

V.Y.Gankin & G.S.Gurevich

**CHEMICAL TECHNOLOGY OF
OXOSYNTHESIS**

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PROLOGUE

This book describes various technological schemes indicating their merits and demerits. Perspectives for the further development of the technology of oxosynthesis are also shown. Recommendations for making a proper choice of apparatuses when designing an oxosynthesis industry are also given. Information on the reaction mechanisms proceeding during oxosynthesis, and kinetic and thermodynamic data of various processes are also included.

This book is meant to help technical engineers who work at oil refining enterprises, at scientific institutions. It is of great help to workers engaged in projection work.

This book is also of value to students of special chemical-technological colleges. It contains 298 pages, 85 drawings, 64 tables; 415 bibliographical entries.

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INTRODUCTION

Oxosynthesis is the process of getting aldehydes and alcohol out of olefins via the reaction:



This reaction was discovered by Otto Roelen in 1938 during the studies of the Fisher-Tropsch synthesis and became known as ***Oxosynthesis*** [1, 2]. Consequently, a more precise name was attached to the interaction of olefin with carbon oxide and hydrogen with the formation of aldehydes, i.e., the ***hydroformylation reaction***.

In scientific literature the word *oxosynthesis* is most often used to define the technological process for getting aldehydes, or corresponding alcohols that include, besides hydroformylation itself, also the catalyst reception stage, its discharge out of the reaction products, the division of the products and the hydration of the aldehydes (if the final product of the process happens to be alcohol).

This term, as a rule, does not signify a concrete chemical reaction, but it signifies a complex that bonds together all the chemical reactions and processes into a common technological system necessary to get aldehydes or alcohol out of olefin and synthetic gas as a final product containing one more carbon atom in the carbon skeleton than in the initial olefin. It is namely in this sense that the term *oxosynthesis* is used in this book.

In spite of the fact that the history of oxosynthesis, as a technological process, is already about 40 years old, scientific literature practically does not contain any information about the technological principles for industrial processes and schemes of its practical use. The main data on the technology of oxosynthesis amounts to only thousands of patents and a great number of commercial descriptions.

If we consider that at present (1991) there are several dozen oxosynthesis installments in the world that produce from 4.5 to 5.5 million tons of products per year [3-5], (Russia is undoubtedly increasing its production) then it becomes clear why the authors of this book are making an effort to fill this gap.

Many publications have recently been devoted to scientific studies of reactions that are combined in the oxosynthesis process. Besides the numerous magazine articles, here we should mention the great collections of reviews and monographs [6 - 12]. However, since

they were published, new data have appeared, which is explained, first of all, by the great interest in this sphere of technical chemistry that allows to get results important not only in respect to applied sciences, but also in respect to making a great contribution to the fundamental problems of homogenous catalysis.

Since it is impossible to study problems of chemical technology processes nowadays without considering kinetics and the mechanism of chemical reactions, this book makes an effort to bond these questions into one whole unit.

Though oxosynthesis, like a complex technological complex, includes not only stages that are based on chemical reactions, but also stages based on physical processes of separation, cleaning, etc, the main attention in the book is given to the *chemical* stages of the process.

The book includes of a lot of researches published in scientific publications, dissertations, reports, etc.

However, considering the monographic character of the book, the authors based it mainly on the results of their own researches and the data taken from their own colleagues who have worked for many years at the USSR Scientific Chemical Research Institute for Petroleum. When choosing experimental data and interpretations, the authors considered their own viewpoints that were elaborated when analyzing and comparing their own and other publicized data.

Considering the novelty of various questions under research, and the efforts to offer new notions about various problems, the authors would be grateful to receive critical remarks that might occur on the part of the readers.

The authors wish to make use of this opportunity to express their hearty thanks to *N.S.Imyanitov* for his friendly help during the work on this book and for giving us the opportunity to get acquainted with his researches. We also thank *A.N.Davidov*, *M.L.Kolesov*, and *Y.B.Tsirkin* for the materials used in section 7. Our thanks also go to *L.F.Kardashina*, *L.A.Arzhanik*, and *L.A.Norkina* for their aid in compiling the manuscript.

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1. TECHNOLOGICAL SCHEMES OF THE OXOSYNTHESIS PROCESS (GENERAL PRINCIPLES)

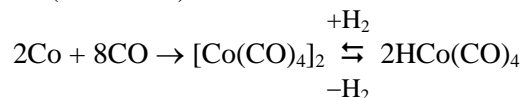
The reaction for olefin hydroformylation, which is the 'heart' of the oxosynthesis process, proceeds in the presence of metal-complex compounds (metal carbonyls) and has a homogenous-catalytic feature.

For quite some time the only hydroformylation catalyst used was cobalt in the various forms of its carbonyls that were in equilibrium with the conditions of the reaction. Recently it was shown that in order to accomplish the hydroformylation reaction catalysts modified by the exchange of carbon oxide in hydrocarbonyl cobalt for various electro-donor ligands could be used. That is, compounds of the $\text{HCo}(\text{CO})_3\text{L}$ type (where L is the trialkylphosphines or triarylphosphines and phosphites) [13] can serve as catalysts.

It has also been shown that rhodium carbonyls can serve as effective hydroformylation catalysts [14]. However, even nowadays the overwhelming majority of industrial oxosynthesis installations are working on the basis of cobalt carbonyls.

The classical oxosynthesis industrial process can be conditionally divided into the following five main stages:

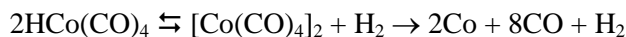
1. *Cobaltization* — the formation of a catalyst (cobalt carbonyl) out of metal cobalt (or its salts). See scheme 1.1:



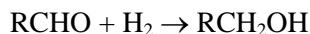
2. *Hydroformylation* — the reaction of olefin with carbon oxide and hydrogen in the presence of cobalt carbonyls:



3. *Decobaltization* — the decay of cobalt carbonyls and the regeneration of cobalt out of the hydroformylation reaction products:



4. *Hydrogenation* — the transformation of aldehydes into relative alcohols (no matter if the final product is 100% or partly alcohol) with the help of the homogenous or heterogenous catalytic reaction:



5. *Rectification* — the division of intermediate products and the discharge of commodity aldehydes and alcohols.

Some of the stages in the processes can be substituted.

The general industrial complex can also include stages for getting initial raw components of the process — olefins, hydrogen, and synthetic gas (mixture $\text{CO} + \text{H}_2$). However, the connection of these stages with the process is actually a formal, administrative factor.

The technological scheme of the process, as a whole, is defined by the principles of realizing separate stages and their interaction. At present there is no common, generally recognized, technology for the oxoprocess. Scientists in various countries, mainly in the USSR, USA, Germany, and Japan, have elaborated numerous technological schemes, as a rule, with great differences.

Various technological process schemes are exploited on an industrial scale even within a single country. In Russia, for example, there are industrial installations made via three different technological schemes. This is explained by historic reasons (rapid progress of the developing process) and by the concrete aims of the industrial installation (receiving alcohol or aldehydes as a final product).

The hydroformylation reaction, especially when it is conducted on cobalt carbonyls (conditionally called 'classical oxoprocess'), transits effectively in quite a definite interval of parameters with a pressure of from 20 to 30 MPa; temperature of 100° to 200° C. Therefore the technical peculiarities for performing the hydroformylation stage cannot significantly influence the general technological oxosynthesis scheme. This, of course, is not related fully to the oxosynthesis processes with the use of modified ligands of cobalt and rhodium catalysts. These comparatively rare variants of the oxoprocess will be detailed later.

The alcohol hydrogenation reaction of the received aldehydes takes place either homogenous-catalytically or without the use of heterogeneous catalysts in a wide range of temperatures and pressures.

On oxosynthesis installations of industrial scale enterprises the hydration stage occurs in one case, for example, at about 30 MPa and at 260°-320° C, while in another case — at about 1 MPa and 120°-160° C. However, it is not the choice of the hydrogenation method that dictates what kind of oxoprocess scheme should be taken. On the contrary, the method of realizing the hydrogenation stage is chosen depending on the technological scheme of the process.

Obviously, the peculiarities of the product rectification stage also cannot define the principle characteristics of the technological scheme.

There are wide opportunities for the construction of various technological schemes thanks to the variety of methods of realizing the

decobaltization stage — the extraction of cobalt from reaction products and the recirculation of the cobalt in this process.

If the required condition for the formation of cobalt carbonyls in the cobaltization stage is the interaction of cobalt (in the form of metal or its compounds) with carbon oxide at an increased temperature (usually 100°-170° C) and a pressure (20-30 MPa), then the decobaltization stage can be realized with the help of various technological approaches.

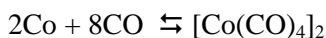
To extract cobalt out of reaction products, the cobalt carbonyls, being homogenous and soluble in the product, are destroyed and transferred to the stable cobalt forms (metallic cobalt, cobalt salts) then they are extracted from the product and returned to the cobaltization stage.

The technological schemes for performing these processes can be divided into three groups: 1) those based on the thermal instability of the cobalt carbonyls; 2) those based on the instability of the cobalt carbonyls relative to the action of the oxidizers including acids; 3) those based on the volatility of cobalt compounds and product oxosynthesis.

These are the factors that define the general technological scheme of the process.

1.1 SCHEMES WITH THERMAL DECOBALTIZATION

In technological schemes of processes that relate to the first group the catalyst is received and discharged via the reaction:



in the direct (cobaltization) and reverse (decobaltization) directions. For the acceleration of the direct or reverse reaction these transitions are conducted at high temperatures. The procedure of either reaction is defined by the partial pressure of the carbon oxide.

The thermal decomposition of cobalt carbonyls is known as the top-chemical reaction. To avoid the deposit of cobalt on the walls of the apparatus and the acceleration of the thermal carbonyl decomposition reaction, technological oxosynthesis schemes with thermal decobaltization of hydroformylation products are realized via three main variants:

1) The cobalt settles upon the developed fixed surface (i.e., decobaltization) then the reverse reaction is conducted in the same apparatus, that is, the cobaltization stage takes place. The so-called '*dyad*' and '*triad*' process schemes are realized in this variant.

2) The cobalt is set upon a developed movable surface after it returns from the decobaltization apparatus onto the cobaltization stage. This is how the '*kieselguhr*' scheme is realized.

3) The cobalt is extracted in the form of powder suspended in the liquid product. The settling of the cobalt on the walls of the decobaltization apparatus is avoided by special methods (mainly by the recirculation of part of the product that contains suspended powder of cobalt onto the decobaltization stage) [15]. The suspension of cobalt, after its separation from the main part of the hydroformylation product, returns to the cobaltization stage. This scheme became known as the '*powder scheme*'.

Technological schemes with thermal decobaltization are the oldest, but, nevertheless, they have not lost their industrial significance.

Judging by literary data, the first industrial technological oxosynthesis scheme was a dyad one [16]. The work of this scheme is illustrated in figure 1.1. Olefin and synthetic gas (a mixture of carbon oxide and hydrogen) are fed into the reactor, filled with immovable pumice, on which the metallic cobalt is settled. The cobalt, interacting with the synthetic gas, forms carbonyls, which catalyze the hydroformylation reaction that is proceeding in the same reactor.

The reaction products with diluted cobalt carbonyls pass through a separator where they are separated from the carbon oxide and then pass on to the second reactor, which is filled with the same kind of immovable pumice but without any cobalt. This second reactor receives some hydrogen. If the partial pressure of the carbon oxide is too low, and the temperature is too high, the cobalt carbonyls fall apart and the metallic cobalt settles down on the nozzle. The product, free of the cobalt, transits to the next stages. When the greater part of the cobalt is thus transferred from the first to the second reactor, the functions of the reactor are changed.

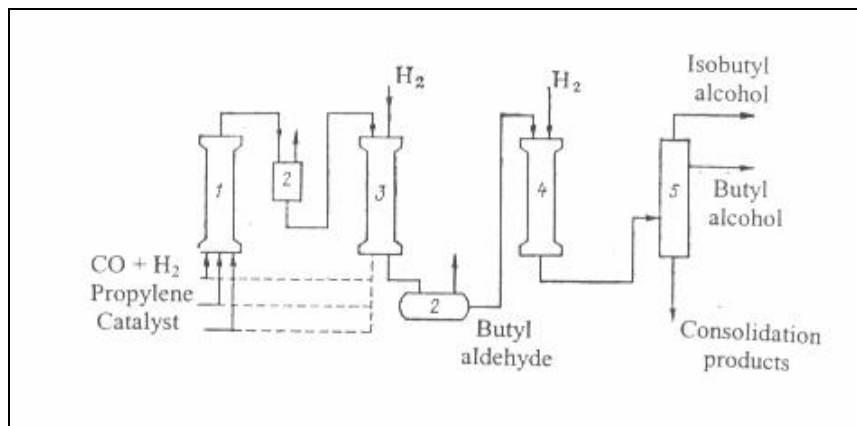


Figure 1.1 Dyad oxosynthesis scheme:

1 — reactor for carbonyl formation and hydroformylation; 2 — separators; 3 — decobaltizer; 4 — hydrogenation reactor; 5 — product-dividing sector.

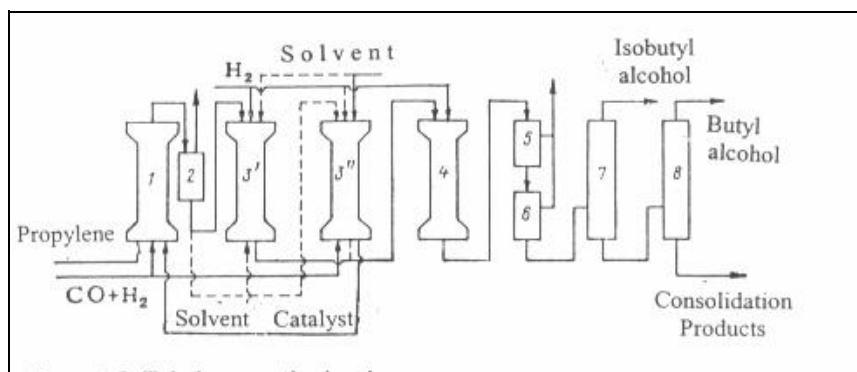


Figure 1.2 Triad oxosynthesis scheme:

1 — hydroformylation reactor; 2 — separator; 3' & 3'' — cobaltization and decobaltization reactors; 4 — hydrogenation reactor; 5 & 6 — separators; 7 & 8 — product-dividing sector

Figure 1.2 shows the triad scheme, which is actually an improved dyad one [17, 18]. Cobalt carbonyls and hydroformylation come from different apparatuses. There are 3 main apparatuses in this scheme: 1) the cobaltizer, where the compound of cobalt carbonyl is formed in an inert a carbon-hydrogen solvent; 2) the reactor proper for hydroformylation; and 3) the decobaltizer, where the cobalt carbonyls break up and the metallic cobalt is extracted from the product. The

cobaltizer is filled with pumice covered with cobalt, while the decobaltizer is of pure pumice. In the course of the cobalt's wasting away in the cobaltizer, and its piling up in the decobaltizer, the functions of these apparatuses change.

It was mentioned that the transition reaction for metallic cobalt in carbonyls proceeds at high temperatures and pressures. In order to guarantee the stability of cobalt carbonyls and the necessary transition speed of the cobalt in the carbonyls, the cobaltizer in the triad scheme works at 30 MPa and at 80°-130°C, and the temperature of the process rises during the decrease of the cobalt concentration on the nozzle of the cobaltizer. The recurrence of the work of the apparatuses for cobaltization and decobaltization makes it necessary to accomplish the decobaltization stage also at 30 MPa (otherwise the operation for the function change in the apparatuses would cause a lot of trouble).

Thus, in the triad scheme (just as in the dyad one), cobaltization, hydroformylation, and decobaltization are accomplished under great pressure (≈ 30 MPa).

The need to make use of a great number of high-pressure apparatuses is a shortcoming of these systems. Other shortcomings are the strict synchronization of the job which does not allow the organization of a fully uninterrupted production (one cycle of work by the apparatuses runs for no more than 24 hours), then there are difficulties connected with the irregularity of the settling of the metallic cobalt on the nozzle of the decobaltization reactor, and finally, there is a comparatively small output from such a great volume of high pressure apparatuses.

These shortcomings were partly done away with in the course of the elaboration of a modernized variant of a triad scheme, known in chemical literature as a '*scheme with a small cobalt*' [19]. The use of this scheme allows increasing the length of a one-job cycle of the apparatuses from 8 to 10 twenty-four-hour days nonstop; and there was a better distribution of cobalt on the cobaltization reactor's nozzle. This scheme is now (1981) working on the industrial scale.

The idea of thermal cobalt carbonyl distribution with metallic cobalt precipitation on the moveable carrier with a developed surface was used when elaborating the kieselguhr scheme [20].

In this variant, the cobalt is introduced to the process in the form of metallic powder suspension spread in the kieselguhr scheme. The process is conducted in two simultaneously working reactors (fig. 1.3). In the first reactor, at 25 - 30 MPa and 150° - 170° C, there is a formation of cobalt carbonyls and a partial hydroformylation reaction.

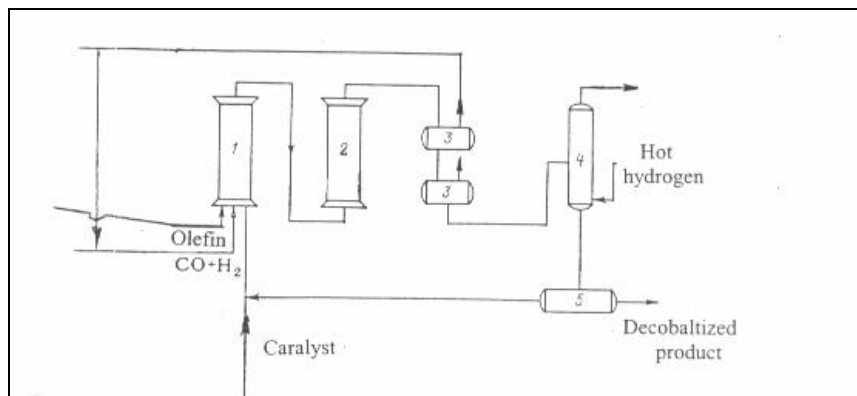


Fig. 1.3 The Kieselguhr scheme for oxosynthesis:

1 — reactor for carbonyl-formation and hydroformylation; 2 — reactor for hydroformylation; 3 — separators; 4 — reactor for decobaltization; 5 — magnetic separator.

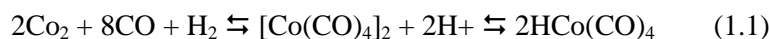
The hydroformylation reaction ends up in the second reactor. In order to intensify the process, the temperature here is 10° - 20°C higher than in the first reactor. The liquid hydroformylation product (after separating from the synthetic gas) with the suspended kieselguhr within, goes to the decobaltization stage which is accomplished in two consecutively working reactors at 120° - 130°C and a hydrogen pressure of 2.5 - 3.0 MPa. The cobalt that settled on the kieselguhr, is separated from the liquid product via magnetic separators. The decobaltization stage is accomplished at a smaller pressure. The main shortcomings of this scheme are due to the erosion of the apparatuses and also with the difficulty in separating the catalyst suspension from the product on the magnetic separators. Still, the scheme is used on the industrial scale.

Among the schemes with thermal decobaltization, it is worth mentioning the powder scheme where the inclusion and exclusion of the catalyst in regard to the system is accomplished by suspending the powder in the product of the metallic cobalt [21, 22]. The scheme was elaborated on the experimental scale.

The characteristic feature of all the technological schemes with thermal decobaltization is the partial hydrogenation of aldehydes in alcohol during the decobaltization stage. After all, the aldehydes in the decobaltization apparatuses are in contact with metallic cobalt, which is quite an active hydrogenous catalyst and under the pressure of hydrogen. This circumstance makes schemes with thermal decobaltization most valuable for the process of getting alcohols but not aldehydes. The oxosynthesis installations with thermal decobaltization, now working in Russia, produce butyl and high quality alcohols as final products.

1.2 SALT-CONTAINING SCHEMES

Technological oxosynthesis schemes that use the instability of cobalt carbonyls for discharging catalysts, are often called salt-containing schemes. In this case, cobalt salt is the source for getting cobalt carbonyls. On the decobaltization stage the cobalt carbonyls are destroyed by oxidizers in the presence of acids with the formation of initial salts. Thus we have the following reaction:



in the direct (cobaltization) and reverse (decobaltization) directions.

To conduct a reaction for the formation of cobalt carbonyls out of its own salts the partial pressure of carbon oxide should be not lower than a certain point, depending on the temperature of the process.

Exactly how the oxosynthesis salt schemes work is clear from figure 1.4. Cobalt in the form of salt, dissolved or suspended in water or in an organic solvent, synthetic gas, and initial olefin, are all put into the reactor, where the processes of carbonyl formation and hydroformylation are combined. Under the influence of the rising temperature and the pressure of the synthetic gas, cobalt carbonyls form in the reactor, and the hydroformylation reaction begins. The liquid product of hydroformylation separates from the gas-synthesis in the separator and goes to the decobaltizer where it is processed by acid. The separated cobalt in the form of a mixture or salt suspension is then separated from the hydroformylation product and returns to the cycle.

The processes of carbonyl formation and hydroformylation, of course, can be accomplished in various reactors.

Technological salt schemes for oxosynthesis processes are being elaborated and exploited by many world famous firms. They differ mostly by the cobalt salt and acid used for spreading cobalt carbonyls.

Thus, in the scheme of the BASF firm in Germany [23, 24] a water mixture of cobalt acetate is used. Decobaltization is accomplished by a mixture of vinegar acid after which the formed compound of cobalt acetate separates from the organic hydroformylation product.

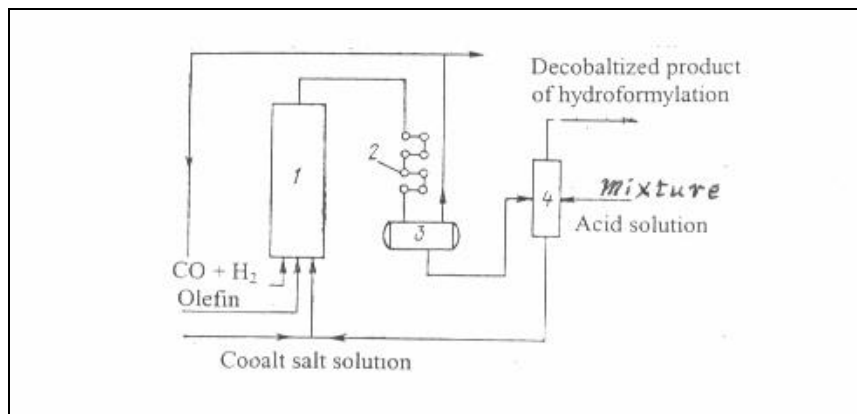


Figure 1.4 Salt-containing oxosynthesis scheme:

1 — reactor for carbonyl-formation and hydroformylation; 2 — refrigerator;
3 — separator; 4 — decobaltizer.

The Ruhrchemie firm (Germany) has elaborated a scheme where a suspension of cobalt salt is introduced in an organic product [25, 26]. The extraction of cobalt from a hydroformylated product is conducted with the help of formic or vinegar acid. The formed cobalt salts are not soluble in hydroformylated products thanks to which they can be singled out in the form of suspensions and returned to the process.

In the technological process of the firm Mitsubishi [27] cobalt is introduced into the system in the form of lauric acid salt. Decobaltization is accomplished by breaking up the cobalt carbonyls with the help of a watery mixture of nitric acid. The formed watery mixture of nitrate cobalt is separated from the products of hydroformylation.

In all the variants of salt-scheme reactions, carbonyl formation and hydroformylation are carried out at high pressures (20 to 30 MPa), while the decobaltization stage runs practically at atmospheric pressure.

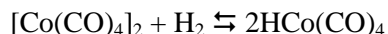
The given examples include only some of the elaborated salt systems, however, these are sufficient to realize that all these processes are based upon one and the same principle, and they came into being not only as a result of the development of the technological process, but also as a result of challenging battles for patents.

The main merits of oxosynthesis salt schemes are that their high pressure installation is smaller thanks to: 1) the possibility of conducting the decobaltization stage at atmospheric pressure; 2) the nonstop work of the installation; 3) a much smaller loss of aldehydes because of the hydrogenation in alcohols, which is important in cases when the main final products of the process are aldehydes.

The shortcomings of technological schemes of this type are the relative complications of the decobaltization technology stage because of 1) the need for introducing additional reagents; 2) the appearance of sewage in the process; 3) the presence of active corrosion reagents.

1.3 EVAPORATIONAL AND MIXED SCHEMES

The separation of the cobalt catalyst from the hydroformylation products can be accomplished by a simple distillation of the organic products. In hydroformylation products the cobalt is mainly in the form of an equilibrium mixture of dicobaltoctacarbonyl and hydrocarbonyl:



Note that dicobaltoctacarbonyl is a poor evaporation compound. The shift of the equilibrium towards the dicobaltoctacarbonyl is possible by lowering the partial pressure of the hydrogen

Thus, the division of the products of hydroformylation and cobalt is possible either by ratification under a vacuum (at a relatively low temperature), or by the ratification of carbon oxide under pressure, because if the temperature is too high in the absence of carbon oxide, the cobalt carbonyls are thermally unstable.

There are schemes given in chemical literature describing how to get volatile aldehydes with decobaltization, based on the various volatile capacities of carbonyls and aldehydes [11].

Technological schemes showing the oxosynthesis process with the division of hydroformylation and catalyst products in the form of carbonyls with the help of evaporation, were mainly elaborated at the outset of the development of oxosynthesis [28]. In this period of time the hydroformylation reaction was thought to have been of a heterogenous catalytic character.

Later on were studied the details of the separation of products of propylene hydroformylation from cobalt carbonyls with the help of evaporation at below atmospheric, equal to atmospheric, and above atmospheric pressures [29]. However, in the classical variant of the oxosynthesis (with the use of cobalt carbonyls as catalysts) such a technological scheme was never used on an industrial scale.

The most perspective process turned out to be the one that combined the principles of the salt and evaporation schemes. In this system the cobalt carbonyls, after hydroformylation, are transferred to a slightly volatile, thermally stable form like the salt of naphthene acid,

well diluted in the organic product. After this the hydroformylation product is easily separated from the cobalt salt that is returned together with part of the hydroformylated product onto the cobaltization stage where the cobalt readily produces carbonyls. The cobalt losses, together with the distillation products, comprise less than 1%. Figure 1.5 demonstrates the described principle, which is put in the basis of the scheme and is called the *naphthene-evaporation process* [30].

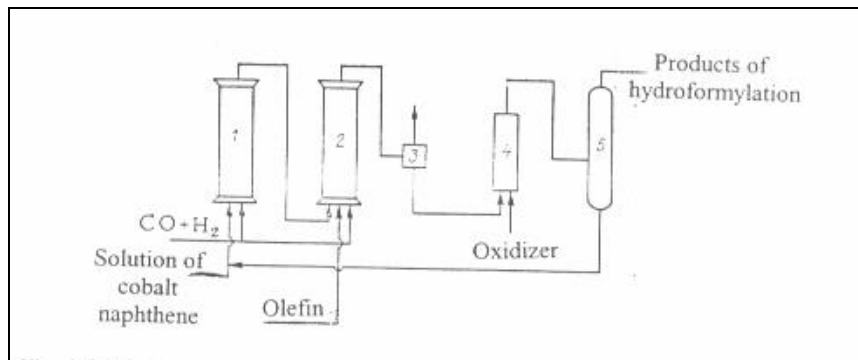


Fig. 1.5 Naphtha-evaporation oxosynthesis scheme:

1 — cobaltizer; 2 — hydroformylation reactor; 3 — separator;
4 — decobaltizer; 5 — rectification column.

Such are the main principles on which is based the classical technology of the oxosynthesis process with a cobalt catalyst. However, for a deeper understanding of the peculiarities of technology and various schemes, it is important to know the mechanism and kinetics of chemical reactions that form the complex of the oxoprocess.

Without such information it is impossible to understand even those features that are introduced, say, into the oxosynthesis technology by using modified phosphines (PH_3) of a cobalt or rhodium catalyst. It is because of this that the following sections of the book are devoted to detailed analyses of each of the stages of the process.

We will return to the technological schemes of the process and detail the most important of them.

2 THE HYDROFORMYLATION STAGE

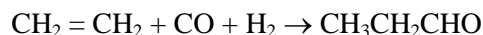
2.1 NOTIONS ABOUT HYDROFORMYLATION REACTION MECHANISMS

Research of the hydroformylation reaction mechanism has been occupying the minds of scientists like G.Natta, W.Reppe, G.Wilkinson, I.Wender, M.Orchin, and others for more than 30 years. This research was necessary because of objective circumstances such as the increase in the use of reactions and the unusualness of the chemical bonding reaction itself that connects such big fragments (formylation groups) with double bonds and with the formation of a new C—C bond.

In the process of widening the knowledge in this sphere, the essence of the word *mechanism* was 'evolutionary', that is, the problems also widened when investigators began studying the hydroformylation of reaction mechanisms. Just like in other analogous cases, it was very important to discover new facts rather than interpret the old ones on the level of knowledge that existed at that time. As a matter of fact, when studying hydroformylation reactions, theoretical works sometimes foretold and defined experiments.

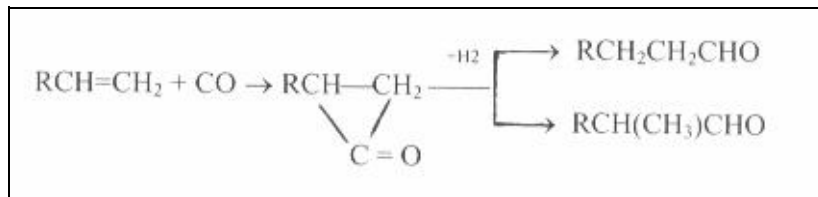
Only those works are mentioned here in the retrospective review that played an important role in modern achievements.

Undoubtedly, one of the most significant periods was O.Roelen's discovery of carbon oxide and hydrogen bonding to olefins in the presence of cobalt-containing catalysts along the following reaction:



which is the very first suggested hydroformylation reaction mechanism.

Then it was found that during the hydroformylation of olefins with more than two carbon atoms in the chain, a mixture of aldehyde isomers is formed. Thus, mixtures of butyl and isobutyl aldehydes were formed out of propylene [31, 32]. In order to explain this, W.Reppe [33] suggested that first the carbon oxide reacted with the olefin, thereby forming a three-part cycle that is then replaced by the hydrogen:

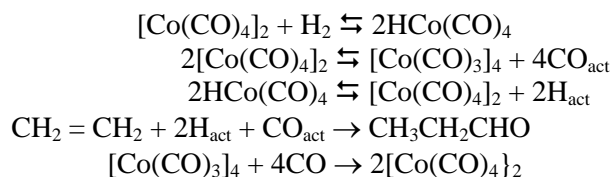


The role of the catalyst in this scheme was never discussed. This scheme, naturally, from the chemical viewpoint, explained the formation of isomer bonds during olefin hydroformylation.

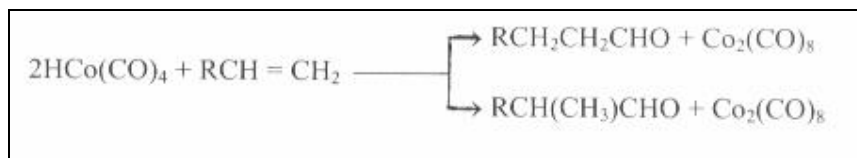
At this time the research on the hydroformylation reaction, the catalyst was introduced to the reaction in the form of a Fisher-Tropsch contact ($\text{Co} \cdot \text{Th} \cdot \text{SiO}_2$) and considered to be a heterogeneous catalytic reaction, during which, part of the cobalt changed into the reaction product in the form of carbonyl compounds before it left the reactor.

D. Rudkovsky and his colleagues [34, 35] found that a compound containing cobalt in the form of carbonyls with no heterogeneous cobalt catalyst can catalyze the hydroformylation reaction. That is, the carbonyl cobalt dissolved in a liquid, served as a catalyst for the hydroformylation reaction, and the reaction itself is a homogenous-catalytic one.

Thanks to this data, a mechanism was suggested that supposed the formation of *active carbon oxide* out of dicobaltoctacarbonyl, and *active hydrogen* out of hydrocarbonyl cobalt with subsequent bonding of the active carbon oxide and hydrogen to the olefin:

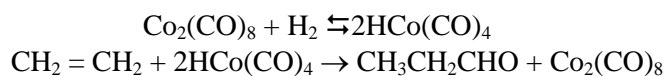


The next step in the study of this reaction mechanism was I. Wender's discovery of the reactions between hydrocarbonyl cobalt and olefin that brought about the isomer mixture of aldehydes [36]:



This reaction was conducted in atmospheric pressure and at temperatures of 10° to 20° C and became known as the *stoichiometric hydroformylation reaction*.

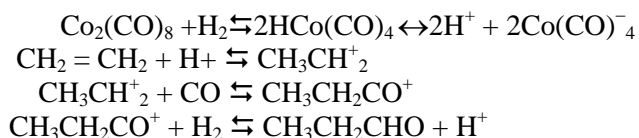
Since the reaction for the formation of hydrocarbonyl cobalt out of dicobaltoctacarbonyl was known, we can presuppose that the catalytic hydroformylation reaction, when cobalt was introduced to the system in the form of dicobaltoctacarbonyl, would proceed along this mechanism:



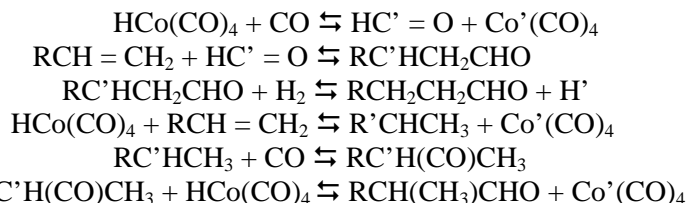
The stoichiometric hydroformylation reaction then became and still is one of the most important objects for research when studying this mechanism as the most convenient experimentally (requiring common conditions) and as the most informative model.

The above given scheme became a reflection of chemism in the hydroformylation reaction, thus, further research was directed towards the question: *How does the interaction hydrocarbonyl cobalt—olefin take place?* Since ions and radicals were then known to be intermediate active particles, suppositions were made to the effect that the interaction occurred along the ionic or the radical mechanism.

Ionic mechanism:

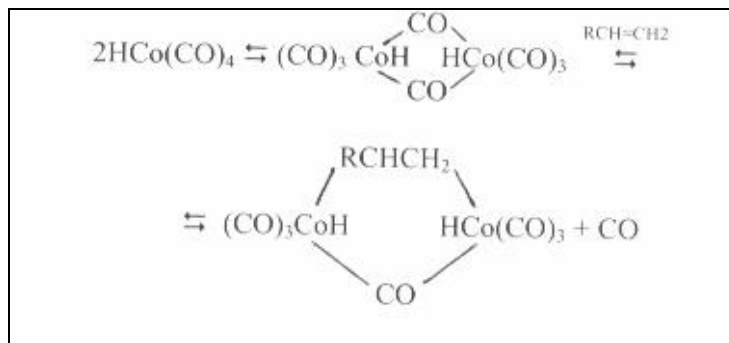


Radical mechanism:

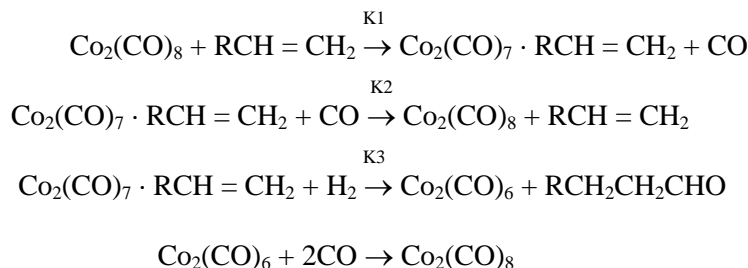


Both were regarded as chain mechanisms. There were no radicals as a result of the catalytic or stoichiometric hydroformylation. The reaction did not slow down when inhibitors of radical reactions were added to the system, which caused doubt about the existence of a radical mechanism. The ionic mechanism also got no experimental proof.

Further research in reaction kinetics, where the slow-down influence of carbon oxide on the hydroformylation reaction speed was observed, was the basis for hypotheses that explained this phenomenon. The main point here was the supposition of the formation of an intermediate complex between the carbonyl cobalt and the olefin with a discharge of carbon oxide. Wender supposed that such a complex was formed of hydrocarbonyl cobalt and olefin via this scheme [39]:



A.Martin considered that the complex is formed via interaction of dicobaltoctacarbonyl with olefin along the following scheme [40]:

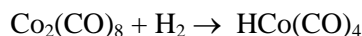


The derived kinetic equation for the initial reaction speed is thus:

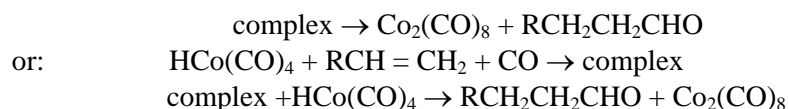
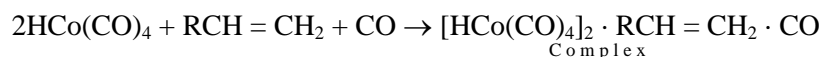
$$r = \frac{K_1 K_3 P_{\text{H}_2}}{K_2 P_{\text{CO}} + K_3 P_{\text{H}_2}} [\text{Co}_2(\text{CO})_8] [\text{RCH} = \text{CH}_2]$$

This well agrees with the experimental data. But this mechanism did not consider the role of the hydrocarbonyl cobalt in the reaction.

Knowing that it was due to the oxosynthesis that a transition reaction of dicobaltoctacarbonyl with hydrocarbonyl was possible, M.Orchin considered it proven that it was namely the hydrocarbonyl cobalt that took part in the formation of the catalyst complex [41]:



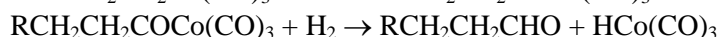
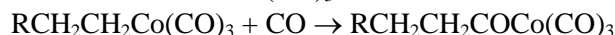
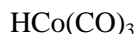
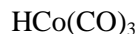
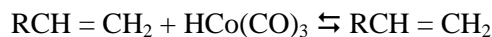
During the development of such research, M.Orchin and L.Kirch offered two alternative mechanisms for hydroformylation [42]:



It is obvious that the nature of the supposed complex out of olefin, carbon oxide, and hydrocarbonyl cobalt remained unclear.

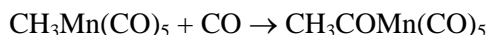
The next step in the development of the hydroformylation mechanism was the Sternberg-Wender hypothesis. Considering Coffield's data on the methyl-manganese-pentacarbonyl interaction with carbon oxide [43], they supposed the interaction of olefin and cobalt hydrocarbonyl

proceeds with the subsequent formation of the olefin π -complex, $\text{HCo}(\text{CO})_4$, alkylcobaltcarbonyl, and acylcobaltcarbonyl [44]:



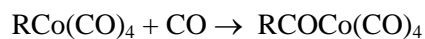
The possibility of forming an olefin π -complex with $\text{HCo}(\text{CO})_4$ was confirmed by data from coordinate compound chemistry where we found that olefins can be ligands and can form π -complexes with metals.

The transition stage of alkylcobaltcarbonyl into acylcobaltcarbonyl was postulated by Sternberg and Orchin analogous to Coffield's transition of alkylmanganeseecarbonyl into acylmanganeseecarbonyl:



The rest of the mechanism's stages were more hypothetical, but even they did not cause any objections.

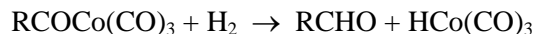
D.Breslow and R.Heck [45, 46] synthesized a substance of the $\text{RCo}(\text{CO})_4$ type, that is, alkylcobaltcarbonyl, that adsorbed the carbon oxide, thereby forming acylcobalttetracarbonyl:



Breslow and Heck thought this was equilibrium:



but acylcobalttricarbonyl is an active compound, and when replaced by hydrogen, offers an aldehyde as follows:



Acylcobalttetracarbonyl does not react; the hydroformylation slows down with the pressure increase of the carbon oxide.

Breslow and Heck proved that during the stoichiometric interaction of hydrocarbonyl cobalt with olefin, acylcobaltcarbonyl was the result. They also proved that compounds with an IR (infra-red) spectrum absorption stripe that corresponded to acylcobaltcarbonyls, are present in the reaction mixture during catalytic hydroformylation [46].

At the same time, Orchin and his colleagues found that the speed of the acylcarbonyl breaking reaction was much smaller than the total speed of the stoichiometric hydroformylation reaction [42]. This caused doubt about the existence of the acylcobaltcarbonyl breaking reaction with the formation of aldehydes under conditions of the oxoprocess.

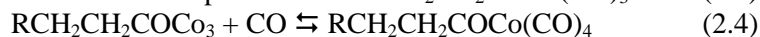
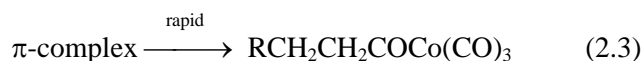
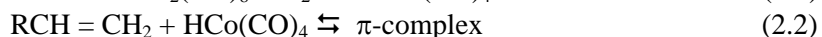
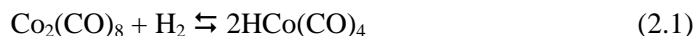
L.Marko and colleagues [47] attempted to find products in the IR-spectra that carbonized the absorption strip, and was characteristic for alkylcarbonyls. However, this attempt failed. M.Niwa and M.Yamaguchi [48] found that the transition reaction speed of the dicobaltoctacarbonyl into hydrocarbonyl was smaller than the total speed of the oxoprocess.

All these facts caused doubts about the correctness of the points of view concerning the hydroformylation reaction mechanism.

A confirmation about the correctness of this mechanism, made by H.Sternberg and I.Wender*, was proof of this mechanism's compliance with the well known kinetics data [49].

* In literature [8] this mechanism was known as the 'Breslow-Heck Mechanism'. However, D.Breslow and R.Heck actually only developed and formulated the ideas originally expressed by Sternberg and Wender. This is why we consider it proper to give the priority to the scientists H.Sternberg and I.Wender.

The Sternberg-Wender mechanism was offered as follows:



This scheme shows the cobalt hydrocarbonyl formation stages (2.1), π -complex (2.2), and acylcarbonyl (2.3), (2.4) as intermediate products of the interaction. The reaction speed equation follows:

$$r = 2K_5\text{CH}_2\text{CCo} / b + \sqrt{b^2 + 8K_5\text{CH}_2\text{CCo} / K_1K_2^2K_3^2\text{C}_{\text{olefin}}}$$

$$\text{when } b = 1 + K_4\text{CCo} + K_5\text{CH}_2 / K_3 (1 + 1 / K_5\text{C}_{\text{olefin}})$$

Here: C_{H_2} is hydrogen concentration; C_{Co} is cobalt concentration; C_{olef} is olefin concentration; C_{CO} is carbon oxide concentration; $K_1 — K_5$ are speed constants to reactions (2.1) — (2.5).

However, this equation could not be used to calculate the hydroformylation reaction speed and compare the results with the known kinetic reaction experimental data because of mathematical difficulties.

To simplify the equation, allowances were made: stage (2.1) was excluded from the mechanism's equilibrium, then it was decided that there was very little dicobaltoctacarbonyl in the system because of the bonding of the cobalt hydrocarbonyl formation, so the equilibrium of the reaction was shifted towards the point of its origin. Excluded were the formation stage of the π -complex out of cobalt hydrocarbonyl, olefin, and the shift of the π -complex to acylcobaltcarbonyl. Stages (2.2) and (2.3) were united into one interaction stage of hydrocarbonyl and olefin, with the formation of acylcobaltcarbonyl.



Now the equation for the reaction speed is simplified as follows:

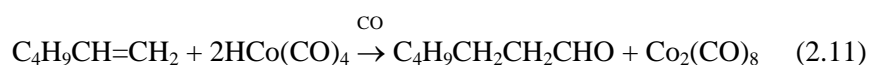
$$r = K_9 K_{11} C_{olefin} C_{H_2} C_{Co} / K_9 K_{10} C_{olefin} C_{Co} + K_{11} C_{olefin} + 1$$

where $K_9 — K_{11}$ are the reaction speed's constants (2.7) to (2.9)

The results of the calculations made with a computer matched the known experimental data in this field. It was shown that this equation very well describes the change in the cobalt hydrocarbonyl concentration during the cyclohexane hydroformylation reaction, which was defined experimentally by Japanese researchers [50].

These calculations, having confirmed the correctness of the Sternberg-Wender mechanism, stimulated the further development of researches dealing with the studies of the elementary stages of the hydroformylation reaction mechanism and with the identification of the intermediate products of the process.

The cobalt hydrocarbonyl interaction kinetics with 1-hexane at 1 atmosphere and 10°C [51] along the reaction shows:



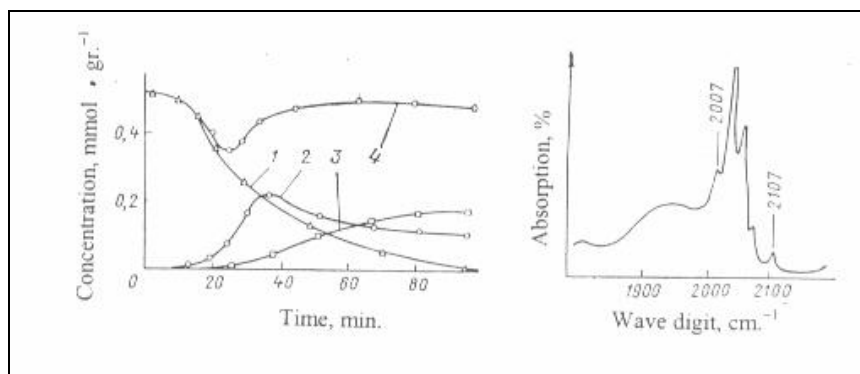


Fig. 2.1 Kinetic curves of 1-hexane hydroformylation reaction:
 1 — $\text{HCo}(\text{CO})_4$; 2 — acylcobaltcarbonyl; 3 — enant aldehyde; 4 — total cobalt w / compound. Temp. — up to 10°C ; partial pressure of carbon oxide, 0.11 MPa; solvent — heptane.

Fig. 2.2 IK-spectrum of sample treated with 40% KOH.

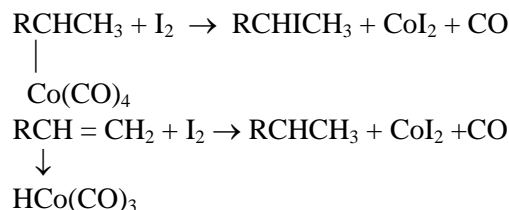
The time spent on keeping the cobalt hydrocarbonyl, acylcobaltcarbonyl, and aldehyde in the reaction mixture was analyzed. It turned out that the curve characterizing the change of the acylcobaltcarbonyl concentration during the reaction, resembles the kinetic curve of the intermediate product that preceded the aldehyde formation (figure 2.1).

The cobalt concentration change during reaction was analyzed. The concentrations of the stoichiometric hydroformylation products, defined via chemical analyses, were summed up: cobalt hydrocarbonyl + acylcobaltcarbonyl + aldehyde, each mol of which was equal to two mols of cobalt in accordance with the stoichiometry of reaction (2.11).

The total curve of the cobalt contents in the reactions' products had the minimum (fig. 2.1) indicating the presence of an analytically not definable cobalt-containing intermediate product in the mixture. The minimum preceded the acylcobaltcarbonyl formation that corresponded to the intermediate compound and preceded the acylcobaltcarbonyl.

To identify the cobalt-containing intermediate compound, samples of the product, containing minimums of cobalt in the reaction mixture, were chosen and analyzed. The samples were treated with alkali [40% - 50% NaOH, at minus 50°C] to do away with the hydrocarbonyl; then iodine was used. A chromatographic analysis showed that a new compound was thus formed (new peak on the chromatogram). A chromatic-mass-spectroscopic analysis showed that this new peak corresponded to mixtures of the 2nd and 3rd iodine-hexane.

The treatment of reaction products of stoichiometric hydroformylation with iodine and no mixture of cobalt hydrocarbonyl, led to the formation of iodine-alkyls, which form via interaction with iodine of alkylcobaltcarbonyl or the π -complex of hydrocarbonyl cobalt — olefin:



Samples of the IR-spectrum were taken under special conditions after taking the cobalt hydrocarbonyl out of it (fig. 2.2), which coincided with the methylcobaltcarbonyl spectrum [52]. On both IR-spectra, in the wavelength range of 2035 cm^{-1} , the stripes coincided with the vibrations of the CO group in the alkylcobalt-carbonyls. There were hardly any absorbing stripes on the spectra, characteristic of dicobaltoctacarbonyl (1860 cm^{-1}), cobalt hydrocarbonyl (2115 cm^{-1}), and the absorption of cobalt acylcarbonyl (2107 cm^{-1}). Some absorbed about 2035 cm^{-1} .

Thus, it became evident that alkylcobaltcarbonyls were formed in the period of time that preceded the formation of acylcobaltcarbonyls. A quantitative analysis of the alkylcarbonyls during the reaction (in the form of iodine-alkyls) confirmed that it was the alkylcarbonyls that were the products that preceded the acylcarbonyls. The total number of analytically defined cobalt-containing compounds in the course of the experiment remained practically unchanged (fig. 2.3 & 2.4).

Alkylcarbonyls, acylcarbonyls, hydrocarbonyls, dicobaltoctacarbonyls are the main forms where cobalt is under stoichiometric synthesis conditions. The role of the π -complex: olefin — hydrocarbonyl cobalt in the hydroformylation mechanism remains unclear.

Though the Sternberg-Wender suppositions about the presence of the π -complex in the reaction's system were also confirmed by Marko and colleagues [47], and though the same hypothesis was made by Lindsey and Cramer when studying the isomerization reaction of hexane under cobalt hydrocarbonyl influence [53], there was no proof that the π -complex was the intermediate product of the hydroformylation reaction.

There was an opinion that the first stage of the hydroformylation reaction was an electrophyl connection of HCo(CO)_4 to the olefin with alkylcobaltcarbonyl formation [54, 55]. The balance of cobalt observed during the reaction (fig. 2.3 & 2.4) spoke in favor of this supposition. This did not negate the existence of small bits of the π -complex in the reaction's mixture, but it did complicate the defining of this product.

Kinetic curve analyses in interaction reaction $\text{HCo}(\text{CO})_4$ with olefins (fig. 2.3) have shown that after the hydroformylation reaction's induction period there are a lot of various carbonyl derivatives of cobalt in the reaction's medium [56]. Such a mixture is practically indivisible. Because of this, an attempt was made to find π -complex $\text{HCo}(\text{CO})_4$ with olefin in the samples that were chosen during the induction period when the reaction mixture contained only $\text{HCo}(\text{CO})_4$ and the π -complex.

Since $\text{HCo}(\text{CO})_4$ can easily be taken out of the system, one can get samples of the reaction's mixture without any cobalt carbonyl derivatives besides a possible π -complex with olefin.

The π -complex is identified by IR-spectroscopy when shifting the valence vibration frequency of CO end groups relative to the frequencies of the hydrocarbonyl cobalt carbonyl groups, which are not connected with the π -complex, as well as the frequency decrease in the double bond because of the coordinate bonding of the olefin with cobalt. According to [57 & 58] the decrease is in the range of 140 to 150 cm^{-1} spectra in the π -complex of transitional metals. Therefore, when the π -complex is formed between $\text{HCo}(\text{CO})_4$ and propylene, there is a shift of the spectrum stripe by 1643 cm^{-1} which belongs to the double bond of the olefin with a frequency of about 1500 cm^{-1} .

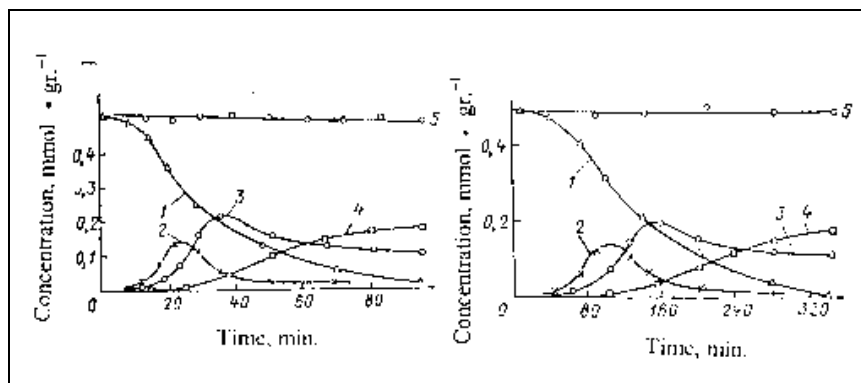


Fig. 2.3 Kinetic curves of 1-hexane stoichiometric hydroformylation

reaction: 1 — $\text{HCo}(\text{CO})_4$; 2 — alkylcarbonyls; 3 — acylcarbonyls;

4 — aldehydes; 5 — total cobalt-containing compounds.

Temperature — 10°C; carbon oxide partial pressure — 0.11 MPa; initial 1-hexane concentration — 3.5 $\text{mmol} \times \text{g}^{-1}$; solvent — heptane.

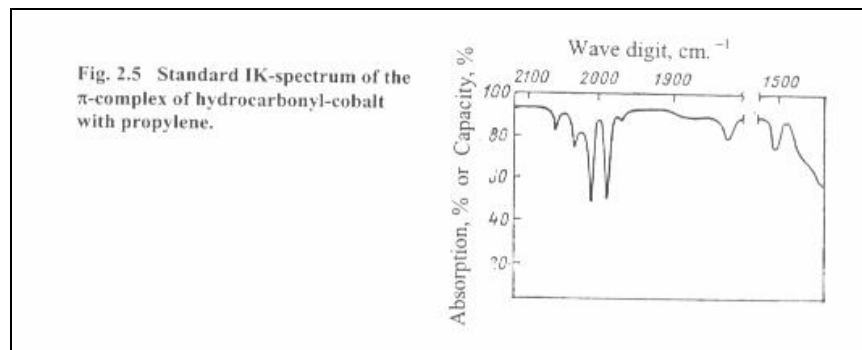
Fig. 2.4 Kinetic curves of 2-hexane stoichiometric hydroformylation

reaction: 1 — $\text{HCo}(\text{CO})_4$; 2 — alkylcarbonyls; 3 — acylcarbonyls;

4 — aldehydes; 5 — total cobalt-containing compound.

Temperature — 10°C; carbon oxide partial pressure — 0.11 MPa;

initial 2-hexane concentration — $3.5 \text{ mmol} \times \text{g}^{-1}$; solvent — heptane.



The sample of the reaction's mixture $\text{HCo}(\text{CO})_4$ and propylene, taken at the end of the induction period, was freed of cobalt hydrocarbonyl with the help of NaOH .

Indeed, the analyzed samples of the reaction's mixture did not contain hydrocarbonyl, alkyl- or/and cobalt acylcarbonyl. The analysis was made on the IR-spectrometer using a cuvette cooled to minus 20°C . In the spectra of the samples, chosen during the induction period of the reaction, and freed of $\text{HCo}(\text{CO})_4$, had intense stripes with valence vibration frequencies of 1990, 2020, 2040, and 2070 cm^{-1} , belonging to the $\text{C}=\text{O}$ bond of the carbonyl group.

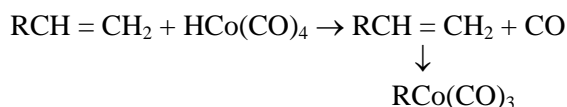
Compared with the IR-spectra of the carbonyl-derivatives of cobalt, these spectra had no stripes like those in the CO group of alkyl- and acylcobaltcarbonyls, and a new absorption stripe of 1990 cm^{-1} was found. Frequency valence vibration stripes of 2020, 2040, and 2070 cm^{-1} had another relative intensity (fig. 2.5). An absorption stripe of 1500 cm^{-1} was found in a spectrum as a result of the formation of a coordinate bond olefin—cobalt. This proves the presence of $\text{HCo}(\text{CO})_4$ and propylene in the sample of the π -complex.

During the reaction there was a change in the intensity of the absorption stripes of 1500 cm^{-1} and 1990 cm^{-1} : The bigger was the 1500 cm^{-1} stripe — the bigger was the 1990 cm^{-1} one. The intensity of these stripes kept decreasing during the reaction, and when samples were taken at the end of the reaction, stripe 1500 cm^{-1} was not there (fig. 2.6). This data characterizes the change in the contents of the π -complex during the reaction that occurred in the IR-spectra as a change in the intensity of the absorption stripe 1500 cm^{-1} .

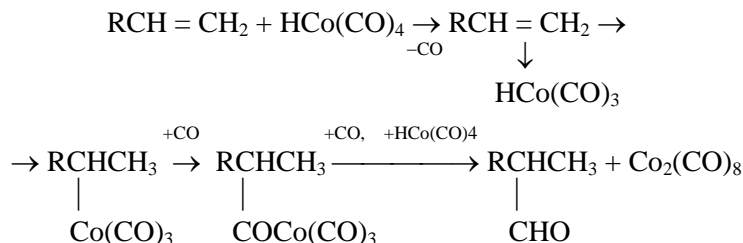
Reaction mixture samples, taken at the induction period, were freed of $\text{HCo}(\text{CO})_4$, then kept at room temperature. The spectral analyses

of the samples showed the valence vibration frequency of the carbonyl group equal to about 2007 cm^{-1} and 2107 cm^{-1} , which is characteristic for acylcobaltcarbonyls. This proved the capability of the π -complex $\text{HCo}(\text{CO})_4$ and propylene to transform into acylcobaltcarbonyl — the next intermediate compound of the hydroformylation reaction.

The qualitative definition of the contents of π -complex $\text{HCo}(\text{CO})_4$ with propylene has shown that on the fifth minute of the reaction, the amount of cobalt bonded to the π -complex, equals 1.43 % to 1.86 % of that introduced into the system in the form of $\text{HCo}(\text{CO})_4$. At the end of the induction period this equaled to about 5.7 % to 6.2 % of the cobalt bonded to the π -complex. The data on the concentration of the π -complex in the system, received via the cobalt analyses, well coincided with the amount of discharged carbon oxide during the π -complex formation via the reaction:.



Thus, it was proven that the stoichiometric interaction of hydro-corbanyl cobalt with olefins proceeds along this scheme:



But is the stoichiometric interaction scheme of $\text{HCo}(\text{CO})_4$ with $\text{RCH} = \text{CH}_2$ proper for aldehyde catalytic synthesis from olefins, carbon oxide, and hydrogen in the presence of carbonyls of cobalt?

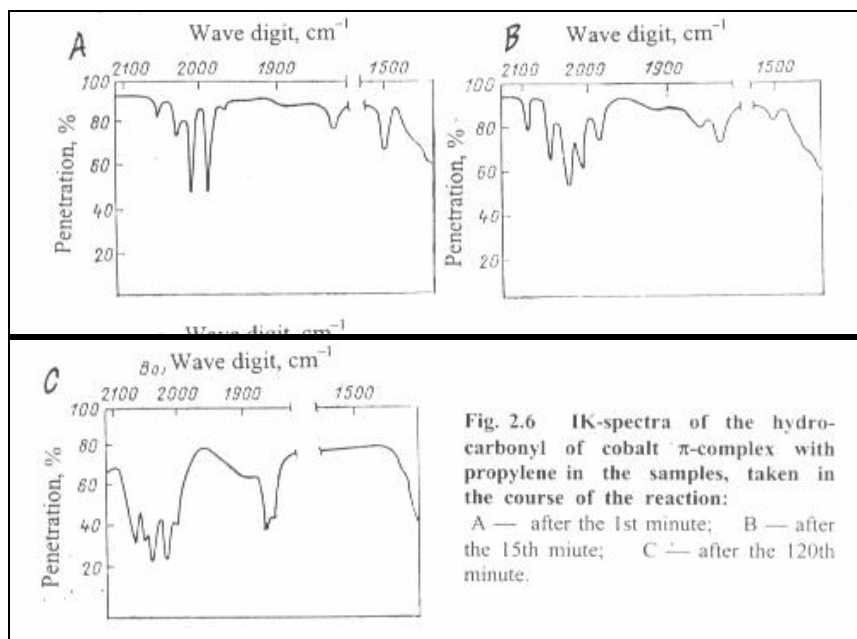


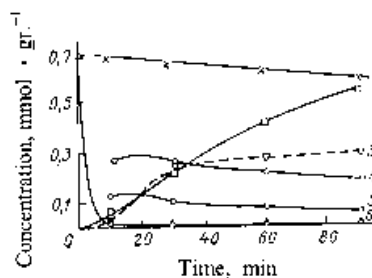
Fig. 2.6 IR-spectra of the hydrocarbonyl of cobalt π -complex with propylene in the samples, taken in the course of the reaction:

A — after the 1st minute; B — after the 15th minute; C — after the 120th minute.

Fig. 2.7 Kinetic curves of hydrocarbonyl-cobalt reactions with 1-hexane under conditions of catalyst synthesis:

1 - total cobalt-containing compounds,
2 - aldehydes C_7 ; 3 - $Co_2(CO)_8$,
4 - acylcarbonyls; 5 - alkylcarbonyls;
6 - $HCo(CO)_4$.

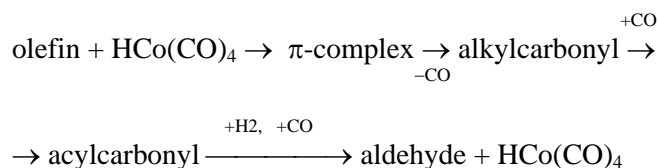
Temperature - $70^\circ C$;
Synthesis-gas pressure - 3.2 MPa;
initial concentration of 1-hexane -
 $3.5 \text{ mmol} \times g^{-1}$; solvent -- heptane.



Studying the kinetics of interaction $HCo(CO)_4$ with 1-hexane under conditions of catalytic synthesis, it was found that when the pressure and temperature increased, the concentration of all the defined cobalt compounds, and their sum does not change, as compared to that of the stoichiometric synthesis.

To make this more convincing, it is enough to compare the kinetic curves showing the change in the product concentration under conditions of catalytic synthesis, shown in fig. 2.7, with kinetic curves — fig. 2.3. Here we have a smooth transition into an area of catalytic synthesis where the concentration of intermediate compounds changes but slightly.

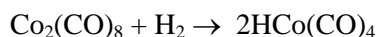
This research allows making a conclusion to the effect that the reaction for the hydro-formylation of olefins, catalyzed by cobalt carbonyls, proceeds along the following scheme:



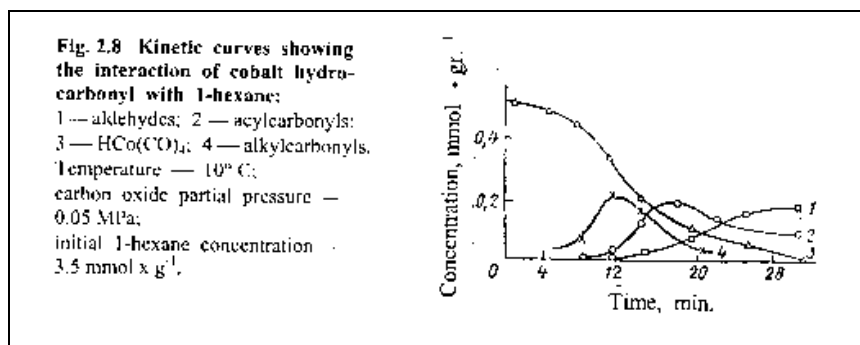
2.2 KINETICS OF COBALT HYDROCARBONYL INTERACTIONS WITH OLEFINS and NATURE OF HYDROFORMYLATION CHAIN REACTIONS

When studying the hydroformylation reaction mechanism, one of the most important kinetic regularities is the negative influence of the carbon oxide concentration on the reaction speed [40, 59]. Namely this was the defining point when most of the hypotheses on reaction mechanisms came into being. Breslow and Heck envisioned the influence of partial pressure (concentration) of carbon oxide on the speed of the breakup of acylcobaltcarbonyl. Indeed, the indicated reaction, with proper treatment, slowed down with the increase of the pressure in the carbon oxide.

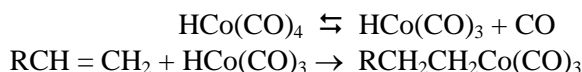
Some authors supposed that the influence of carbon oxide concentration is observed on the interaction stage of cobalt hydrocarbonyl with olefin. There were also suggestions made to the effect that the increase of the carbon oxide pressure slows down the transition of dicobaltoctacarbonyl into hydrocarbonyl as follows:



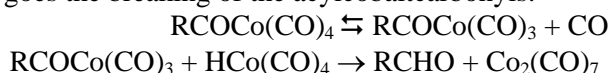
that is, into the initial stage of the process [60, 61].



Then it was found that the decrease of the carbon oxide concentration accelerates the alkylcarbonyl formation stage and the breaking of the cobalt acylcarbonyls (fig. 2.8 & 2.3). Two hypotheses were experimentally confirmed that presupposed a negative influence of carbon oxide concentration when alkylcarbonyl is formed:



likewise goes the breaking of the acylcobaltcarbonyls:



It was found that the curve showing the decrease in the hydrocarbonyl of cobalt concentration during the reaction with olefin has an S-like form with a prominent induction period (fig. 2.8) that is, there was auto-acceleration in this reaction.

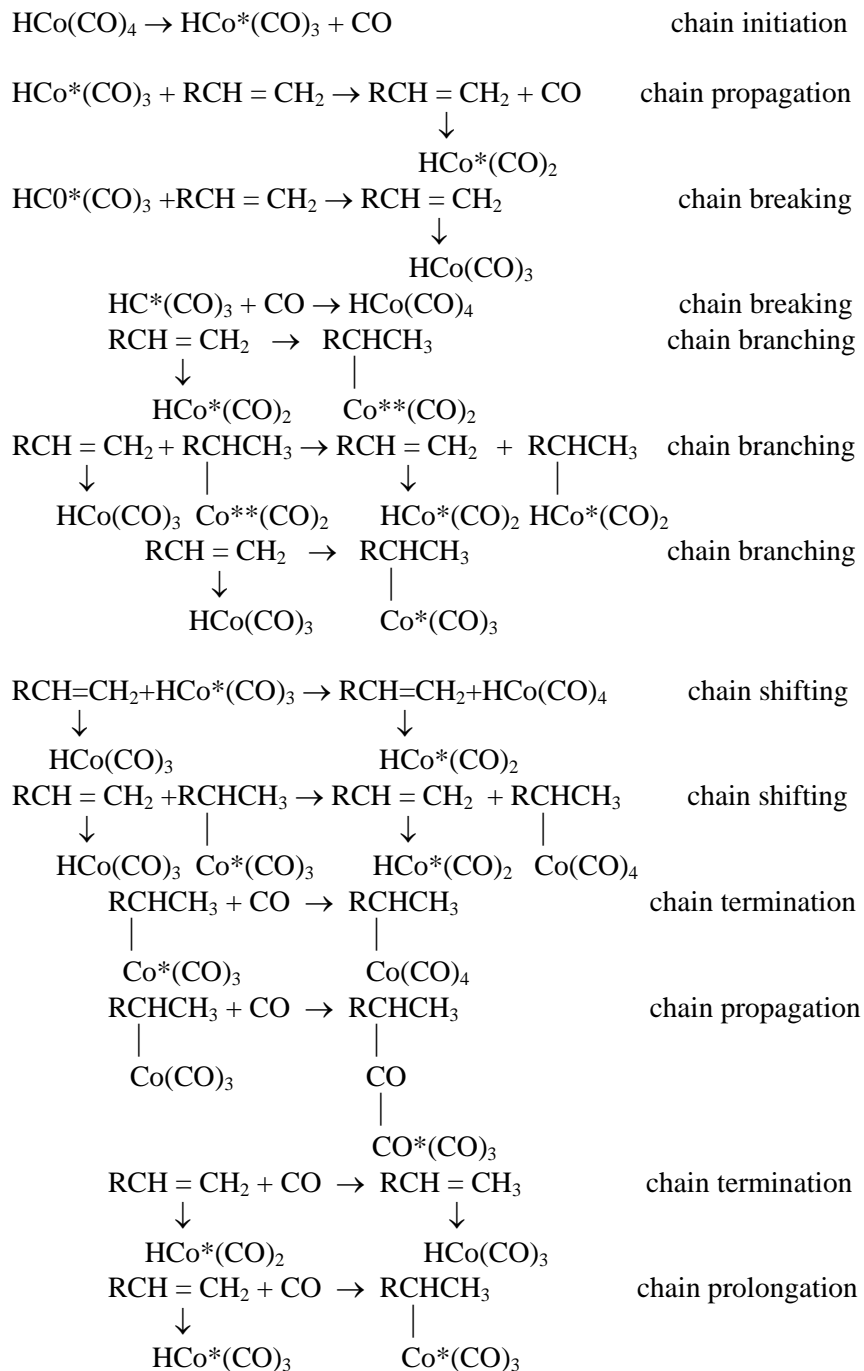
One can readily explain the observed kinetic regularities by imagining that the catalytic active compounds in the hydroformylation reaction are coordinate unsaturated complex compounds [62]. Conences are formed along the chain mechanism [63, 64].

Note: *Unsaturated complex compounds* will further be referred to as *conences*. This contraction will allow forming combinations like *conence reactions*.

(P.S. The hypothesis about the catalytic activity of the unfilled complexes, very well explains the negative influence of the increase of the carbon oxide concentration on the reaction speed).

The hydroformylation reaction mechanism, including the stages of interaction of $\text{HCo}(\text{CO})_4$ with olefins, can be presented in the form of

the following scheme which shows the chain process. The conences are marked with asterisk (*) symbols.



Aldehydes are formed via the following reactions:



The correctness of this scheme is certified by a number of experimental facts. As already mentioned, the interaction reaction of $\text{HCo}(\text{CO})_4$ with olefins has a definite induction period and is conditioned by the need to first form conences. If this supposition is proper, the addition to the initial reaction mixture of the product's sample that was taken at the end of the induction period and stored without carbon oxide, in order to avert the transition of the conences into saturated compounds, causes the disappearance of the induction period.

Indeed, it is obvious that the samples introduced to the reaction mixture on the third minute (fig. 2.9), taken from a previous test (for example, *on the 15th minute — the end of the induction period, connected with the preliminary conence formation in the reaction system, or on the 60th–70th minute — the end of the reaction, there are conences in the reaction system*) and having been stored in an atmosphere of nitrogen at minus 60° C, this completely liquidates the induction period. Another such operation with a sample, held in an atmosphere of carbon oxide, did not cause a decrease in the induction period [65].

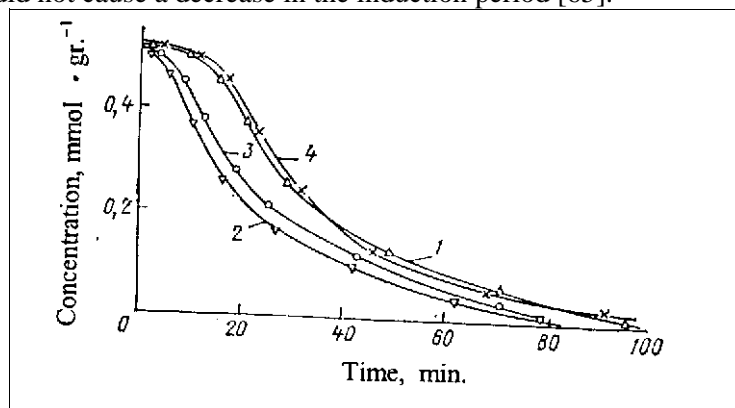


Fig. 2.9 Kinetic interaction curves of $\text{HCo}(\text{CO})_4$ with 1-hexane in the presence of initializing additions:

1 — without additions; 2 — with additions of interaction products taken at the alkylcarbonyl formation stage; 3 — with additions of interaction products taken at the end of the reaction; 4 — with the addition of interaction products preliminarily treated with carbon oxide.

To substantiate the value of the chain reaction mechanism, the influence of additives on the interaction speed of $\text{HCo}(\text{CO})_4$ with 1-

hexane was studied. The additives used were $\text{Co}_2(\text{CO})_8$, $[\text{Rh}(\text{CO})_2\text{Cl}]_2$, and coordinate-unsaturated forms of conences, received from dicobalt-octacarbonyl and rhodium carbonylchloride by blowing argon through the mixtures of these compounds in heptane at room temperature. The reverse saturation of conences up to coordinate-saturated forms was conducted by blowing carbon oxide under the same conditions.

The influence of the additives on the hydroformylation reaction speed of 1-hexane in the presence of $\text{HCo}(\text{CO})_4$ was defined by the absorption speed of carbon oxide. (fig.2.10 & 2.11). The introduction of small additives to the reaction's mixture, independently of the received conences, caused an abrupt decrease of the induction period, while the introduction of these additives after the conence absorption (up to the coordinately-absorbed complexes or initial carbonyls) did not influence the hydroformylation reaction speed at all. The effect of the additives depended on the concentration of the introduced conences.

Thus the accelerated action of the additives with conences confirms the fact that hydroformylation reactions proceed via conence formation that play the role of intermediate active particles.

The change of the degree of the coordinate non-saturation of cobalt during hydroformylation can be evaluated quantitatively. Samples of the reaction's mixture were analyzed at different times during the process after a stoichiometric 1-hexane hydroformylation reaction to find out the contents of carbon oxide.

The calculation of the degree of conence contents in the cobalt of the samples was carried out in accordance with the amount of carbon oxide that was discharged during the breaking of the cobalt carbonyls via the iodine, and by the initial $\text{HCo}(\text{CO})_4$ concentration in the system. See the data in fig. 2.12. It was found that the amount of carbon oxide, bonding to the cobalt, changes in the course of the reaction. The degree of 'conecity' first increases from 1 (coordinate saturated form) to 1.20 – 1.31, then gradually diminishes towards the end of the reaction until it becomes 1 again, which corresponds to the absence of conences.

Simultaneously, the coordinate saturation of cobalt in the samples, gathered in the course of the reaction, and kept in an atmosphere of carbon oxide, is equal to 1, which proves that the conences have transited into coordinate-saturated forms.

The maximum on the curve of the coordinate unsaturated cobalt corresponds to the maximal reaction speed along the kinetic curve showing the absorption of carbon oxide, which, naturally, is explained by the proportionality of the reaction speed in the hydroformylation of the concentration of the conences in the system.

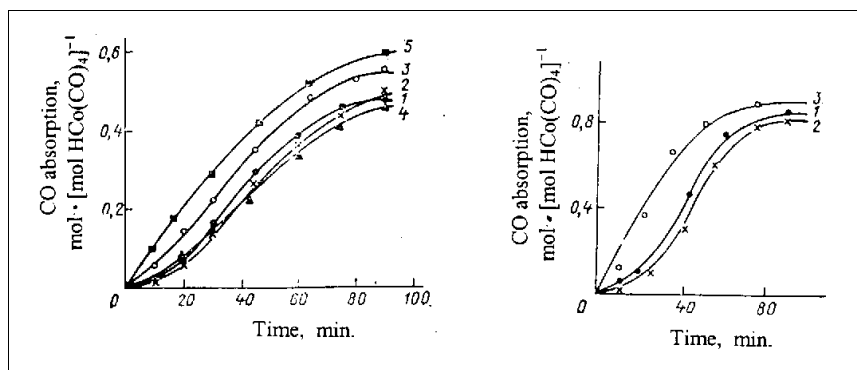


Fig. 2.10 Kinetic curves showing absorption of carbon oxide during the hydro- formylation reaction of 1-hexane, catalyzed by hydrocarbonyl of cobalt with the addition of cobalt conences:

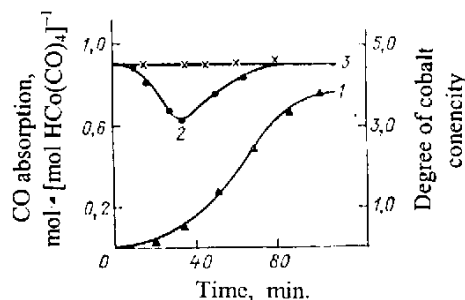
1 – no additions; 2 – with $\text{Co}_2(\text{CO})_8$ (blown with argon and carbon oxide); 3 – with $\text{Co}_2(\text{CO})_8$ added (degree of 'conency' 1.12; received via blown nitrogen); 4 – $\text{Co}_2(\text{CO})_8$ added; 5 – $\text{Co}_2(\text{CO})_8$ added (degree of conency 1.23); received via blown nitrogen.

Fig. 2.11 Kinetic curves showing carbon oxide absorption during the hydro- formylation reaction of 1-hexane, catalyzed hydrocarbonyl of cobalt with the addition of rhodium conences:

1 – no additions; 2 – $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ added;
3 – addition of conences received from $[\text{Rh}(\text{CO})_2\text{Cl}]_2$.

Fig. 2.12 Change of the 'conency' degree in cobalt during the 1-hexane hydro-formylation reaction:

1 – carbon oxide absorption;
2 – degree of 'conency' of cobalt in samples of reaction mixtures treated before being broken up by carbon oxide.
Temp. 10°C ; carbon oxide's partial pressure 0.11 MPa;
initial concentration:
 $\text{HCo}(\text{CO})_4$, $0.35 \text{ mmol} \times \text{g}^{-1}$,
1-hexane $2.5 \times \text{g}^{-1}$, solvent – heptane.



The received data speaks to the effect that the offered conence branched chain hydroformylation reaction mechanism is confirmed by the following experimental facts:

- 1) The reaction is accelerated thanks to the conence additives (independent of their nature).
- 2) There is no influence of these additives after their absorption.
- 3) There is a common influence of the conence additives on the hydroformylation reaction, on the induction period, and on their coordinate non-saturation.
- 4) The S-formed kinetic curves show the use of the reagents and the formation of the reaction's products.
- 5) The braking (slow-down) action of the carbon oxide on the speed of the hydroformylation reaction is obvious.

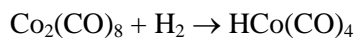
The conence branched chain hydroformylation reaction mechanism explains the contradictions between the reaction speeds of the dicobaltoctacarbonyl transition into hydrocarbonyl of cobalt [41], the transition of acylcobaltcarbonyls into aldehydes [37], and the total hydroformylation reaction speed, found in a separate study of kinetics in separate stages of the total process. Though the speed of each of these stages '*in the pure form*' is smaller than the total speed of the process, they all accelerate when there is a big concentration of coordinate unsaturated particles in the reaction's system, which are formed on other stages of the mechanism, since both reactions are of the conence type.

The received kinetic data is also explained by the radical mechanism of the process. In this case the first stage of the process is the homolytic stage of the breaking of the cobalt hydrocarbonyl as follows:

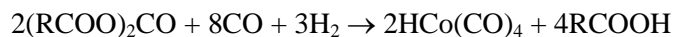


In spite of this, unexplainable was the braking (slow-down) action in the process of molecular carbon oxide, and the dissociation of $\text{HCo}(\text{CO})_4$, which was quite problematic being of a radical type.

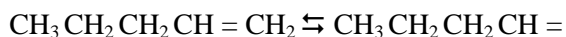
It is known that there are many reactions where metal carbonyls have common kinetic regularities (like the reverse dependence of the chemical reaction speed on the partial pressure of carbon oxide when it increases beyond a certain level and is close to the minimum required to guarantee stability of the metal carbonyls). Such a phenomenon was observed when studying the formation reactions of cobalt hydro-carbonyl out of dicobaltoctacarbonyl [60]:



the formation of carbonyl cobalt out of its salts [61]:

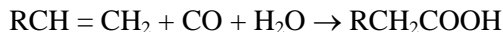


the isomerization of olefins in the presence of metal carbonyls [66]:





hydrocarboxyl olefin treatment in the presence of metal carbonyls [67]:



hydrometoxyformylation [68]:



In each concrete case the negative influence of carbon oxide on the reaction speed was explained with the help of various schemes. It is clear that the observed kinetic regularities in all these reactions can better be explained on the basis of the hypothesis concerning the catalytic activity of the coordinate-unsaturated complex compounds.

The decrease in the reaction speed with the participation of metal-complex catalysts during the ligand concentration increase in the reaction's mixture, was observed in other cases too, for example, during the oxidation and isomerization of olefins on chloride palladium [69, 70].

When L.Nikolayev studied the breaking of hydrogen peroxide into copper complexes, he spoke to the effect that it was the coordinate unsaturated compounds that were catalytically active in this process [71].

Thus, considering the importance of reactions with conence participation for many oxosynthesis process stages and their common character for the metal-complex catalyst, it is worth dwelling upon conence reactions and the catalysis of coordinate compounds, and even put such material into a separate section.

2.3 THEORY OF CONENCE REACTIONS

The above given scheme of the hydroformylation mechanism is made up of a number of consecutive and parallel reactions of complex compounds. Further in this book you will find material on the reaction mechanisms for the formation and breaking of cobalt carbonyls, which is also the result of studying the reactions of complex compounds.

For better understanding and additional confirmation of the value of the suggested reaction mechanisms, the authors considered it necessary to give more details on the reactions of complex compounds. In the framework of this book, it is important if we consider that the new precepts, or those that are given for the first time, when describing the coordinate compound reactions, were expressed and developed, first of all, as a result of researches in the field of reaction mechanisms.

As any theory in general, the theory of conence reactions is a chance theory, a theory of probability, and, as all chemical theories, this is a qualitative one, that is, its predictable power is limited by *'whatever*

happens'. The degree of this prediction increases when evaluating reactions with close chemical properties in their compounds, for some of which the experimental results are known.

The main task of this theory, however, is to explain the available experimental material with the fewest possible additional suppositions.

The method of naming the reactions according to the type of particles that enter the reaction spontaneously is widely accepted in chemistry. For example: ionic and radical reactions.

There is a more fractional division. Ionic reactions include cation reactions (such as carbon-cation ones, carbon-anion ones, etc.).

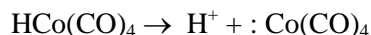
The intermediate active compounds in complex compound reactions (i.e., particles that react with other compounds) are the above mentioned three types of intermediate active compounds since the coordinate bond can dissociate with the formation of ions and radicals:



and the Lewis acids and bases:



All three of the formed particles M^*L_{n-1} are coordinate and unsaturated, and have unfilled orbitals with the exception of a rare dissociation case of the following type:



Such complex compounds that have vacant orbitals are considered as being *coordinate unsaturated* ones. As a rule, the number of electrons in the central atom of such compounds is smaller than that in the following one — in the Mendeleyev Table of inert gases.

Conence reactions are those where the conences are the intermediate compounds. The name itself: '*coordinate unsaturated compound*' has long been used in chemical literature to indicate coordinate compounds with the number of ligands smaller than that in the coordinate saturated compound [73].

The new term has additional sense since it singles out the types of reactions that differ from ionic and radical ones, relative to the character of the intermediate particles. The main mass of conences, besides those in the free orbital in the outermost shell, also contains non-bonding electrons, i.e., acids and Lewis bases simultaneously.

The logic of singling out the conences into a separate class with a special name is not only due to the specific realm of phenomena where

conences play a role, but also to the width of this realm (coordinate compound reactions, complex catalyst catalysis).

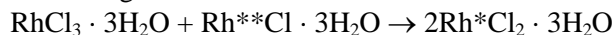
Coordinate unsaturated compounds were chosen as intermediates in the ligand substitution reactions. The studies of these reactions were conducted on a wide front and are described in a wonderful monograph by F.Basolo and R.Pearson [73]. The reaction substitution mechanism, proceeding via the dissociation mechanism, presupposed intermediate conence formation.

The hypothesis for chain reactions was meant to explain a number of complex compound reactions and, first of all, the interaction of cobalt hydrocarbonyl with olefins [64]. At first it was supposed that the coordinate compounds enter reaction in the form of conences, that is, the reaction speed is controlled by the speed of their formation. Further it was supposed that new conences were formed not only as a result of dissociation, but also as a result of the interaction of the conences with coordinate saturated compounds (chain origin) or as a result of the reaction inside the complex (introduction reaction, chain branching).

The theory of conence reactions presupposes the following:

1) As a rule, coordinate compounds enter the reaction process in the form of conences.

2) Conences, no matter what kind (ion conences, radical conences, etc.) are capable of taking part in analogous reactions. Thus, if we know the following reaction:



which is generally presented as:



we can suppose there is a reaction like:

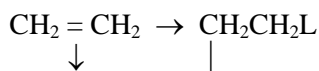


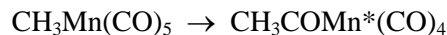
Regarding the original hypothesis concerning the mechanism for complex compound reactions, it is necessary to consider all the possible interactions (to begin with — known or analogous ones) both initial ones, and those forming compounds during the reaction. The last rule is a common one, for theoretically structuring a mechanism for any reaction, and is mentioned here only because it will be widely used later in reference to conence reactions.

Conences can be formed as a result of dissociation reactions:



introduction reactions:





and elimination restoration reactions:



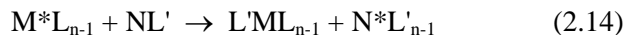
Conences can interact with ligands, with coordinate saturated compounds, and with themselves. The interaction of a conence with a ligand can lead to the formation of a coordinate saturated compound along the following scheme:



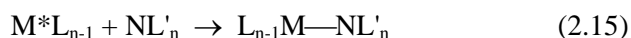
or it can lead to a replacement (or knock out) of the ligand at the expense of the energy discharged during the bonding of the entering ligand:



The interaction of the conence with the coordinate saturated compound can proceed with the formation of another conence:



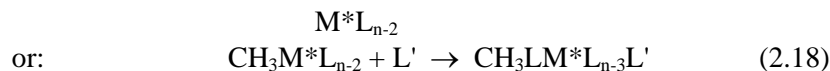
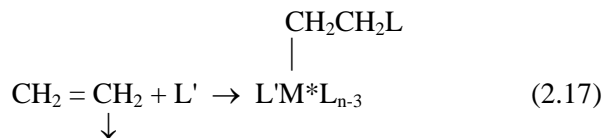
or with the formation of a cluster:



The interaction of two conences can also proceed with a cluster formation as follows:



Interactions such as conence — ligand can lead to the introduction reaction as follows:



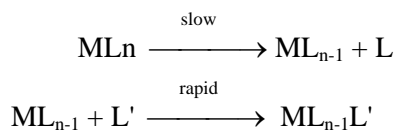
All the above-indicated types of conence reactions are *common coordinate compound* reactions.

Reaction 2.12 is the second stage of the ligand substitution reaction that proceeds along the dissociation mechanism. Reaction 2.13 is a ligand substitution reaction proceeding along the association mechanism. As a rule, the ligand substitution reaction proceeds by the conences along the association mechanism, for example, the ligand substitution reactions — in flat square complexes [73]. Reaction 2.14 is a ligand redistribution reaction along whose mechanism numerous oxide restoration reactions take place. Reaction 2.16 is typical for many carbonyl complexes.

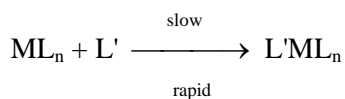
The given reactions are elementary in reference to many transformations that had been studied in coordinate compound chemistry (ligand substitution and exchange, introduction, oxide bonding, and elimination restoration).

2.3.1 LIGAND SUBSTITUTION AND LIGAND EXCHANGE REACTIONS

Substitution reactions (exchange of one ligand in a complex for a different one) and *exchange reactions* (exchange of one ligand for an identical radioactive one) are the most widely studied of the complex compound reactions. In order to explain their kinetic regularities, two main mechanisms have been offered — the dissociation mechanism:



and the association mechanism:





The *dissociation mechanism* describes the reactions with the first order of magnitude in the complex and the zero order of magnitude in the ligand, while the *association mechanism* has the first order of magnitude in both the complex compound and in the ligand. To explain the often-observed significant deviations in the orders of magnitude in the reagents, a suggestion was made to the effect that both of the above mentioned mechanisms are extreme and part of the reaction proceeds via a mixed mechanism in which one of the indicated routes prevails.

The additional suppositions, however, did not explain any other observed anomalies in the procedure of the ligand *substitution* and *exchange* reactions. For example:

1) The speed exchange constants CO in row Ni(CO)₄, Fe(CO)₅, Cr(CO)₆ comprise relatively $7.8 \times 10^{-4} \text{ sec}^{-1}$ at 0°C, four years (half-period exchange) at 25°C and $2 \times 10^{-5} \text{ sec}^{-1}$ at 117°C (the reaction proceeds via the dissociation mechanism, therefore the constants are calculated as reaction constants of the first order of magnitude) while the bonding energy M—C decreases in this row [73];

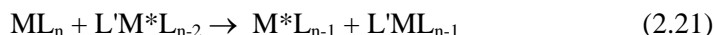
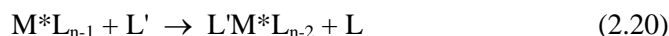
2) The speed constants and the activation parameters of the substitution and exchange reactions CO in Ni(CO)₄ into P(C₆H₅)₂ and ¹⁴CO are very much alike since both reactions proceed along the dissociation mechanism. Contrary to what was expected, for the substitution reaction we have $K = 4 \times 10^{-4} \text{ sec}^{-1}$ at 0°C, $\Delta H = 85 \text{ kJ}$ and $\Delta S = +2 \text{ e.u.}$ while for the exchange reaction: $K = 8 \times 10^{-4} \text{ sec}^{-1}$, $\Delta H = 49 \text{ kJ}$ and $\Delta S^* = -26 \text{ e.u.}$. Analogous anomalies have also been observed when comparing the kinetic exchange and substitution parameters in reactions like Hg[Co(CO)₄]₂ and other compounds.

3) From the position of substitution reaction kinetics it is impossible to explain the high exchange speed of CO in Co₂(CO)₈ as compared to the carbonyls of other metals.

The above-mentioned anomalies point to the incompleteness of the description of the ligand substitution and exchange reactions' mechanisms with the help of simple dissociation or association schemes.

According to the conence reaction theory, two types of substitution and exchange reactions are possible when: 1) a coordinate *saturated* compound is introduced to the reaction; 2) a coordinate *unsaturated* compound is introduced to the reaction.

In the first case the reaction mechanism includes these stages:



Interactions *conence* — *conence* and *conence* — *coordinate saturated compound* that lead to cluster formation, and the interaction of conences with solvents, were not considered in this mechanism, since the consideration of these interactions would only complicate the comprehensibility of the question — without introducing nuances that were required for further discussions. This is why the given mechanism can be regarded as the first (most simplified) approximation.

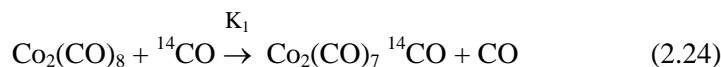
Compared with the above given dissociation mechanism, this one has additional stages 2.20 and 2.21 whose possibilities have been previously described.

The mechanism that includes reactions 2.19 to 2.23 is called a *chain conence mechanism* analogously to the *chain radical mechanism*; 2.19 — *chain origin reaction*, 2.20 — *chain continuation*, 2.21 — *chain transfer*, 2.22 and 2.23 — *chain break*. Route 2.19 — *simple dissociation scheme*, 2.22 — *special case*.

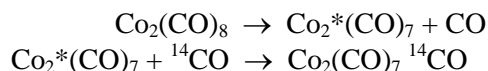
Any non-chain mechanism can be regarded as a special case of a chain mechanism with a chain length of zero. Reaction 2.19 is greatly endothermic; from the energy viewpoint route 2.19, 2.20, 2.21, is more preferable than 2.19, 2.22 because one endothermic act is accompanied by n exchange acts proceeding along the reaction with an exothermic (in the case of substitution) or a zero thermal effect (in the case of exchange). During the reaction along this route, the most characteristic shift of energy from the forming particles to the initial ones is observed (i.e., positive energetic reverse bonding of reactions 2.20, 2.21).

The positive energy reverse bonding is the main physical essence of chain processes and a sufficient sign to characterize this process as a chain one, i.e., the reaction mechanism which includes stages 2.19 — 2.21, can be regarded as a chain mechanism.

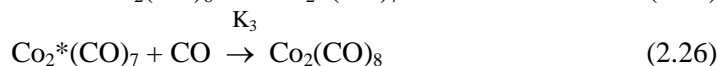
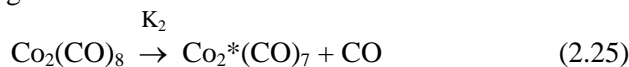
The principles of chain conence reactions offer mechanisms of concrete reactions that fully agree with their kinetic characteristics. Thus the following exchange reaction:



has a speed constant of $K_1 = 1.5 \times 10^{-3} \text{ sec}^{-1}$ [74]. When using the simple dissociation scheme, the mechanism of this reaction includes the following stages:



However, having studied kinetic reactions:

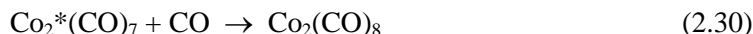
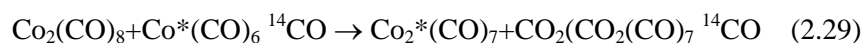
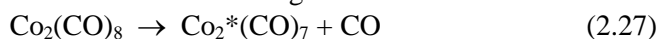


It was found that $K_2 = 2 \cdot 10^{-5} \text{ sec}^{-1}$, and $K_3 = 1.1 \cdot 10^{-2} \text{ L} \cdot (\text{mol} \times \text{sec})^{-1}$

It is quite evident that a comparison of the speed constant values of reactions 2.25 and 2.24 allows doing away with the use of the dissociation scheme for describing reaction mechanism 2.24.

The use of the principles of conence chain reactions serves as a record of possible interactions like *conence* — *coordinate saturated compound*, and *conence* — *ligand* with the formation of new conences.

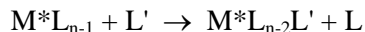
This record leads to the following mechanism of reaction 2.24:



Since this reaction has the first order of magnitude along $\text{Co}_2(\text{CO})_8$, it is obvious that the speed of stage 2.29 does not limit the process. Considering this fact, it was found that 2.28 has a speed constant of $K = 10 \text{ L} \cdot (\text{mol} \cdot \text{sec})^{-1}$ with an activation energy of $E = 21 \text{ kJ/mol}^{-1}$.

The much greater reaction speed constant of 2.28 as compared to that of reaction 2.30, and the much smaller activation energy when including carbon oxide with the simultaneous elimination of the ligand, signifies that this reaction proceeds more readily than the simple saturation process. That is, it signifies that this reaction's speed is being controlled by spatial difficulties, and not by the energy of bond M—L.

The chain character of the mechanism and the defining role of the following chain continuation reaction:

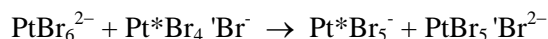
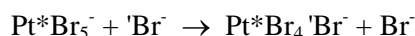
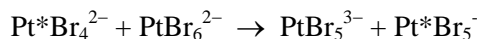
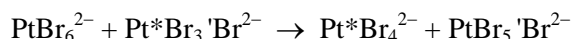
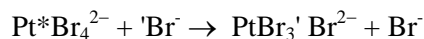


which proceeds practically with a zero thermal effect and very well explains the above given anomalies. The increase in the exchange speed of CO in the carbonyl row $Ni(CO)_4 > Fe(CO)_5 > Cr(CO)_6$ is explained by the consistent increase of the screening of the central atom. The various reaction exchange speeds for ligands of various structure [for example, CO exchanges for ^{14}CO more readily than CO exchanges for $P(C_6H_5)_3$] can be explained by the various volumes of the ligands, that is, by spatial difficulties for the chain continuation reaction.

The chain mechanism is also proven to exist in photochemical ligand exchange reactions in $PtCl_6^{2-}$ and $PtBr_6^{2-}$ on marked Cl^- and Br^- [75]. It was supposed that the chain carriers would be $PtCl_5^{2-}$ and $PtBr_4^{2-}$ that are actually conences. Therefore, the indicated reactions proceed along the chain conence mechanism. The complete mechanism schemes of these reactions are given here.

[The single quotes (') signify marked bromine ions.]

$_{hv}$



The branched chain mechanism reaction very well agrees with the high quantum discharge ($\phi \gg 1$).

When studying the ligand substitution reactions, it was found that as a rule, the substitution reaction in octahedron complexes proceed along the dissociation mechanism (S_{N1}), while in the flat-square complexes — along the association mechanism (S_{N2}). The number of exceptions to this rule, however, is great. Thus, the ligand substitution reaction in octahedron halogen complexes Pt(IV) has the first order of magnitude in the complex and ligand, which is characteristic for the association mechanism [76]. Some complexes Pt(IV) had reactions of

the second order of magnitude, and their reaction speeds depended on the type of substitution ligand [77].

Complexes $\text{Pt}(\text{NH}_3)_2\text{Cl}_3^+$ and $\text{PtEn}(\text{NH}_3)_3(\text{NO}_2)\text{ClBr}$ where En is the ethylene-diamine that reacts with pyridine along the reaction of the second order of magnitude, $\text{Pt}(\text{NH}_3)_4\text{Cl}_2^{2+}$ also reacts along the reaction of the second order of magnitude with ammonia. Pyridine reacts with $\text{trans-Pt}(\text{NH}_3)_4(\text{NO}_2)\text{Cl}^{2+}$ more rapidly than with ammonia. There are exceptions to the substitution rules in respect to carbonyl-octahedron complexes.

In most of the metal carbonyls, the ligand substitution reaction has the first order of magnitude along the complex, and the zero order along the ligand substitution reaction. Reactions $\text{Co}(\text{NO})(\text{CO})_3$, $\text{Fe}(\text{NO})_2(\text{CO})_2$, $\pi\text{-C}_5\text{H}_5\text{Rh}(\text{CO})_2$ and some others have the second order of magnitude in the substitution reaction. Relatively, it was supposed that the indicated reactions proceeded along mechanism $\text{S}_{\text{N}2}$ [73].

Mechanism $\text{S}_{\text{N}2}$ in these cases, is not only an exception to the rule concerning substitution reactions for complex compounds, but it contradicts the first principle of the conence theory according to which complex compounds enter reaction in the form of conences, since octahedron complexes are coordinate saturated compounds. The observed diversions and seeming contradictions can be explained in the framework of the theory by the greater role of the chain route (by the longer chain route).

Besides a qualitative explanation, one could expect that in some cases the chain transition reaction (2.21) could limit the process speed which should be reflected in its kinetics. Indeed, when studying the kinetics of the ligand exchange and substitution reactions in $\text{Pt}(\text{IV})$ complexes (for example: Cl^- in $\text{PtEn}_2\text{Cl}_2^{2+}$ on radioactive Cl^- and NO_2^-) it was found that the speed of the exchange reaction in the darkness adheres to the equation that amounts to the following [78]:

$$r = K [\text{Pt (II)}] [\text{Pt (IV)}] [\text{Cl}^-]$$

and the substitution reaction speed was equal to [79]:

$$r = K [\text{Pt (II)}] [\text{Pt (IV)}] [\text{NO}_2^-]$$

which well coincides with the chain conence scheme of the given reactions [that is, the interaction of the coordinate unsaturated complex Pt (IV) as the limiting stage of the process].

When introducing conences or compounds into the system (items that readily dissociate in solvent) the substitution reaction proceeds via equation 2.13, that is, along the scheme analogous to that of the

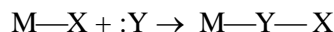
association mechanism. This reaction has the first order of magnitude in both the initial complex and the ligand substitute. Indeed, the substitution and exchange reactions for flat-square complexes, whose main mass consists of conences, have a total second order of magnitude. Still, further dissociation of the complex via the following equation is not excluded:



2.3.2 LIGAND INTRODUCTION REACTIONS

The ligand introduction reaction in complex compounds can be described by the following general scheme [80].

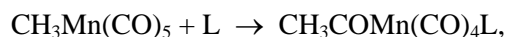
The details of this reaction are given in note [73].



where $X = H^-$, R^- , OR^- , NR_2^- , Cl^- , Br^- , I^- , or NR_3 , OH^- , or H_2O ; $Y = CO$, olefin, dyad, acetylene, $RCHO$, RCN , SO_2 , O_2 , or other unsaturated systems.

Group Y is coordinated to the metal before the reaction begins [73]. It is group X that migrates to group Y after coordination.

The most studied ligand introduction reaction is the already mentioned reaction:

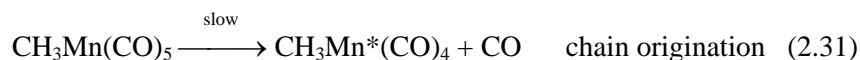


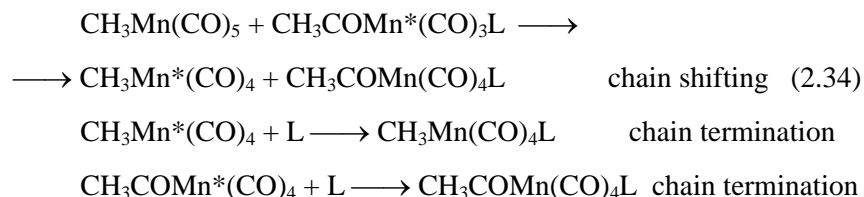
which depicts the introduction of carbon oxide to the acylpentacarbonyl of manganese.

It was supposed that the reaction proceeded via an intermediate reaction [81-83] that was either in the fifth-coordinated or had a solvent (S) molecule somewhere in the sixth-coordinated space:



However, the bond breaking force $CH_3 - Mn$, whose energy is very large, is unclear. This contradiction becomes understandable if we presuppose that the reaction proceeds along the chain conence mechanism as follows:

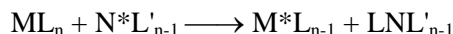




The unlikely endothermic reactions 2.31 and 2.32 serve only to originate the chain (appearance of conences in the system). The next stages of the mechanism are either exothermic 2.33, or proceed with a thermal effect close to zero 2.34.

2.3.3 OXIDIZING-RESTORATION REACTIONS IN COMPLEX COMPOUNDS

Oxidizing-restoration reactions in complex compounds are often described by the following equation:



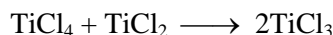
that is, such reactions are examples of chain transfer reactions in a chain conence mechanism.

If we put such reactions into a separate group of conence reactions, the ligand is usually transferred with a charge.

This group of reactions is on the borderline between oxidizing-restoration reactions and conence reactions. They can be regarded as either. Thus, reactions of the following type:



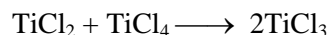
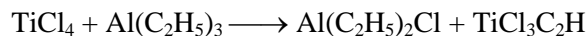
are related to conence reactions of the chain shift, while this type:



is related to oxidizing-restoration reactions.

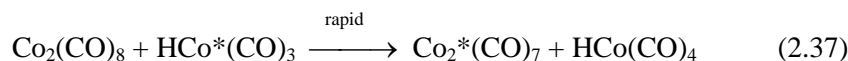
Generally, the reactions of both types stress the need to consider interaction reaction mechanisms that lead to chain transfer or chain branching. The presence of chain oxidizing-restoration reactions and that of conences confirms N.Semyonov's hypothesis about the increasing usage of chain processes.

An example of a chain branched oxidizing-restoration reaction is the reaction for catalyst formation and polymerization of olefins:

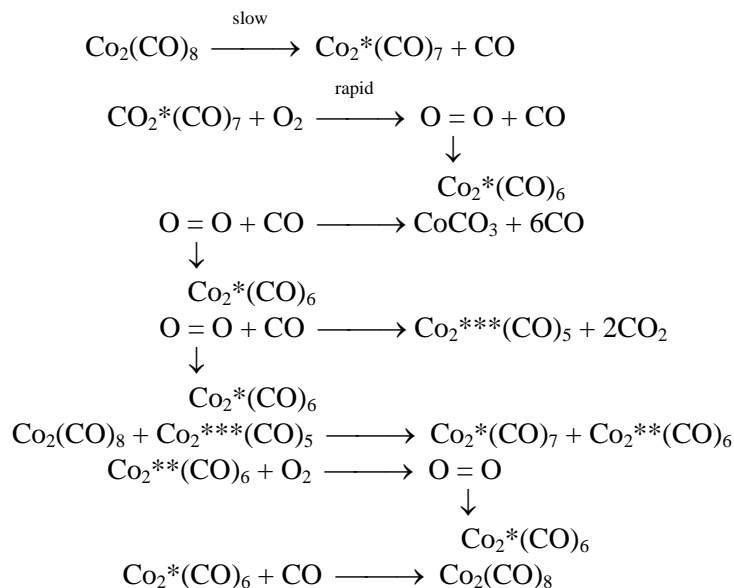


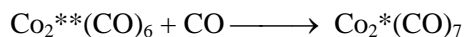
2.3.4 COMPLICATED CONENCE REACTIONS

Complicated conence reactions that include various types of the above described conence reactions as elementary stages, are regarded by us mainly as additional experimental confirmation of the reality of chain conence mechanisms. An example of a complicated conence reaction is the transition of dicobaltocarbonyl into hydrocarbonyl cobalt:



and the oxide carbonyl cobalt reaction with oxygen:





Data on kinetic reactions of 2.35 to 2.38 are given in section 3.1

The given dicobaltoctacarbonyl oxidation mechanism with oxygen is confirmed by the auto-catalytic nature of the reaction's (S-shaped kinetic curves in figure 2.13) to slow down the influence of the carbon oxide on the reaction speed (fig. 2.14) and on the contents of the gas phase when processing dicobaltoctacarbonyl with oxygen (table 2.1).

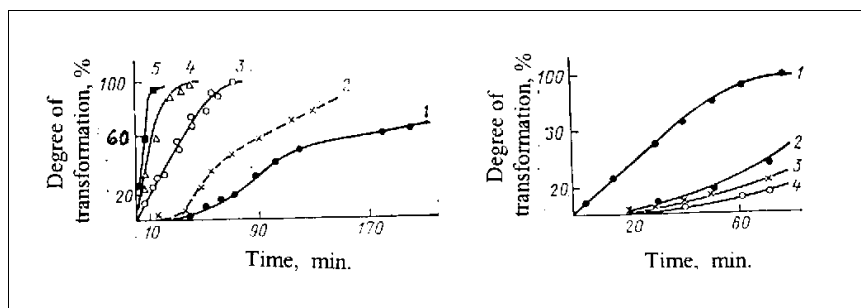


Fig. 2.13 Kinetic curves showing oxidation of dicobaltoctacarbonyl in cobalt carbonate:

Concentr. of cobalt in the initial product $0.047 \text{ mol} \times \text{L}^{-1}$; solvent – toluene. Temp. (in °C): 1 – 0°; 2 – 10°; 3 – 20°; 4 – 30°; 5 – 40°.

Fig. 2.14 Speed dependence of the dicobaltoctacarbonyl oxidation reaction on the contents of carbon oxide:

Temperature of oxidation: 20°C; contents of CO in oxygen-containing gas (% of volume): 1 – 0%; 2 – 38%; 3 – 50%; 4 – 69%.

TABLE 2.1

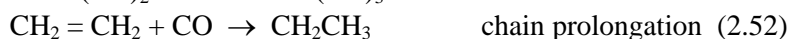
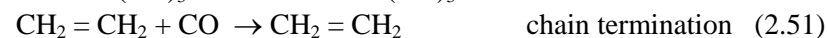
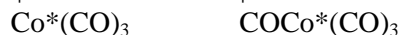
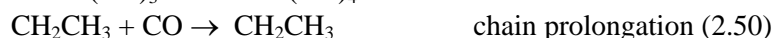
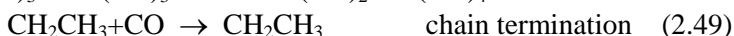
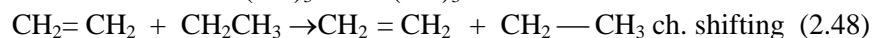
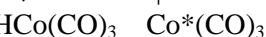
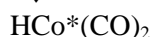
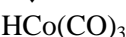
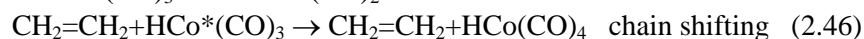
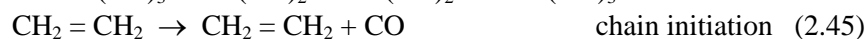
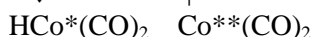
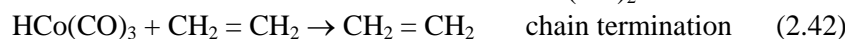
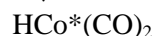
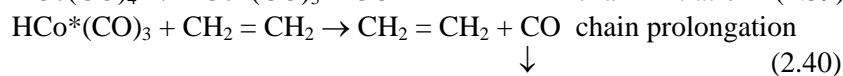
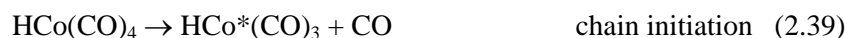
Contents Of Gas Mixtures When Oxidizing Dicobaltoctacarbonyl With Oxygen

Cobalt concentration in the initial compound is 0.61 mols per liter⁻¹

Temperature in °C	Composition of gas phase, in % of volume		Ratio CO : CO ₂ mol · mol ⁻¹
	CO	CO ₂	
50	94.7	6.3	≈ 15 : 1
30	81.5	18.5	4.4 : 1
35	79.0	21.0	3.8 : 1
20	80.0	20.0	4 : 1

The chain conence reactions were suggested after researches in cobalt hydrocarbonyl interactions with olefins, i.e., stoichiometric

hydroformylation reactions, which are widely studied conence chain reactions and are the most convenient when illustrating the main types of conence reactions or structuring a reaction along a conence chain mechanism. The reaction routes of stoichiometric hydroformylation up to the stage of alkylcarbonyl formation can be presented as follows:



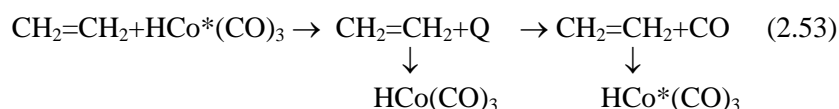


The main regularities of chain conence reactions coincide with those of chain reactions in the full sense of the word *chain* [85], namely:

1) The conence concentration during the reaction is higher than the balance (equilibrium) [64].

2) There is a positive reverse bonding (connection) which is used along routes 2.43, 2.45, and 2.48.

3) The energy of the previous stages is utilized to accomplish the next, for example, along routes 2.39 and 2.53:



4) The conence (active particle) does not disappear during the reaction except during the chain breaking.

5) When introducing coordinate saturated compounds into the reaction, the latter has an induction period that shortens when the conences are added.

The reaction capabilities of conences are defined by their electronic structure.

Conences, depending upon the number of valent electrons in the central atom and the nature of the ligands surrounding it, can be divided into *low-spin* and *high-spin* conences. Low-spin conences are actually acids or Lewis bases depending on the degree of acidity or baseness of the compound reacting with them. Since they are soft acids, the conences react actively with soft bases and acids (even among themselves) with the formation of clusters. The high-spin conences, in the main state, are bi-radicals so they can enter reactions just like radicals do.

Both the occupied and the vacant orbitals in the low-spin conences have practically the same energies, while in the high-spin conences the non-paired electrons are situated on orbitals with identical energies. Relatively, all conences, besides those in the main state, are in an agitated state with almost identical energies. For low-spin conences, the non-paired state is regarded as an agitated state, while for high-spin ones it is visa versa. Likewise does the reaction mechanism change, depending on the types of conences.

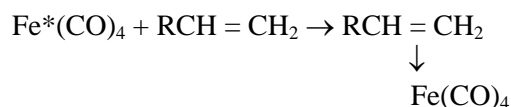
The use of this data allows, on many occasions, to offer a new reaction mechanism or give preference to one of the best. For example, it

is known that $\text{Fe}(\text{CO})_5$ reacts with olefins forming a π -complex, and also with CCl_4 forming radicals.

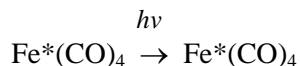
It is therefore obvious that we can explain the interactions of $\text{Fe}(\text{CO})_5$ + olefin and $\text{Fe}(\text{CO})_5$ + CCl_4 which are different in respect to the mechanism, but have a common first stage — the dissociation stage of the pentacarbonyl iron molecule:



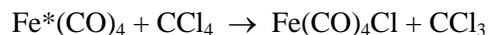
The dissociation of iron pentacarbonyl leads to the formation of conence $\text{Fe}^*(\text{CO})_4$. Carbon oxide — a strong field ligand [with conence $\text{Fe}^*(\text{CO})_4$] is a low-spin conence with a vacant orbital in the main state and with an energy close to that of a fully occupied orbital. A vacant orbital conditions the possibility of the formation of a π -complex during interaction with a soft basis (olefin molecule):



and with a bi-radical in the excited state:



The formed bi-radical enters reaction with CCl_4 with the formation of two radicals:



Experimental data well agrees with this explanation. Thus, if the formation of the π -complex with $\text{Fe}(\text{CO})_5$ can occur in the darkness, then the interaction of $\text{Fe}(\text{CO})_5$ with CCl_4 and the formation of radicals occurs only during light radiation.

The reaction capabilities of conences with vacant orbitals are defined mainly by the possibility of the electrons to bond to the vacant orbital of the conence. The degree of activity depends on the properties of the central atom and ligands that surround it. The activity of the conences increases in accordance with the increase of the electrophylity of the central atom, that is, when moving along the Mendeleyev Table of Elements upwards and to the right.

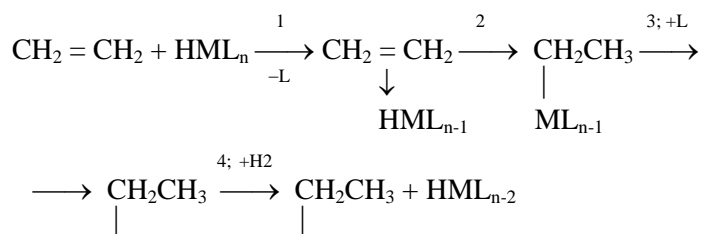
Electronegative ligands increase the activity of conences. The presence of easily transiting electrons in the ligands, like that of the π -electrons, causes a decrease in the conences' reaction capabilities. Analogous is the influence of ligands whose electrons with energies and

1) when the reaction speed is defined by the conence formation speed (such reactions proceed mainly as chain reactions);

Thus, the theory of conence reactions explains the main types of complex compound reactions — *ligand substitution*, *ligand exchange*, *ligand introduction*, and *oxide-restoration reactions*.

On the basis of understanding its elementary stages, this theory allows to offer schemes of complex reaction mechanisms with the involvement of complex compounds. Thus the theory of conence reactions allows to better realize the power of processes from the energetic viewpoint.

Catalysis in complex compounds of metals, being one of the most important directions in theoretical and applied research nowadays, we would like to offer the main catalysis mechanism scheme for complex compounds as follows: *A more complete scheme is proven experimentally for the hydroformylation reaction [64, 86].*





This scheme includes substitution reactions (stages 1 and 4) and introduction reactions (stages 2 and 3) as elementary stages.

In the catalysis of complex compounds, conence reactions are considered as elementary.

Catalyst mechanisms are based on possible conence reactions in the given system and are constructed in accordance with the main types of the given reactions. Thus we have three types of conence catalyses:

Type I — here the speed is defined by the conence formation speed (in all the studied cases the chain mechanism was obvious). *This is a chain conence catalysis.*

Type II — here the conence formation speed is great, while its reaction capabilities are small. *This is a specific conence catalysis*, since the reaction speed almost completely depends on the capability of the conences being formed.

Type III — here chain reactions take place on some stages of the catalytic cycle, while specific conence reactions take place on other stages. *This is a mixed conence catalysis.*

This is but a relative division since all depends not only on the type of reaction, but also on the conditions under which the reactions proceed. Indeed, when the temperature rises, in the common case, the number of conences will increase, that is, with the increase of the temperature it is possible there can be a transition of the chain conence reactions into specific conence reactions and, naturally, a change in the type of catalysis.

A conence chain catalysis is characteristic of slow dissociation in the reaction media of complex compounds. This is the best illustration of a catalyst chain mechanism. It is the only case when a catalyst is connected with the substratum throughout the chain process and guarantees the reaction process along the chain mechanism. For this type of conence catalysis, the conclusions about the mechanism on the basis of macro-kinetic data seem hardly effective because of the numerous routes and energy connections with other stages.

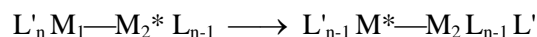
More reliable are the ideas about mechanisms based on possible and already known types of conence reactions. Most characteristic for conence chain catalysis is the reaction acceleration at the expense of accumulating the energy that is discharged in the course of the reaction, that is, the positive energy straight line and reverse bonding.

The main driving force for a specific conence catalysis is the formation of intermediate compounds which are more capable of reacting than the initial ones with a decreased activation energy and

running along a non-catalytic path. The conence concentration in the course of the reaction is close to that of the equilibrium.

The catalysis is actually a series of successive stages not connected energy-wise, where the conclusions about the mechanism and calculation of the constants of the mechanism's stages, considering the macro-kinetic data, are quite logic. Such catalysis is characteristic of rapid dissociation in reactions of complex compounds. In this case we can use the catalyst to perform a reverse reaction.

Coordinate unsaturated cluster compounds are known as *conence clusters*. Besides simple clusters, the conence clusters also pass on the chain to another reactor center not via a crash, but via an intermolecular shift of the ligand:



The surface metal atoms are surface cluster conences with a large number of metal—metal bonds. Relatively, the chain reactions on the surface of metal can proceed according to the conence mechanism along the cluster scheme, that is, with the shift of the ligand.

As already said, on various stages of the homogenous catalytic act, thanks to the energy discharge during the *conence—ligand* interaction, there can be a dissociation of other ligands (that used to belong to this conence) or a reaction between these ligands and the introduction reaction. As for the clusters, the discharged energy, as a result of the interaction of one of the cluster conences with a ligand, can cause reactions of the given atom with either the neighboring coordinate saturated ones or the coordinate unsaturated ones.

Besides the indicated reactions, there can be a change in the chemical nature of the conences closest to the reacting atom. Radicals, for example, can be formed (in the case of low-spin complexes) or visa versa, bi-radical conences (in the case of high-spin complexes) and can transit into acid and main Lewis centers. This allows supposing that there can be new active centers on the catalyst running the reaction, and the nature of the old active centers can change.

The conence catalysis allows better understanding, from the energetic and chemical viewpoints, at the expense of what forces the acceleration reaction actually takes place:

1. *The catalyst allows to use the energy of the previous stage for the accomplishment of the next stage, or to use the energy of the next stage to accomplish that of the previous one. Chemical activation is accomplished on the catalyst.*

2. *The catalyst accumulates kinetic energy.* The dissociation of a complex in a mixture with a conence formation is an illustration of a molecule's transition energy accumulation (in an inert solvent) in the form of potential energy (conence). An analogous phenomenon was noted during conence dissociation not in inert solvents but in acid dissociation and in bases. In this case, there is not only a transition of kinetic energy into potential, but a process occurs in which weak chemical actions lead to the accumulation of energy on some particles.

3. *The catalyst accomplishes a reaction along a route that requires a smaller activation energy on each stage.* From the chemical viewpoint, there is no doubt that the following route — appearance of the conence as a result of dissociation; its interaction with the olefin; the consequent introduction reaction; etc. — proceeds more readily (i.e., with a smaller activation energy) than a direct interaction of chemically neutral components relative to each other, like carbon oxide and olefin.

From the chemical viewpoint the acceleration of the catalyst is observed in two ways as follow:

1. *Chemical reactions — the interaction of chemically active particles between themselves and with molecules.* Relatively to the type of active particles, reactions can be ionic, radical, conence, etc. Catalyst — a substance that offers an active particle (conence, ion, radical) while the reacting molecules of these particles cannot, as yet, produce them.

2. *The catalyst activates chemical bonding.* In the well known complex model, which is well detailed in chemical literature, two types of interaction are considered: the transition of the dual bonds' π -electrons to the vacant orbital of the central atom, and the transition of the electrons of the central atom (that do not take part in the bonding) onto the rough orbital of the bond like that of the $C\equiv C$. Both interactions lead to the roughening of the dual bond.

This model allows making some conclusions about the chemical action of the catalysts. Obviously, the main form of action exerted by the catalyst upon the bond is the introduction of a compound that weakens the bond but does not cause its breaking to form new bonds like metal — catalyst. The formation of new bonds, most likely, is a rare case of interaction where the border between the subsequent chemical reaction and the catalytic reaction is fading away.

The main types of interaction that lead to the weakening of the bond are as follows:

- 1) the interaction of a vacant orbital with the electrons of a bonding orbital;
- 2) the interaction of free electrons with orbit-roughening bonds.

The bond weakens while transiting from the interaction of non-bonding electrons with one roughened orbital to the interaction of electrons with two non-bonding orbitals, and the transition of bonding electrons to the vacant metal orbitals.

The transition of free metal electrons onto a roughened orbital, say, on saturated hydrocarbon, is a convenient model for the explanation of the activation of bond carbon — hydrogen in saturated hydrocarbon metal complexes.

Interactions with roughening orbitals envisage definite positions for the reacting spatial molecule in reference to the catalyst and its spatial fixation, since the interaction even with one catalyst atom proceeds via two or three points. Out of this precept we get the principle of spatial compliance and stereo-specific action of the homogeneous catalysts.

Bond roughening in catalyst reactions that precedes its breakage at the expense of the electrons' shifting to the roughening bond orbitals, allows to expect the same kind of mechanism for bond breaking in other cases that have nothing to do with the catalyst.

For example, the influence of a solvent on the reaction speed, the hydrogen bond, or the substitution reaction, that proceed along the association mechanism. In this last case we can suppose that the introduced substitute first forms a bond on the roughing orbital, and then (after the exit of the substituting fragment) — along the bonding orbital.

The general theoretical studies of the energetic and chemical forces that define the essence of catalysis, allow making several general conclusions about the possibility of formulating a theory for the selection of catalysts for various reactions.

Even if we exclude the citing of multi-stage and multi-route catalytic reactions and the problem of foreign particle influence, we can say that catalysis is a much more difficult phenomenon qualitatively than a simple chemical reaction. At present the theoretical calculations of chemical reaction speeds are hardly effective (partly because of mathematical difficulties) and practically all the chemical 'intuition' is based on experimental data of the past.

A correlational approach to chemical reactions proved to be of value only in regard to their systematization, and in some cases, in regard to the initial studies of mechanisms. Therefore the existing catalysis

theories can be regarded as correlational in the sphere of catalysis on the first stage of their development. It is doubtful that a new general theory on catalysis will ever appear, one that would allow a selection of catalysts for new reactions.

However, the systemization that can be done depending on whether the electrophyl or nucleophyl catalyst properties play an important role in the given case, of course, is the proper direction to follow. The catalysis theories, undoubtedly, will maintain their principle applied meaning, that is, the motivation of the search for new catalysts and the generalization of the available experimental material.

An exception can be made to this general rule which could include some phenomena untouched upon in this work, for example, oxidized replacement catalysis where the catalyst is given in the capacity of an intermediary that passes on the electron.

We can expect a great role for conence reactions in biochemistry since ferments (catalysts of the main biochemical reactions) are complex compounds. The fact that conence chain reactions are important reactions in biochemical processes does away with the main contradiction of the chain reaction hypothesis in biochemistry [87]. Biochemical reactions are examples of the most economical use of energy in the catalyst cycle, which can be explained by their chain character.

The supposition that radical chain processes play a leading role contradicted the second feature of biochemical processes — their high selectivity, since the radical chain processes are almost non-selective reactions in complex systems. As for conence chain reactions, this is the most probable chemical basis for biochemical processes of the known chemical chain reactions.

2.4 STAGES OF HYDROFORMYLATION REACTION MECHANISM

On the basis of the above given information on conence chain reactions and their role in homogeneous catalysis, we can examine the mechanisms in separate stages of the hydroformylation reactions and summarize this data into a single reaction mechanism.

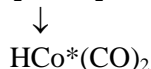
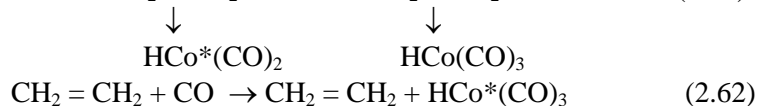
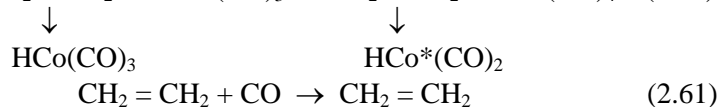
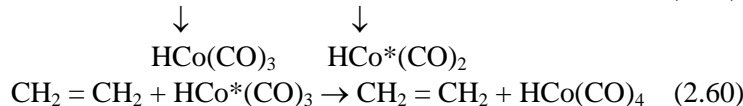
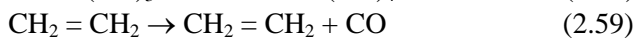
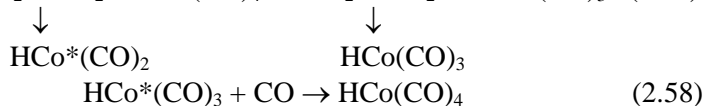
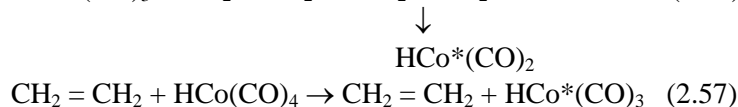
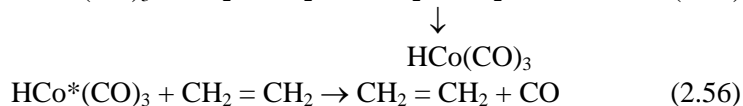
2.4.1 FORMATION OF THE π -COMPLEX

The formation reaction for the π -complex of hydrocarbonyl cobalt with olefin is a common ligand substitution reaction in a coordinate compound. According to the main precepts in the theory of such

reactions, the first stage in the π -complex formation is the dissociation of the coordinate saturated carbonyl cobalt up to the conence:

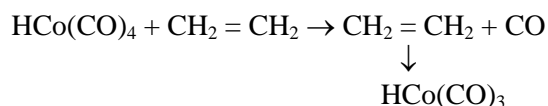


The reaction scheme proceeding further is as follows:



The available experimental data including the above-mentioned reactions, gives the priority to one of the routes. It has been proven that the preliminary exposure of $\text{HCo}(\text{CO})_4$ in the absence of olefin, does not decrease the reaction's deduction period. Therefore, the formation of conence $\text{HCo}^*(\text{CO})_3$ does not limit the process of π -complex formation. This fact proves that if stage 2.57 takes place, it plays a significant role.

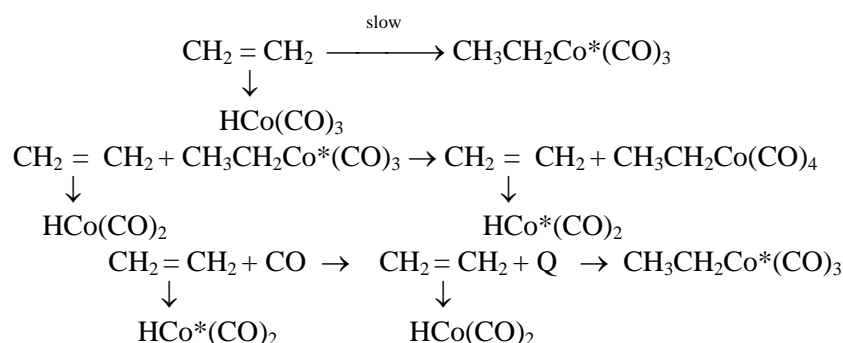
The routes for the formation of the π -complex are stages 2.54 and 2.55 that describe a simple dissociation scheme of the mechanism. Exception: there is a π -complex formation along the following reaction:



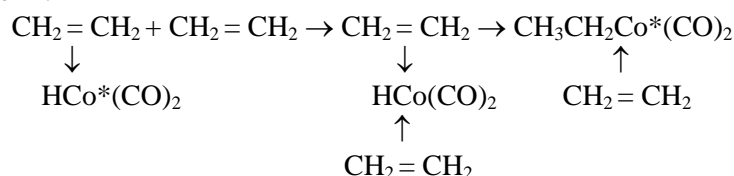
— at the expense of bond formation in the transition state between the roughening orbitals of the dual carbon–carbon bond and the cobalt filled in with d-orbitals.

2.4.2 TRANSITION OF THE π -COMPLEX INTO ALKYLCOBALTCARBONYL

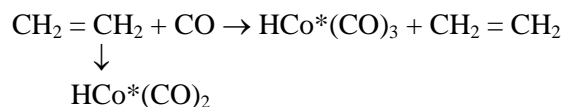
The transition reaction of the π -complex of hydrocarbonyl cobalt with olefin into alkylcobaltcarbonyl is an introduction reaction, and its mechanism can be described as follows:



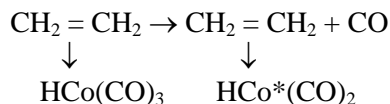
The π -complex transits into alkylcobaltcarbonyl when interacting with olefin:



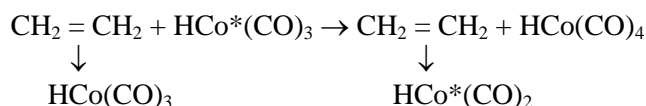
The interaction of carbon oxide with a conence can lead to the knock-out of the olefin:



The initiation of the chain can occur, as already indicated, as a result of a common dissociation of the π -complex:

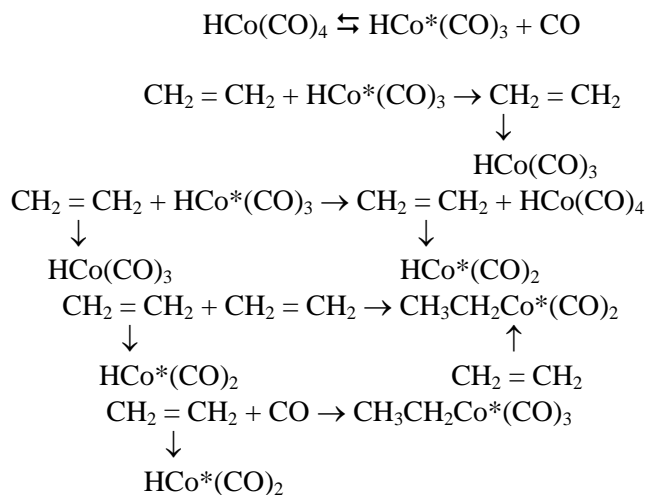


When there are conences in the system like $\text{HCo}^*(\text{CO})_3$, the formation of the coordinate unsaturated π -complex can occur as a result of an interaction of a conence with a π -complex along the scheme:



It is experimentally proven that in the absence of hydrocarbonyl cobalt, the actual time for a semi-transformation of a π -complex into alkylcarbonyl, is one hour, while in its presence the semi-transformation time is several minutes. It has also been found that the same kind of acceleration is produced by other conences, independently received and introduced into the system, for example, $\text{Co}_2^*(\text{CO})_7$. It has been noted that the π -complex transition reaction into alkylcobaltcarbonyl is slowed down when the pressure of the carbon oxide increases.

Considering these experimental data and the theory of conence chain reactions, we can undoubtedly consider the following route for the formation of alkylcobaltcarbonyl out of π -complexes in the presence of hydrocarbonyl cobalt (or conence):



The presence of conences in the system at the beginning of the reaction accelerates the initiation of the chain. In the absence of conences, the initiation of the chain occurs via one of the above shown mechanisms. Here, as in all the following schemes of conence chain reactions, are given not all the possible reaction routes, but only the idea about how to find them.

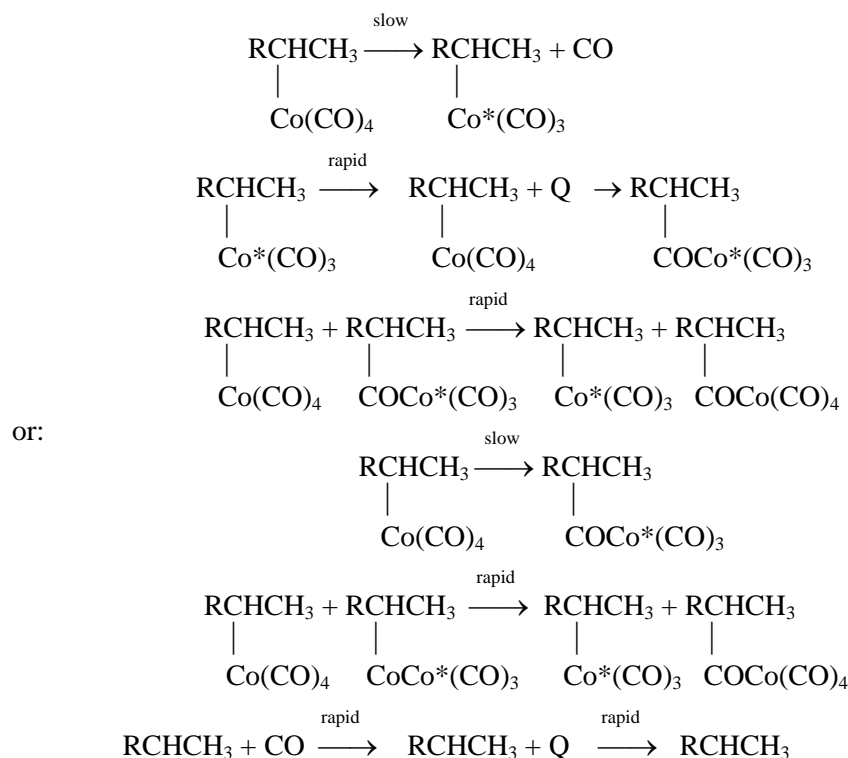
The supposed formation of a coordinate unsaturated π -complex
 $\text{CH}_2 = \text{CH}_2$
 of the type indicated here: \downarrow as an intermediate product
 $\text{HCo}^*(\text{CO})_2$

of the π -complex transition reaction into alkylcobaltcarbonyl on the one hand, is confirmed by the high degree of 'conecency' of the system, during the alkylcobaltcarbonyl formation stage (see fig.2.12), on the other hand, it very well illustrates the action of the catalyst.

The coordinate unsaturated π -complex (π -complex—conence) has a double bond roughened much more than that in the saturated one. It is supposed that there is a step-by-step roughening of the dual bond during catalysis. By bonding a carbon oxide molecule or an olefin in the vacant space, the π -complex gets additional energy necessary for the breaking of a double bond.

2.4.3 TRANSITION OF ALKYLCOBALTCARBONYL INTO ACYLCOBALTCARBONYL

The reaction for the transition of alkylcobaltcarbonyl into acylcobaltcarbonyl is an introduction reaction. Their routes can be represented thus:





Of the two indicated variants of chain initiation when transiting alkylcobaltcarbonyls into acylcobaltcarbonyls, experimentally the second proved to be the best. The spectra of the alkylcobaltcarbonyl mixtures reveal absorption stripes like those of the acylcobaltcarbonyls.

Just as in the transition reaction of π -complex into alkylcobaltcarbonyls, during the transition reaction of alkylcobaltcarbonyls into acylcobaltcarbonyls, the system has a large number of conences, which means that the initial chain routes do not play a significant role.

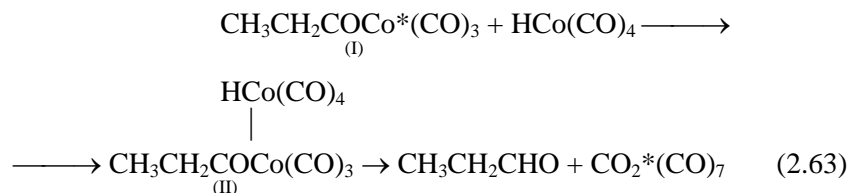
2.4.4 TRANSITION OF ACYLCOBALTCARBONYL INTO ALDEHYDE

Alternate mechanisms for the transition of acylcobaltcarbonyls into aldehydes were hardly studied, so they are the most hypothetical.

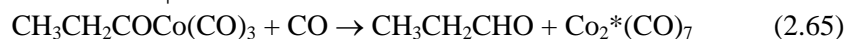
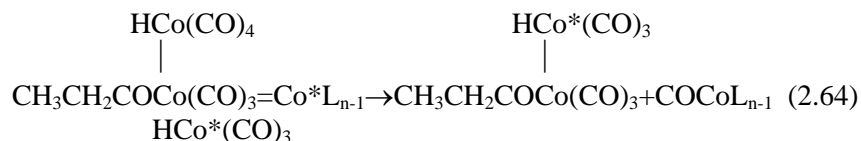
If the mechanisms mentioned in the previous stages of the general hydroformylation mechanism could be foreseen, guided by theoretical knowledge, and the main routes could be chosen on the basis of experimental material, the transition stage of acylcobaltcarbonyl \rightarrow aldehyde, judging by the general conception of conence reactions, we can only suppose that acylcobaltcarbonyls enter reaction in the form of conence-like acylcobalttricarboxyls. In the case of stoichiometric hydroformylation, this reaction is described by the following equation:



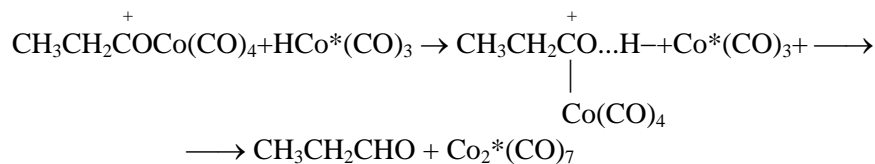
Further details of the mechanism on this stage can be gathered on the basis of analogies. For example, we know that the formation of a cluster develops at the expense of 1) a vacant orbital of a coordinate unsaturated acylcobaltcarbonyl and 2) a full d-orbital of a hydrocarbonyl of cobalt. Therefore, the reaction is possible along this scheme:



The transition of compound (II) into aldehyde in the presence of conences can be eased by passing it via the chain mechanism:



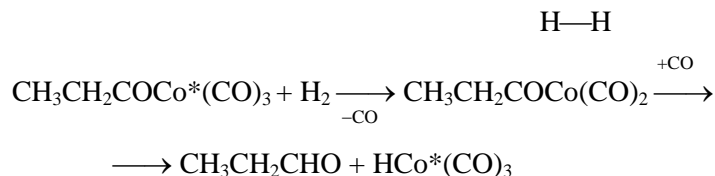
The analogy between acylcobaltcarbonyls and halogen-anhydrides carbon acids is shown in the works of N.Imyanitov [88]. Both substances give acids (or ether) when water (or methyl spirit) is applied. Therefore, analogous to the reaction mechanism where chlorine-anhydrides react with water (or spirit), the interaction of acylcobalt-carbonyl with hydrocarbonyl can be described thus:



Here group Co(CO)_4 is more electrophorus than proton, and group Co(CO)_3 is less electrophorus. Such a scheme has no internal contradictions, it explains the slowdown influence of carbon oxide on the speed of aldehyde production out of acylcobaltcarbonyls (conence concentration decrease in the system) and it gives a single interpretation about the mechanism for the formation of aldehydes, acids, and ethers.

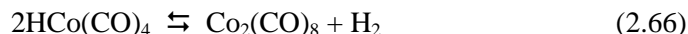
Still, this mechanism scheme has many assumptions, of which the most hypothesis-like is the supposition about the change of the sign of the charge on the hydrogen for plus to minus during the transition from HCo(CO)_4 to $\text{HCo}^*(\text{CO})_3$. The mechanism for forming acids out of acylcobaltcarbonyls can be illustrated thus:

The most probable mechanism stages are those of 2.63 to 2.65. During catalytic hydroformylation, the breaking of the acylcobalt-carbonyl can proceed under the influence of the hydrogen:



The possibility of such a reaction was shown experimentally.

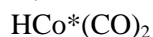
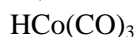
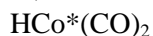
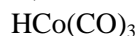
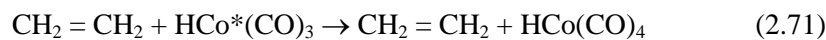
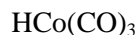
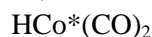
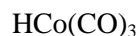
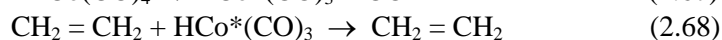
Nevertheless, in real conditions of catalytic synthesis it does not play a significant role. Indeed, if the breakage of acylcobaltcarbonyl took place via the action of hydrogen, the concentration of dicobaltoctacarbonyl in the system would be defined by the equilibrium of the reaction:

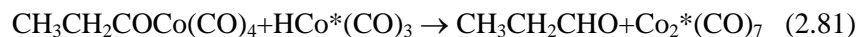
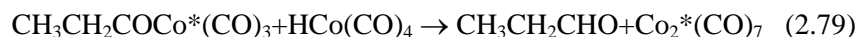
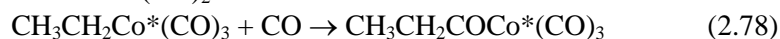
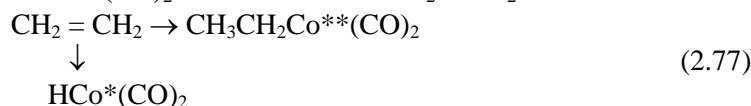
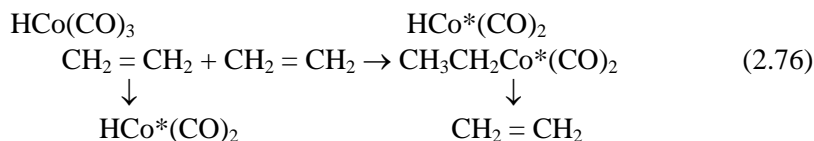
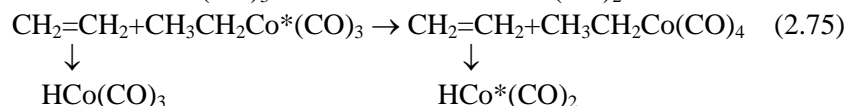
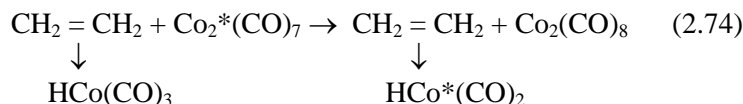
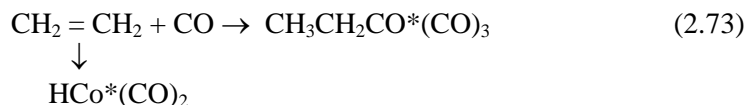


However, the experimentally defined dicobaltoctacarbonyl concentration during catalytic hydroformylation (see fig. 2.7) is greater than expected, considering the data on the equilibrium between dicobaltoctacarbonyl and cobalt hydrocarbonyl of in the liquid phase [89].

Thus, at 70°C, 3 MPa at mol gas ratio of $\text{CO}:\text{H}_2 = 1:1$ and concentration of $\text{HCo}(\text{CO})_4$, $0.1 \text{ mol} \cdot \text{gram}^{-1}$ the equilibrium concentration $\text{Co}_2(\text{CO})_8$ is about $0.01 \text{ m-mol} \cdot \text{gram}^{-1}$, while the experimentally defined concentration of $\text{Co}_2(\text{CO})_8$ with a catalytic hydroformylation of 1-hexane in these conditions comprises about $0.3 \text{ mol} \cdot \text{gr}^{-1}$, that is, it exceeds the equilibrium by 30 times. The concentration of $\text{Co}_2(\text{CO})_8$ is defined not by K_p of reaction 2.66, but by its formation along reaction 2.63.

Considering the material on the mechanism of separate stages of hydroformylation, we offer the full scheme of the reaction's mechanism:





The contribution of each of the stages to the mechanism of the process is difficult to evaluate quantitatively, but a qualitative evaluation to each stage is possible. Because of this, the main routes of the processes do not have any additional indexes next to their number; the increased number of little strokes by the number of the stage corresponds to the decrease in its quantitative contribution to the total mechanism.

2.5 ISOMER FORMATION MECHANISMS; INFLUENCE OF REACTION CONDITIONS ON ISOMER CONTENTS OF FINAL PRODUCTS

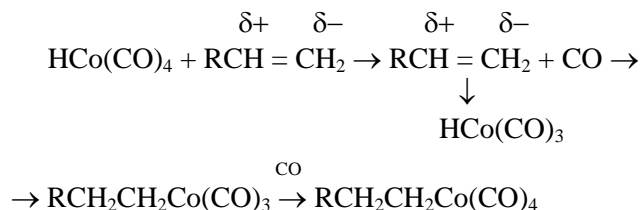
In the early stage of the study of the hydroformylation reaction, it was found that the reaction proceeds by forming normal and abnormal aldehydes (those olefins from which isomer aldehydes cannot be formed no matter where the carbonyl group was bonded — to ethylene, cyclohexane, etc., are exceptions.)

The first hypothesis that described the mechanism for isomer distribution of aldehydes was offered by W. Reppe who found that, as a result of the direct interaction of carbon oxide and olefin, an intermediate

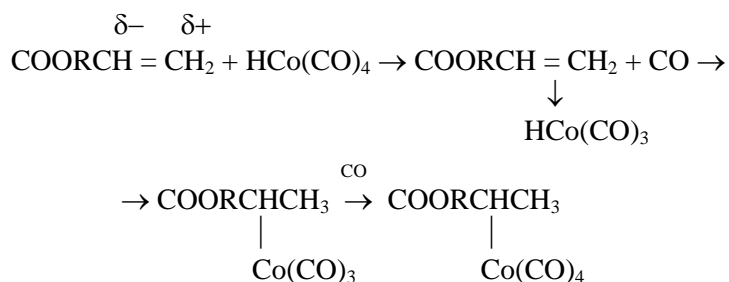
compound is formed with a triple cycle. It is the breaking of this compound that defines the isomer correlation of the aldehydes.

When Sternberg and Wender resolved that the hydroformylation reaction proceeds via intermediate formation of alkylcobaltcarbonyls, Breslow and Heck proposed that the isomeric distribution of aldehydes is defined by the contents of the products in the initial bonding of $\text{HCo}(\text{CO})_4$ to the olefin via a double bond.

How is $\text{HCo}(\text{CO})_4$ bonded to the olefin? This question was answered on the presumptions of the hydride qualities of the hydrogen in cobalt hydrocarbonyl [90-93]. In concert with such presumptions, cobalt was supposed to form bonds mainly with the carbon atom that has unlimited bonding and has the greatest negative charge. The olefin, with a double bond at the end of the chain at the expense of the induction influence of the alkyl groups, was said to realize the following scheme:



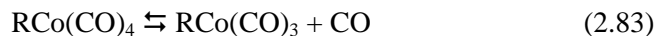
At the same time, say, for the unlimited compound ether with the greatest negative charge in the carbon atom and in the α -position, the interaction continued in the realistic experiment along the scheme:



However, Imyanitov [94, 95] confirmed the fact that "hydrocarbonyls are undoubtedly acids, and there is no substantial evidence that the hydrogen in hydrocarbonyl of cobalt has a hydride character."

P.Pino and his colleagues found that the amount of butyl aldehydes received from the hydroformylation of isomer propylene depended on the partial pressure of the carbon oxide and temperature, and that the carbon oxide's pressure increase favorably increases the

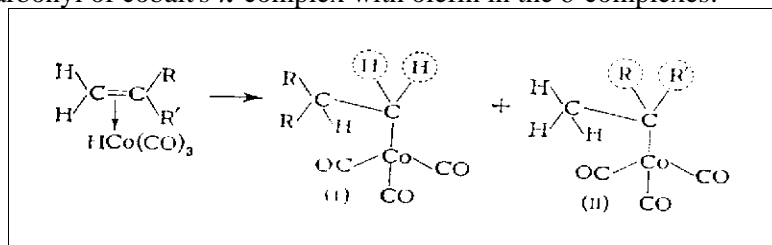
output of butyl aldehyde [96]. To explain this fact, Pino supposed that the isomer distribution is controlled by equilibrium reactions:



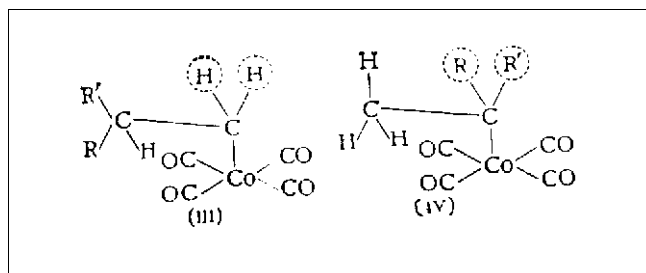
The pressure increase of the carbon oxide causes the shift of the reaction's equilibrium to the left (2.83); at the same time the reaction's equilibrium is much more shifted to the right than reaction's equilibrium (2.85) because of the steric factors.

This fact about the increase of the output of aldehydes of normal structure when increasing the partial pressure of carbon oxide has been often mentioned also in later works [97, 98].

J.Falbe made an effort to explain the isomer distribution of the forming aldehydes via steric factors [11]. According to his judgement, the isomer distribution 'forms' during the transition stage of the hydrocarbonyl of cobalt's π -complex with olefin in the δ -complexes:



The alkyl substitute increase of the carbon atom causes difficulty during alkylcarbonyl formation, therefore δ -complex (I) forms more readily than does (II). Simultaneously, the increase of the pressure of the carbon oxide aids the formation of the alkylcobalttetracarbonyls:



Since the formation of (IV) is sterically hampered even more than the formation of (II), we get mainly alkylcobalttetracarbonyl (III), which leads to aldehydes of normal structure.

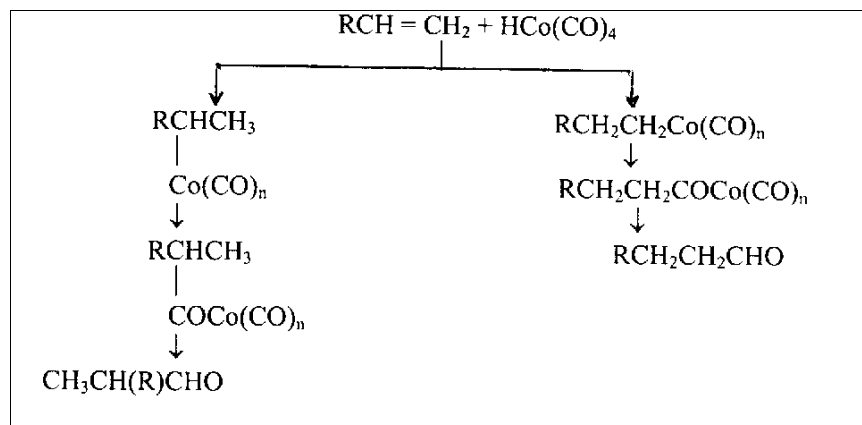
Falbe explained the increase of the output of normally structured aldehydes during the modification of the cobalt catalyst with phosphine, and the decrease of the output when transiting from a cobalt catalyst to a rhodium one. The substitution of a CO molecule in hydrocarbonyl for a phosphine one significantly increases the steric obstacles to the interaction of cobalt with a carbon atom with substitutes. The rhodium atom is larger than the cobalt one; so, in Falbe's words, "the rhodium atom has *plenty of space*" for the formation of isostructural products.

According to Imyanitov's remarks, the radii of cobalt atoms (0.125 nm) and rhodium atoms (0.134 nm) are not so different as to affect the steric difficulties.

The most serious reason against the hypothesis of the decisive role of structural alkylcobaltcarbonyls in isomer distribution of aldehydes [99] is the fact that during studies about the isomer contents of alkylcarbonyls formed via the interaction of HCo(CO)_4 with 1-hexane, there were no alkylcobaltcarbonyls of normal structure (1-cobaltcarbonylhexane) in the reaction's products. Samples of the reaction's hydrocarbonyl of cobalt mixtures and 1-hexane, taken at the beginning of the reaction, were freed of hydrocarbonyl of cobalt, and treated with iodine. The alkylcobaltcarbonyls transited to their relative iodinehexanes. Studies of the received product's mass-spectrums showed that 1-iodinehexane was not present in the mixture; but there was some 2-iodinehexane (and possibly, 3-iodinehexane).

Experiments with model mixtures have showed that the methods used allowed to find 1-iodinehexane in a mixture with other isomers in the ratio of 2:100. That is why only 2% of the cobaltcarbonylhexane isomer was formed as a result of bonding against the Markovnikov rules.

It is obvious that all the hypotheses on the mechanism of isomer distribution, based upon the following scheme are not well based:



Outwardly all scientists seem to agree with the observed regularities for isomer distribution of the reactor's products.

Interesting results were received when studying the isomer contents of acylcarbonyl. The transition stage of alkylcarbonyls into acylcarbonyls precedes the formation of aldehydes, therefore the isomer distribution of the forming aldehydes can be defined namely by the correlation of the structures of the acylcarbonyls.

In figures 2.15 and 2.16 are shown the experimental data on the time changes in the isomer contents of the acylcarbonyls (intermediate reaction product) and the aldehydes which are received during the interaction of $\text{HCo}(\text{CO})_4$ with 1- and 2-hexanes.

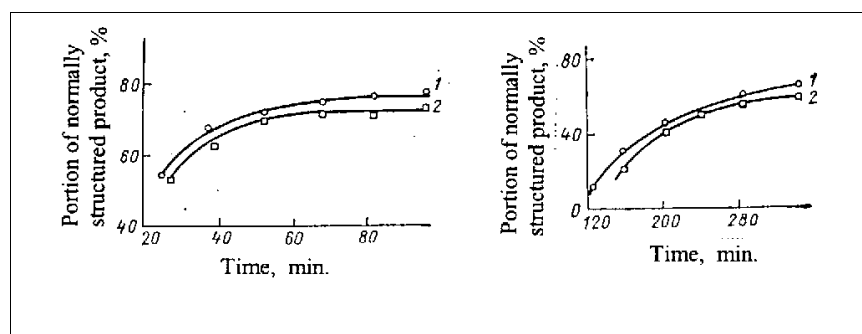


Fig. 2.15 Dependence of normally structured product contents in isomer mixtures of acylcobaltcarbonyls: (1) and aldehydes (2), received via the interaction of hydrocarbonyl of cobalt with 1-hexane, on time in minutes.

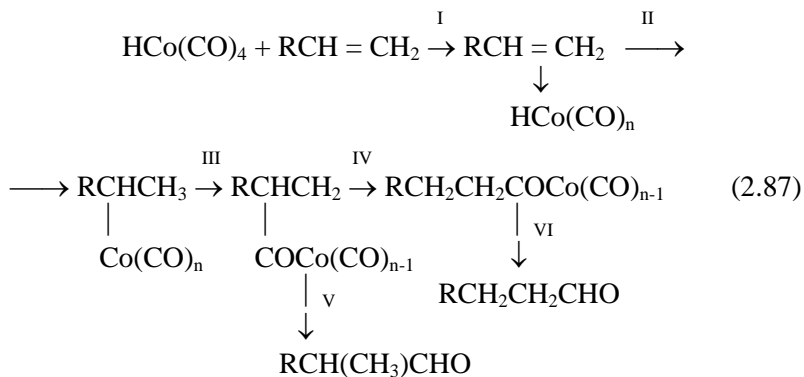
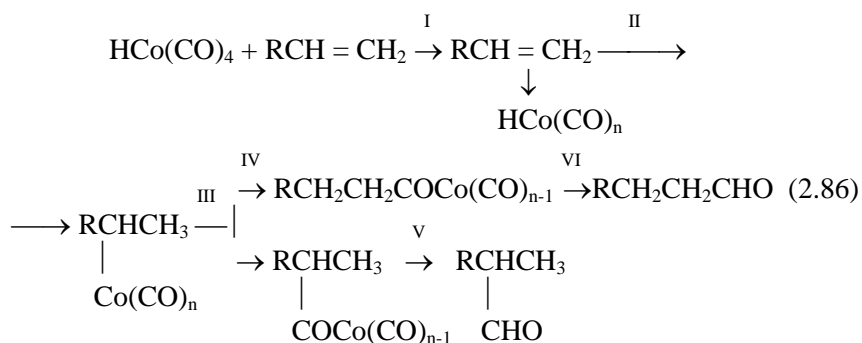
Fig. 2.16 The same with 2-hexane.

During a stoichiometric interaction of $\text{HCo}(\text{CO})_4$ with olefin, part of the products of normal structure in the forming mixtures of isomer acylcobaltcarbonyls and aldehydes increases in the course of the reaction. This is best observed via reaction $\text{HCo}(\text{CO})_4$ with a 2-hexene. As a result, the final product's contents of the hydroformylation of a 2-hexene is very close to that of a 1-hexene.

This data allows to confirm the facts that: 1) there is a correlation between the isomer contents of the acylcobaltcarbonyls (the reaction's intermediate product) and the aldehydes (the final product) during the interaction of hydrocarbonyl of cobalt with olefins; 2) during the synthesis there occurs isomerization of the acylcobaltcarbonyls (the reaction's intermediate products).

The change of the isomer contents of acylcobaltcarbonyls cannot be explained by isomerization of alkylcobaltcarbonyls, which precede them during the synthesis, since, as already mentioned, there were no normally structured alkylcobaltcarbonyls in the reaction's mixture.

Thus, we should prefer scheme (2.86), which considers the direct transition of the 2-cobaltcarbonylalkane into acylcobaltcarbonyl as being both isostructural and of normal structure, or scheme (2.87), which considers the isomerization of acyls:



Scheme (2.86), explaining the observed experimental facts, still does not agree well enough with the known kinetic process regularities.

It is known (fig. 2.3) that the alkylcobaltcarbonyl concentration in the reaction mixture proceeds through the maximum, preceding in time, the acylcobaltcarbonyl concentration maximum. Moreover, the reaction mixture contains a great concentration of acylcobaltcarbonyls even after the almost complete disappearance of alkylcobaltcarbonyl.

If the isomer distribution of aldehydes is defined by the speed of stages III and IV during the transition of alkylcobaltcarbonyl into acylcobaltcarbonyl, then after the disappearance of the former, it cannot change any more. However, the increase of the normal part of the aldehyde in the reaction's mixture is observed throughout the reaction period, i.e., even after the complete disappearance of the alkylcobaltcarbonyl (see fig. 2.15 and 2.16).

Scheme 2.87 offers the best available kinetic data. In this case the isomer distribution of aldehydes is defined by the correlation of the speeds in stages IV and V which change during the reaction in favor of stage IV because HCo(CO)_4 plays a role in reaction V whose concentration, during the test, decreases (see fig. 2.3).

The isomerization of acylcobaltcarbonyls was first introduced by Y. Takegami [100] who synthesized isoacylcobaltcarbonyl thereby proving the possibility of its transition into acylcobaltcarbonyl.

Quantitatively, the influence of the main parameters in the hydroformylation process (temperature, partial carbon oxide pressure, catalyst concentration) on the isomer contents of the produced aldehydes, are given in detail in the hydroformylation of propylene [97, 98, 101].

With the increase of the temperature, the correlation of the received butyl and isobutyl aldehydes always changes in favor of the increase of the isostructural product. An analogous correlation has been found in regard to other olefins [102].

The increase of the carbon oxide's partial pressure to a certain point, leads to the increase of the output of aldehydes of normal structure. Thus, with the increase of the pressure from 0.65 to 10 atm the correlation of the discharge of aldehydes to that of isoaldehydes changes from 1:1 to 3:1 [96]. Further increase in pressure hardly influenced the isomer distribution of aldehydes.

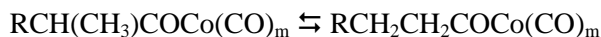
During olefin hydroformylation of branched structure with a branch by the dual bond (isobutylene) the output of products of the end-

attachment abruptly increases as compared to that of the olefins of normal structure.

The concentration of catalyst has little influence on the isomer contents of the received products. Only a modification of the catalyst will change the isomer distribution. An addition of tributylphosphine to the reaction's mixture greatly increases the output of normally structured aldehydes [103, 104]. The switch from cobalt catalysts to rhodium ones increases the output of isoaldehydes [105].

All the factors accelerating the reaction (besides catalyst concentration) lead to an increased output of isostructural products. To explain this, some hypotheses came forth with suppositions about the influence of the parameters of the process on the bonding of HCo(CO)_4 to the double olefin bond or about the equilibrium between various forms of alkylcarbonyls. There is no sense to dwell upon these in detail after the proof of their illogic notions about the defining influence of the alkylcobaltcarbonyl formation stage on the isomer distribution.

The isomer distribution of hydroformylation products depends on the speed correlation of stages IV and V on the offered mechanism for isomer formation (2.87). The increase of the carbon oxide's pressure has influence on the isomer distribution because it has influence on the speed of stage V (reaction proceeds via conences). The carbon oxide's pressure influence was observed experimentally before equilibrium is reached:



Indeed, the increase of the carbon oxide's partial pressure from 0.05 to 0.11 MPa (fig.2.8 and 2.3) decreases the hydroformylation reaction speed by two times. The reaction speed for the isomerization of isoalkylcobaltcarbonyl into acylcobaltcarbonyl depends on this factor only to a small extent, which was proven by Y.Takegami (table 2.2).

Analogously is explained the influence of temperature on isomer distribution. The increase of the reaction temperature from 10° to 20° C increases the hydroformylation reaction by 1.7 times (compare fig. 2.17 and 2.3), but this is hardly noticeable on the reaction speed during the isomerization of acylcobaltcarbonyls (table 2.2).

Therefore, the temperature increase does accelerate the isoaldehyde formation reaction along the route I – II – III – V via scheme 2.87, having hardly any influence on the speed of normal structure aldehyde formation along the route of I – II – III – IV – VI.

TABLE 2.2
Formation of Isomer Acylcarbonyls in Reactions of Chlorine
Anhydride Isobutyl Acids with NaCo (CO)₄

MEDIUM	TEMPERATURE IN ° C	RELATION OF ACYL- CARBONYLS H : ISO
CO	25	4.6
CO	0	5.0
N ₂	25	8.8
N ₂	0	7.5

Unlike other hypotheses about the mechanism of the influence of process parameters on isomer distribution of aldehydes, this scheme considers the experimentally proven fact of the bonding of $\text{HCo}(\text{CO})_4$ to the olefin only in accordance with the Markovnikov rule and also the presence of the isomerization reaction for acylcobaltcarbonyls under conditions of hydroformylation.

An experimental checkup on the correctness of the regularities, found while studying the stoichiometric hydroformylation of olefins under conditions of catalytic synthesis, has shown that the isomer correlation of the aldehydes is close to that of acylcobaltcarbonyls. But there are also regularities that are not explained by the scheme. The increase of carbon oxide pressure stabilizes the isomer distribution of acylcarbonyls in the course of the reaction and decreases the dole of isoacylcobaltcarbonyl. The temperature increase increases the contents of isoacylcobaltcarbonyl and leads to a great change in the isomer distribution of the latter in the course of the reaction.

When hydroformylation is conducted at 70°C, the portion of isoacylcobaltcarbonyl in the isomer mixture is smaller than that of the isoaldehyde in the aldehyde mixture; at 100° C the reverse is observed.

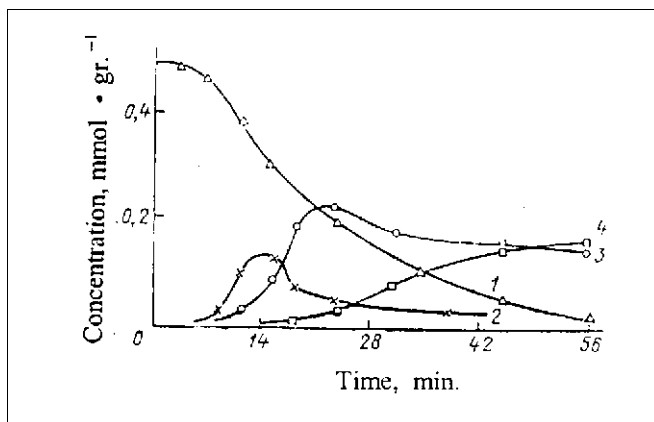


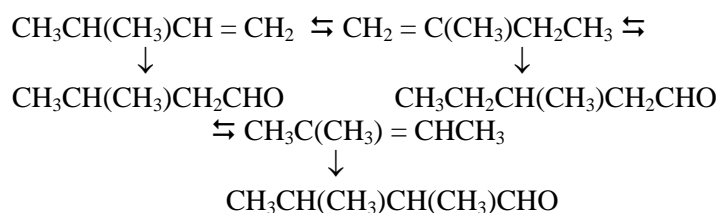
Fig. 2.17 Kinetic curves of the stoichiometric hydroformylation reaction with a 1-hexane at 20°C:

1 – $\text{HCo}(\text{CO})_4$; 2 – alkylcarbonyls; 3 – acylcarbonyls; 4 – aldehydes.
Carbon oxide partial pressure – 0.11 MPa; initial 1-hexane concentration – $3.5 \text{ mmol} \cdot \text{g}^{-1}$; solvent – heptane.

It is obvious that the influence of parameters on the isomer distribution of aldehydes and, in particular, the influence of the partial pressure of the carbon oxide, is not limited only by the mechanism seen above (scheme 2.87). Various shifts of the equilibrium in some stages also take place.

The hydroformylation reaction is accompanied by a parallel migration reaction of a double bond in olefin. There is a supposition that, to a great extent, it is the isomerization of olefin that defines the isomer contents of the products of hydroformylation.

Way back in the early stages when Rudkovsky and Pazhitnov studied the oxoprocess [106], they found that 3-methyl-1-butylene showed that at the initial period of the reaction, the olefin isomerizes into an equilibrium mixture of methyl-butylenes. The following scheme for the formation of isomer aldehydes was offered:

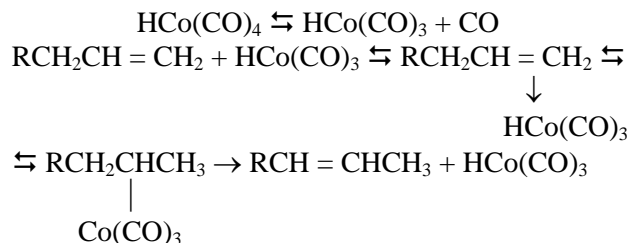


The same kind of supposition was made by Johnson [107] who proved that during the hydroformylation of 4-methyl-1-pentene, olefin isomerization precedes the arrival of isomer aldehydes. However, when Goldfarb and Orchin investigated the hydroformylation of 1-heptene, they failed to find any olefin isomerization though they did observe the formation of isomer aldehydes [108].

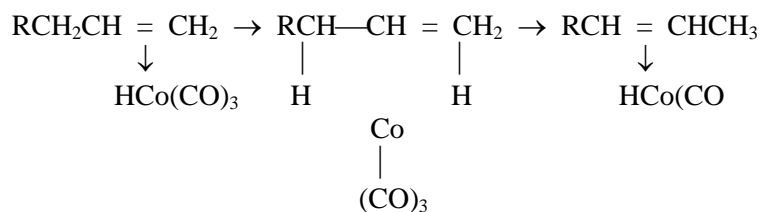
Today, the most widely spread viewpoint is that though olefin isomerization does precede the carbon—cobalt bond formation during hydroformylation, it does not play a foremost role in the isomer distribution of aldehydes because the isomerization proceeds much slower than the hydroformylation [11, 109].

Nevertheless, olefin isomerization, under conditions of hydroformylation, has been widely studied. A lot of explanations have been presented about the mechanism for the transition of a double bond along the olefin chain,

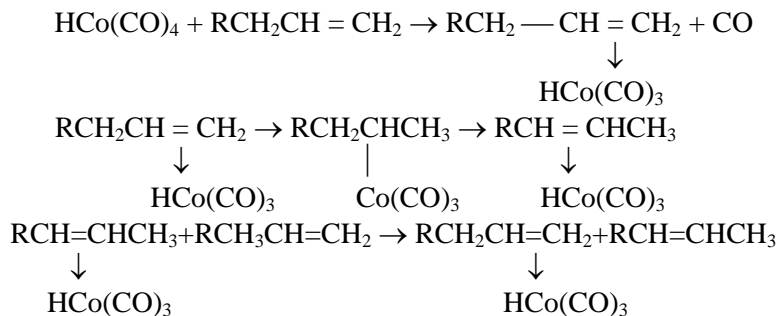
Breslow and Heck supposed that isomerization proceeds via a consecutive 1-, 2-bonding and chipping off $\text{HCo}(\text{CO})_4$:



Also offered was an olefin isomerization mechanism, which included the exchange of a hydrogen atom of the allyl olefin group with the hydrogen of hydrocarbonyl of cobalt via a six-part π -allyl complex:



The authors found the experimental confirmation of this scheme when they studied the isomerization of allyl alcohol under the influence of deuteriocarbonyl of cobalt $\text{DCo}(\text{CO})_4$. All the atoms of the deuterium in propionic aldehyde (product for alcohol isomerization) belong only to the carbon of the methyl group. But when studying the isomerization of allyl-benzene into propylene-benzene under the action of $\text{DCo}(\text{CO})_4$, Rooz and Orchin found that during isomerization, there was no deuterium exchange nor formation of $\text{HCo}(\text{CO})_4$ [111]. Cramer and Lindsey [112] offered a scheme to interpret the Rooz-Orchin scheme for olefin isomerization suggesting the replacement of isomerized olefin in the intermediate complex with a non-isomerized one:



The correctness of this explanation was confirmed later. When examining the isomerization of 1-hexane in the presence of $\text{HCo}(\text{CO})_4$, it was found that the isomerization reaction has an induction period and proceeds auto-accelerated. The induction period is close to that of the hydroformylation reaction, and is proven by the comparison of the data on kinetic isomerization of 1-hexane (fig. 2.18) with kinetic hydroformylation of the olefin. It was also found that the isomerization of olefins proceeds mainly while the alkylcobaltcarbonyls are in the system.

The isomerization reaction speed under conditions of stehio-metric interaction is about 6 times greater than the hydroformylation reaction. Thus, in equal periods of time and under equal conditions, 1.25 mol of olefin was isomerized, while only 0.25 mol reacted.

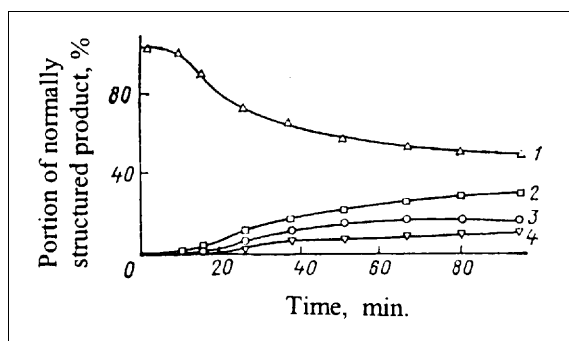
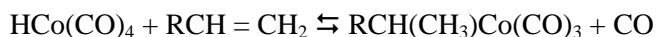


Fig. 2.18 Kinetic isomerization curves of 1-hexane in the presence of $\text{HCo}(\text{CO})_4$: 1 – 1-hexane; 2 – trans-2-hexane; 3 – trans-2-hexane; 4 – 3-hexane. Temp. + 10°C; carbon oxide partial pressure 0.11 MPa; initial 1-hexane concentration $3.5 \text{ mmol} \cdot \text{g}^{-1}$.

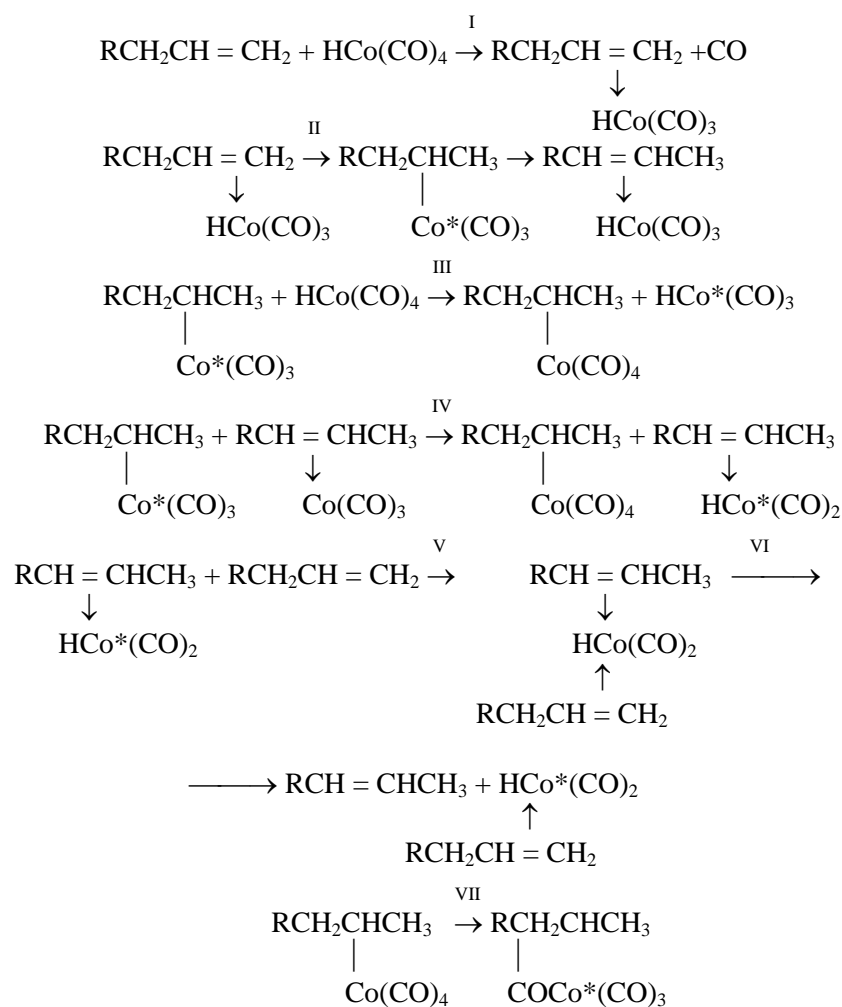
The above-mentioned results agree with the Cramer-Lindsey mechanism. The correlation of the time required for the isomerization reaction, and the time of existence in the alkylcobaltcarbonyl system is witness to the fact that it is the alkylcobaltcarbonyls that are the intermediate products of the isomerization reaction. The Breslow-Heck mechanism also presupposed alkylcobaltcarbonyls to be the intermediate products of the isomerization reaction; but if we accept their mechanism, with chip-off $\text{HCo}(\text{CO})_4$, then, with an isomerization speed 6 times greater than that of the hydroformylation, an equilibrium is the result:



However, it has been experimentally proven that in the course of the reaction, the concentration of alkylcobaltcarbonyls increases while the concentrations of $\text{HCo}(\text{CO})_4$ and olefins decreases.

At present, the experimentally proven existence of the π -complex $\text{HCo}(\text{CO})_4$ and olefin in the system speak in favor of the Cramer-Lindsey mechanism. After all, this mechanism is based on the hypothesis on the existence of a complex that was impossible to find.

Considering the available experimental information and the interpretation of reactions with metal carbonyls, as chain conence ones, the reaction mechanism for the isomerization of olefins under conditions of hydroformylation can be presented as follows:



This scheme does not show the breaking stages of the chain (the saturation of the conences with carbon oxide) though they do exist.

The offered scheme well explains the auto-accelerated feature of the isomerization of olefins and the negative influence of the carbon oxide's pressure on the reaction speed.

In accordance with the scheme, this pressure on the isomer distribution of aldehydes is explained by the fact that stages I, II, IV, V, and VI that define the isomerization of 1-olefin, include many more elements that proceed with the participation of conences, than stages I, III, and VII that define the acceptance of the hydroformylation products.

Therefore, the increase of the carbon oxide's partial pressure slows down the reaction speed of the olefin isomerization. Besides, Takegami has found that the carbon oxide's partial pressure and temperature have a greater influence on the alkylcobaltcarbonyl isomerization reaction than that on the acylcobaltcarbonyl isomerization reaction [100].

The influence of the temperature on the isomer contents, obviously, is explained by the fact that the activation energy of the isomerization reaction is greater than that of the hydroformylation reaction, which makes the isomerization reaction accelerate to a greater extent at high temperatures.

The given material allows to better understand the macro-mechanism of the isomer aldehyde formation, summarized in part, in work [113]. Before that a conclusion was made to the effect that [114] the extreme viewpoints on the influence of isomerization reactions on the isomer distribution of aldehydes [106 - 108], indeed, are extreme, and the truth, as we all know, often lies in between these viewpoints.

Modern methods allow us to differently interpret the known experimental results. According to the reaction mechanism scheme, it is not olefin isomerization that defines the formation of isomer aldehydes, but it is the alkylcobaltcarbonyl isomerization, which leads to a simultaneous production of both isomer olefins and isomer aldehydes.

Everything that was said here about the role of the olefin and alkylcobaltcarbonyl isomerization reactions, of course, should not be confused with the role of acylcobaltcarbonyls and their isomerization in isomer distribution, for which they are entirely responsible in such a case, for example, as the hydroformylation of propylene.

2.6 THERMODYNAMIC AND KINETIC REGULARITIES RELATIVE TO THE HYDROFORMYLATION REACTION

In accordance with thermodynamic data, hydroformylation reactions are possible at 0.1 MPa since the equilibrium of the reaction is shifted to the right limit (aldehyde formation) [114].

In chemical literature [114-116] are given the data on equilibrium constants and free energy of the ethylene hydroformylation reaction, but since the procedure of the hydroformylation reaction in the intervals, that have a practical significance, the pressures and temperatures are not limited by the equilibriums, and there is no sense in taking them up in detail. Generally, we can say that the choice of pressure and temperature depends not on thermodynamics, but on the kinetic process, and also by the need to guarantee the stability of the catalyst in conditions of the process.

This reaction is exothermic. The thermal effect during propylene hydroformylation is equal to 126 kJ/mol^{-1} [117].

The hydroformylation reaction speed is proportional to the concentration of olefin and catalyst, it increases with the increase of the hydrogen pressure and it decreases with the increase of the carbon oxide pressure. Thanks to the mutual compensation effects received during the increase of the pressure of carbon oxide and hydrogen, the hydroformylation reaction speed practically does not depend on the total pressure if the constant relation of $\text{CO} : \text{H}_2$ is maintained.

Natta and colleagues offered the following equation for the reaction speed [118]:

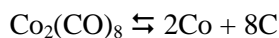
$$r = kC_{\text{ol}} \cdot C_{\text{Co}}p_{\text{H}_2}/p_{\text{CO}}$$

However, there is a more precise equation presented by Wender [119, p. 128]:

$$r = kC_{\text{ol}} \cdot C_{\text{Co}}ap_{\text{H}_2}/(ap_{\text{H}_2} + bp_{\text{CO}})$$

C_{olef} — olefin concentration; C_{Co} — cobalt concentration; p_{H_2} and p_{CO} — partial pressure of hydrogen and carbon oxide; a, b , — constants.

The stable cobalt catalyst concentrations in the solution is defined by equilibrium:



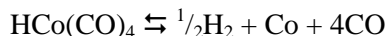
and therefore, the following equation:

$$K_p = C_{\text{Co}_2(\text{CO})_8} / p_{\text{CO}}^8$$

In this case, the minimal partial pressure of carbon oxide for an equilibrium concentration ($\approx 0.2\%$) can be expressed by an empiric equation [120]:

$$p_{\text{CO}} = 7.94 - 2660 / T$$

Equilibrium research of various cobalt carbonyl forms have shown that in the field of their low concentrations ($> 0.02\%$) during hydroformylation the reaction mixture practically contains only cobalt hydrocarbonyl [121], therefore the equilibrium is defined by a stoichiometric equation:



In such cases the equilibrium concentration of cobalt carbonyls can be defined by the following equation [122]:

$$\lg C = -24.38 + 6400/T + 4 \lg p_{\text{CO}} + \frac{1}{2} \lg p_{\text{H}_2}$$

where C — carbonyl concentration in recalculation for metallic cobalt.

The hydroformylation reaction speed increases with the increase of temperature; the reaction's temperature coefficient is from 1.4 to 1.7. The data about the temperature coefficient of the hydroformylation reaction of 1-buten being equal to 3 to 4 is doubtful [123].

The reaction speed for the hydroformylation of 2-methyl-1-penten can be calculated by the equation:

$$K = 8.7 \cdot 10^{12} \exp (13,000 / T)$$

When studying the kinetics of propylene hydroformylation [120], the following dependence was received:

$$\ln K = 21.9 - 20,000 R / T$$

Later the dependence on the temperature, the speed constant, the formation of butyl and isobutyl aldehydes were defined separately [124]:

$$\ln K = 19.4 - 18,000 / RT$$

$$\ln K = 23.2 - 22,000 / RT$$

The given dependencies allow to accomplish the technical calculations and to define the optimal temperature intervals, the pressure and the concentration of the catalyst, necessary to guarantee the desired reaction speed of the reactor's production center, and also the isomer relations of the received products.

The hydroformylation reaction speed depends on the structure of the olefin. The influence of olefin structure on the reaction speed was studied by Wender [125]. The received data are given in table 2.3.

TABLE 2.3

**DEPENDENCE OF HYDROFORMYLATION REACTION SPEED ON
OLEFIN STRUCTURE**

Conditions: temperature — 110° C; initial pressure at room temperature — 24 MPa; olefin — 0.5 mol; methylcyclohexane (solvent) — 65 ml; dicobaltoctacarbonyl — 2.8 gr.; ratio CO : H₂ = 1 : 1.

	Speed constant for reaction		Speed constant for reaction
Olefins	K · 10 ³ min. ⁻¹	Olefins	K · 10 ³ min. ⁻¹
With straight chain and end position of double bond		With branched chain and end position of double bond	
1-Pentane	68.3	4-Methyl-1-pentane	64.3
1-Hexane	66.2	2-Methyl-1-pentane	7.32
1-Heptane	66.8	2,4,4-Trimethyl-1-pentane	4.79
1-Octane	65.6	2,3,3-Trimethyl-1-butane	4.26
1-Deutsane	64.4		
1-Tetradetsane	63.0	With branched chain and inside position of double bond	
		4-Methyl-2-pentane	16.2
		2-Methyl-2-pentane	4.87
With straight chain and inside position of double bond		2,4,4-Trimethyl-2-pentane	2.29
		2,3-Dimethyl-2-butane	1.35
		2,6-Dimethyl-3-heptane	6.23
2-Pentane	21.3		
2-Hexane	18.1	C y c l i c a l	
2-Heptane	19.3		
3-Heptane	20.0	Cyclopentane	22.4
2-Octane	18.8	Cyclohexane	5.82
		Cycloheptane	25.7

	Cyclooctane	10.8
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The presence of substitutes in the double bond offers the greatest influence on the reaction speed. The molecular olefin mass practically does not have influence on the hydroformylation speed. The straight-chain olefins with double bonds at the end enter the reaction with the greatest speed.

The branched carbon-hydrogen chain with a double bond decreases the reaction speed, but if the carbon-hydrogen substitute is far from the double bond, the speed decrease is insignificant. [Compare the hydroformylation speeds of 1-pentane, 1-hexane, and 4-methyl-1-pentane.] The shift of a double bond inside the chain slows down the hydroformylation reaction. [Compare the 1- and 2-pentanes.] The situation of the double bond inside the chain hardly influences the speed. [Compare the 2- and 3-heptanes.]

Note that the hydroformylation reactions of various olefins have various activation energies. This means that the dependencies received by Wender at 110° C, can have quite different characters at much higher temperatures. The data offered by A.A.Polyakov on the activation energies for some of the olefins are given as follows:

Olefin	Seeming activation energy E in kJ/mol ⁻¹
Ethylene	96.1
Propylene	83.6
Isobutylene	83.6
1-Pentane	62.7
2-Methyl-1-Pentane	54.3
Cyclohexane	121.2

The data received later on the formation speed of aldehydes of various structure during olefin hydroformylation (at 140° C) principally agreed with the data received by Wender:

Aldehyde	Constant of the reaction speed in min ⁻¹
Propionic	0.3
Butyl	0.066
Isobutyl	0.02
Iso-valerian	0.04
Pival	0.0017

2.6.1 INFLUENCE OF SOLVENTS ON REACTION SPEEDS

The hydroformylation reaction, especially on the industrial scale, is most often accomplished with solvents. Solvents improve the reaction process since they help the transition of the olefins to the liquid phase, especially during the formylation of the lower olefins. Solvents are often used for the transport of catalysts.

Simultaneously the nature of the solvent, it is well known, can significantly influence the mechanism and the kinetics of the reaction.

The best aliphatic and aromatic carbon-hydrogens and alcohols are used as solvents in the oxosynthesis process. Hard-boiling oxygen - containing byproducts received in the course of the process can also be used. Some patents recommend water as a solvent [126].

The influence of solvent on the hydroformylation reaction was studied in detail. Besides the mentioned, also were studied the aliphatic, the alicyclic, and the aromatic ethers, nitriles, organic acid anhydrides, ketones, complex ethers, lactones, lactams, etc. The received data was rather contradictory.

Wender and colleagues studied the influence of heptane, methylcyclohexane, benzol, chloride-benzol, methylethylketone, acetone, butane-ether, methanol, ethanol, 2-ethyl-gexanola, on the speed of the cyclohexane hydroformylation reaction [125] and found that it hardly changed ($K = 5.7 \cdot 10^{-3}$ to $8.9 \cdot 10^{-3} \text{ min}^{-1}$).

The same results were received when studying the hydroformylation kinetics in the following: propylene in acetone, diethyl ether, tetra-hydro-furan, and cyclic-hexane [127]. At the same time Ivanaga and colleagues [128, 129] found that the reaction speed of hydroformylation of acryl-nitrile in methanol is 6 times greater than in benzol, while the hydroformylation reaction speed for metocryolite in methane, ethane, butane is by 3 to 4 times greater than in acetone, methylethylketone, and tetrahydrofuran.

It was found that the hydroformylation reaction speed for propylene in toluene and in the cubic leftover have close values [129].

In general, we can consider that, on the one hand, the influence of the solvent on the hydroformylation reaction speed greatly depends on the nature of the unlimited compound, on the other hand, it depends on the total speed of the process to a greater extent than the simple change of speed of the chemical reaction proper because the solvent also has influence on the phase equilibriums in the system: hydrodynamics, mass transition, etc.

Finally, it is necessary to consider the fact that some solvents are capable of entering reaction with forming aldehydes. Thus, when using alcohols as a solvent, a great amount of acetylene is formed [130].

2.6.2 INFLUENCE OF PARAMETERS ON ISOMER CONTENTS OF PRODUCTS

Considering the practical significance of the problem, about the quantitative data on the influence of various conditions on the product's isomer contents during catalytic hydroformylation, many scientists have studied the influence of temperature, pressure, and solvent on the correlation of isomers. Most of the attention was devoted to the hydroformylation reaction of propylene.

Olefin hydroformylation with a direct aim and a final position of a double bond proceeds mostly forming normally structured aldehydes, especially at 100° to 140° C. The portion of iso-structured aldehydes increases with the increase of temperature. Table 2.4 shows the influence of the temperature on the product's isomer contents received during the hydroformylation of propylene, 1-butane, and 1-heptane according to data [123, 131]. At temperatures up to 100° C the discharge of normally structured aldehydes reaches 80%. In the case of propylene, even at a temperature higher than 200° C the portion of normally structured aldehydes in a mixture of isomers comprised about 66%.

TABLE 2.4 Dependence of Isomer Contents of Hydroformylation Products on Temperature

Initial Olefin	Temperature	Correlation CO : H ₂	Contents of aldehydes in mixture — in %		Correlation N : Iso
			Normal	Iso	
Propylene	90	1 : 1	75.4	24.6	3.06
	135	1 : 1	76.1	23.9	3.18
	140	1 : 1	75.3	24.7	3.04
	170	1 : 1	69.7	30.3	2.30
	182	1 : 1	67.3	32.7	2.06
	234	1 : 1	61.3	38.7	1.58
1-Butane	70	1 : 3	73	27	2.70
	90	1 : 3	71	29	2.40
	140	1 : 1	60	40	1.50
	180	1 : 1	45	55	0.80
1-Heptane	70	1 : 3	80	20	4.00
	85	1 : 3	75	25	3.00
	100	1 : 3	72	28	2.60
	180	1 : 3	43	57	0.75

The increase of the carbon oxide's partial pressure also favors the preferential formation of aldehydes with a direct aim. Quantitative data on the influence of carbon oxide pressure on the discharge of butyl aldehyde isomers during propylene hydroformylation have been received in work [131] and are shown in figure 2.19. The increase of the carbon oxide's partial pressure increases the discharge of straight-chain aldehydes to a certain extent. After this, the relations between the products of normal and iso-normal structure become stabilized. The absolute value of this limit depends, in part, on the temperature.

The hydrogen's partial pressure also increases the output of normally structured products (fig. 2.20). There is a limitation here too, after which there is no pressure influence at the output of the isomers.

There is also an influence of the total pressure on the isomer contents of hydroformylated products of propylene and 1-heptane [130, 131]. Just like for partial pressure, there is a limit to the influence of the total pressure on the isomer contents of the aldehydes that depends on the temperature, and, most likely, on the structure of the initial olefins.

Olefins of normal structure with an inside position of a double bond during hydroformylation offer a greater output of iso-structural aldehydes. At temperatures over 140°C the contents of the products of hydroformylation (like 1- and 2-heptanes) is practically the same. The same is observed during the hydroformylation of 1- and 2-hexanes. This is because of the greater activation energy value of the isomerization reaction as compared with that of the hydroformylation reaction.

Because of this, in most works where the hydroformylation reaction was studied under usual conditions for technical oxosynthesis (20-30 MPa, 140°-180°C) there was no dependence of the isomer contents on the double bond position in the olefin chain.

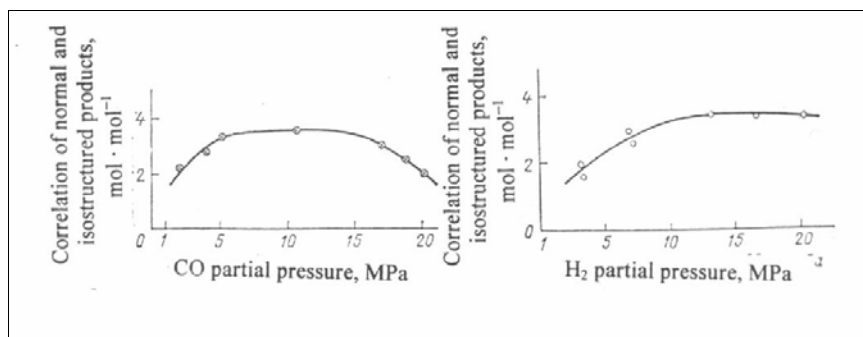


Fig. 2.19 Dependence of isomer contents of products of propylene hydroformylation on the partial pressure of carbon oxide.

Fig. 2.20 Same on the partial pressure of hydrogen.**TABLE 2.5**

Dependence of the isomer contents of products of hydroformylation on the temperature. Pressure ≈ 25 MPa.

Initial olefin; concentration	Temper- ature	Ratio CO:H ₂	Pres- sure MPa	Contents of aldehydes in mixture; %		Ratio nor:iso
				Norm	Iso	
Propylene; 0.1 % (mass.)	180	1 : 1	23	60	40	1.5
			28	67	33	2.0
			38	73	27	2.8
	140	1 : 1	10	67	33	2.0
			15	76	24	3.1
1-Heptane; 0.5 % (mass.)	85	1 : 1	25	78	22	3.5
			10	78	22	3.5
			25	79	21	3.6
	85	1 : 3	4.2	45	55	0.82
			25	75	25	3.0
			35	75	25	3.0

TABLE 2.6

Dependence Of Reaction Speed And Isomer Contents Of Hexane Hydroformylation Products On Temperature

Conditions: pressure 29 MPa; ratio CO : H₂ 1 : 1; cobalt concentration 0.1 % (mass.)

Olefin	Temperature ° C	Ratio of aldehydes norm : iso	Speed constant of reaction K · 10 ⁻³ , min ⁻¹
1-Hexane	110	4.4	32.0
	130	3.0	96.3
	150	2.0	300.0
	170	1.5	540.0
Hexane with a statistic distribution of double bond via conditions 1, 2, and 3.	120	2.1	12.8
	140	1.9	51.7
	155	1.7	145.0
	175	1.5	413.0

However, when studying the hydroformylation reaction of the 1-hexane and the isomerized hexane with the statistic distribution of double bonds along positions 1, 2, and 3 in a wide range of temperatures, it was found that at temperatures of 110°-120°C the hydroformylation of the 1-hexane offers a significantly greater output of normally structured aldehydes than does the hydroformylation of hexane with a statistic distribution of double bonds (see table 2.6). Note that if there is an increase of temperature up to 170°C, the isomeric contents of the hydroformylation products of 1-hexane and the isomeric hexane are practically the same.

Relative to the comparison of the reaction speed of the hydroformylation of the 1-hexane with the end and inside positions of the double bond, just as expected, at comparatively low temperatures the 1-hexane entered the reaction with a much greater speed than the isomeric hexane, while at high temperatures the hydroformylation speed practically did not depend on the position of the double bond.

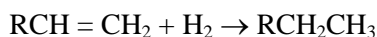
It was already said that during the hydroformylation of branched olefins practically no quarterly carbon atoms were formed. This is probably because during hydroformylation of iso-butylene, besides the iso-valerian aldehydes we also got the Pivalev aldehydes, though the formation speed of the latter, indeed, was about 20 times smaller than the speed for the formation of a 3-metyl-butanal.

2.7 SIDE REACTIONS DURING OLEFIN HYDROFORMYLATION

The percentage of side reactions under various conditions can differ, but, as a rule, the output of side products comprises 10%-20% of all the chemical transformations. The studies of side reactions proceeding under conditions of hydroformylation are of great practical value.

Some of the methods of decreasing the output of side products in the hydroformylation process will better be understood only when we comprehend the mechanism of their formation.

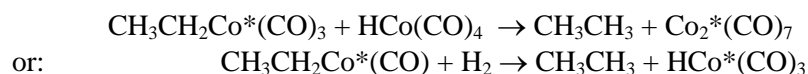
Out of a large number of side reactions, only one is the main hydroformylation reaction — the hydrogenation of olefins in the presence of metal carbonyls:



The hydrogenation of olefins on metallic cobalt that can be present in the reaction's system, under conditions of hydroformylation, does not occur because of the poisoning of the surface of the cobalt by carbon oxide [132].

The influence of the main parameters of the process and olefin structure on the reaction speed of olefin hydrogenation, and therefore, on the correlation of the hydrogenation and hydroformylation reactions were studied by Marko [132, 133], Rudkovsky and Imyanitov [6, p.17; 134; 135]. They found that the straight-chain mono-olefin hydrogenation of double bonding hardly has any influence. When the double bond is in the third branch of the carbon chain, the degree of hydrogenation increases.

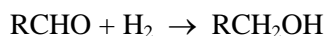
The hydrogenation mechanism of double bonding, most likely, is in the interaction of alkylcobaltcarbonyls with cobalt hydrocarbonyls or hydrogen along the scheme:



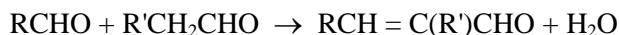
The hydrogenation reaction speed is proportional to the cobalt carbonyl concentration; it increases with the increase of the hydrogen's partial pressure and it slows down with the increase of the carbon oxide's partial pressure. In the case of the α -methyl-sterol, the order of the hydrogenation reaction along the substratum is smaller than the order of the hydroformylation reaction.

Other side reactions proceed with the participation of aldehydes and continue in succession relative to the hydroformylation reaction. Among them are the following:

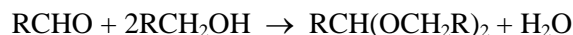
hydrogenation of aldehydes in alcohol:



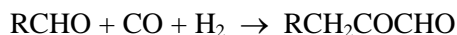
croton condensation of aldehydes:



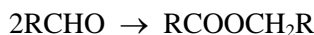
acetylation of aldehydes:



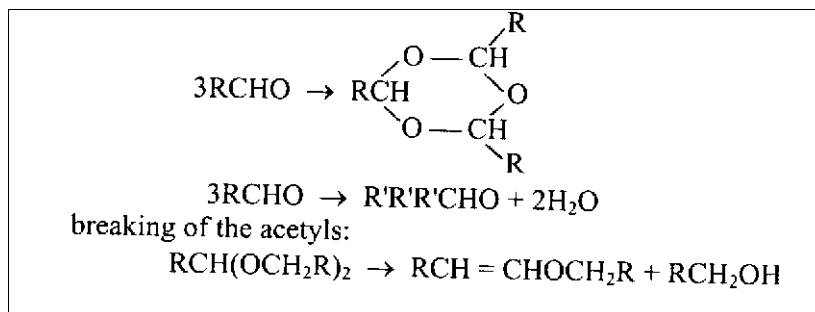
hydroformylation of aldehydes:



complex-ether condensation:



condensation reaction with formation of tri-measured products:



There are some more side reactions of the *second generation* that lead to the formation of complex (usually unidentified) high-boiling side products at the expense of the condensation and packing reaction along the unlimited bonds $\text{C}=\text{C}$ and the carbonyl group.

The mechanism for the formation of side products out of aldehydes in the hydroformylation process can be, in some cases, explained by the chemical properties of cobalt hydrocarbonyl.

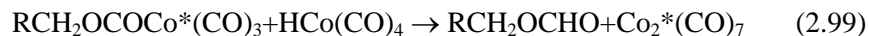
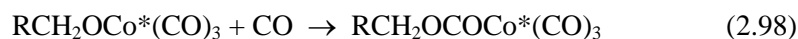
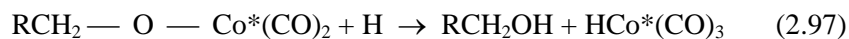
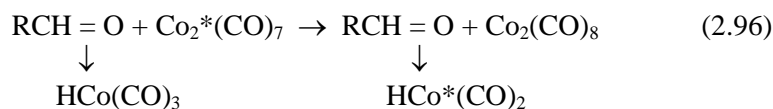
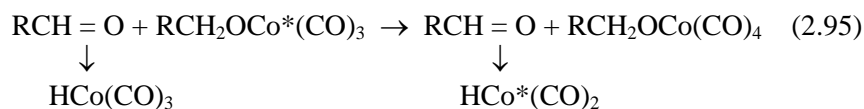
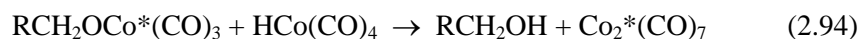
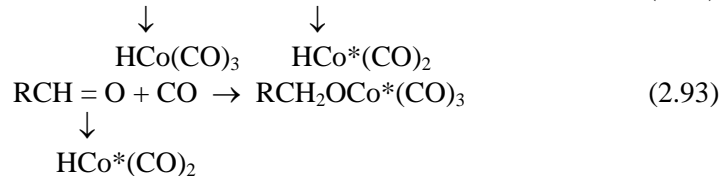
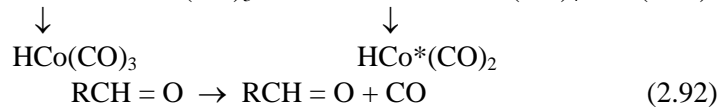
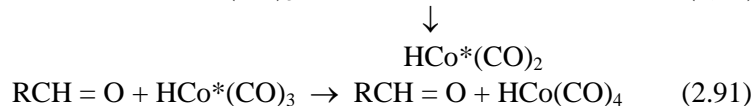
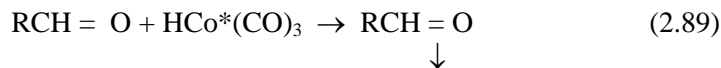
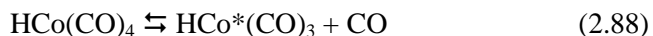
On the one hand, cobalt hydrocarbonyl can react with the double bond $\text{C}=\text{C}$ of the carbonyl group via the intermediate formation of metal-organic compounds just like with the double bond $\text{C}=\text{C}$ in the case of olefins.

The π complex *olefin — hydrocarbonyl* consequently offers aldehyde or carbon-hydrogen. Analogously, the π -complex *aldehyde — hydrocarbonyl* offers formyl or alcohol as the reaction product.

On the other hand, cobalt carbonyl is a strong acid (like nitric acid) that catalyzes many chemical reactions of the acid-based type. These reactions include such bonding as acetylation, aldolization, etc.

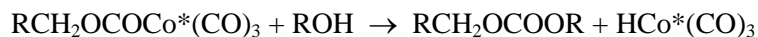
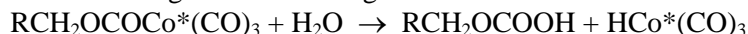
Thus, the mechanisms of most of the side reactions can be related to the catalytic properties present in the cobalt hydrocarbonyl system. The presence of two different kinds of mechanisms (as a minimum) for the formation of side products, presupposes the possibility of gaining an influence on their correlation.

The reaction mechanism for the interaction of cobalt hydrocarbonyl with aldehyde (analogously to the cobalt carbonyl plus olefin interaction mechanism) can be offered as follows:



Such an interaction reaction mechanism for cobalt hydrocarbonyl with aldehydes explains the hydrogenation of aldehydes in alcohol under conditions of hydroformylation and the formation of formates. See (2.94), (2.97), (2.99), and (2.100).

Besides these products, the offered reaction mechanism allows to expect the formation of carbon acid ethers in the capacity of side products according to the following reaction:

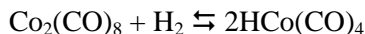
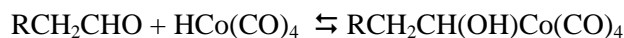


However, as yet, there is no information about the identification of these compounds as side products of hydroformylation.

An analogous scheme was offered by Marco [136] who considered only the possibility of bonding hydrogen (or carbon oxide) to conences with electronic vacancies in the d-shell of the cobalt atom.

2.7.1 HOMOGENOUS HYDROGENATION OF ALDEHYDES IN ALCOHOL

This reaction is one of the most studied of all the side reactions dealing with hydroformylation. Wender offered the first mechanism of this reaction [137]:



The hydrogenation reaction has the first order of magnitude in respect to the aldehyde, hydrogen, and catalyst. It is slowed down by carbon oxide to a greater extent than by the hydroformylation reaction. The kinetics of the reaction can be described as follows [136]:

$$r = kC_a C_{\text{Co}} P_{\text{H}_2} / (P_{\text{Co}})^2 \quad (2.1)$$

The speed constant dependencies for the hydrogenation reaction of aldehydes in alcohol on the concentration of cobalt during propylene hydroformylation have been found [138]. (See figure 2.21.)

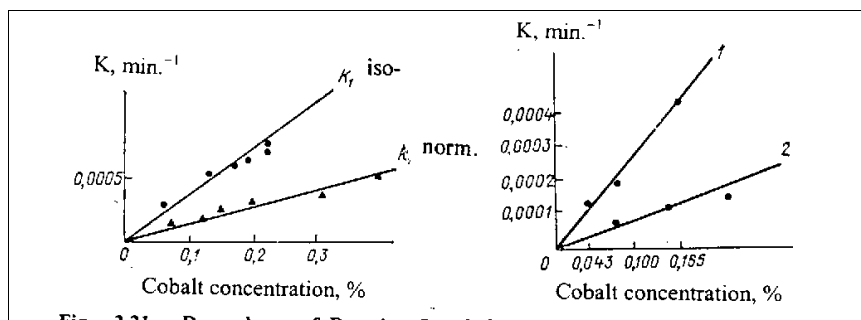


Figure 2.21

Fig. 2.21 Dependence of Reaction Speed Constants for Hydrogenating Butyl Aldehydes on Cobalt Concentration when Hydroformylating Propylene:

K_i^{norm} , K_i^{iso} – reaction speed constants for hydrogenating butyl and isobutyl aldehydes.

Figure 2.22

Fig. 2.22 Same for Hydrogenating Propylene Aldehyde when Hydroformylating Ethylene: 1 – cobalt introduced into system as naphthyl; 2 – introduced as carbonyls.

The speed constant of the hydrogenation reaction, relative to isobutyl aldehydes, is higher than in butyl aldehydes. Thus at 140°C the speed constant of the hydrogenation reaction of butyl aldehyde is equal to $K \cdot 10^{-3} = 0.157 \text{ min}^{-1}$; and the speed constant of the isobutyl aldehyde is: $K \cdot 10^{-3} = 0.285 \text{ min}^{-1}$.

The kinetic dependencies received in this work confirm the correctness of equation (2.1). Analogous data was received by Polyakov when studying the kinetics of hydrogenating the propane aldehyde under conditions of hydroformylation of ethylene. (See figure 2.22)

The production of butyl alcohol at the expense of homogenous hydrogenation of butyl aldehydes under hydroformylation is obvious only at high temperatures.

Thus, when studying the kinetics of the transformation of butyl aldehydes under conditions of hydroformylation [30 MPa, $\text{CO} : \text{H}_2 = 1 : 1$, cobalt concentration $\approx 0.4\%$ (mass)] it was found that in 180 minutes, at 120°C only about 1.5% (mol.) of the butyl aldehyde hydrated into butane, while at 140°C — about 7% (mol.).

The dependence of the homogenous hydrogenation reaction speed on the temperature was put in the basis of the idea to elaborate a one-stage scheme for the production of alcohol out of olefins [139].

Figure 2.23 Dependence of reaction speed of propionic aldehyde genation in the presence of $\text{Co}_2(\text{CO})_8$ on carbon oxide partial pressure.

Cobalt concentration 0.2 % (mol); hydrogen partial pressure 9,5 MPa;
a – initial concentration of aldehyde; x – concentration of formed alcohol.

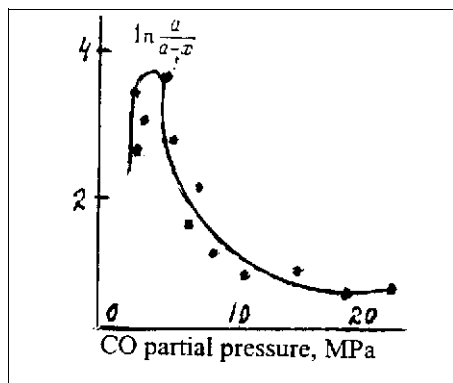
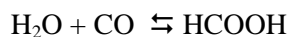


Figure 2.23

The dependence of the homogenous hydrogenation reaction speed in regard to aldehydes in the presence of dicobaltoctacarbonyl on the partial pressure of carbon oxide is shown in figure 2.23 [136]. When the partial pressure of the carbon oxide is small, the reaction speed increases and so does the CO concentration, which is explained by the acceleration of the cobalt carbonyl formation process. The maximum on the curve corresponds to the equilibrium between the conence formation reaction and the reaction that changes them into saturated complexes, after which there is a slow-down of the reaction caused by the carbon oxide. The hydration mechanism is shown in reactions (2.88) to (2.100).

2.7.2 FORMATION OF ALKYLFORMYLS

The presence of formic acid ethers in hydroformylation products was discovered at an early stage of the studies of the process mechanism [140–142]. Originally it was thought that formyls were received as a result of the interaction of alcohol with formic acid [142, 143], that were formed under hydroformylation conditions according to this reaction:



which is not confirmed by later works.

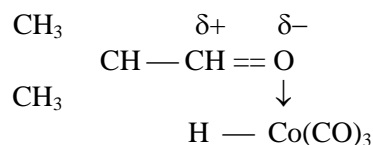
Obviously, the hypothesis offered by Marco about the formation of alkylformyls via alkyloxycobalttetracarbonyls parallel with the homogenous hydration of aldehydes through alkyloxycobalttetracarbonyls is quite logic. In this case the equation for the reaction speed of formyl formation has the following resemblance:

$$r = kC_a C_{CO} P_{H_2} / P_{CO}$$

The data in chemical literature [144] to the effect that the reaction speed for the formation of alkylformyls is in proportion to the carbon oxide concentration, most likely, is a mistake, since this data contradicts the notion about the catalysis with metal-complex compounds. The observed dependencies, probably, are connected with the studies of reactions in cases where the cobalt carbonyls are unstable.

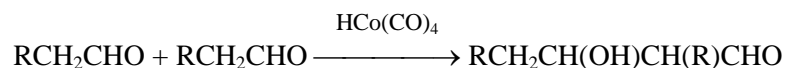
The reaction speed for the isobutylformyl formation during propylene hydroformylation is greater than the butylformyl formation speed [144]. An analogous speed correlation, as indicated above, was observed also during the formation of isobutyl and butyl alcohol at the expense of hydrogenating corresponding aldehydes. This coincidence corresponds to the offered reaction mechanism since the alkylformyls and alcohols are formed on different paths for their further transformation into one and the same kind of intermediate products (i.e., alkyloxycobalttetracarbonyls).

Most likely, this is explained by the extremely powerful induction effect of the isopropyl group during the formation of the following complex [145]:



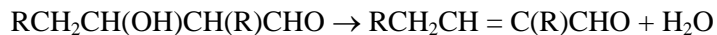
2.7.3 ALDOL CONDENSATION OF ALDEHYDES

The formed aldehyde partly enters the aldol connection reaction during hydroformylation as follows:



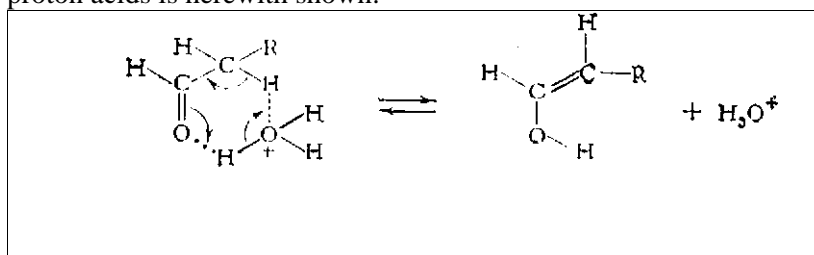
which is catalyzed by $\text{HCo}(\text{CO})_4$ thanks to its acidity.

Under conditions of hydroformylation (T over 100°C) aldol quickly liquidates the water-forming α - and β -unsaturated aldehydes:

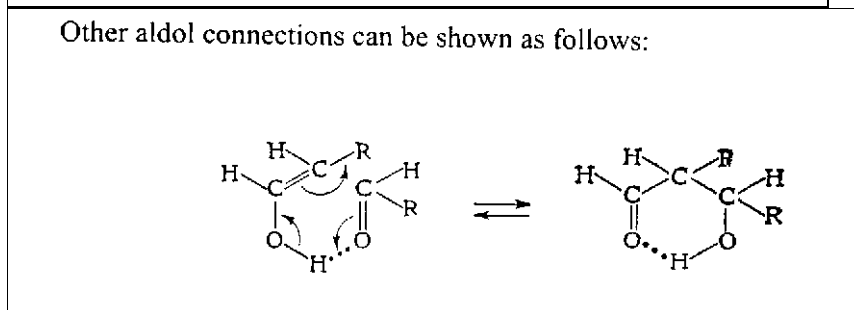


Big and small enols appear as intermediate products of the aldol compounds catalyzed by acids — compounds which, thanks to the strong positive mesomere effect of a hetero-atom, have a great nucleophilicity of olefin bonding and well react with electrophil carbonyl groups.

The mechanism for the formation of an enol in the presence of proton acids is herewith shown:



Other aldol connections can be shown as follows:



A molecule with a reaction-capable carbonyl group is called a *carbonyl component (CC)* while a molecule that gives an intermediate enol is called a *methylene component (MC)*. The aldol condensation reaction speed is usually controlled by the speed of the aldol connecting stage and can be expressed by the formula:

$$r = kC_{\text{CC}}C_{\text{MC}}$$

In our pure case, when one and the same aldehyde is the '*initial material*' for both of the components, the speed is proportional to the square of its concentration:

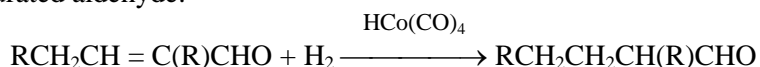
$$r = kC_a^2$$

But under the conditions of hydroformylation, the reaction speed of the aldol condensation has the first order of magnitude in respect to the aldehyde:

$$r = kC_a$$

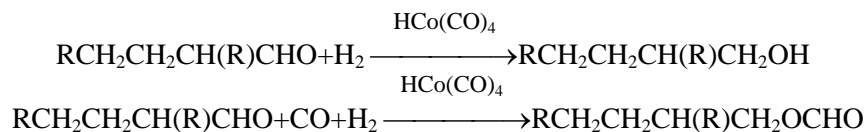
This makes one suppose that in the presence of hydrocarbonyl of cobalt, the limiting stage is the enolization.

The 'dyad' structure of α - and β -unsaturated aldehyde hydrogenates easily in the presence of $\text{HCo}(\text{CO})_4$ thereby forming saturated aldehyde:



Joined with the double bond of a carbonyl group $\text{C}=\text{O}$, the bond $\text{C}=\text{C}$ does not enter the hydroformylation reaction, and therefore it does not offer bifunctional side products.

Saturated aldehyde can be subject to further transformation with the formation of alcohol and formate:



The transformation of 2-ethylhexane under conditions of propylene hydroformylation has been studied in work [146].

TABLE 2.7
Transformation of 2-Ethylhexenal Under Conditions of Propylene Hydroformylation

Conditions: Temperature 146° C; Pressure 29 MPa; Ratio $\text{CO} : \text{H}_2 = 1:1$;
Cobalt Concentration 0.1% (mass.)

Time in min.	C o n c e n t r a t i o n i n % (mass.)			
	2-ethyl- hexenal	2-ethyl- hexanal	2-ethyl- hexylformyl	2-ethyl- hexanol
0	14.0	—	—	—
10	10.9	3.1	—	—
20	8.8	5.2	—	—
30	7.0	7.0	—	—
40	5.0	9.0	—	—
50	3.7	10.3	—	—
60	2.4	11.6	—	—
90	0.6	12.1	0.8	0.7
120	—	10.7	1.4	1.3

180	—	9.6	1.8	1.8
240	—	6.3	2.1	2.5
360	—	4.8	2.7	2.8

This work has shown that the 2-ethylhexenal offers a 2-ethylhexanol, and a 2-ethylhexylformyl, and the hydroformylation reaction speed and the hydrogenation of the carbonyl group are much smaller than the hydrogenation speed of the conjugated double bond (table 2.7). The hydrogenation reaction of the 2-ethylhexenal into the 2-ethylhexanal has the first order (of magnitude) relative to aldehydes, cobalt carbonyls, and the activation energy being 113 kJ/mol^{-1} .

The capability of the aldehydes to enter reaction of aldol condensation with the formation of α - and β -unsaturated aldehydes and the further hydrogenation of these aldehydes up to alcohols, is used in the modification of the oxosynthesis process known as the *aldox-process*. In this case the hydroformylation of propylene is accomplished in the presence of substances that accelerate the condensation of butyl aldehydes in 2-ethylhexenal (compounds Mg, Zn, Sn, Ti, Zr, Hf, Th, Pb, Cd, Hg, Al, Cu) [147]. KOH can also be used as a condensing agent [148]. The final products received are a 2-ethylhexanol and a mixture of butyl alcohol isomers.

Though the reaction of 2-ethylhexenal hydrogenation proceeds much quicker than the hydrogenation or hydroformylation of 2-ethylhexanol, it seems to be much slower than the reaction for propylene hydroformylation. Thanks to this, the presence of the 2-ethylhexenal in the hydroformylation product slows down the propylene hydroformylation reaction because of the bonding of the cobalt hydrocarbonyl in the complex that comes before the 2-ethylhexanal formation [149, 150]. In table 2.8 is shown the influence of a 2-ethylhexenal concentration on the reaction speed of propylene hydroformylation.

TABLE 2.8
Dependence of Propylene Hydroformylation Reaction Speed
on 2-Ethylhexenal Concentration in Reaction Mixture

Conditions: Temperature 130°C ; Pressure 29 MPa;
Ratio $\text{CO} : \text{B}_2 = 1 : 1$; Cobalt Concentration 0.1% (mass.)

Initial Concentration in % (mass.)	Speed Constant for Reaction $K \times 10^2, \text{min}^{-1}$
27.5	2.30

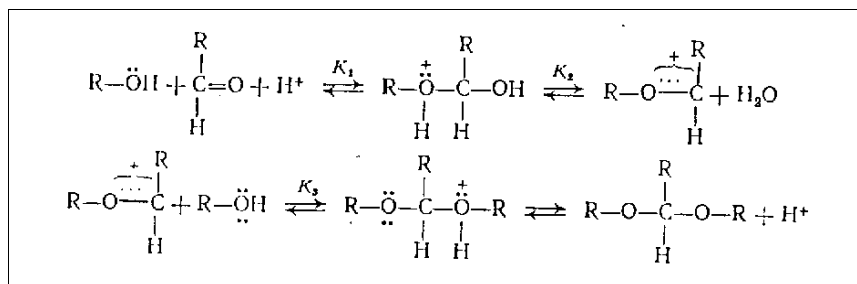
20.3	3.50
10.5	4.90
5.0	7.25
0	11.25

2.7.4 FORMATION OF ACETYL

The formation of acetyls out of aldehydes and alcohols almost always accompanies the hydroformylation reaction. In some cases, for example, when using alcohols as solvents, there are many more acetyls formed than aldehydes [131, 151].

However, acetyls are also formed when using carbon hydrogen as a solvent, like toluene during propylene hydroformylation [138].

The acetyl-forming reaction is catalyzed with acids [152] whose role is played by HCo(CO)_4 [153]. This reaction proceeds thus:



The slowest stage of the process is the cation-forming one, that is why the acetalization (and the reverse reaction — acetyl hydrolysis) proceed, as a rule, with the kinetics of a monomolecular reaction.

It is possible, that acetyl formation can be catalyzed by HCo(CO)_3 [144] along the following mechanism:

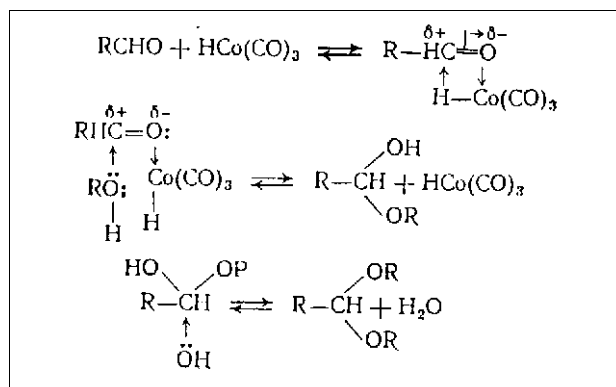
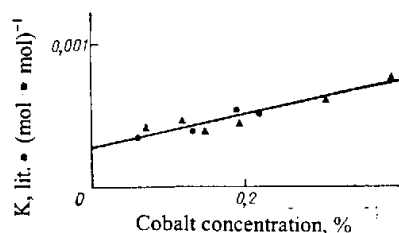


Fig. 2.24 Dependence of the constant of the reaction speed for the formation of the sum of acetyls on cobalt concentration under conditions of propylene hydroformylation:

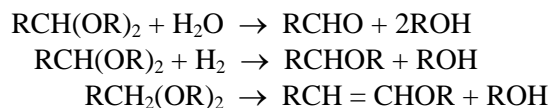
▲ acetal of normal structure
● acetal of iso-structure



It was found that under the conditions of propylene hydroformylation the reaction speed only slightly depends on the cobalt concentration (figure 2.24) [138]. Therefore this variant of the mechanism for forming acetyls is hardly possible.

When hydroformylating propylene, from 1% to 5% (mol) of the butyl aldehydes turn into acetyls. Since six isomer acetyls are formed out of butyl aldehydes and butyl alcohol, it is impossible to evaluate the value of each isomer.

The received acetyls can be subjected to hydrolysis, hydrogenolysis, and thermal breaking:



Aldehydes, alcohols, common ethers, and unsaturated common ethers are simultaneously formed; i.e., side products of the second generation.

Though sometimes the formation of acetyls in the course of the reactions play a positive role, for example, when producing unstable aldehydes [11], as a whole, the hydroformylation process is carried on in conditions that are not favorable for acetyl formation (wrong temper-

ature, or solvent, etc.) This is mainly because there are acetyl-breaking reactions among the side reactions of the *second generation* with the formation of saturated and unsaturated common ethers. The presence of common ethers in the main products complicates the rectification schemes and decreases the output of final products.

The kinetics of the rest of the side reactions that proceed under the conditions of hydroformylation, haven't been well studied. On the whole we can say for sure that the activation energy of the main and side reactions (excluding the aldehyde hydration reaction) hardly differ from each other. That is why the change of the conditions of the process are hardly noticeable relative to the reception of the main and side products.

Thus, if the activation energy of the hydroformylation reaction comprises $54 - 96 \text{ kJ/mol}^{-1}$ for various olefins, then for the formyl formation reaction it is equal to about 100 kJ/mol^{-1} , which hardly depends on the structure of the aldehyde, for the acetyl-formation reaction — 50 kJ/mol^{-1} , for the condensation reaction — 46 kJ/mol^{-1} , and the last two also hardly depend on the structure of the initial compounds. The activation energy of the hydrogenation of the propane aldehyde is equal to 121 kJ/mol^{-1} , that of butyl aldehyde $\approx 125 \text{ kJ/mol}^{-1}$, that of isobutyl and isovalerian aldehydes $\approx 138 \text{ kJ/mol}^{-1}$.

As already noted, the great activation energy for the homogenous hydrogenation of aldehydes in the presence of HCo(CO)_4 is used for guarantying the production of alcohol instead of aldehydes in case of hydroformylation at high temperatures.

However, the large activation energy is characteristic not only for the hydrogenation of aldehydes, but also of olefins ($\approx 150 \text{ kJ/mol}^{-1}$ for propylene, $\approx 125 \text{ kJ/mol}^{-1}$ for iso-butylene). Therefore, hydroformylation at high temperatures is always accompanied by increased losses of the initial olefin at the expense of its transformation into paraffin.

The correlation of final and side reactions can be greatly influenced by changing the degree of the initial olefin transformation because practically all the side reactions proceed in succession (not at all parallel) in regard to the main reaction. By decreasing the degree for the propylene transformation, it is possible to decrease the output of side products during hydroformylation from 10%-20% to 1%-2% (mass.).

The data on the influence of the propylene transformation degree (characteristic of circulation brevity (f) on the correlation of the outputs of main and side products are given in figure 2.25 [154].

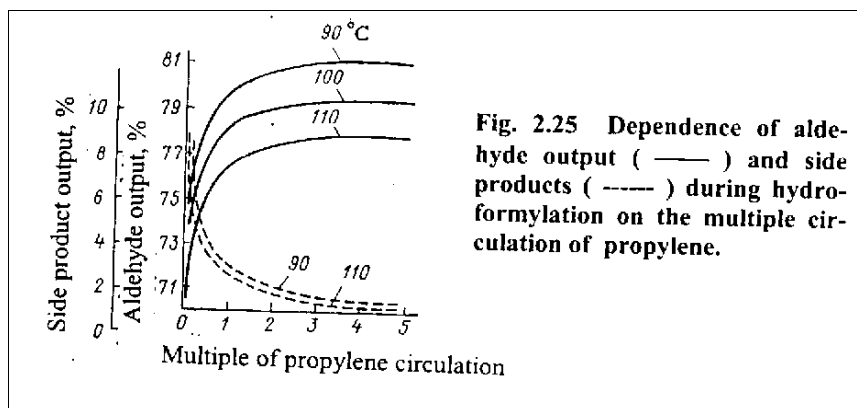


Fig. 2.25 Dependence of aldehyde output (—) and side products (----) during hydroformylation on the multiple circulation of propylene.

2.8 INFLUENCE OF PHASE EQUILIBRIUMS AND REACTOR STREAM STRUCTURES ON HYDROFORMYLATION

When choosing a construction and calculation in regard to a reaction apparatus for a chemical process, besides kinetic data, many other factors should be considered that are connected with masso- and thermo-exchange in the apparatus.

In the case of olefin hydroformylation, one of the important factors that influence the choice of optimal technological and constructive characteristics of the reactor's assembly is its dual-phase system. Here the most important (and also the most capable of being regulated by a parameter) is the distribution of the olefins between the gas and liquid phases of the system. It is quite natural that the role of this factor increases with the decrease of the molecular mass of the olefins, thereby gaining dominating significance in the case of ethylene and propylene hydroformylation. The influence of olefin distribution between the phases in the reaction system on the output of the main product and the effect of having used the reaction volume, have been studied in detail for the case of propylene hydroformylation [155].

According to the phase equilibrium, the propylene is distributed between the gas and liquid phases via the following equation:

$$N_{\text{ж}}^{\text{C}_3\text{H}_6} = N_0^{\text{C}_3\text{H}_6} \frac{1}{K_{\text{C}_3\text{H}_6}} \frac{N_{\text{ж}}}{N_{\text{r}}} \left(1 + \frac{1}{K_{\text{C}_3\text{H}_6}} \frac{1}{\frac{N_{\text{ж}}}{N_{\text{r}}}} \right)$$

$N_{\text{ж}}^{\text{C}_3\text{H}_6}$ is the amount of propylene in the liquid phase, in mols;

$N_0^{\text{C}_3\text{H}_6}$ is the total amount of propylene in the system, in mols;

$K_{\text{C}_3\text{H}_6}$ is the propylene's phase equilibrium constant;

$N_{\text{ж}}, N_{\text{r}}$ amount of substance in the liquid and gas phases, in mols.

If we consider that the equilibrium contents of propylene in the phases is reached at each moment of time of the process, then the equation for the main and side reactions will be observed thus:

$$d\lambda/dt = AK_1 (1 - \lambda) \quad (2.II)$$

$$d/dt = AK_1 (1 - \lambda) - K_2 y \quad (2.III)$$

λ is the transformation degree of the initial propylene; y is the transformation degree of the initial propylene in the main product.

In figure 2.26 are shown the data on the influence of the distribution of propylene between the gas and liquid phases [value A from equation (2.II)] on the output of the final product which is characterized as a ratio y_a/y , where y_a is the transformation degree of the initial propylene in the aldehydes at $A < 1$, and y being the transformation degree of the initial propylene in the aldehydes, in case if the propylene is completely in the gas phase, that is, $A = 1$.

In figure 2.27 we see the data on the influence of the distribution of propylene between phases A on the effectiveness of the reaction volume characterized by the relation of time t_A necessary to gain the necessary degree of propylene transformation at $A < 1$, and time t , necessary for gaining the same degree of transformation at $A = 1$.

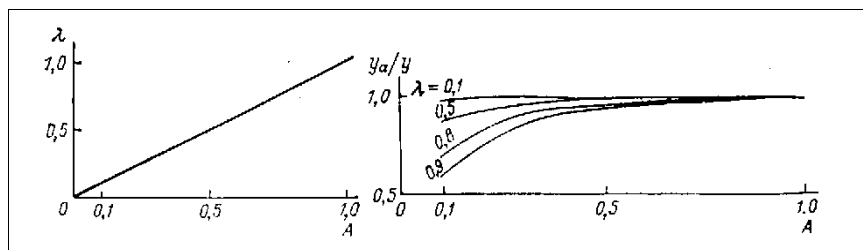


Fig. 2.26 Dependence of Final Product Output at Various Degrees of Propylene Transformation on Amount of Propylene in the Liquid Phase. (Designations are in the text.)

Fig. 2.27 Dependence of the Effectiveness Using the Reactor's Volume on the Portion of Propylene in the Liquid Phase. (Designations are in the text.)

The increase of the amount of propylene in the gas phase decreases the output of the main product, which is better observed at big degrees of transformation and this increases the necessary contact time.

The value A , according to equation (2.II), depends on $K_{C_3H_6}$ and N_{liq}/N_{gas} and, therefore, on the type of solvent, temperature, pressure, and amount of liquid in the gas passing through the reactor. The more liquid products and the less gas pass through the reactor, the greater is the value A . In the industrial enterprises that produce butyl aldehydes and butyl alcohol via the oxosynthesis method, A varies from 0.65 to 0.95.

The example of propylene hydroformylation also evaluates the influence of longitudinal (linear) mixing and circulation inside the reactor (i.e., the flowing structures in the reactors) on the effectiveness of the use of the reaction's volume and output of the main products. To evaluate the influence of the longitudinal mixing, a model reactor with an ideal ejecting and mixing system was used [156]. As a measure of effectiveness of the use of the reactor's volume, this equation was used:

$$\eta = t_1/t_2$$

where t_1 and t_2 are the contact times, needed to reach a definite degree of propylene transformation in an ideal reactor with an ideal mixing system. This equation can be transformed into the following:

$$\eta = \frac{\ln C_0/C_K}{(R + 1) \ln \left[\frac{RC_K + C_0}{C_K (R + 1)} \right]}$$

where C_0 (C_{in}) and C_K (C_{fin}) are the initial and final propylene concentrations; K is the coefficient of multiple circulation, that depends on the space of the longitudinal transition.

Figure 2.28 shows the data of the negative influence of the longitudinal shifting on the degree of the use of the reaction's volume.

The negative longitudinal transition influences the output of final products during hydroformylation, especially during deep transformation of propylene (fig. 2.29). The dependence of the final product output on the longitudinal transition was evaluated via the following equation:

$$\frac{C'}{C} = \frac{\frac{1}{1 - K_2/K_1} \left[\frac{C_K R + 1}{R + 1} C_0^{K_2/K_1} - \left(\frac{C_K R + 1}{R + 1} \right)^{K_2/K_1} C_K \right]}{\frac{C_K^{K_2/K_1}}{1 + K_2/K_1} (1 - C_K^{1 - K_2/K_1}) \left[\left(\frac{R C_K + 1}{R + 1} \right)^{K_2/K_1} - \frac{R}{R + 1} C_K^{K_2/K_1} \right]}$$

where C' is the concentration of aldehydes at the exit of the reactor with a longitudinal shifting; C is the concentration of aldehydes at the exit of a reactor with ideal mixing.

In the case of a small degree of olefin transformation, when η and C'/C are close to 1, a circulation can be used. Chemical literature has the data on the non-acceptance of recirculated products in the synthesis zone, but industrial enterprises do recirculate products to ease the conditions of thermal removal in some cases.

For the quantitative evaluation of the influence of recirculation on the output of products during propylene hydroformylation, calculations were made via this equation:

$$y_1/y = 1 - D [1 - (1 - \lambda)^{K_2/K_1}] / (1 - K_2/K_1) / [(1 - \lambda) K_2/K_1 - (1 - \lambda)]$$

y_1 is the output of the final product with the use of recirculation; y is the same without recirculation; D is the indicator of multiple recirculation.

It has been shown that recirculation decreases the output of final products (fig. 2.30) and with the increase of the temperature, the negative influence of recirculation decreases (see **a** and **b** in fig. 2.30).

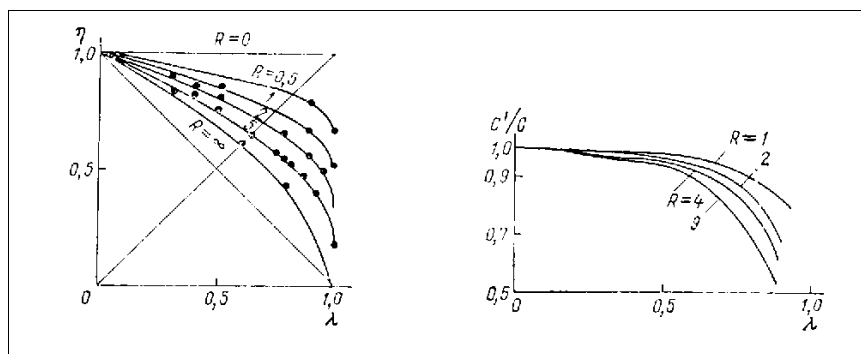


Fig. 2.28 Dependence of the effective use of the reactor's volume on the linear transition: $\lambda = (C_0 - C_K)/C_0$; other designations – in the text.

Fig. 2.29 Dependence of final product output C/C in the process of propylene hydroformylation on the linear transition: Same condition.

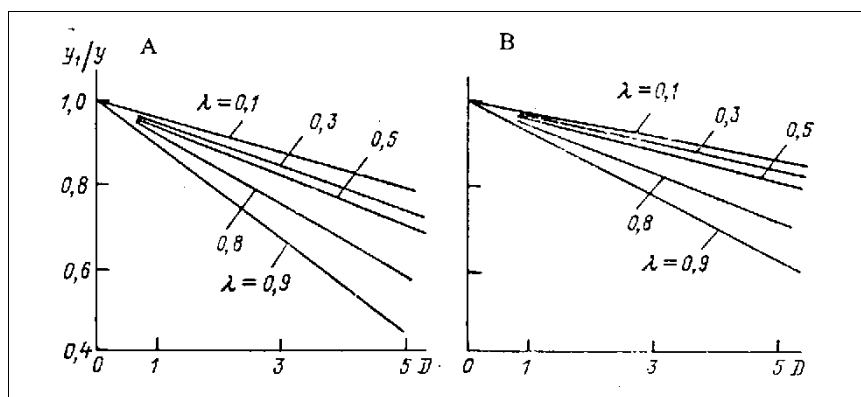


Fig. 2.30 Dependence of final product output at 120°C (A) and 160°C (B) on recirculation of propylene hydroformylation products. Designations are given in the text.

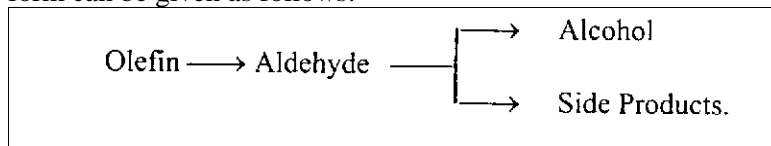
2.9 PRINCIPLES FOR CONSTRUCTING HYDROFORMYLATION CENTERS

2.9.1 CHEMICO-TECHNOLOGICAL SPECIFICS OF HYDROFORMYLATION AS A PRECONDITION WHEN CHOOSING REACTORS

The hydroformylation reaction in industrial processes of oxosynthesis proceeds mainly in the liquid phase. The reaction speed in the gas phase is by about two orders of magnitude smaller than in the liquid phase. Because of this, the construction of the reactor should guarantee rapid transition of the gaseous reagents (carbon oxide, hydrogen, and olefins — after the hydroformylation of the lower olefins) to the liquid phase. This is accomplished by a non-intensive preliminary mixing of the reaction's mixture close to the area where the reagents were introduced, or by passing gaseous reagents through special apparatuses.

The hydroformylation reaction is exothermic, therefore, it has to provide an effective thermal output. But the temperature increase is undesirable for the isomer distribution of the final product (increase of the output of isostructured products with the increase of temperature). An ideal hydroformylation reactor should be close to an iso-thermal one relative to the temperature.

A kinetic model of the hydroformylation process in the simplest form can be given as follows:



Here **olefin** is the initial raw material for the process; **aldehyde** is the final product of the process; **alcohol**, as a rule, is also the final product of the process; **side product** needs no explanation.

The side product formation reactions are sequential relative to the main reaction of hydroformylation. Since the order of side reactions relative to aldehyde is the first, and sometimes the second, the speed of the side reactions is proportional to the aldehyde concentration or even to the square value of the concentration's speed.

Because the reactor is expected to provide a minimal output of side products, the most effective apparatus for hydroformylation is one that does a good job at ousting (as the 'finale' of the reaction, i.e., where the aldehyde concentration is greatest). Such an apparatus provides an average concentration of aldehydes and a minimal contact time.

In most of the technological schemes cobalt is put into the reactor in the non-active form (in the form of salt). This is why when there is no special apparatus in the scheme, where the formation of cobalt carbonyl takes place, a high concentration of cobalt carbonyls in the first zone of the reaction can be provided either by recirculating part of the product, or by accomplishing the process in an apparatus with an ideal mixing capacity where the concentration of cobalt carbonyls is high.

The optimization of technological and constructive designing of the reactor's center for hydroformylation should be accomplished with consideration for the kinetic characteristics of the process, the specifics of the physical condition and properties of the components of the reacting mixture, the phase transitions, and requirements of optimal production together with thermal stability of the process, etc.

Contradictions that arise when changing various parameters (like the opposite influence of temperature on the production of an apparatus, and the isomer distribution of the main products) require decisions on the basis of compromises.

2.9.2 APPARATUSES FOR DESIGNING HYDROFORMYLATION REACTORS

Reactors With Inner Heat Collectors

To take away the heat from an exothermic hydroformylation reaction and to keep a stable temperature regime in the process, reactors with inner heat collectors can be used. These are apparatuses where the heat of the reaction is absorbed at the expense of putting cold raw materials or products right into the reaction zone.

Such apparatuses include the widely used high-pressure reactors of the *column type*. In oxosynthesis, these are columns with a high pressure ($H = 12,000 \text{ mm} - 18,000 \text{ mm}$, $\varnothing = 1,000 \text{ mm} - 1,200 \text{ mm}$) at the bottom of which the reactor components and catalyst are provided. The heat collecting regulation in this system is accomplished by blowing cold products of hydroformylation into each zone in turn. In most such apparatuses there is a circulation of a gas stream (CO and H_2), which improves the thermal exchange between the reactor's mixture and the blown in cold products that does away with the possibility of local overheating. The merit of this apparatus is its simple construction, and therefore, simple to manufacture.

However, the physical and mathematical modeling of column apparatuses up to nowadays has always been a problem. The dual-phase system with difficult-to-manage transition phases, the combined system of blowing in the cold products, and the gas circulation, all this provides a stream of complex hydrodynamics. These circumstances allow us to regard the column type of apparatuses as the most reliable.

However, the great experience gained when projecting and working with these reactors allowed to receive workable reaction centers for oxosynthesis machines at a time when the methods of mathematical modeling of chemical technology was just taking form. These circumstances explain the popularity of the column type of reactor with an inner thermal cutback regulator in the oxoprocess.

The shortcomings of the *column type* apparatus are connected with, first of all, the violation of those chemical-technological premises concerning the optimization of the hydroformylation process, already touched upon. This is why reactors of this type inevitably have a greater output of side products.

Besides this, the circulation of liquid and gaseous products increases the cost of repairs and energy usage. It also worsens the effective use of the reactor's volume (for 1 m^3 of liquid material, 2 m^3 of the reactor's volume is used).

Another variant of a reaction center with an inner heat collector can be the apparatus with an ideal mixer. Here the mixing is done at the expense of either outer or inner circulation.

This *ideal mixing* apparatus has some priority over the column type apparatus. Since there is no need to preliminarily heat the raw material, there is no need for the thermo-exchange-and-heating apparatus in the technological scheme. There is no circulation of gaseous products and carbonyl-containing products. Finally, apparatuses of this type are readily modeled and calculated. Not without substantiation, apparatuses of this type are calculated via quasi-homogeneous models.

However, in this apparatus of ideal mixing, when accomplishing a process with high degrees of transformation for the initial raw material, there will always be a high concentration of aldehydes, which will cause the formation of a multitude of side products. This makes apparatuses of the '*ideal mixing type*' not very welcome as reactors for hydroformylation '*in the pure form*'. The possibility of using such reactors in combined schemes will be touched upon later.

Reactors With Outer Heat Collectors

Out of numerous reaction apparatuses with outer heat collectors used in the hydroformylation process, it is most advisable to use column apparatuses with built-in tubes or thermal-exchange apparatuses of the *tube-in-tube type*. In practice, most workers prefer to use the *column type* of apparatus.

In published patent lists of the last years (1980) we come across descriptions for the use of hydroformylation reactors of the column type with built-in heat collectors with elements of the Field tube type. Water and alcohol were used as cooling liquids. Heat collecting can also be accomplished with built-in coiled pipes.

Of great interest is the use of high pressure reactors with a vertical system of pipes — where the reaction contents is within the pipes. This apparatus needs no additional high pressure.

Reactors with outer heat collectors are modeled and calculated much easier, because in this case we can use (just as in the case of the apparatus with *ideal ejection*) quasi-homogenous single-phase modeling.

There is a preference for reactors with outer heat collectors over those with inner ones. This is because the former are closer related to apparatuses with ideal ejection.

However, a serious shortcoming of these apparatuses is their unusual length when carrying out a process with a high degree of initial olefin transformation. The preliminarily heating of the initial products is

retained and the recirculation part of the carbonyl-containing liquid product for decreasing the induction period, connected with the transition of the cobalt salts into carbonyls, is also retained. As a result, this apparatus for ideal ejection is not used to the full extent.

Reactors of Combined Types

The merging of the advantages of the above reviewed types of reactors can be accomplished in the reactor center where a zone working like an apparatus that offers *ideal mixing* is merged with another zone working like an apparatus of *ideal ejection*. The 'first part' of the hydroformylation reaction is accomplished in the zone of *ideal mixing*, i.e., the process runs up to 50%-70% of the initial olefin transformation. Then the reactor's mixture passes on to the zone of *ideal ejection*.

The reactor center of the combined type of heat collecting apparatus can be regarded as a number of separate apparatuses connected consecutively, or just one sectional apparatus.

This effective heat collector works mainly at the expense of the input of cold raw material, and is accomplished in the zone of *ideal mixing*. Intensive mixing provides a satisfactory concentration of the active form of catalyst in all parts of the zone. The average concentration of aldehydes in the zone is not high thanks to the incomplete transformation of the initial olefin. This is why the secondary side reactions proceed with a small speed. A high concentration of initial olefin in this zone guarantees sufficient reaction speed even at comparatively low temperatures. The possibility of conducting a process at low temperatures, in turn, favorably influences the isomer distribution of hydroformylated products.

The circulation of products in the *ideal mixing zone* is accomplished at the expense of the built-in elements (which is most desired) or at the expense of the outer circular contour.

The reaction mixture transits from the ideal mixing zone to the ideal rejection zone. The heat collecting is accomplished at the expense of the outer thermal-exchange. Here the reaction ends most rationally, with a minimal discharge of side products.

The reaction center of the combined type of heat collector allows not only to decrease the portion of side reactions, but also to cut down on the volume of thermal-exchange-heating equipment, as well as a cut down on the volume of the ideal rejection zone.

However, this combined type of heat collector does not do away with the problems of cutting back chemical reaction heat completely because indirect cooling remains to dominate in this respect. In

connection with this, to give the process more thermal stability, longitudinal mixing of the reactor's mixture is still used in many cases.

Patent lists of hydroformylation reactors [157] show that the reactors at industrial enterprises are mostly of the combined types.

2.9.3 CALCULATING AND OPTIMIZING HYDROFORMYLATION REACTORS

Methods of mathematical modeling during the construction, calculation, and optimization of chemical reactors are developing simultaneously with the widening of our knowledge on chemical and physical processes that occur in industrial reactors.

On the first stages of the development of chemical technology, the calculation of the reactor was limited to defining the volume of the reactor's apparatus, needed to provide the necessary depth of transformation for the initial raw material with the given technological parameters, on the basis of experimentally defined dependencies of *time–degree* of transformation, *temperature–degree* of transformation, *pressure–degree* of transformation, etc.

Actually, the work of an industrial reactor is defined by a complex of chemical and physical processes that have individual or joint influence on the distribution of concentrations of reacting substances and temperature profiles in the reactor's volume that are, after all, the driving forces of the proceeding processes. The optimal distribution of the concentration and temperature fields in the reactor and the guarantee of the stability of this optimal distribution — such are the main problems to be solved before the creation of an industrial chemical reactor.

To solve problems, we need information about the chemical and physical processes in the apparatus.

What is this information about?

Firstly, it is about chemical model processes, about the system of equations that deal with the laws, and about the dependence of the change of chemical reaction speeds proceeding in the apparatus on the reagent's concentration and temperature. The development of modern methods of studying the kinetics of chemical reactions allows (if backed up by experiments) to get detailed kinetic models of chemical processes, especially of homogeneous catalytic reactions. To simplify the consequent calculations, complete kinetic models can be substituted by simple ones, and some chemical reactions can be excluded from the model if their contribution is too small to influence the transformation.

Secondly, it is about a physical model of a process, that is, a system of equations describing the influence of inter-phase substances

and temperature exchange on the concentration of reacting substances and temperature distribution. The physical model of a process should also consider the influence of the reactor's constructive specifics on the mechanism and speed of the physical processes in the apparatus. The mechanism of physical processes in technological apparatuses is quite complex. Indeed, the full physical model of a chemical reactor is regarded as unattainable. This is why only approximate physical models are used, though the degree of approximation in most cases is hardly substantial as compared with the well-substantiated chemical models

Thus, the mathematical model of an apparatus, including the simplified chemical and physical models, are approximate. However, the use of such models, when calculating and optimizing chemical reactors, is still a very useful and widely practiced phenomenon.

Methods of calculating and optimizing chemical reactors with the help of mathematical modeling are described in a number of monographs [158-163]. Relative to the hydroformylation process, methods for the calculation of apparatuses for ideal mixing and ideal ejection with an outer heat collector [164] are often suggested.

The kinetic model of the process given below, and the approximate single-phase physical model of the process are used for the calculation of a reactor for propylene hydroformylation with the help of an outer heat collector and a set of Field tubes:

$$C_i = C_i^0 + \tau \sum_{j=1}^{j=13} v_{ij} r_j$$

where C_i^0 and C_i are concentrations of the i component at the exit and the entrance of the reactor; i being the number of the substance in the kinetic scheme; j is the number of the reaction in the kinetic scheme; v_{ij} is the stehiometric reaction coefficient with the corresponding sign; r_j is the reaction speed; τ is the time of contact that is calculated via formula:

$$\tau = V (1 - \varepsilon) / Q_{liq}$$

where V is the free volume of the reactor; ε is the gas contained in the reactor; Q_{liq} is the amount of liquid used at the exit of the reactor.

The stability of the reactor's regime is calculated thus:

$$\frac{1}{\tau} - \frac{G C_3 H_6 q_y}{K F + C_{liq} C_{liq} + Q_g C_g} - \frac{R T^2}{E} \left(\frac{1}{\tau} + K \right)$$

$$K F + Q_{liq} C_{liq} + Q_g C_g > q G C_3 H_6 y / R T^2 / E - B (1 / \tau + K)$$

$$B = V (1 - \varepsilon) C_{\text{liq}} P_{\text{liq}} + V \varepsilon C_g P_g + V_{\text{st}} P_{\text{st}} C_{\text{st}}$$

where $G C_3 H_6$ is the amount of propylene fed into the mixture; y is the propylene's transformation degree; q is the reactor's heat effect; F is the size of the heat exchanger's surface; C_{liq} , C_g , & C_{st} are the heat capacities of the fluid, gas, and steel; Q_{liq} & Q_g are the expenditures in the liquid and gas phases; P_{liq} , P_g , & P_{st} are the condensations of liquid, gas, and steel; K is the speed constant for propylene utilization; V_{st} is the steel construction volume in the reactor.

The system of equations for calculating the temperature in the Field tubes goes as follows:

$$\begin{aligned} \frac{dT_{\text{in}}}{dx} &= \frac{\pi d_{\text{in}} N K}{Q C_p} (T_{\text{out}} - T_{\text{in}}) \\ \frac{dT_{\text{out}}}{dx} &= \frac{\pi d_{\text{out}} N K}{Q C_p} (T - T_{\text{out}}) + \frac{dT_{\text{in}}}{dx} \end{aligned}$$

where T_{in} & T_{out} are the cooling agents' temperatures in the inner and outer tubes; T is the reactor's temperature; d_{in} & d_{out} are the diameters of the inner and outer tubes; N is the number of Field tubes; Q is the amount of cooling agent; C is the heat capacity of the cooling agent; p is the density of the cooling agent; x is the coordinate along the top of the reactor ($x = 0$ corresponds to the entrance of the reactor).

The initial conditions for this system as a whole are chosen in a way that the thermal balance conditions of the reactor would be fulfilled:

$$\begin{aligned} T_{\text{out}} - T_{\text{in}} / x = H &= \\ = 1 / Q c [q G C_3 H_6 y + (Q_{\text{liq}} C_{\text{liq}} + Q_g C_g)_{\text{en}} T_{\text{en}} - Q_{\text{liq}} C_{\text{liq}} + Q_g C_g)_{\text{ex}} T_{\text{ex}}] \end{aligned}$$

where H is the height of the efficient part of the reactor; indexes **en** and **ex** indicate the values at the *entrance* and *exit* of the reactor.

When choosing a hydroformylation reactor, one must remember that the expenditures made on the reactor relative to the total volume of capital investment on the industrial installations of the oxosynthesis system comprises $< 1 - 2 \%$.

Besides, when optimizing the construction of the reactor and the parameters of the process, no use minimizing the reactor's volume because the economical effect is comparatively small.

The 'reserve' in the reactor's volume allows not only the smoothening out of inconsistencies in research and calculations, but also offers additional possibilities for flexible regulation of the process.

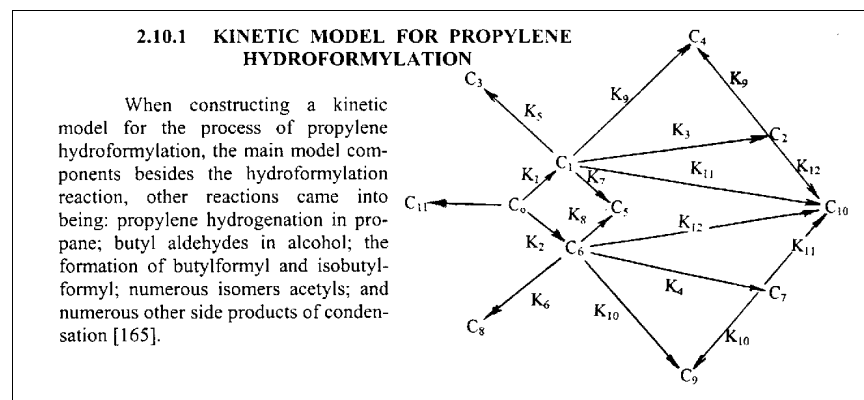
Undoubtedly, these ideas have nothing to do with optimization of parameters, which directly or indirectly influence the output of the final products, the heat stability of the reactor, etc.

2.10 MATH MODELING OF KINETICS IN HYDROFORMYLATION

The mathematical methods of modeling chemical processes as a way of solving problems connected with the elaboration of industrial technologies, is of primary importance nowadays.

One of the conditions that offer a possibility for practical usage of mathematical modeling for calculating reactor apparatuses, is to have plenty of data on the kinetic process in the form of kinetic models.

That is — a system of equations characterizing the dependence of the reaction speed on the reacting substance concentration and conditions for performing the process. This is why the kinetic model structure is a natural finale of the kinetic process research, which has a practical significance.



Here: C_0 — propylene concentration; C_1 — butyl-aldehyde concentration; C_2 — butyl-alcohol concentration; C_3 — butyl-formyl concentration; C_4 — normal structure acetal (N—N—N) concentration; C_5 — concentration of high-boiling condensed products; C_6 — concentration of isobutyl-aldehydes; C_7 — isobutyl alcohol concentration; C_8 — isobutylformyl concentration; C_9 — concentration of acetal isostructure (I—I—I); C_{10} — concentration of mixed acetals (N—I—I,

N—N—I, I—N—I, I—I—N); K_1 — K_{13} — speed constants of corresponding chemical reactions.

The above scheme reflects the main directions of chemical transformations in reaction mixtures. The concentration change of substances in time, relative to the accepted scheme, is described by the following system of differential equations:

$$\begin{aligned} dC_0/dt &= -(K_1 + K_2 + K_{13}) C_0 \\ dC_1/dt &= K_1 C_0 - (K_3 + K_5 + K_7) C_1 - 2K_9 C_1 C_2 - 2K_{11} C_1 C_7 \\ dC_2/dt &= K_3 C_1 - 3K_9 C_1 C_2 - 3K_{12} C_2 C_6 - K_{10} C_6 C_7 - K_{11} C_1 C_7 \end{aligned}$$

$$\begin{aligned} dC_3/dt &= K_5 C_1 \\ dC_4/dt &= K_9 C_1 C_2 \\ dC_5/dt &= K_7 C_1 + K_8 C_6 \end{aligned}$$

$$\begin{aligned} dC_6/dt &= K_2 C_6 - (K_4 + K_6 + K_8) C_6 - 2K_{10} C_6 C_7 - 2K_{12} C_2 C_6 \\ dC_7/dt &= K_4 C_6 - 2K_{10} C_6 C_7 - 3K_{11} C_1 C_7 - K_9 C_1 C_2 - K_{12} C_2 C_6 \end{aligned}$$

$$\begin{aligned} dC_8/dt &= K_6 C_6 \\ dC_9/dt &= K_{10} C_6 C_7 \end{aligned}$$

$$dC_{10}/dt = 2K_{11} C_1 C_7 + 2K_{12} C_2 C_6 + K_9 C_1 C_2 + K_{10} C_6 C_7$$

$$dC_{11}/dt = K_{13} C_0$$

At $t = 0$; $C_1 = C_2 = C_3 = C_4 = C_5 = C_6 = C_7 = C_8 = C_9 = C_{10} = C_{11} = 0$.

TABLE 2.9
Values of Parameters in Equation $\ln K = \ln K_0 - E/RT$
in the Kinetic Model of the Propylene Hydroformylation Process
 Pressure 30 MPa; ratio $\text{CO:H}_2 = 1:1$; cobalt concentration 0.1% (mass.)

n	$\ln K_0 n$ (in minutes ⁻¹)	E, kJ x mol ⁻¹
1	19.4 ± 3.0	75 ± 12
2	23.2 ± 3.0	92 ± 12
3	27.8 ± 6.0	126 ± 20
4	32.4 ± 2.0	139 ± 8
5	21.7 ± 4.0	105 ± 12
6	17.3 ± 3.5	88 ± 12
7	5.9 ± 4.0	46 ± 6
8	0.87 ± 2.0	29 ± 8
9	1.2 ± 4.5	31 ± 16
10	5.02 ± 2.7	46 ± 9
11	1.2 ± 4.5	31 ± 16

12	5.0 ± 2.7	46 ± 9
13	35.9 ± 5.0	150 ± 21

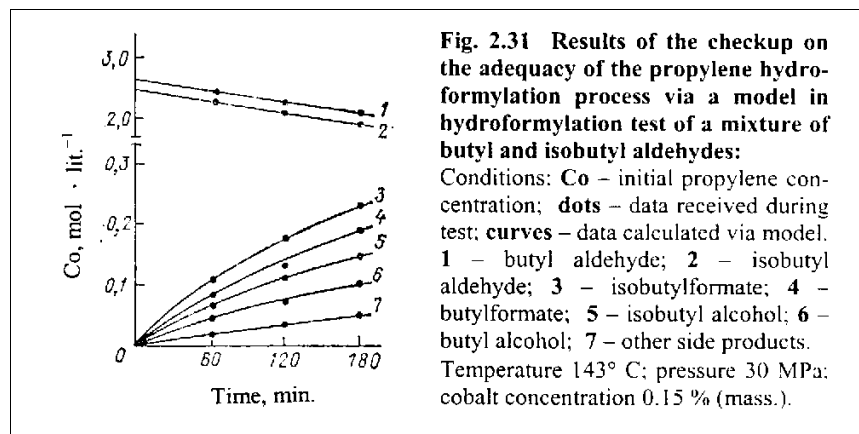
Note: All the constant values are based on the cobalt concentration of 0.1% (mass.) For all reactions $K = f(C_{Co})$, with the exception of : K_9 — K_{12} , where K does not depend on the cobalt concentration.

TABLE 2.10 Adequacy checkup results on the model in the propylene hydroformylation process

Conditions: temperature 148°C; pressure 30 MPa; cobalt concentration 0.05% (mass.); propylene transformation degree 98%.

Product	Product Concentration *, % (mol.)	
	Experimental	Calc. via model
Butyl aldehyde	70.00	69.00
Isobutyl aldehyde	23.00	23.80
Butyl alcohol	0.72	0.87
Isobutyl alcohol	0.53	0.54
Butylformate	1.09	1.10
Isobutylformate	0.45	0.50
Total other side products	4.30	4.30

* Recalculated to consider the total amount of oxygen-containing products.



The value of the parameters in equation $\ln K = \ln K_o - E/RT$ for all reactions related to the kinetic model of the hydroformylation process, are given in table 2.9.

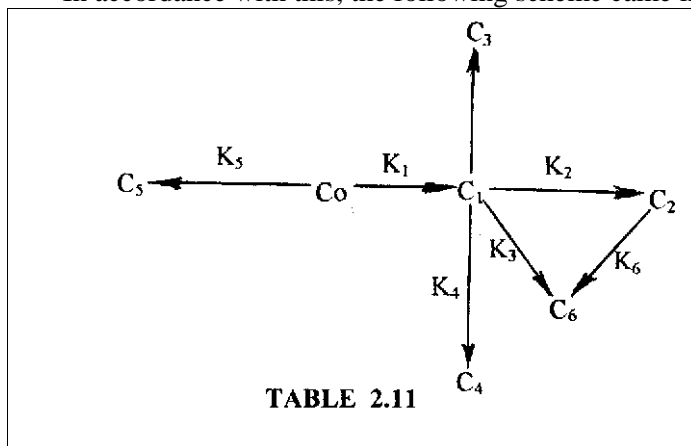
The adequacy of the experimental data on the elaborated model has been checked on two samples: propylene hydroformylation in the solvent toluol (table 2.10), and hydroformylation of an isomer mixture of butyl aldehydes in a solvent of toluol (fig. 2.31). The good coincidence of the data allows considering the offered kinetic model as quite adequate.

2.10.2 KINETIC MODEL FOR ETHYLENE HYDROFORMYLATION

Constructing a kinetic model for an ethylene hydroformylation process, one must take into account the reactions for the formation of propionic aldehydes, alcohol, propylformate, acetyl, and a number of reactions for the formation of high-boiling condensation products, and diethylketone.

The formation of ketone parallel with the formation of aldehydes is a specific case, most likely for the hydroformylation of the one and only olefin, namely, ethylene. At least, when hydroformylating other olefins, no ketones were formed.

In accordance with this, the following scheme came into being:



Values of parameters in equation $\ln K = \ln K_0 - E/RT$ of the kinetic model in the ethylene hydroformylation process

n	$\ln K_0 n$ (in min^{-1})	E, $\text{kJ} \times \text{mol}^{-1}$
1	26.7 ± 4.9	96.3 ± 12.6
2	27.9 ± 1.0	121.4 ± 4.2
3	21.7 ± 1.0	100.5 ± 4.2

4	10.3 ± 1.0	58.6 ± 4.2
5	22.5 ± 4.9	96.3 ± 12.6
6	11.9 ± 2.4	62.8 ± 12.6

Note: The constant values are based on the cobalt concentration of 0.1 % (mass.). For all reactions $K = f(C_{Co})$, except K_6 which does not depend on the cobalt concentration.

Here C_0 — C_6 are concentrations of ethylene, propynal, propanola, propylformyl, condensation products, diethylketone, and propylal, relatively, K_1 — K_6 are speed constants of the corresponding reactions. A kinetic scheme is described by a system of differential equations:

$$\begin{aligned} dC_0/dt &= -(K_1 + 2K_5) C_0 \\ dC_1/dt &= K_1 C_0 - (K_2 + K_3 + K_4) C_1 - K_6 C_1 C_2 \\ dC_2/dt &= K_2 C_1 - 2K_6 C_1 C_2 \\ dC_3/dt &= K_3 C_1 \\ dC_4/dt &= K_4 C_1 \\ dC_5/dt &= K_5 C_0 \\ dC_6/dt &= K_6 C_1 C_2 \end{aligned}$$

$$\text{At: } t = 0; C_0 = C_0^0; C_1 = C_2 = C_3 = C_4 = C_5 = C_6 = 0$$

The values of the parameters in equation $\ln K = \ln K_0 - E/RT$ for the reactions included in the kinetic model for ethylene hydroformylation is given in table 2.11. A checkup of the adequacy of the suggested kinetic model has shown good results.

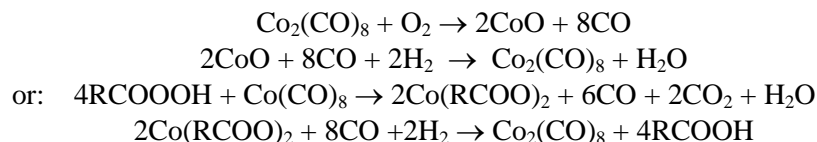
2.11 INFLUENCE OF FOREIGN PARTICLES ON THE HYDROFORMYLATION PROCESS

Both the initial olefin-containing raw material and synthesis gas ($CO + H_2$) can contain various foreign particles that have influence on the hydroformylation reaction, which is very important when accomplishing processes on the industrial scale. The main kinds of foreign particles that olefin raw materials could bring into the process are dyad, acetyl, sulfur, and super-sour compounds.

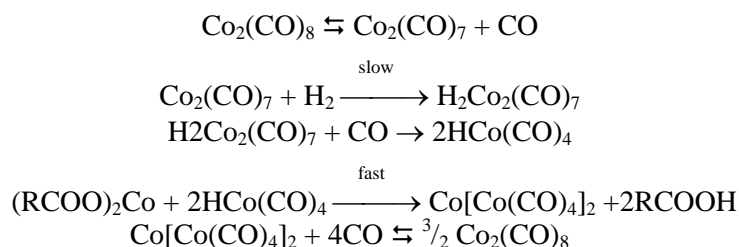
2.11.1 INFLUENCE OF OXYGEN AND PEROXIDE COMPOUNDS ON THE HYDROFORMYLATION PROCESS

The synthesis gas contained in oxygen can influence the oxosynthesis process directly or via hydroxyhydroperoxide, which is formed in the interaction of oxygen and aldehydes

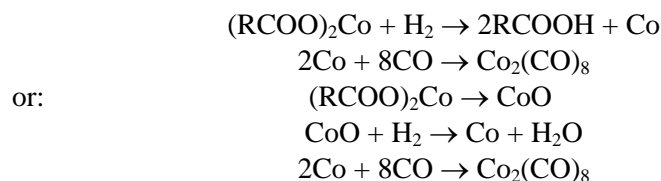
It is known that cobalt carbonyls readily oxidize under the influence of oxygen or peroxide with the formation of oxide and cobalt carbonate. However, both cobalt oxides and cobalt salts under conditions of hydroformylation again form carbonyls:



However, the reaction for the formation of cobalt carbonyls out of acids and salts is auto-catalytic (cobalt carbonyls serve as catalysts in this reaction) which proceeds along the scheme:



If there are no carbonyls, the reaction for the formation of carbonyls out of salts proceeds extremely slowly along this scheme:



further it proceeds along the auto-catalysis mechanism.

The reaction of direct restoration of cobalt salts with hydrogen becomes noticeable only at $\approx 130^\circ \text{C}$. At $140^\circ\text{--}150^\circ \text{C}$ it requires about two hours to form cobalt carbonyls out of salts, while in the presence of cobalt carbonyls, only about ten minutes.

Thus, the oxidation of foreign particles inevitably has influence upon the reaction speed when they are concentrated. The cobalt carbonyls will almost all be destroyed, transferring the oxidizer into the water, and for the replacement of their concentration in the process, a lot

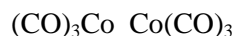
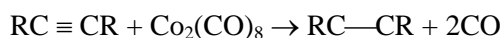
of time is required. At small concentrations of oxygen or peroxide, their influence on the process is hardly noticeable. Thus, when concentrating cobalt in raw material (about 2 gr. per liter⁻¹) there is an allowance for oxygen up to 0.2% or peroxide compounds up to 10 mg per liter⁻¹.

Here we are not considering the possible influence of oxygen (and peroxide compounds) on the process via the formation of corrosion-active compounds that destroy the apparatuses.

2.11.2 INFLUENCE OF DYADS AND ACETYLENE

Foreign particles of dyad and acetyl carbon-hydrates have an inhibiting action on the hydroformylation reaction. This inhibiting action is caused by the forming of the complex of diolefin with cobalt hydrocarbonyl $C_4H_6 \cdot HCo(CO)_4$ [168, 169].

Under conditions of hydroformylation, the complex falls apart with the hydrogenation of the dyad up to the olefin. Analogous is the action of the acetylene; only in this case the complex is formed with dicobaltoctacarbonyl as follows [170]:

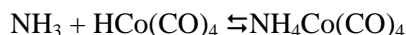


The structure of the complex is defined by spectroscopy. The breaking of the complex in the presence of hydrogen leads to the hydrogenation of the triple bond to a double one. The action of allen on the hydroformylation process is analogous to that of acetylene [171].

2.11.3 INFLUENCE OF AMMONIA

Foreign particles in synthesis gas have influence on the quality of the products since aldehyde-ammonium will form; then the following hydrogenation will cause the formation of amines. The influence of ammonia on the reaction speed of the hydroformylation reaction has not been studied as yet (1980)

It is known that ammonia and cobalt hydrocarbonyl form salts:



These do not catalyze the hydroformylation reaction. Therefore we can suppose that ammonia in concentrations, close to those of cobalt, will slow down the process.

2.11.4 INFLUENCE OF SULFURIC COMPOUNDS

Information on the influence of sulfuric compounds on the hydroformylation process, published in chemical literature, is very contradictory. Positive influences of sulfuric compounds on the process have been found. Ordinary sulfur, hydrogen sulfate, and carbon sulfate were offered as pro-motors as a catalyst for hydroformylation [172, 173].

Simultaneously there was also information on the slow down of the hydroformylation reaction caused by sulfuric compounds [175, 176]. Marco and his colleagues [177-179] published data to the effect that common sulfur carbon sulfate slow down the hydroformylation reaction by bonding cobalt in the form of sulfides. Mercaptans (RSH) have a much smaller influence on the hydroformylation reaction speed. The slowdown influence of sulfuric compounds can be evaluated by the ratio:

$$S : CS_2 : C_2H_5SH = 100 : 71 : 1.6.$$

The influence of the thiophene and the tetrahydrothiophene on the speed of hydroformylation went unnoticed.

When studying the influence of foreign particles of sulfuric compounds with olefin-containing raw materials on the oxosynthesis process via the triad scheme with thermal decobaltization, it was found that the reaction speed of the hydroformylation process actually does not depend on the amount of serum foreign particles there are in the raw material [180].

The olefin-containing fractions 55°-140°C various types of gasoline from a catalytic cracking mill, containing 0.06% and 0.29% (mass.) of serum, had almost the same hydroformylation speed. On the hydroformylation stage there was no 'tying' of cobalt into sulfuric compounds.

However, on the stage of thermal decobaltization there was an interaction of cobalt with a sulfuric compound, and here the cobalt bonded to the serum practically does not transform back into carbonyls under the conditions of hydroformylation.

Thus, most proven is the precept about the fact that under conditions of hydroformylation, the sulfuric compounds do not react with

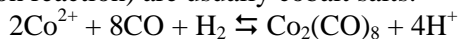
cobalt carbonyls, they don't form catalytic non-active compounds with them, and therefore, they do not have influence on the reaction speeds.

However, under conditions of thermal decobaltization, the formation of cobalt sulfides does take place.

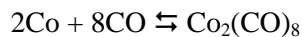
3 COBALTIZATION AND DECOBALTIZATION STAGES

3.1 COBALT CARBONYL FORMATION

The sources for producing cobalt carbonyls (catalyst of the hydroformylation reaction) are usually cobalt salts.



or direct metallic cobalt:



3.1.1 KINETICS OF COBALT CARBONYL FORMATION OUT OF OWN SALTS

Cobalt carbonyls (decobaltoctacarbonyls and hydrocarbonyls) are received via the interaction of cobalt halogens with carbon oxide in the presence of halogen acceptors [181] or via the interaction of synthesis gas (CO and H₂) with solutions of cobalt salts in organic solvent [182].

In the oxosynthesis process, the most convenient way of getting cobalt carbonyls is to get them from own salts via the interaction of synthesis gas with solutions of salts in organic solvents [183], since in this case, the conditions for the formation and storing cobalt carbonyls are practically the same as the conditions for the existence of the hydroformylation reaction.

The temperature for this reaction (carbonyl formation) is equal to 130°-180° C. Conducting the reaction for producing carbonyls at a temperature higher than 180 C is not desired because of a possible thermal breakup of the forming carbonyls. The direction of the reaction (direct or reverse) is defined by the partial pressure of the carbon oxide.

There are factors that allow us to act upon either the direct or reverse reaction. For example, the use of oxidizers accelerates the breakup of carbonyls with the formation of salts, as expected, because, as a result of the action of the oxidizers, the cobalt transits to the dual-valence condition.

The use of restoration devices accelerates the direct reaction of the formation of carbonyls out of salts. The restoration device can be carbon carbonyl itself in the presence of carbon oxide, which defines the autocatalytic nature of the reaction.

Influence of Type of Salt on Reaction Speed

The reaction speed for forming carbonyls out of salt solutions during interaction with synthesis gas hardly depends on the type of salt used if this salt is well diluted in the solvent [184]. Thus, the kinetic curves of the reaction for the formation of carbonyls out of solutions of cobalt acetate, cobalt butylene, and cobalt naphthene, are almost analogous (see fig. 3.1)

If the salt does not dilute in the chosen solvent, the kinetic curves of the reaction are of a different form. Most likely, in this case the reaction proceeds in the diffusion area. For example, when cobalt carbonyls are formed, the interaction of the synthesis gas with the cobalt acetate in toluol, the reaction speed hardly depends on the temperature and it does not increase during the increase of the cobalt carbonyl concentration (see fig. 3.2)

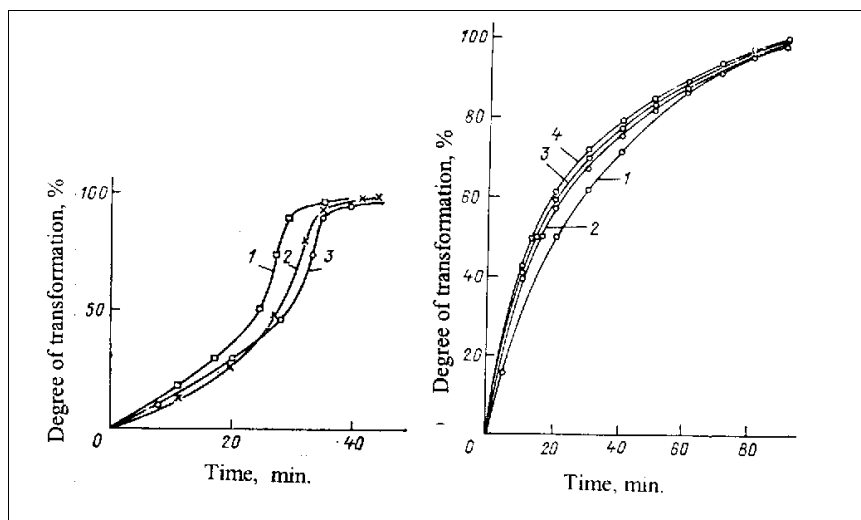


Fig. 3.1 Kinetic curves showing the cobalt carbonyl formation reaction out of compounds of various cobalt salts:

1 — cobalt naphthenate ; 2 — cobalt butyrate; 3 — cobalt acetate.

Fig. 3.2 Kinetic curves showing the cobalt carbonyl formation reaction out of a compound of cobalt acetate in toluol:

C u r v e	Temperature, °C	Initial concentration of carbonyls, % (mass.)
1	180	0.4
2	142	0.8
3	140	0.4
4	142	0.4

Therefore, the choice of salts, that serve as *initial raw material* on the stage of carbonyl-formation, is defined mainly: a) by the dilution of the salt in the product that is used as a solvent in the process; b) by the corrosion properties of the acid discharged during carbonyl formation (during carbonyl formation the acid leftovers are discharged from the salts in the form of free acid). The most desired of these suggestions are the cobalt salts of the highest aliphatic and naphthene acids.

Influence of Partial Pressure, Carbon Oxide, and Temperature

According to Chini [185, 186], the data received when researching the reactions for forming cobalt carbonyls out of cobalt 2-ethylhexanate. The speed constant of this reaction can be calculated via the equation of the autocatalytic reaction of the zero (or pseudo-zero) order of magnitude along the initial component:

$$K = 2.3 / \tau \lg (a + x/a)$$

where **a** — initial cobalt carbonyl concentration; **x** — present cobalt carbonyl concentration; **τ** — time in minutes.

The equation for the reaction speed constant includes, besides the cobalt concentration, the concentration of the rest of the components that influence the reaction speed (carbon oxide and hydrogen). In Chini's experiments these values remained unchangeable, and it was conditionally understood that the reaction speed does not depend on carbon oxide and hydrogen in solutions. Considering that the carbonyl-forming reaction, as a rule, is conducted under the high pressure of the mixture CO and H₂ (up to 30 MPa), it will practically always have a pseudo-zero order of magnitude along these components.

Accomplishing the cobalt formation reaction out of its own salts, the partial pressure of the carbon oxide should be not lower than a certain value, depending on the temperature. With the increase of temperature, the pressure of the carbon oxide increases as well. Thus, at 110°C, to accomplish the reaction, it is enough to have a partial pressure of carbon oxide equal to 0.3 MPa, while at 170°C this value runs up to 2.2 MPa.

The dependence between $\lg p_{\text{CO}}$ (p_{CO} is the partial pressure of the carbon oxide, necessary for the reaction) and the reverse temperature is given in fig. 3.3 An analogous dependence was observed [187] when studying the reaction for the formation of carbonyls out of metallic cobalt. However, the necessary partial pressure for the reaction, that forms carbonyl out of cobalt salts, is smaller than in the case of the interaction of CO with metallic cobalt.

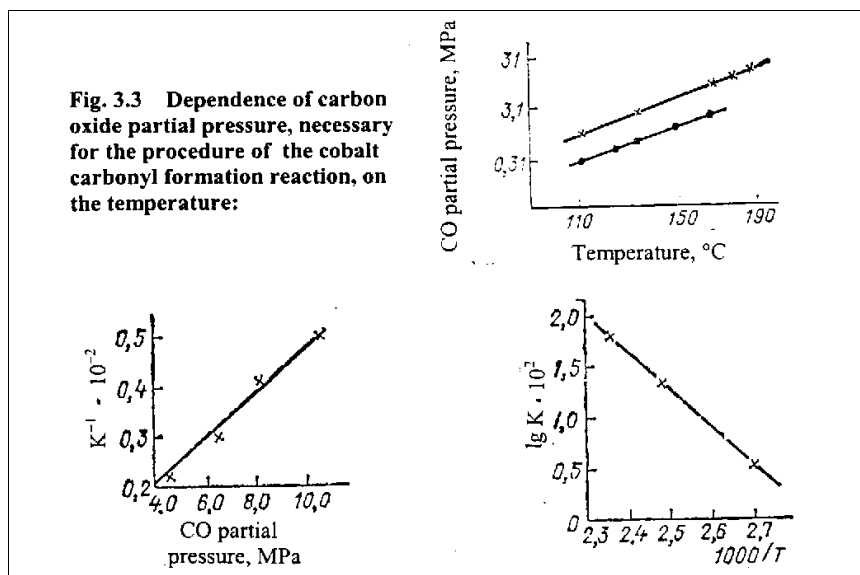


Fig. 3.4 Dependence of the reaction speed for the formation of cobalt carbonyls out of own salts, on the partial pressure of the carbon oxide:

Temperature 100° C; partial pressure of the hydrogen 10 MPa.

Fig. 3.5 Dependence of the reaction speed for the formation of cobalt carbonyls out of own salts, on the temperature.

The increase of carbon oxide's partial pressure beyond the norm at the given temperature, will slow down the reaction speed (see fig. 3.4)

The apparent activation energy of the reaction for the formation of cobalt out of own salts, defined on the basis of the data on the dependence of the reaction speed on the temperature (fig. 3.5) corresponds to 70 kJ/mol⁻¹.

Influence of Aldehydes, Ketones, Alcohols, Amines on Reaction Speed

The reaction speed for cobalt carbonyl formation out of salts significantly increases in the presence of small quantities of aldehydes, ketones, alcohols, amines, that is — the main substances, according to Lewis (see table 3.1)

Aldehydes, ketones, and alcohols at equal molar concentrations, offer acceleration to about the same degree. The reaction accelerates to a greater extent with amines (pyridine, aniline, and dihexylamine).

In fig. 3.6 to 3.8 are given the kinetic curves for the cobalt carbonyl formation reaction out of solutions of its own salts in toluol in the presence of butyl aldehydes, acetone, and methyl alcohol [184]. It is

of interest to note that when keeping aldehydes, ketones, and alcohols in a reactor's mixture up to about $0.5 \text{ mol} \times \text{liter}^{-1}$ their presence hardly has any influence on the reaction speed. An increase in the concentration of the Lewis principles leads to the proportional increase of the reaction speed. However, when conducting the reaction in pure methyl alcohol, its speed is close to that of the toluol reaction and much smaller than that of the alcohol concentration which is about $4 \text{ mol} \cdot \text{liter}^{-1}$.

TABLE 3.1

Reaction Speeds for Cobalt Carbonyl Formation out of Own Salts in the Presence of the Lewis Bases

Conditions: temperature 100°C ; cobalt concentration $\text{C Co}^0 - 0.42\%$ (mass.), $\text{CCo}^{8+} - 1.35$ (mass.); solvent — toluol.

Lewis Base	Concentration of the Base in C mol / liter	Speed constant of reaction $\text{K} \times 10^2 \text{ min}^{-1}$	$\text{K} \times 10^2$ shifted to $\text{C} = 1 \text{ mol} \times \text{liter}^{-1}$	Induction period in minutes
A c e t o n e	0.53	4.0	8.0	35
	1.06	6.3	6.0	6
	4.54	41.0	9.0	1
Butyl aldehyde	0.43	3.0	6.4	25
	1.72	11.0	7.0	6
Methyl alcohol	0.97	3.8	3.8	4
	1.94	10.0	5.1	3
	3.88	20.0	5.1	1
Ethyl alcohol	1.35	14.0	10.0	2
	2.70	27.0	10.0	1
Amyl alcohol	0.72	4.8	6.3	15
	1.44	9.2	6.7	3
Theophen	0.94	8.4	9.0	30
Dihexilamine	0.41	14.0	33.0	1
Anilin	1.65	70.0	42.0	1
Pyridine	0.46	85.0	185.0	1
	0.92	35.0	38.0	8
	1.84	Reaction does not proceed.		

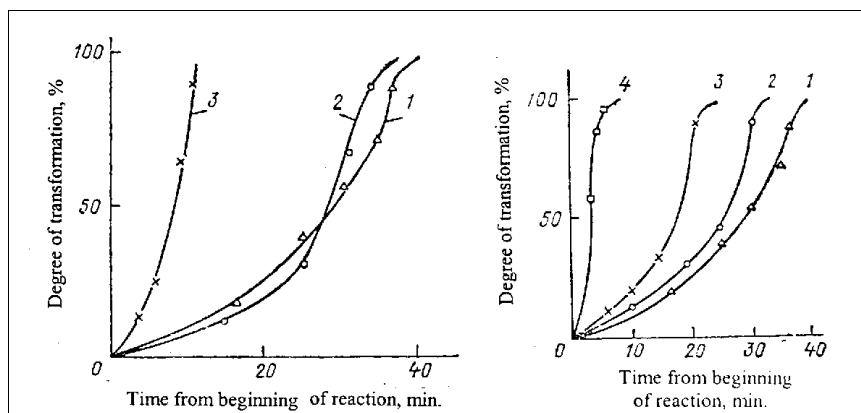


Fig. 3.6 Kinetic curves showing reaction of cobalt carbonyl formation from a solution of its own salts in toluol in the presence of butyl aldehyde.

Aldehyde concentration (in $\text{mol} \cdot \text{lit}^{-1}$): 1 – 0; 2 – 0.43; 3 – 0.72.

Fig. 3.7 Same, but in the presence of acetone.

Acetone concentration (in $\text{mol} \cdot \text{lit}^{-1}$): 1 – 0; 2 – 0.53; 3 – 1.06; 4 – 4.54.

In the case of pyridine, this phenomenon is even more prominent. When concentrating pyridine in a reaction mixture of $0.92 \text{ mol} \times \text{liter}^{-1}$, the reaction speed is slower than at $0.45 \text{ mol} \times \text{liter}^{-1}$, but higher than in pure toluol or in the presence of other substances that encourage acceleration. During the concentration of pyridine $1.84 \text{ mol} \times \text{liter}^{-1}$ the carbonyl-formation reaction does not proceed at all.

When there is olefin in the reaction's system, first comes the reaction for the transformation of cobalt salts into carbonyls, and then comes the hydroformylation reaction.

In fig. 3.9 we see the characteristic fall of pressure (expenditure of carbon oxide) in time (i.e., reaction speed) when researching, under analogous conditions, the cobalt carbonyl formation reaction and the hydroformylation of paraffin cracking in the presence of cobalt salts.

We see that in the area where the salts change to carbonyls, the kinetic curves of these two reactions coincide. Therefore, until there is a complete transition of the cobalt salts into carbonyls, the hydroformylation reaction does not proceed.

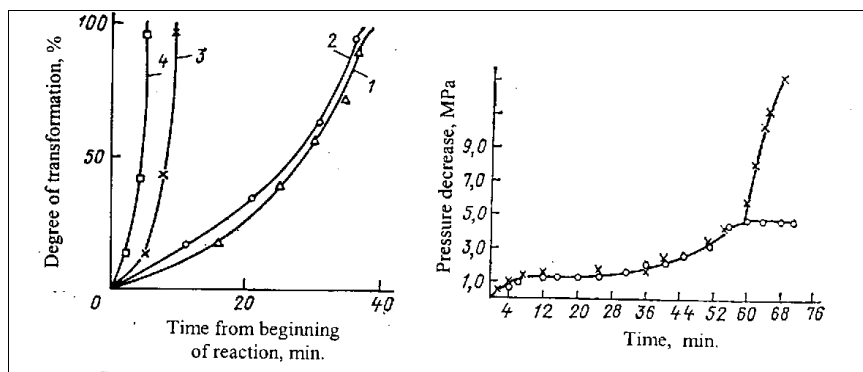
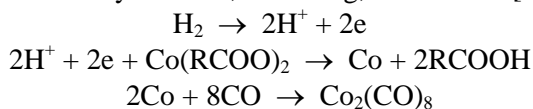


Fig. 3.8 Kinetic Curves for the Cobalt Carbonyl Formation Reaction out of Solutions of Own Salts in Toluol in the Presence of Methyl Alcohol. Alcohol concentration (in mol x liter⁻¹): 1 — 0; 2 — 0.97; 3 — 1.94; 4 — 3.88.

Fig. 3.9 Kinetic Curves for the Cobalt Carbonyl Formation Reaction out of Own Salts (o) and Cracking-Paraffin Hydroformylation on Cobalt Salts (x).

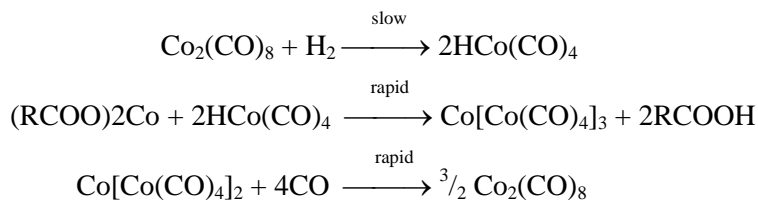
Mechanism for Cobalt Carbonyl Formation out of Own Salts

The first reaction mechanism for cobalt carbonyl formation from own salts was offered by Wender, Sternberg, and Orchin [119 p.78]:



These chemists supposed that the dual-valent cobalt is reduced by hydrogen to a zero-valent one, which then changes under the action of the carbon oxide, into decobaltoctacarbonyl analogous to the known reaction for metallic cobalt [188]. However, such a reaction mechanism does not explain its auto-catalytic nature, or its slowdown reaction with the increase of the carbon oxide's pressure.

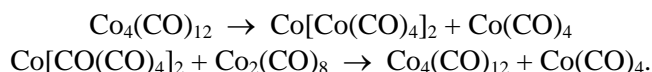
Having studied cobalt carbonyl formation out of salt of 2-ethylhexane acid, Chini offered the following scheme as a '*working hypothesis of a reaction's mechanism*' [186]:



Chini's scheme explains the accelerating action of the decobaltoctacarbonyl on the reaction, and therefore, its auto-catalytic nature.

Having resolved that the first stage of the mechanism (formation of cobalt hydrocarbonyl) is a slow one, Chini explained why the reaction speed increased with the increase of the hydrogen's pressure. However, even this scheme does not explain slowdown action of carbon oxide on the reaction speed, and therefore, is not sufficiently authentic.

In an effort to explain the slowdown effect of the carbon oxide, Chini suggested that the carbon oxide's pressure increase causes a decrease in the tetracobaltdodecarbonyl concentration $\text{Co}_4(\text{CO})_{12}$ in the presence of which there can be an occurrence of $\text{Co}(\text{CO})_4$ in the system along the following reaction:



while the formation speed of cobalt hydrocarbonyl out of $\text{Co}(\text{CO})_4$ is much higher than out of decobaltoctacarbonyl. The possibility of these reactions was proven on the basis of the well-known reactions of cobalt carbonyls [189]. However, this scheme is also doubtful since it does not explain the influence of the hydrogen concentration on the reaction speed and does not explain the negative influence of carbon oxide from the quantitative viewpoint.

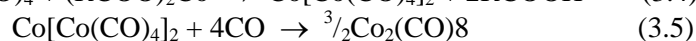
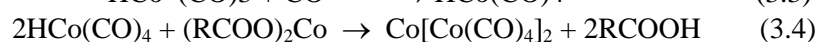
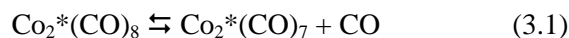
Though Chini practically gave up his initially suggested mechanism, since it did not explain the slowdown effect of carbon oxide, from the chemical point of view, his scheme is attractive because each of the stages of this mechanism is authentic and understood. Namely this allowed supplementing the Chini mechanism by using the hypothesis about the role of the conences in a metal-complex catalysis [184].

When studying the kinetics of cobalt carbonyl formation out of own salts in the presence of olefins, it was found that the olefin hydroformylation reaction precedes the induction period whose value depends on the amount of decobaltoctacarbonyl introduced together with the salt. After the induction period, the hydroformylation reaction speed corresponds to that reaction speed which is observed when all the cobalt is introduced to the reaction system in the form of carbonyls.

The speed for absorbing carbon oxide in the system: **cobalt salt — cobalt carbonyls — olefin**, completely coincides with the speed for the absorption of carbon oxide by the reactor which contained no olefin throughout the whole of the kinetic curve and showed the time of the transition of the cobalt salt into carbonyls (fig. 3.9). This allows us to conclude that in the system: **cobalt salt — cobalt carbonyls — olefin**, formed via the action of synthesis gas, the cobalt hydrocarbonyl does not

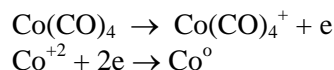
catalyze the olefin hydroformylation reaction up to the complete transition of the cobalt salts into carbonyls. This can be explained only by the fact that the formed cobalt hydrocarbonyl does not offer a π -complex with the olefin, but enters another reaction — with cobalt salt.

Therefore, the mechanism for the formation of cobalt carbonyls out of own salts should be described as follows [190]:



All the stages of this mechanism have their true confirmations.

Undoubtedly, there is a possibility for realizing a stage for the formation of cobalt hydrocarbonyls out of decobaltoctacarbonyls. Cobalt hydrocarbonyls a powerful acid, close to that of nitric acid in a solution of water, therefore its reaction in exchange interactions with the cobalt salt of weak acids is quite realistic. The formation of decobaltoctacarbonyls out of cobalt hydrocarbonyl salt are described in patents [191]; its theoretical opportunities are proven on the basis of the comparison of the acid-replacement potentials of the following reactions:



This mechanism explains carbon oxide's slowdown influence on the reaction speed since it presupposes that under conditions of the decobaltoctacarbonyl reaction (itself being inactive) is in equilibrium with decobaltheptacarbonyl that is formed as a result of dissociation.

The kinetic equation of the process with the suggested mechanism should be as follows:

$$r = K_2 (C_1 - x) C_{\text{H}_2} \quad (3.I)$$

where K_2 is the speed constant of reaction (3.2); C_1 is the concentration of decobaltheptacarbonyl in a solution without considering its expenditure relative to reaction (3.1); x is the decobaltoctacarbonyl concentration; C_{H_2} is the hydrogen concentration. For reaction (3.1) we get the following:

$$K_p = (C_1 - x) C_{\text{CO}}/x \quad (3.II)$$

where K_p is the reverse value of the reaction's equilibrium constant; C_{CO} is the carbon oxide concentration.

From equation (3.II) we get:

$$x = C_1 C_{CO} (K_P + C_{CO})$$

By substituting the value of x in equation (3.I) we get:

$$\begin{aligned} r &= K_2 C_1 C_{H_2} K_P / (K_P + C_{CO}) \\ \text{or: } r &= dC_1/d\tau = K_2 C_1 A \\ A &= K_P C_{H_2} / (K_P + C_{CO}) \end{aligned} \quad (3.III)$$

During the unchangeable hydrogen concentration (C_{H_2}) in the course of the reaction, carbon oxide (C_{CO}) and temperature (usual conditions for tests) A is an unchangeable (constant) value.

Therefore, when integrating equation (3.III) we get:

$$\frac{\ln C_1/\alpha}{\tau} = \frac{K_P C_{H_2}}{K_P + C_{CO}} = K \quad (3.IV)$$

where K is the constant calculated from the experimental data;
 α is the initial decobaltoctacarbonyl concentration

In this case, by integrating equation (3.III) we get:

$$\frac{1}{K} = \frac{1}{K_2 C_{H_2}} + \frac{C_{CO}}{K_P K_2 C_{H_2}} \quad \text{or} \quad \frac{C_{H_2}}{K_2} = \frac{1}{K_2} + \frac{C_{CO}}{K_P K_2} \quad (3.V)$$

Since in the studied area of pressure and temperatures the concentration of CO and H₂ in liquid form is proportional to the partial pressures of these gases, there should be a linear dependence between: ρ_{H_2}/K and ρ_{CO} (where ρ_{H_2} and ρ_{CO} are hydrogen partial pressures and carbon oxide, relatively).

To check the truth of this conclusion, experiments were conducted on the production of cobalt carbonyls out of own salts at various partial pressures of carbon oxide and hydrogen. The constant value of reaction speed K in the course of the experiment was practically the same. This is why the average value was used in calculations K (K_{av}) for each experiment that dealt with ρ_{CO} and ρ_{H_2} . These values together with the necessary data on ρ_{H_2} are given in table 3.2.

As seen in fig.3.10, the experimental results are well described in equation (3.V), which confirms the correctness of the offered reaction mechanism for cobalt carbonyl formation out of own salts.

TABLE 3.2 Average Values of Speed Constants for Reactions of Cobalt Carbonyl Formation out of Own Salts

$K_{av} \times 10^2, \text{ min}^{-1}$	$\rho_{H_2 \text{ av}}, \text{ MPa}$	$\rho_{CO \text{ av}}, \text{ MPa}$	$(\rho_{H_2 \text{ av}}/K_{av}) \times 10^{-2}$
2.9	19.7	6.5	6.8
2.1	17.4	7.8	8.3
1.6	14.6	10.1	9.1
1.3	13.8	12.5	10.6
1.2	14.1	12.2	11.7
1.2	13.4	12.7	11.2
0.9	11.5	14.4	12.8

On the basis of these results, and also on the solvability data of carbon oxide and hydrogen in toluol and toluol solvent of cobalt naphthene (fig. 3.11), the values of constants K_2 and K_{eq} in equation (3.V). The value K_r reaction for the formation of cobalt decobaltoctacarbonyl out of decobaltoheptacarbonyl at 95° C comprised 0.17 mol x liters⁻¹. The value of the speed constant reaction of the cobalt hydrocarbonyl formation out of decobaltoheptacarbonyl K_2 at 95° C was found to be equal to 0.19 lit. x mol⁻¹ x min⁻¹.

In order to confirm the correctness of this reaction mechanism the speed of the transition from decobaltoctacarbonyl to cobalt hydrocarbonyl was also defined. It was found (fig. 3.12) that the transition speed of decobaltoctacarbonyl into hydrocarbonyl relative to the decobaltoctacarbonyl concentration of 1 mol x lit.⁻¹ at $T = 100^\circ \text{ C}$ and pressure of 20.4 MPa ($\rho_{CO} = \rho_{H_2} \approx 10 \text{ MPa}$), comprises 0.42.

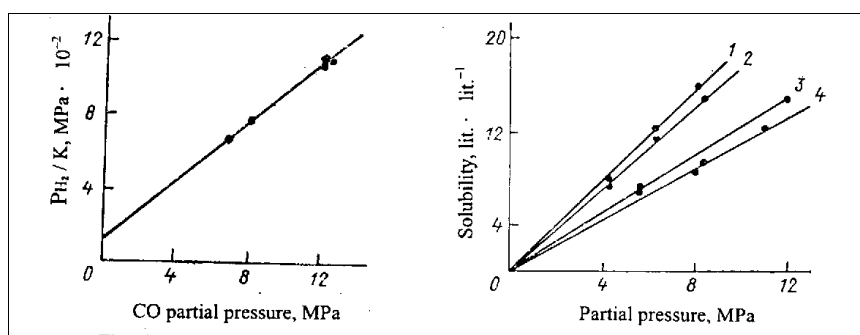
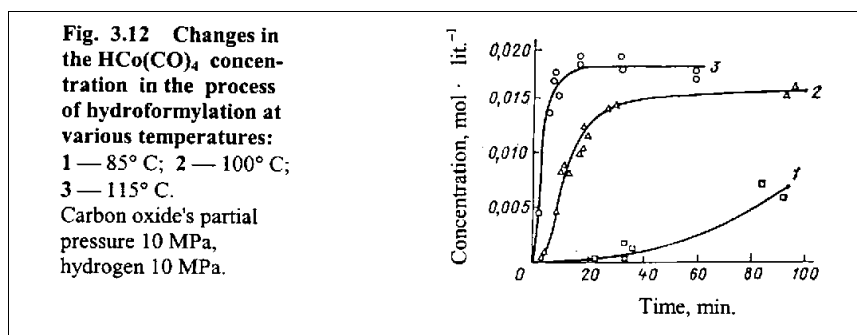


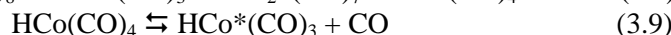
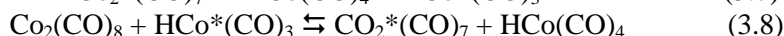
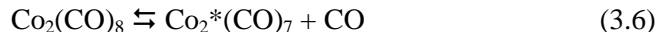
Fig. 3.10 Dependence between ρ_{H_2}/K and carbon oxide's partial pressure reaction for cobalt carbonyl formation out of own salts.

Fig. 3.11 Carbon oxide solvency (1, 2,) and hydrogen (3, 4) in their mutual presence in toluol (1, 3) and in a toluol cobalt naphthenat compound (2, 4). Cobalt concentration in the form of salt 0.9 % (mass.); temperature 95° C.



The speed value of the above-mentioned reaction, calculated on the basis of the data on the formation of cobalt carbonyls out of own salts (fig.3.1), comprises 0.49. The surprising coincidence of the resulting values additionally confirms the correctness of the choice of the reaction's mechanism.

When researching the kinetics of the cobalt hydrocarbonyl formation reaction, a supposition was made to the effect that there were also elements of the chain conence mechanism (fig. 3.12) in the induction period. Then the reaction mechanism for the formation of cobalt hydrocarbonyl out of decobaltoctacarbonyl can be presented thus:



According to this scheme, the auto-acceleration phenomenon is observed in a number of cases: for example, if the reaction speed (3.6) in the direct and reverse directions is commensurable with the reaction speed (3.7) and much smaller than the reaction speed (3.8); or, if the formation of $\text{Co}_2(\text{CO})_7$ along route (3.7) or (3.9), and then (3.8) are quicker than route (3.6). The set dependence between the carbon oxide's partial pressure, necessary for the formation of cobalt carbonyls out of own salts, and a temperature (see fig.3.3), reflect, most likely, the conditions under which the last stage of the given mechanism proceeds.

Thus, the derived equation based on the suggested reaction mechanism for the formation of cobalt carbonyls out of own salts, the reactor's dependence of the speed constant on the partial pressures of the carbon oxide and the hydrogen very well agree with the experimental data, which (considering the chemical possibilities of each of the stages of the mechanism) speaks in its favor of the correctness of this mechanism.

Generalizing the main regularities for the reaction of cobalt carbonyl formation out of own salts in the given mechanism, we have not cited the case when there is no decobaltoctacarbonyl in the system, i.e., this is a possible variant when starting the apparatus and experimentally introducing cobalt salt alone (without decobaltoctacarbonyl).

In this case, obviously, at first a small amount of dual-valent cobalt is restored by hydrogen up to cobalt with a zero valence, then the latter, under the influence of carbon oxide, changes to dicobaltoctacarbonyl. This process is a very slow one.

At identical temperatures and pressures, ($T = 100^{\circ}\text{C}$, $p_{\text{CO} + \text{H}_2} = 20.4 \text{ MPa}$) for 5 hours there was no fall in the pressure when introducing only salt into the autoclave. At 140°C the reaction time was 2 hours, while under the same conditions, in the presence of dicobaltoctacarbonyl, the reaction ends in 5 minutes. After the formation of a small amount of decobaltoctacarbonyl, the reaction proceeds in accordance with the main regularities mentioned above and described in the above given mechanism.

Thus, when studying reactions where cobalt carbonyls are formed out of own salts, the influence of the restoration of dual-valent cobalt with hydrogen can be overlooked even though this reaction is an addition to the above given mechanism. Most likely, it is the overestimation of this stage's value, or the misunderstanding of the mechanism given in materials printed in patent literature and articles written by Wender and colleagues [119, p.78] that the idea to the effect that when using cobalt salts as a source for getting catalyst oxosynthesis — cobalt carbonyls, higher temperatures are required ($150^{\circ}\text{--}200^{\circ}\text{C}$) as well as higher pressures (20-30 MPa), than when introducing a cobalt carbonyl solution into the reactor.

When studying the mechanism for forming cobalt carbonyls out of own salts, the mechanism that influences the reaction speed — one of Lewis's main substances — was not touched upon. The influence of the solvent (mainly the Lewis substances) can be imagined as follows: on the one hand, solvability leads to the change of the nature of the conence. In the case of accelerating the reaction, we can suppose that solvability increases its reactor capability. On the other hand, at the expense of solvability, the amount of conences in the solution decreases that causes the slowdown of the reaction.

3.1.2 COBALT CARBONYL FORMATION OUT OF METALLIC COBALT

Just like most of the other metal carbonyls, cobalt carbonyls are easily formed via the interaction of metallic cobalt with carbon oxide. The reaction proceeds with a noticeable speed even at room temperature and a carbon oxide pressure of 4-5 MPa. The reaction of metallic cobalt with carbon oxide is regarded as being heterogenous (gas — hard body), and its kinetics are like those of heterogenous processes.

To improve the contact of the phases, it is necessary to enlarge the surface of the cobalt. This is why the carbonyl formation reaction runs smoothly when the metallic cobalt is in the form of powder (especially if it is freshly replaced) or if it is put onto a developed surface of a carrier, like, for example, pumice (powder from volcanic rock).

To ease the transportation problem of the received carbonyls, the reaction for receiving carbonyls out of metallic cobalt and carbon oxide is conducted in the presence of a solvent (most often - hydrocarbon) in which carbonyls dilute most readily. The kinetics and mechanism of the carbonyl-formation reaction of metallic cobalt have been studied in works Rudkovsky & colleagues [34, 192, 193].

The increase of the carbon oxide's partial pressure proportionally increases the reaction speed of the carbonyl formation. The temperature increase also increases the reaction speed. When approaching the threshold of the temperature stability of the carbonyls, the speed process begins to decrease because of the noticeable procedure of the reverse reaction. The optimal temperature for carbonyl forming out of metallic cobalt depends on the partial pressure of the carbon oxide, and can be expressed by the formula:

$$1,000/T = 3.16 - 0.4 \lg p_{CO}$$

where **T** is the optimal temperature of reaction **K**.

In the case of conducting a cobalt-carbonyl formation reaction in the presence of hydrogen (i.e., with the help of synthesis gas, but not pure carbon oxide) the increase of the hydrogen's partial pressure increases the reaction speed. This is connected with the transformation of the forming decobaltoctacarbonyl into a much lighter cobalthydrocarbonyl, which more easily transits into the liquid and gas phase freeing the surface of the metallic cobalt.

This supposition very well agrees with the mechanism of cobalt carbonyl formation out of metallic cobalt according to which the limiting stage of the process is desorption of reaction products (cobalt carbonyls) off the top of the metal.

The reaction speed for the formation of cobalt carbonyls strongly depends on the conditions at which the metallic cobalt was received, mainly the temperature. Thus, a comparison of two samples of metallic cobalt was made to check the speeds of cobalt carbonyl formation. The first was received by breaking up cobalt carbonyl at 170° - 180°C , while the second — at 280° to 320°C .

At identical conditions of carbonyl formation [155°C , 30.6 MPa; contents of carbon oxide in synthesis gas 40% of the volume] the cobalt received at a low temperature (170° - 180°C) almost completely changed to carbonyls in 35 minutes (see fig.3.13), while the cobalt, received at a high temperature (180°C - 320°C) changed to carbonyl only by 30%. The initial speed for transformation into carbonyls for the first sample comprised 7 % in 1 minute; for the second sample — 1 %.

Thus, the speed for forming carbonyls out of metallic cobalt, received at $\approx 170^{\circ}\text{C}$, was 7 times greater than that from cobalt, received at $\approx 300^{\circ}\text{C}$. Still smaller is the transformation speed of carbonyls out of cobalt, received by carbonate restoration at 400°C . At identical conditions of carbonyl formation (130°C , 17.2 MPa) the cobalt, received from cobalt carbonyls via thermal breakup at 170° - 180°C , almost completely transforms into carbonyls in ≈ 20 minutes, while the cobalt, received via the restoration of carbonate at 400°C , in 80 minutes is transformed into carbonyls only by 28 % (fig. 3.14).

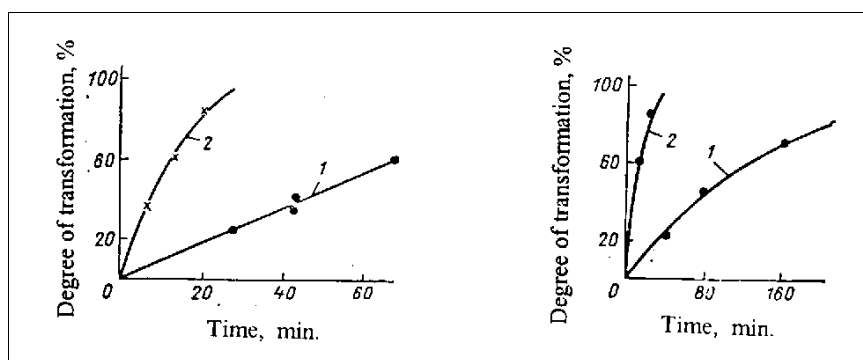


Fig. 3.13 Kinetic curves showing cobalt carbonyl formation out of metallic cobalt received by carbonyl breakup at 280° - 320°C (1) & 170° - 180°C (2).

Fig. 3.14 Kinetic curves showing cobalt carbonyl formation out of metallic cobalt received by carbonyl breakup at 170° - 180°C (2) and by restoration of carbonate at 400°C (1).

The initial speed for the transformation into carbonyls in this case, for the cobalt sample, received out of carbonate, is by 10 times smaller than for the sample received at low temperature out of carbonyls. Meantime, the metallic cobalt dispersion, defined sediment-metrically, was practically the same. Obviously, the variety of speeds for carbonyl-formation is defined, in this case, by the change of the micro-relief on the surface of metallic cobalt crystals received at various temperatures and from various substances.

Distorted places in the crystal net and cracks possess the highest energy. Namely these micro-defects are those active centers where the chemical reaction begins. The temperature increase (in this case, in the process of receiving) increases the transition of the atoms on the surface of the crystal being formed and allows them to occupy the best places energy-wise, which causes an orderly structure of the crystals and lowers their reaction capabilities.

3.1.3 TECHNOLOGICAL PRINCIPLES FOR ACCOMPLISHING COBALTIZATION STAGES

Having dwelled upon the kinetics and mechanism of the reaction for getting cobalt carbonyls 1) from metal and 2) from own salt, let's find out how to choose the proper technical means for this stage of the process. Carbonyls are received either way under high pressure of the synthesis gas (usually ≈ 30 MPa) i.e., with the use of reactors that can supply high pressure.

When getting cobalt carbonyls from salts, for example, from naphthene acids, a mixture containing 2 % - 3 % (mass.) of cobalt is put into the reactor for carbonyl formation. That is why, in spite of the great exothermal effect of the carbonyl formation reaction, there is no need to have a special thermal regulator in the reactor to cut down the heat.

The auto-catalytic character of the reactor for cobalt carbonyl formation out of salts requires reactors that guarantee complete mixing in this process. Such a type of apparatus will provide a maximal reaction speed and therefore, the most effective use of the reactor's volume.

The production and exploitation of industrial reactors with high pressure and mixing devices, is a difficult problem. A good effect could be gained by using apparatuses of the column type with a small ratio in regard to the height of the apparatus and its diameter, and with devices for introducing synthesis gas. With ratio $H : \varnothing \approx 3 : 1$, such apparatuses, by their characteristics, are close to reactors of ideal mixing. The use of apparatuses like reactors of ideal mixing, also allows to introduce cold raw materials, thereby making good use of the heat of the reaction.

When getting carbonyls out of metallic cobalt, as already said, the reaction proceeds with acceptable speeds so long as the metal has a developed surface, which is, actually, the metal settled on the developed surface of the carrier. It is best if the carrier and the settled cobalt are in the carbonyl-formation reactor in the form of a fixed layer. It is most advisable to use column reactors of high pressure of the shelf type (for more details see section 4.2).

As a whole, the technology of the carbon-formation stage of the oxosynthesis process is quite simple. The calculation of the apparatus can be made with the help of the simplest methods.

3.2 COBALT EXTRACTION FROM HYDROFORMYLATED PRODUCTS

After conducting the hydroformylation reaction, it is necessary to accomplish the extraction of cobalt from the product and recirculate it into the process. This stage is generally called decobaltization.

In spite of the fact that in principle, the separation of cobalt from the aldehydes that were received during the reaction, especially lower ones, can also be achieved without breaking the carbonyls that catalyze hydroformylation (more about this later), this separation is usually transferred into the so-called *thermally stable form*. Metallic cobalt and cobalt salt are of the same form.

The method of regenerating cobalt and recirculating it into the process, in various ways defines the features of the technological scheme of the whole of the oxosynthesis process, and the degree of cobalt extraction has a mighty influence on the cost of the received product.

3.2.1 THERMAL DECOBALTIZATION

In the simplest case, metallic cobalt can serve as a stable thermal form of cobalt convenient for extracting from an organic product. In order to get metallic cobalt out of carbonyls, it is enough to heat the carbonyls in the absence of carbon oxide (or at small partial pressures of carbon oxide).

In order to prevent fallout of metallic cobalt on the walls of the apparatus and ease its further separation from the organic products, the breakup of the carbonyls under the influence of increased temperature most often is accomplished in the presence of some kind of inert carrier with a developed surface (like pumice — hard porous volcanic rock). The carrier can be used as a fixed layer or in a suspended manner.

Oxosynthesis schemes of this type are called either *thermal* or *schemes with thermal decobaltization*. These include the previously

described and realized on a wide industrial scale, *triad* and *kizelgur* schemes of the process.

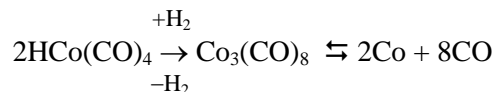
As a matter of fact, the process of thermal decobaltization can be accomplished also in the absence of the nozzle that serves for coating cobalt onto (i.e., the so-called powder scheme of the oxoprocess).

Among the schemes with thermal decobaltization, the most successful is the *triad*, that is, the scheme with the fixed layer of a carrier that is coated with metallic cobalt and off which cobalt is 'washed off' in the form of carbonyls for recirculating into the process. In spite of the seeming archaism, this scheme contains high technical and economic data, especially in concert with the principle of using low concentrations of cobalt on the hydroformylation stage (the so-called *thermal scheme with a small cobalt* that will be touched upon later in detail).

In connection with this, the principles of thermal decobaltization are cited in this book in conformity with just this variant.

Cobalt carbonyls, in part — hydrocarbonyls, ordinarily are quite stable compounds. Thus, the period of semi-transformation for cobalt hydrocarbonyl under normal conditions comprises, for a solution of hexane with a concentration — 0.62 % (mol.) at a period of ≈ 5 hours [194]. But the water solution of hydrocarbonyl of the same concentration breaks up in 14 days (336 hours) and only by 20 %

However, when heated, the carbonyls readily break up along the following reaction:

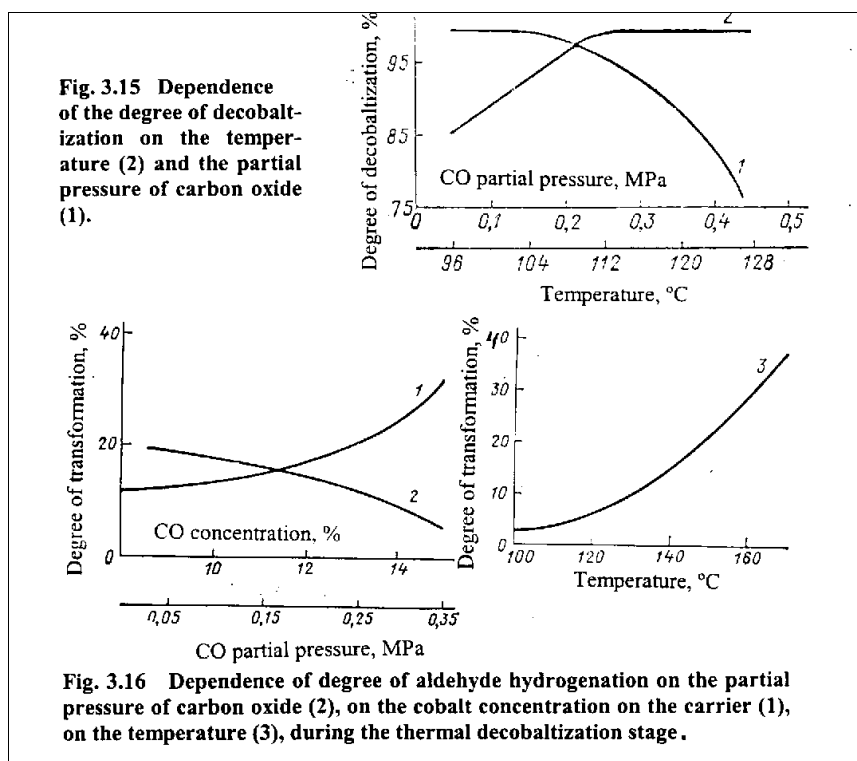


This reaction has the second order of magnitude and a speed constant $K = 3 \times 10^{-3} \text{ mol}^{-1} \times \text{c}^{-1}$ at 25°C and general pressure of 0.1 MPa [194, 195]. Activation energy $E \approx 49 \text{ kJ} \times \text{mol}^{-1}$.

Under industrial conditions thermal breakups of carbonyls are good to conduct with pressure close to the pressure value on the stage of carbonyl formation, that is, at 20 – 30 MPa. The pressure in the system is produced by hydrogen.

When studying the influence of temperature on the degree of carbonyl breakup when the general pressure $P = 26 \text{ MPa}$ and the partial pressure $p_{\text{CO}} < 0.1 \text{ MPa}$ it was shown that practically the complete extraction of cobalt out of the product is possible at $115^\circ - 120^\circ\text{C}$ (fig. 3.15). The decrease of temperature to 100°C lowers the degree of decobaltization to about 90 %. When studying the dependence of the degree of decobaltization on the partial pressure of carbon oxide, it was

found that at 130° – 140°C practically the complete extraction of cobalt is possible at $p_{\text{CO}} \leq 0.1$ MPa (see fig. 3.15). The increase of partial pressure of carbon oxide up to 0.24 MPa lowers the degree of decobaltization to 97 %; at 0.43 MPa the degree of extraction of cobalt comprises only 77 %. Close data are given in works [196, 197]. Thermal breakup of carbonyls at 170° – 180°C allowed to get an extraction of 99% of cobalt at $p_{\text{CO}} = 0.24$ MPa; and 98 % at $p_{\text{CO}} = 0.43$ MPa.



The concentration of metallic cobalt on the carrier can also have influence on the degree of decobaltization. For a complete extraction of cobalt from products of hydroformylation, the cobalt concentration on a stationary carrier should not exceed 15 % - 20 %.

Contact of aldehyde-containing hydroformylated products on the thermal decobaltization stage with metallic cobalt under hydrogen pressure, at a raised temperature causes side reactions, the main one of which is the hydrogenation reaction because the slightly dispersing metallic cobalt is an active hydrogenated catalyst. Condensation reactions with the formation of high-boiling products also proceed.

In fig. 3.16 we see the data concerning the dependence of the degree of butyl aldehyde hydrogenation during thermal decobaltization of products of propylene hydroformylation on the carbon oxide's partial pressure in the system, on the temperature and cobalt concentration on the stationary carrier.

The increase of the carbon oxide's partial pressure slows down the hydrogenation reaction. Thus, at 140° C and a cobalt concentration of 12 % (mass.) the change of p_{CO} from 0.05 to 0.35 MPa lowers the degree of hydrogenation of butyl aldehydes from 19 % to 6 %. The increase of cobalt concentration and temperature increases the degree of hydrogenation. However, even at minimal values of these parameters of the process, the portion of products of the hydrogenation reaction (butyl alcohol) was big enough.

It is obvious that the oxoprocess schemes with thermal decobaltization are necessary mainly for alcohol-production apparatuses. If the final product of the apparatus is the aldehyde, then the use of the scheme with thermal decobaltization is most desirable.

3.2.2 ACIDIC DECOBALTIZATION

When treating hydroformylated products with acidic water solutions, the cobalt carbonyls break up and cobalt salts that dilute very well in water are formed. These can be separated from the organic product in the form of water solutions.

For this, it is worth using sulfuric acid since this acid and its salts in a water solution more thoroughly separate from the aldehyde product, as compared with, say, organic acids, because of the much smaller solubility of cobalt sulfate in organic products.

In order to accelerate the reaction for the transformation of cobalt carbonyls into cobalt sulfate, it is recommended to add hydrogen peroxide to the acid. When studying decobaltization with the help of sulfuric acid and hydrogen peroxide, it was found that a sufficiently deep decobaltization of hydroformylated products is gained when using an 8 % solution of sulfuric acid, which, in quantity, corresponds to about 2 mols of acid per 1 mol of cobalt.

A noticeable influence on the decobaltization speed is caused by the temperature (fig. 3.17), mixing intensity, which defined the hydrodynamic regime of the process, and therefore, the effectiveness of mass-exchange (fig. 3.18) and the amount of hydrogen peroxide (fig. 3.19).

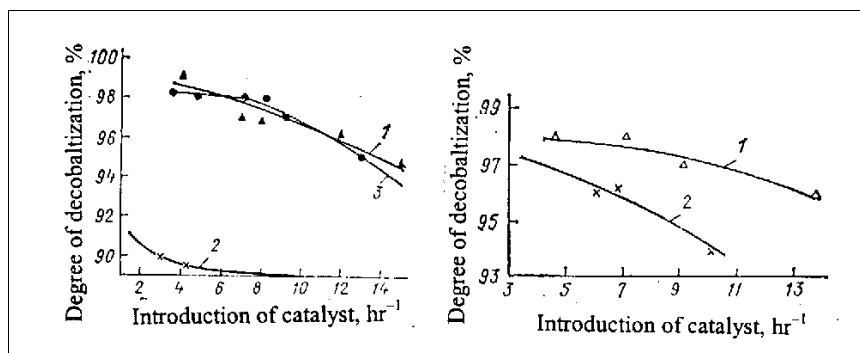


Fig. 3.17 Dependence of the Degree of Decobaltization on the Voluminous Speed and the Temperature:

1 — 40°C; 2 — 20°C; 3 — 65°C.

Fig. 3.18 Dependence of the Degree of Decobaltization on the Voluminous Speed and Intensity of Mixing.

Frequency of mixer rotations per minute: 1 — 2,500; 2 — 700.

It was also found that in the absence of aldehydes the breakup of cobalt carbonyls proceeds slower. Indeed, during the decobaltization of aldehyde-containing products in the presence of sulfuric acid and 3 mols of hydrogen peroxide with 1 mol of cobalt, in 6 minutes 90 % of the cobalt was extracted from the mixture, while the time for decobaltizing a solution of cobalt carbonyl in carbonic hydrogen with sulfuric acid and hydrogen peroxide concentration preceded less than 10 %.

There was no noticeable increase in the degree of decobaltization even at a longer period of time. By increasing the amount of hydrogen peroxide to 10 mol per 1 mol of cobalt, decobaltization of this solution was reached in 16 minutes. Under identical conditions, products containing aldehydes decobaltize in 4 minutes (fig. 3.20).

The indicated observations allowed drawing a conclusion to the effect that aldehydes take part in the reaction for breaking up cobalt carbonyls. We herewith offer the mechanism of a reaction [198, 199] according to which the hydrogen peroxide reacts with aldehydes thereby forming hydroxyhydroperoxides that cause the breakup of the cobalt carbonyls along the following scheme:

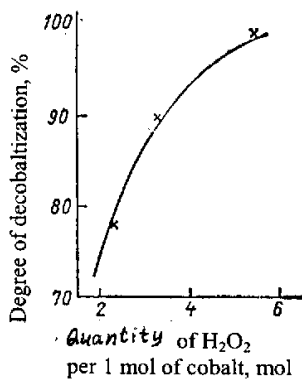
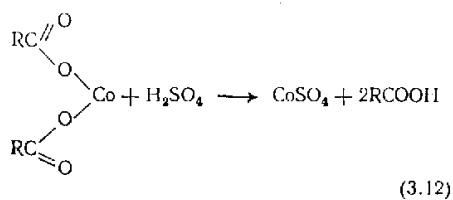
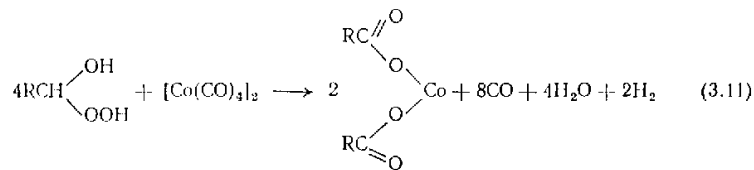
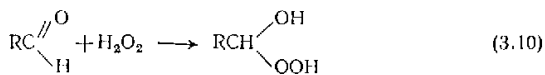


Fig. 3.19 Dependence of decobaltization degree on amount of hydrogen peroxide.

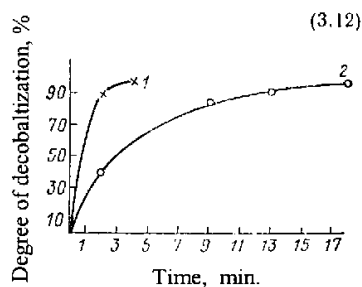
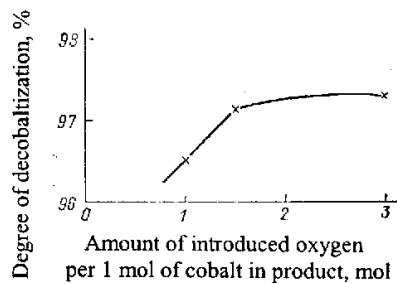


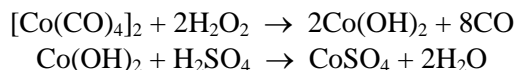
Fig. 3.20 Kinetic curves of decobaltization in the presence and in the absence of aldehydes in the product:

1 - H₂SO₄ + H₂O₂ + aldehydes + cobalt carbonyls; 2 - H₂SO₄ + H₂O₂ + cobalt carbonyls.

Fig. 3.21 Dependence of the degree of decobaltization on the amount of oxygen served.



In the absence of aldehydes, the breakup of cobalt carbonyls is also possible, but proceeds, undoubtedly, much slower thus:



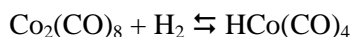
It is known that organic peroxides can be formed via the interaction of aldehydes with oxygen as well. Researches in the decobaltization process of hydroformylated products have shown the hydrogen peroxide can be substituted by oxygen (fig. 3.21).

Considering the mechanism for the process of decobaltizing aldehyde-containing products of hydroformylation via sulfuric acid in the presence of an oxidizer (3.10 to 3.12), we can suppose that the decobaltization process will be well accomplished in the presence of any acid capable of entering the exchange reaction (3.12).

Indeed, firms have suggested decobaltization processes in the presence of the most diverse acids. *Ruhrcheie* has patented a process of decobaltizing hydroformylated products with the help of formic or vinegar acid [200, 201]. The BASF firm suggests extracting cobalt out of hydroformylated products with the help of water solutions of vinegar acid with a simultaneous introduction of air into the process [202]. The Mitsubishi firm uses a process whereby a water solution of sulfuric acid is used as the oxidizer to break up the cobalt carbonyls [203].

3.2.3 EVAPORATIONAL DECOBALTIZATION

In the products of hydroformylation, cobalt resembles two forms of equal weight — decobaltoctacarbonyl and hydrocarbonyl:



Cobalt hydrocarbonyl is a volatile compound, while decobaltoctacarbonyl is quite stable. Because of this, we can separate the hydroformylation product especially in the case of lower olefin hydroformylation — ethylene and propylene — from cobalt decobaltoctacarbonyl via a simple transition without any kinds of chemical transformations.

In order to shift the equilibrium of reaction (3.13) to the side where the decobaltoctacarbonyl forms, it is necessary to have a low partial hydrogen pressure in the system.

Data on the distillation of cobalt aldehyde products and high-boiling side products from the catalyst of the propylene hydroformylation process at various pressures in a flowing system in the presence of

circulating gas (3 -5 M³ of gas per 1 kg initial catalyst) have been received [204]. Experimental results are given in the table 3.3.

Thus, at atmospheric pressure the separation of the aldehyde product from the cobalt can occur even in the flow of synthesis gas since the hydrogen's partial pressure comprises about 0.05 MPa.

TABLE 3.3

Dependence of Cobalt Distribution on Catalyst Evaporation Conditions During Propylene Hydroformylation at Atmospheric and Increased Pressure.

Temperature in °C	Pressure In MPa	Feeding gas M ³ / kg catalyst	Contents of gas, % (vol.)	
			CO	H ₂
In the flow of synthesis gas				
45	Atmospheric	2.5	47	50
	»	2.5	47	50
140	29	5	47	50
	29	5	47	50
In the flow of carbon oxide				
140	11	3	92	0
	9	3	92	5

Contents of cobalt, % (mass.)			Distribution of cobalt in %		Losses in %
in initial product	In distillation	in leftover	in distillation	in leftover	
In the flow of synthesis gas					
0.20	0.0014	0.51	0.4	94.0	5.6
0.22	0.0016	0.51	0.51	96.0	3.5
0.30	0.30	0.20	33.5	34.1	32.4
0.25	0.32	0.18	55.5	31.7	12.8
In the flow of carbon oxide					
0.246	0.0063	0.75	1.2	95.3	3.5
0.246	0.0120	0.72	2.1	97.2	0.7

When the pressure rises, the evaporation should be carried out in a flow of carbon oxide. In such conditions keeping cobalt in remote butyl aldehydes comprises about 0.006 % - 0.012 %, that is, 1 % - 2 % went into the distillation form the cobalt, contained in the product taken for evaporation. From 95 % to 97 % of the initial amount of cobalt that is used for circulation in the process, remains in the boiler product.

When using synthesis gas instead of carbon oxide for evaporating aldehyde products for circulating gas, a significant amount of cobalt (most likely in the form of hydrocarbonyl) was distilled together with the distillate and only about 30 % of the cobalt remained in the boiler (see table 3.3). Obvious, also, were the great losses of cobalt.

The choice of the conditions for evaporation decobaltization (temperature, pressure) is defined by the thermal stability of cobalt carbonyls defined by a well-known equation:

$$\lg p_{\text{Co}} = 7.94 - 2,660 / T$$

The chosen conditions should guarantee the stability of cobalt carbonyls in the process of distillation.

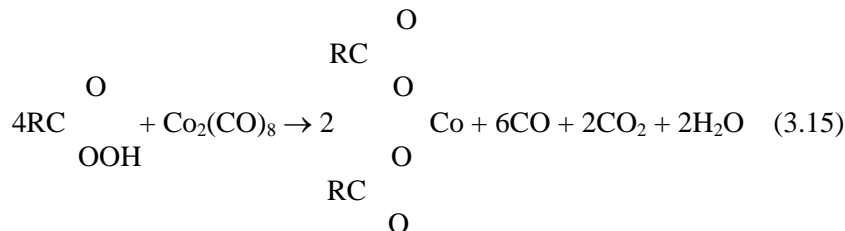
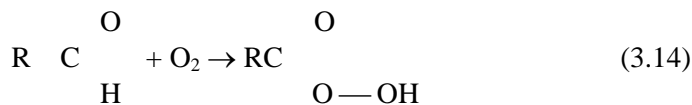
3.2.4 ACIDIC-EVAPORATIONAL DECOBALTIZATION

The main shortcoming of the method of acidic decobaltization of hydroformylation products (independent of which acid is used) is the need to use water solutions of powerful acids, therefore, the formation of a lot of drain water and the corrosion activity of the surroundings.

A shortcoming of the evaporation method is the low stability of the cobalt carbonyls at high temperatures, which actually complicates the accomplishment of the process without any loss of cobalt.

We can unite the merits and exclude the demerits of methods by using the combined acidic-evaporation method of decobaltization.

For this, the aldehyde product of hydroformylation, containing cobalt carbonyls, is treated with oxygen from the air in the presence of, for example, naphthene acids. Here oxygen interacts with the aldehydes thereby forming hydroxihydroperoxides that form salts together with cobalt carbonyls. The latter interact with the naphthene acid thereby forming cobalt naphthene:



Cobalt naphthene, dissolved in a product of hydroformylation, is thermally stable, hardly volatile, and can easily be separated from the aldehyde product with the help of evaporation.

The product being hydroformylated after the breakup of cobalt carbonyls, contains a mixture of cobalt salts with carbonic acid, formed during the interaction of aldehydes with oxides and cobalt with naphthene acid. When instilling the product, the more volatile carbonyl acid, being 'in equilibrium' with the naphthene acid, evaporates, and in the boiler-product only the naphthene cobalt salt remains.

We will further refer to the mixture of cobalt salts, formed during the breakup of carbonyls, as *cobalt naphthene*, which it actually is after instilling the aldehyde product from the circulating cobalt solution.

It is namely on this principle of combining the acidic and evaporative decobaltization that the naphthene-evaporation scheme of the oxosynthesis process is based [205 to 208]. This scheme allows to accomplish the process of regeneration and recirculating cobalt with minimal losses and without the formation of drain water.

3.2.5 TECHNOLOGICAL PRINCIPLES FOR ACHIEVING DECOBALTIZATION

Thermal decobaltization of hydroformylation products is most often accomplished under the pressure of hydrogen (about 30 MPa). High pressure column reactors were used.

When the cobalt settles on the stationary carrier, a column reactor of the shelf type is used. Heat is introduced to this kind of reactor by passing hot hydrogen into it. To guarantee an even distribution of the heat and the settling of the cobalt, hot hydrogen is introduced into each zone at several points at the top of the reactor. The reactor's temperature increases towards the movement of the product under decobaltization.

During the settling of the cobalt onto the moving carrier, or in the form of metallic powder, reactors with empty columns are used. The separation of the powder from the decobaltized products is performed with the help of magnetic separators or by waiting until the powder settles at the bottom of the container. In this case it is wise to preliminarily enlarge the cobalt powder grains in a direct magnetic pole.

Acidic decobaltization is accomplished at low pressure in apparatuses with intensive mixing because its speed is usually defined by the diffusion. Apparatuses of the Vishnevsky mixer type can be used.

Oxidized decobaltization is conducted in an empty apparatus with a nozzle or plates that guarantee an even distribution of the entering oxygen (or air) for the oxidation.

4 THE HYDROGENATION STAGE

Practically all the schemes and apparatuses dealing with the oxosynthesis as the main, or one of the main final products on the industrial scale, produce alcohols that correspond to the number of carbon aldehyde atoms received during hydroformylation. This is also relative to those oxosynthesis apparatuses that use low olefins (ethylene, propylene) as initial raw material, thereby producing propylene aldehydes and propylene alcohols, butyl aldehydes and butyl alcohols. In particular, this is relative to the apparatuses where olefins C₆, C₇, C₈, C₉, C₁₂ are used as initial raw materials received from propylene and butylene, which produce isoheptane, isooctane, isononyl, isodicyl, and isotridicyl alcohols.

The isobutyl aldehyde, received as a side product, is treated in isobutyl alcohol during the hydroformylation of propylene even on the apparatuses of the Mitsubishi firm, where the main final product is butyl aldehyde, later used for the synthesis of 2-ethylhexanole,

The Ruhrchemie firm has worked out and is advertising an oxosynthesis process where the only final product of propylene hydroformylation is the butyl aldehyde, while the simultaneously received isobutyl aldehydes break up into propylene and synthesis gas and are returned to the process. However, there is no confirmation about the industrial use of such an oxoprocess technology.

At any rate, the confirmation that *'compared to alcohols, all the other products received via hydroformylation nowadays play a small role'* [10], is still valid (1980).

Thus, all the known technological schemes for the oxosynthesis process include, as one of the main stages, a center for catalytic hydrogenation of alcohols in corresponding alcohols.

In principle, the reaction for the hydrogenation of aldehydes, received as a result of olefin hydroformylation, can be accomplished in a homogeneous-catalytic manner in the presence of a hydroformylation catalyst with the use of the same gas mixture (synthesis gas) or with the use of other homogeneous catalysts. The elaboration of technological schemes in processes with the use of homogeneous hydrogenation of aldehydes in alcohol has been described in many works.

However, in practice, the hydrogenation process is almost always accomplished separately with the use of heterogeneous catalysts. The latter, in any case, is characteristic for classical schemes of the oxoprocess on cobalt carbonyls. This is explained by the fact that the homogeneous hydrogenation of aldehydes in the presence of cobalt carbonyls proceeds too slow. Small speeds in the reaction need more

contact time and comparatively higher temperatures, but these circumstances cause the procedure of side reactions, and therefore, a decrease in the output of the final product. At the same time, the heterogeneous-catalytic hydrogenation can be accomplished with practically the quantitative output of the final product with a high output for the reactor's apparatus.

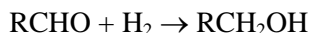
Because of the fact that the homogeneous-catalytic and the heterogeneous-catalytic hydrogenation of aldehydes are quite different reactions, relative to the mechanism and kinetics on the one hand, and to technology on the other, it is best to take up these processes separately.

The heterogeneous-catalytic hydrogenation of hydroformylated products, as a more important process from the practical point of view (at least nowadays, 1980) will be taken up first.

4.1 HYDROGENATION OF HYDROFORMYLATED PRODUCTS USING THE HETEROGENOUS CATALYTIC SYSTEM

As already mentioned, when hydroformylating olefins, besides aldehydes, a certain number of simple and complex ethers, acetals, aldols, dimers, trimers of aldehydes, etc. are formed. The number of such side products can amount to 20 % of the whole mass of the received oxygen-containing compounds. In connection with this, the product that arrives at the hydrogenation stage of the oxosynthesis process quite often resembles not only aldehyde, and the hydrogenation process is not at all limited to carbonyl restoration reaction group up to the hydroxyl group.

Since the main reaction in this complex amounts to:



when choosing catalysts and parameters for the process, the studies of kinetics and mechanics are alerted in order to get some optimal conditions for this reaction and accomplish it with optimal results.

Further we will keep to this principle as we give the information on the transformation of other substances in the course of the process.

4.1.1 HETEROGENOUS CATALYSTS FOR ALDEHYDE HYDROGENATION IN OXOSYNTHESIS

Studies of the aldehyde replacement reaction up to the alcohols in the heterogeneous-catalytic system and the choice of catalysts for this reaction actually began with the discovery of the catalytic hydrogenation of organic compounds. At the beginning of the XX century Sabatye and

Senderen accomplished this reaction having passed a mixture of hydrogen steams and acetaldehyde through a heated tube filled with thoroughly chopped up nickel.

Ipatyev elaborated an instructive manual and apparatus for the hydrogenation of organic compounds under high pressure accomplished, in part, a reaction of liquid-phase hydrogenation of aldehydes under a pressure of up to 30 MPa.

During the 70 years that have passed since then, a great number of publications have appeared where the reaction for the replacement of the carbonyl group is mentioned, and it is difficult to find an element in the Periodic Table which had never been offered as a catalyst for this reaction or for part of it.

Many of the publications, mainly patents, are devoted to the hydrogenation of aldehydes in alcohol in respect to the technological process of oxosynthesis.

Cobalt Catalysts

For quite some time the only hydroformylation catalysts used at industrial enterprises were cobalt carbonyls. It is commonly known that metallic cobalt is capable of catalyze hydrogenation reactions including aldehyde hydrogenation in alcohol. In connection with this, it is not difficult to understand the efforts of many researchers to use the cobalt catalyst for the hydrogenation stage of the oxoprocess. [Here we mean not the hydrogenation in the presence of cobalt carbonyls, but only the heterogeneous hydrogenation on cobalt catalysts.]

The next step is described thus: At the end of the hydroformylation reaction in the stationary system, the cobalt carbonyls were broken up in a hydrogen atmosphere at 10 MPa and 120° - 140°C, thereby receiving metallic fine-grain dispersible cobalt, then the hydrogen pressure was increased to 20 MPa and the temperature was increased to 180° – 200°C. Under these conditions there occurred hydrogenation of the previously formed aldehydes in alcohol [209].

One of the first descriptions of a nonstop oxosynthesis apparatuses [210] was based on the same principle. After the process of hydroformylation and thermal decobaltization, the reaction's products together with the metallic cobalt, having been weighed, entered the hydrogenation reactor where, at 20 MPa and at about 200°C the aldehydes were restored to alcohol. After the main reactor, the product entered the second reactor with a suspended catalyst for additional hydrogenation for those aldehydes that failed to react before. The total

time of the reaction comprised about 4 hours. Analogous situations are described in numerous patents [211, 212].

In order to improve the process of decobaltization and the formation of a well-developed surface in the hydrating catalyst, it is recommended to accomplish the settling of the cobalt onto some kind of carrier (infusorian soil, pumice, etc.) [213, 214]. The best results are obtained when using stationary carriers [215]. Thermal decobaltization on a stationary carrier is combined with aldehyde hydrogenation as described in many patents [213 - 215]. However, the results are inferior to those than can be received in other variants of accomplishing the process of aldehyde hydrogenation.

Even the singling out the process of hydrogenation into a separate stage and a separate reactor being filled with cobalt catalyst on an inert carrier, does not allow to get high production and a sufficiently complete transformation. Thus, according to the data [216], the hydrogenation of butyl aldehydes in the presence of a catalyst containing up to 40 % (mass.) cobalt on pumice at 30 MPa and about 180°C, with a voluminous raw material feeding speed of 0,1 hours⁻¹ proceeded with a transformation degree for the initial aldehydes not more than 98 %. The increase of temperature up to 320°C allowed increasing the voluminous speed only up to 1.0 hr⁻¹ with the preservation of about the same degree of transformation. In the case of aldehyde hydrogenation of C₈ in a cobalt catalyst [20 % (mass.) cobalt on pumice] feeding liquid raw material at voluminous speed 0.5 hr⁻¹, a satisfactory degree of transformation was reached only at about 25 MPa and 350°C.

More active were the mixed cobalt catalysts. The use of such catalysts was described in part, the cobalt-chromate [217], though the received data cannot be regarded as satisfactory.

Much more interesting were the results received when using propylene hydroformylation products (butyl aldehydes) for hydrogenation in a cobalt-calcium catalyst. In this case, at 30 MPa, the voluminous speed for feeding the reactor with raw material is equal to 2.0 hr⁻¹ at 140° - 150°C and practically the complete and selective transformation of butyl aldehydes in alcohol was achieved.

Good results were received when using cobalt catalysts with additions of copper, chrome, manganese, etc.[218]. However, these are but patent data that can't be properly evaluated because of the brevity of the information.

According to Thomas [218], the American firms Chemetron Corporation and Harshaw Chemical Company are producing cobalt catalysts on an industrial scale, and are used on the hydrogenation stage of the industrial oxosynthesis apparatuses. These catalysts contain about

30 - 60 % of cobalt in the form of oxide on carriers that can serve as pumice, or other porous materials. Before being used, the catalysts are restored by hydrogen for the transition of cobalt oxide into metallic cobalt.

According to these data, Chemetron produces five kinds and Harshaw produces four kinds of cobalt catalysts for the hydrogenation stage of the oxoprocess. However, the data on the concrete use of one or the other catalyst on the industrial scale and the result of their work is unknown.

Sulfurous Catalysts

Chemical literature has dwelt in detail on the use of oxo-synthesis sulfurous catalysts for the hydrogenation of products — sulfides of nickel (NiS), wolfram (WS₂), molybdenum (MoS₂), their mixtures in pure form, or with various additions like Al₂O₃.

The use of sulfurous catalysts in the process, at first sight, seems quite advantageous, that is, catalysts of this kind are extremely strong and sturdy against poisoning. Probably this is why so many patents offer sulfurous catalysts [220].

The information in chemical literature on the results of studies of carbonyl compound hydrogenation, including those of aldehydes, is doubtful as to the logic of the wide use of sulfurous catalysts in the hydrogenation process of oxosynthesis. Landa and colleagues [221 - 223] found that when hydrogenating carbonyl compounds on molybdenum sulfide, the output of alcohol does not exceed 77 %, while that on wolfram sulfide — 25 %. Sulfides of wolfram and molybdenum catalyze dehydration reactions with the formation of olefins that further hydrate into paraffin hydrocarbons and ethers.

Mistrik and colleagues [224] have studied the hydrogenation of butyl and isobutyl aldehydes and their mixtures, received via propylene hydroformylation in the presence of nickel-molybdenum sulfide catalyst NiS x MoS₂ [33.8 % (mass.) of nickel, 14.7 % of molybdenum, 26.7 % sulfur], sulfide of wolfram [64.3 % (mass.) of wolfram], and nickel-wolfram-sulfide catalyst on γ -Al₂O₃ [20.2 % (mass.) of wolfram, 2 % of nickel, 8.8 % of sulfur]. They have shown that at high degrees of transformation of the initial aldehyde, the output of butyl alcohol on the nickel-molybdenum catalyst comprises 78.4 %, on the wolfram-sulfide — only 43.2 %, and on the nickel-wolfram catalyst — 74.6 %.

Analogous results [225] came from the studies of hydrogenation reaction of aldehydes C₆ — C₈, received by hydroformylation of fraction 27° — 100°C benzene thermal cracking, on catalyst NiS x WS₂ on γ -

Al₂O₃. At 30 MPa, 230°C and voluminous speed for feeding raw material 2.0 hours⁻¹ the depth of aldehyde transformation comprised about 90 %, but only half of the aldehydes transformed into alcohol.

Results, acceptable from the viewpoint of industrial practice, were received by using a sulfide nickel-wolfram catalyst via the formula:



[50 - 56 % (mass.) of wolfram, 24 - 28 % of nickel, 26 - 29 % of sulfur] [225, 226].

The process of hydrogenating aldehyde fractions C₆ - C₈ in the wide interval of technological parameters on the same catalyst has been studied. When studying the influence of the pressure on the process (table 4.1) it was shown that to get a high degree of aldehyde transformation, we need a pressure higher than 20 MPa. Good selectivity was observed at temperatures not higher than 200°C (table 4.2). Raising the temperature to 220°C led to an abrupt violation of the selectivity — the alcohol output fell from 99.6 % at 190°C to 70 %. This seems to be characteristic for all sulfide catalysts. Namely in this area their dehydrogenation properties are most prominent which, after all, leads to the formation of large amounts of hydrocarbons.

The use of catalyst 2NiS x WS₂ allows to run the process of aldehyde hydrogenation with a large production — the voluminous speed for feeding liquid raw material can comprise 2 - 3 hours⁻¹ (table 4.3).

This catalyst has a high stability. Tests, under conditions of many hours on a pilot apparatus, have shown that the catalyst maintained uninterrupted activity and selectivity for over 5,000 hours. Of interest are the data on the chemical contents of the catalyst (table 4.4).

As a result of lengthy jobs performed, about 6 % of the iron and about 9 % of the cobalt settled on it (% of the catalyst's mass). This occurred as a result of the carbonyls of these metals getting into the hydrogenation solution and the breakup of the carbonyls in the catalyst. However, after a recount, it turned out that the contents of the main components in the used catalyst were the same as in the fresh one.

Out of the offered sulfurous catalysts, for the hydrogenation stage of the oxosynthesis process, the most desirable catalyst is the 2NiS x WS₂. However, when hydrogenating on a sulfide catalyst, we cannot get alcohol without a tinge of sulfur. If the initial aldehyde raw material is non-sulfuric, the received alcohol will still contain about 10 mln⁻¹ of sulfur at the expense of the desulfurization of the catalyst, which worsens the quality of the alcohol and deactivates the catalyst.

The use of sulfurous catalysts can be justified during the processing of olefin fractions on the hydroformylation stage. The latter are received via thermal cracking of various oil products, with the discharge, for example, of the alcohol-photo-reagents.

TABLE 4.1

Dependence of the Aldehyde Hydrogenation Process C₆—C₈ in Catalyst 2NiS x WS₂ on the Pressure

Conditions: temp. 180°C; voluminous speed for feeding raw material 1.0 hr⁻¹; ratio of hydrogen : raw material 1200 lit x kg⁻¹.

Pressure (MPa)	Degree of Transformation of Aldehydes (%)	Output of Alcohol (%) of Transf. Aldehydes & Alcohols Introduced w / Initial Raw Material
5	42.4	100
10	78.5	100
15	93.4	100
20	96.9	95.8
25	97.2	94.5
30	97.6	90.0

TABLE 4.2

Dependence of the Aldehyde Hydrogenation Process C₆—C₈ in Catalyst 2NiS x WS₂ on the Temperature

Conditions: pressure 30 MPa; voluminous speed for feeding raw material 1.0 hr⁻¹; ratio of hydrogen : raw material 1600 lit x kg⁻¹.

Temperature in °C	Degree of Transformation of Aldehydes (%)	Output of Alcohol (%) of Transf. Aldehydes & Alcohols Introduced w / Initial Raw Material
160	65.2	100
170	82.0	100
180	92.7	100
190	95.2	99.6
200	97.3	92.7
220	98.0	70.0

TABLE 4.3

Dependence of Aldehyde Hydrogen. Process C₆—C₈ in Catalyst 2NiS x WS₂ on Volumin. Speed of Raw Material Feeding

Conditions: pressure 30 MPa; temperature 200° C;
ratio hydrogen : raw material 1600 lit. x kg⁻¹.

Voluminous Speed for Feeding Raw Material, hrs ⁻¹	Degree of Transformation of Aldehydes (%)	Output of Alcohol (%) of Transf. Aldehydes & Alcohols Introduced w / Initial Raw Material
1.0	98.5	88.5
1.5	97.3	92.7
2.0	97.1	95.0
3.0	94.0	97.0
4.0	90.3	100

TABLE 4.4

Change of Chemical Contents of Catalyst 2NiS x WS₂ under conditions of hydrogenation of aldehydes C₆—C₈.

Condition: running time 5,000 hours.

Component	Contained in the Catalyst, % (mass.)		
	Fresh	used up	in used up form but recalculated onto initial cont.
Wolfram	42.0	36.1	42.4
Nickel	28.0	23.4	27.4
Sulfur	29.0	25.6	30.2
Graphite	1.0	-----	-----
Iron	-----	6.2	-----
Cobalt	-----	8.8	-----

Skeleton Catalysts

The use of skeleton nickel catalysts (of the Renei type) for the hydrogenation of products of hydroformylation was studied on the early stages of the elaboration of the oxosynthesis process, and is described in patents [227].

In Russia researchers studied and introduced the hydrogenation of products of propylene hydroformylation on a nickel-titanium melting catalyst [228 - 232]. The use of this catalyst at a pressure higher than 5

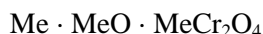
MPa, temperature 120° – 150°C, and with a voluminous speed of about 2.0 hrs⁻¹, allows to reach a deep degree (over 95 %) of transformation of butyl aldehydes in butyl alcohol and a partial hydrogenation of oxygen-containing compounds, side products, contained in the total product of hydroformylation

There is a difficulty involved here connected with the preliminary activation of the catalyst accomplished by knocking out the aluminum with the help of NaOH. An attempt to accomplish this operation right inside the hydrogenation reactor gave no positive results [230, 233], in connection with which we had to decline the activation of the molten nickel-titanium-aluminum catalyst right in the industrial reactor and to conduct this operation separately (outside the reactor). This greatly complicates the operation of loading the active catalyst into the reactor, especially in winter.

Chemical literature has also mentioned the use a copper skeleton catalysts for the hydrogenation of butyl aldehydes that lixiviated the alloy of copper and aluminum [234]. The use of such a catalyst at low pressure (0.2 MPa) and a temperature of 150°C allows feeding of raw material at a voluminous speed of 170 gr./lit. catalyst per hour to get 99.9% of aldehyde transformation at the output of 98.5% alcohol.

Chromic Catalysts

This class of chromic catalysts includes *contacts*, the contents of which can be expressed by the following formula:



The correlation of metallic, oxide, and chromic phases can be quite different depending on the variations of the composition, conditions of preparation, and the reconstruction of the catalysts. However, in spite of the great difference in the compositions, all these catalysts unite the commonness of the reactions and the phase transformations proceeding in the preparatory process, the closeness of their physical and chemical characteristics, and the correlation of activity with the phase contents.

The best-known chromic catalysts are the copper-chromic ones (Adkins catalysts), zinc-chromic catalysts, and nickel-chromic catalysts. The active role in chromic catalysts is played by metal (in the case of copper and nickel) or oxide (in the case of zinc) [235]. All the chromic catalysts are active in the hydrogenation of oxygen-containing compounds including aldehydes. This circumstance predetermined a

number of studies and publications on the use of various chromic catalysts for the stage of hydrogenating the oxosynthesis process.

Today there are many 'prescriptions' for copper-chromic catalysts for the hydrogenation of hydroformylation products, and all of them offer good results [236 - 238]. Well described are the propylene and butyl aldehydes hydrogenation (products of the hydroformylation of ethylene and propylene), nonyl aldehydes (product of the hydroformylation of deisobutylene), aldehydes, received via hydroformylation of olefin-containing fractions of coal tar.

Thus, the Adkins copper-chromic catalysts and their numerous modifications can be successfully used for the hydrogenation of any aldehyde products received via oxosynthesis.

TABLE 4.5
Dependence of Reaction Speed for Hydrogenating Butyl Aldehydes
in a Copper-Chromic Catalyst in the Steam Phase
on the Pressure and Temperature

Pressure in MPa	Temperature in °C	Reaction's Speed Constant, $\text{mol} \times (\text{hr} \times \text{cm}^3 \text{Catalyst})^{-1}$
0.15	160	10
0.5	160	15
1.0	160	19
0.15	200	16
0.5	200	28
1.0	200	31

Copper-chromic catalysts are very active in reference to hydrogenating the carbonyl group, and this allows accomplishing a reaction at a pressure close to that of the atmosphere and a temperature up to 200°C, that is, in very convenient conditions. The process, in such a case, as a rule, is accomplished in the steam phase (table 4.5).

The reaction speed of the steam-phase hydrogenation decreases with the increase of the mol correlation *hydrogen : aldehyde*; therefore, it is best to accomplish this process at a minimal surplus of hydrogen, which is defined, in part, by the phase equilibrium of the system.

When the pressure is close to that of the atmosphere, the reaction proceeds effectively even at the mol correlation of hydrogen : aldehyde equal to 1.1 to 1.2.

Below you see the dependence of the reaction speed of the steam-phase for hydrogenating butyl aldehydes in a copper-chromic catalyst on the mol correlation hydrogen : aldehyde:

Hydrogen : aldehyde, mol x mol ⁻¹	5	10	17.5	20
Reaction's speed constant, mol x (hr x cm ³ of catalyst) ⁻¹	7	6	5	4

Copper-chromic catalysts can also be used for hydrogenating products of hydroformylation at high pressure. In this case it is wise to conduct the process in the liquid phase because the paraffin process requires great amounts of hydrogen. Thus, the hydrogenation of butyl aldehydes received from hydroformylating propylene at 20 - 30 MPa, and 150° - 200°C with a voluminous speed for feeding liquid raw material equal to 1-3 hr⁻¹ proceeds with a high degree of transformation (more than 97 %) and, with practically full selectivity. However, here there is a serious problem: providing a high stability of the catalyst and a longer period of exploitation.

The process of steam-phase aldehyde hydrogenation, according to the data of lab experiments, the life span of copper-chromic catalysts comprises 4,000 to 5,000 hours, whereas the life span of liquid phase catalysts decreases by 1,000 to 2,000 hours.

The widely used methyl alcohol zinc-chromic catalyst also proved to be very hopeful as a hydrogenation contact for oxosynthesis [239 - 242].

When studying the conditions of the reaction for hydrogenating butyl aldehydes on a zinc-chromic catalyst, it was found that at 20 -30-MPa, at 300° - 320°C and at a voluminous speed of raw material feeding at about 2 hours⁻¹, the aldehyde degree of transformation reaches 100 %, and the output of alcohol amounts to 96 - 98 %. When hydrogenating the total product of hydroformylation on a zinc-chromic catalyst a partial hydrogenation up to the alcohol takes place for the oxygen-containing side products.

The zinc-chromic catalyst hardly reacts to the poisoning by sulfuric compounds [243, 244]. Besides, this catalyst is hardly active during the hydrogenation of dual carbon-carbon bonds. This makes zinc-chromic catalysts hopeful in schemes with incomplete transformations of initial olefins, but it complicates receiving high quality alcohols. The zinc-chromic catalyst with an addition of oxide aluminum has a better developed surface and a greater activity which allows to lower the temperature of the process to 230° - 260°C [245, 246].

However, the best results of all the chromic catalysts are offered by the nickel-chromic catalyst [247 - 256]. This catalyst has a great activity relative to the aldehyde hydrogenation reaction in alcohol, which allows conducting the process in a wide variety of pressures and under a moderate temperature ($120^{\circ} - 140^{\circ}\text{C}$), and also with a high selectivity at an optimal temperature. It has been shown that there is a possibility of using this nickel-chromic for hydrogenating a wide variety of products of hydroformylation with the production of alcohols from the propylene kind to $\text{C}_7 - \text{C}_9$ and even higher.

Other Catalysts

Besides the above-described groups of catalysts, in chemical literature (especially in patent sections) we find articles about the possibility of using on the hydrogenation stage. It is suggested that nickel should be used on the pumice [257], on powdered glass [258], on Al_2O_3 [259], and many other nickel catalysts [260], the real quality of which is practically impossible to evaluate because of the lack of information.

The book by Thomas [219] reads to the effect that the American firms Chemetron, Harshaw, and UOP are producing catalysts on a wide industrial scale which contain 30 to 60 % of nickel on the pumice or oxide aluminum, for use in the hydrogenation stage of the oxoprocess.

It is recommended to use copper-magnesium catalyst on pumice [24.5 % (mass.) copper, 5.7 % magnesium] [261], and also catalysts on the basis of cadmium [262], titan, and zirconium [263] and some others.

4.1.2 KINETICS AND MECHANISMS FOR ALDEHYDE HYDROGENATION REACTIONS

The kinetics and mechanism of hydrogenation reactions, just like carbonyl compounds in general, and aldehyde oxosynthesis in part, are hardly studied. This is, most likely, explained by the difficulty of the topic and lack of hope in the possibility of generalizing the kinetic regularities and mechanisms of the heterogenous-catalytic reactions, by the numerous types and complex constitution of the catalysts in use.

All this hinders the possibility to generalize all the known data. Also to blame, most likely, is the circumstance that under the conditions of the industrial heterogenous-catalytic process very rarely do we find an opportunity for conducting a chemical reaction in a purely kinetic realm, that is, variants when the speed of the chemical reaction itself does not

influence the physical factors (mass shift in the stream, mass shift in the seed of the catalyst, heat shift, etc.).

In connection with this, theoretical researches in the field of kinetics and mechanisms of carbonyl compound hydrogenation reactions, very little concerns applied research in this field, and therefore, they hardly have any influence on each other.

To understand the expression *mechanism of the heterogenous-catalytic process*, to a certain extent, is not at all so simple.

On the one hand, from the position of the mechanism of heterogeneous-catalysis, reactions invariably proceed via the following stages: 1) mass-passing of reagents from stream to the outermost layer of catalyst; 2) diffusion of reagents via pores inside the grain of the catalyst; 3) absorption of reagents on the hard surface of catalyst; 4) chemical reaction between adsorbed reagents; 5) desorption of chemical reaction product from surface of catalyst; 6) diffusion of products from pores of catalyst; 7) mass-passing of products from surface of catalyst to stream.

Stages 1 and 7 characterize not a chemical reaction, but rather its procedure from the viewpoint of the conditions of mass-exchange; stages 2 and 6 are defined by the physical structure of the grain of the heterogenous catalyst, and only stages 3, 4, and 5 are characteristic signs of chemical reactions proper and of reacting substances.

Relative to bimolecular reactions, to which the aldehyde hydrogenation reaction is related, the indicated general mechanism can be supplemented by a so-called '*rush-on mechanism*' when one of the substances taking part in the reaction, is not adsorbed on the surface of the catalyst. However, this does not change the general principles of approach to defining the mechanism of the reaction built on the basis of the studies of kinetic reactions.

On the other hand, the mechanism of the heterogenous-catalyst reaction should reflect the form of adsorption of reacting substances, and, what is most important — the form of interaction of the reacting molecules. Such information cannot be extracted only from the data on kinetic reactions.

Practically, researchers prefer to keep to only one approach — to study the mechanism of the reaction.

Among the works devoted to define the mechanism of reactions for the hydrogenation of various carbonyl compounds with the help of kinetic methods are those of a cycle of articles of Soviet and Czechoslovak [264, 265] researchers. On the basis of kinetic data, they suggested equations of the Langmeur-Hinshelwood type that allow

making certain suppositions concerning the mechanism of the reaction. Analogous duality is obvious in works, as well, which are devoted to the studies of the kinetics of aldehyde hydrogenation reactions.

The absence of good methods of modeling industrial reactors on the basis of *pure kinetic* data with a generalized account of facts about the outer and inner diffusions and heat-exchange leads to the fact that most of the researches in this field, that actually conform to the needs that arise during the elaboration of this or that variant of the process, cannot be used for generalizing into one system of data concerning the kinetics of chemical reactions proper — the interaction of aldehydes with hydrogen.

Propionic and Butyl Aldehyde Hydrogenation on Copper-Chromic Catalysts

The kinetics of hydrogenation of propionic, isobutyl, and butyl aldehydes in relative alcohols on a copper-chromium catalyst, containing about 80% (mass.) oxide copper and about 18 % (mass.) oxide chromium in the steam phase at a low pressure have been studied [266].

The speeds of all the three studied reactions almost directly and proportionally depend on the concentrations of the initial reagents and can well be represented by this equation:

$$r = KC_a C_{H_2}$$

(where r is the reaction speed; K is the speed constant; C_a and C_{H_2} are the concentrations of aldehyde and hydrogen).

The influence of temperature on the reaction speed is defined quantitatively for propionic aldehyde thus:

$$\ln K = 19.5 - 9,000 / RT.$$

On the basis of the received data on the influence of partial pressure of components (aldehydes and hydrogen) on the chemical reaction speed (fig. 4.1 & 4.2) the following kinetic equation is offered:

$$dp_a/d\tau = -Kp_a \sqrt{p_{H_2}^0} / [1 + b_{H_2} \sqrt{p_{H_2}^0} + b_a p_a + b_c (p_a^0 - p_a)]^2 \quad (4.1)$$

where $p_{H_2}^0$ and p_a^0 — initial values of the partial pressure for hydrogen and aldehyde; p_a — current value of the aldehyde partial pressure; b_{H_2} , b_a , b_c — adsorption coefficients for hydrogen, aldehyde, and alcohol; K — speed constant of the hydrogenation reaction.

This model postulates that the limiting stage of the reaction's mechanism is the interaction between the molecular-adsorbed aldehyde and atom-adsorbed hydrogen. The supposition that atom-adsorbed hydrogen takes part in hydrogenating aldehydes was known previously [267].

This is true relative to the reaction in the presence of a nickel catalyst. Later it was shown [265] that when hydrogenating acetone on a copper catalyst, a molecular adsorption of hydrogen occurs. In connection with this, a checkup was conducted on a number of models that presupposed molecular adsorption of hydrogen for the description of the kinetics of the aldehyde hydrogenation reaction: Designations are the same as in (4.1)

$$\begin{aligned}\frac{dp_a}{d\tau} &= \frac{-Kp_a p_{H_2}^0}{1 + b_{H_2} p_{H_2}^0 + b_a p_a + b_c (p_a^0 - p_a)} \\ \frac{dp_a}{d\tau} &= \frac{-Kp_a p_{H_2}^0}{[1 + b_{H_2} p_{H_2}^0 + b_a p_a + b_c (p_a^0 - p_a)]^2} \\ \frac{dp_a}{d\tau} &= \frac{-Kp_a}{1 + b_a p_a + b_c (p_a^0 - p_a)} \frac{p_{H_2}^0}{1 + b_{H_2} p_{H_2}^0}\end{aligned}$$

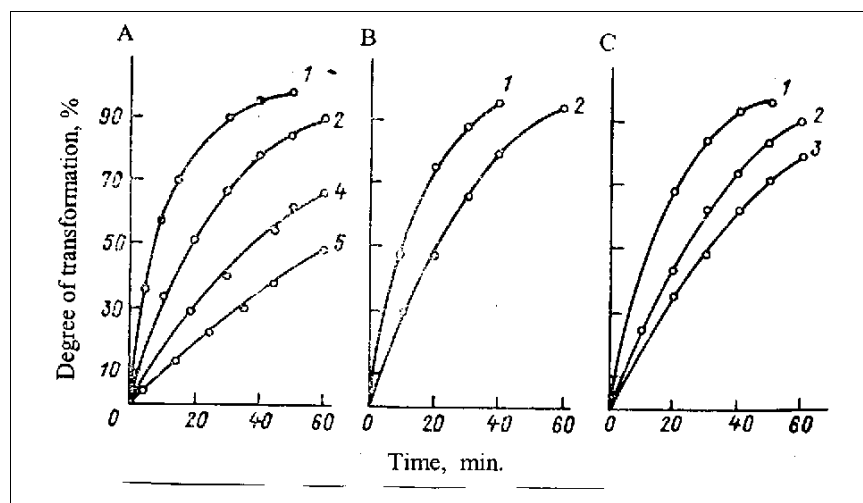


Fig. 4.1 Dependence of Hydrogenation Reaction Speed on Partial Pressure of Aldehydes:

A – propylene aldehyde; B – butyl aldehyde; C – isobutyl aldehyde.

Partial pressure (MPa): 1 – 0.025; 2 – 0.05; 3 – 0.075; 4 – 0.1; 5 – 0.15.

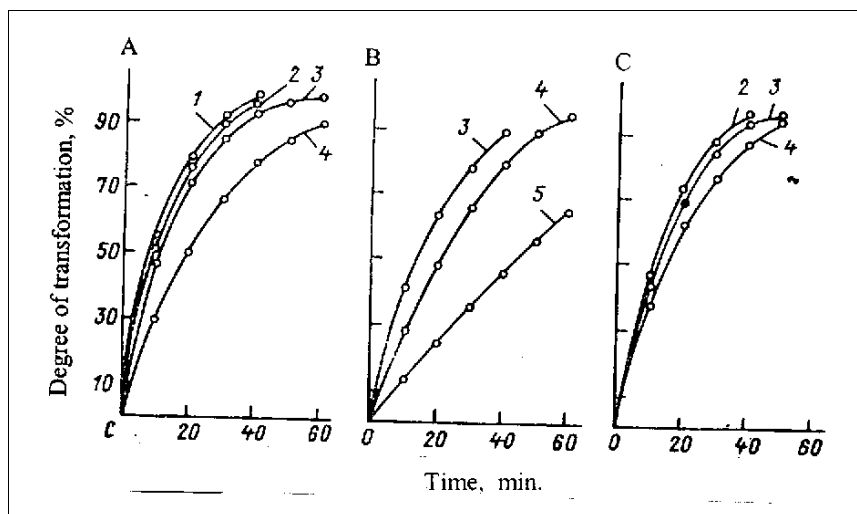


Fig. 4.2 Dependence of Hydrogenation Reaction Speed on Partial Pressure of Hydrogen

A – propylene aldehyde; B – butyl aldehyde; C – isobutyl aldehyde.
 Partial pressure (MPa): 1 – 0.4; 2 – 0.3; 3 – 0.2; 4 – 0.1; 5 – 0.05.

However, the indicated models did not offer an adequate description of the available experimental data.

Thus, we should consider that in the case of hydrogenating aldehydes, atom-adsorbed hydrogen does take part in the reaction on the copper-chromic catalyst. The aldehyde structure, in general, hardly influences hydrogenation reaction speed in the presence of a copper-chromic catalyst at a temperature of 180°C and a pressure of 0.1 MPa:

Aldehyde	Speed constant of reaction $K \cdot 102, \text{mol} \cdot (\text{hr} \cdot \text{gr. catalyst})^{-1}$
Propylene	0.741
Butyl	0.726
Isobutyl	0.713

Aldehyde Hydrogenation on Nickel-Chromic Catalysts

Multiple researches have shown that the nickel-chromic catalyst [$\approx 50\%$ (mass.) nickel, $\approx 28\%$ Cr_2O_5] is one of the best for hydrogenating products of hydroformylation in alcohol, especially in cases when the initial product for the oxosynthesis process are the lower olefins (ethylene, propylene).

Studying the reaction mechanism of the steam-phase of the aldehyde propionic hydrogenation in the presence of a nickel-chromic catalyst [255] via the Hougen kinetic method [268, 269] it was found that the received kinetic dependencies (fig. 4.3 - 4.5) best of all agree with the mechanism where the reaction proceeds between atom-adsorbed hydrogen and molecule-adsorbed aldehyde, and the aldehyde adsorption stage limits the process. In this work the experiments were conducted under purely kinetic conditions (without any influence of outer diffusion and, most importantly, inner diffusion difficulties) with small degrees of transformation of the initial aldehyde, which allowed using the equation for the reaction speed of the zero order of magnitude for the calculations.

The nickel-chromic catalysts produced by the Soviet Union and the German Democratic Republic on an industrial scale, look like tablets ($4 - 6 \cdot 4 - 6$ mm) and it is absolutely impossible to accomplish an aldehyde hydrogenation reaction on it without the influence of the mass-transition processes inside the grain on the reaction speed.

It is obvious that for problems, connected with the elaboration of technologies for industrial processes, this kinetic data is useless.

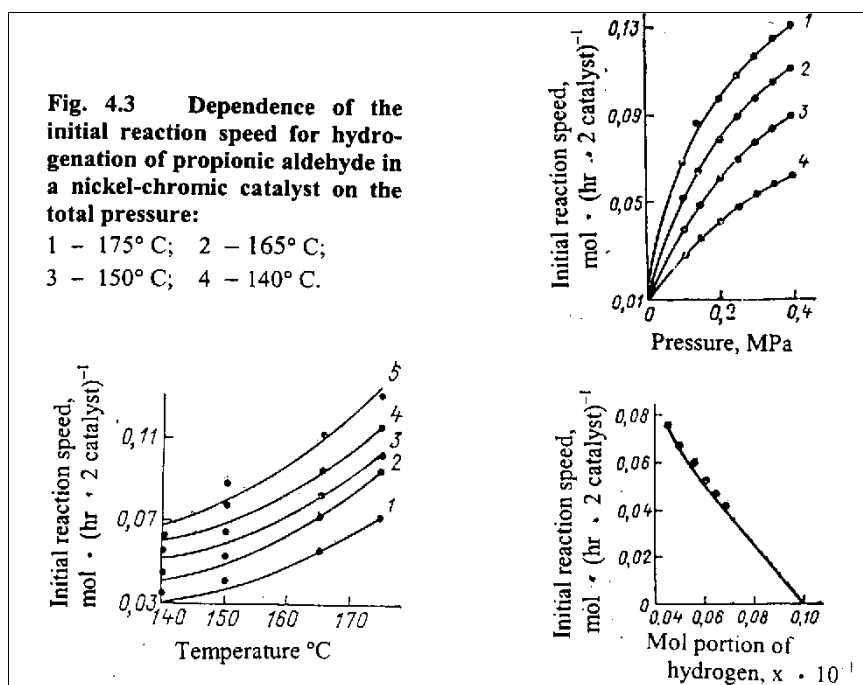


Fig. 4.4 Dependence of initial reaction speed for propylene aldehyde hydrogenation in nickel-chromic catalysts on the temperature:

General pressure (MPa): 1 - 0.4; 2 - 0.3; 3 - 0.2; 4 - 0.15; 5 - 0.1.

Fig. 4.5 Same — on the mol correlation of reagents.

For this experiment, whole tablets from industrial catalysts were used since the influence of the inner-diffusion slowdown on the process was possible. Under such conditions, the mathematical model of the process is not used to expose the delicate mechanism of the catalytic act, though it is convenient for modeling and calculating industrial reactors.

The received data — influence of linear speed of a raw material stream in the reactor (factor of outer-diffusion braking), influence of the concentration of aldehydes and hydrogen, influence of the temperature on the hydrogenation reaction speed, and also the kinetic curves of the reaction are given in fig. 4.6 to 4.9. An analysis of the received kinetic dependencies allows presenting the following reaction speed equation:

$$dC_c/d\tau = K [C_a^\alpha C_{H_2}^\beta / (1 + b_a C_a + b_{H_2} C_{H_2} + b_c C_c)^{\alpha+\beta}] \quad (4.11)$$

where C_a , C_{H_2} , & C_c — aldehyde, hydrogen, & alcohol concentrations;
 b_a , b_{H_2} , b_c — adsorption coefficients of these substances;
 α , β — order of reactions in reference to aldehyde & hydrogen;
 τ — time defined as ratio of catalyst volume to voluminous speed for feeding raw material.

Equation (4.11) presupposes a single-centered catalysis mechanism with challenging adsorption of hydrogen and aldehyde. The limiting stage is the surface interaction of molecular homo-absorption of hydrogen and aldehyde. The molecular form of hydrogen adsorption on nickel does not correspond to the data of the above given reaction's mechanism because it is difficult to suppose there are various forms of hydrogen adsorption in the presence of propionic and isobutyl aldehydes. This distortion of the good mechanism is, most likely, the result of the inner-diffusion of the slowdown of the chemical reaction proper.

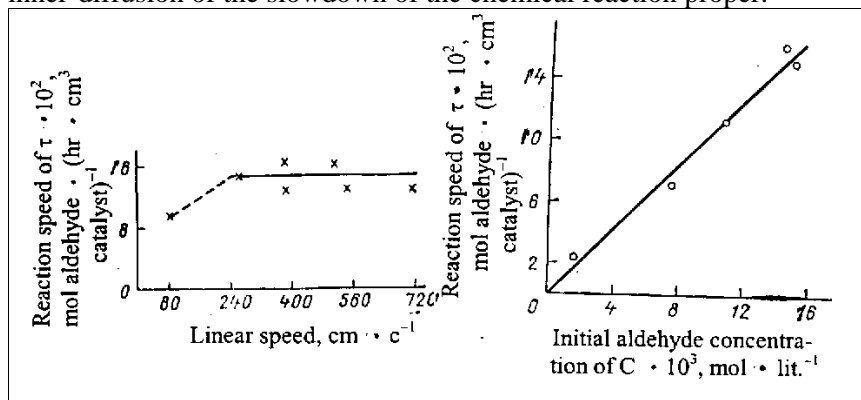


Fig. 4.6 Dependence of reaction speed for hydrogenation of isobutyl aldehydes in nickel-chromic catalyst on the linear speed of raw material steam-gas stream in the reactor.

Fig. 4.7 Same — on the contents of aldehyde in the raw material.

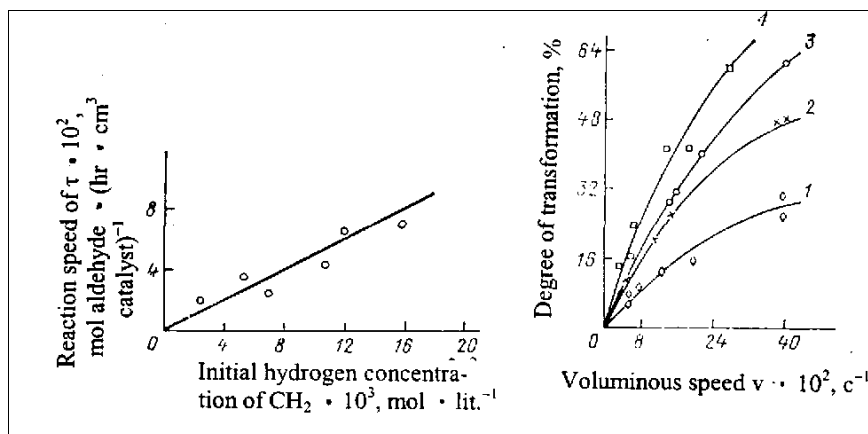


Fig. 4.8 Dependence of reaction speed for hydrogenation of isobutyl aldehydes in nickel-chromic catalyst on hydrogen concentration.

Fig.4.9 Kinetic curves of hydrogenation reaction for isobutyl aldehydes on a nickel chromic catalyst: 1 - 120° C; 2 - 130° C; 3 - 140° C; 4 - 160° C.

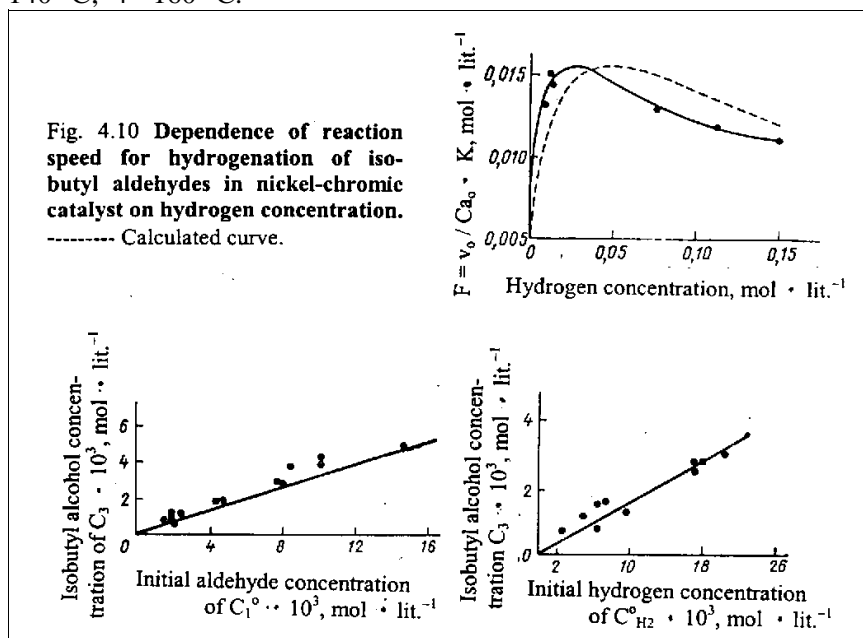


Fig. 4.11 Dependence of isobutyl alcohol concentration during hydrogenation of isobutyl aldehydes on initial aldehyde concentration.

Dots – experimental data; straight line – calculation result via model. Temp. 140° C; initial hydrogen concentr. 0.01346 mol x lit.⁻¹; τ average = 0.125 sec.

Fig. 4.12 Same – on initial hydrogen concentration.

Dots – experimental data; straight line – calculation result via model. Temp. 140° C; initial aldehyde concentration 0.00782 mol x lit.⁻¹

Though equation (4.II) does not offer any true data about the mechanism, nevertheless, it was well used for modeling the reactor's center. For practical calculations this equation can be reduced to:

$$dC/d\tau = K [C_a^\alpha C_{H_2}^\beta / (1 + b_{H_2} C_{H_2})^{\alpha+\beta}] \quad (4.III)$$

For equation (4.III) $\alpha \approx 1$, $\beta \approx 1$ therefore:

$$dC/d\tau = K [C_a C_{H_2} / (1 + b_{H_2} C_{H_2})^2] = K C_a f(C_{H_2}) \quad (4.IV)$$

Let's take the dependence of the concentration function $f(C_{H_2})$ in equation (4.IV) on hydrogen concentration. In fig. 4.10 the function values $f(C_{H_2})$ are shown along the ordinate axis:

$$f(C_{H_2}) = \frac{dC_c/d\tau}{K C_a} = \frac{\Delta C_c^0 / \Delta \tau}{K C_a}$$

Here index C_c^0 indicates that the corresponding values of concentration and transformation are taken for initial moments of time. According to this data the adsorption coefficient for hydrogen

$$b_{H_2} = 23.5 \text{ lit. x mol}^{-1}.$$

The parameters of the Arrhenius equation for the given reaction can be expressed by the formula:

$$\ln K = 16.9 - 9,400 / RT \quad (4.V)$$

With the help of constants received via the equations (4.IV) and (4.V) integrating the systems of differential equations:

$$\begin{aligned} dC_a/d\tau &= -K [C_a C_{H_2} / (1 + 23.5 C_{H_2})^2] \\ dC_{H_2}/d\tau &= -K [C_a C_{H_2} / (1 + 23.5 C_{H_2})^2] \\ dC_c/d\tau &= K [C_a C_{H_2} / (1 + 23.5 C_{H_2})^2] \end{aligned}$$

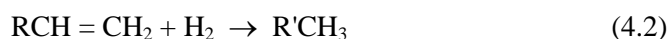
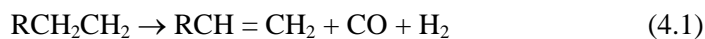
A theoretical calculation of kinetic curves was made under conditioned suitable to the experiment. On fig. 4.11 and 3.12 are shown the coincidence of the experimental and calculated data on the dependence of the alcohol concentration on the aldehyde and hydrogen concentrations. The laws of formal kinetics allow distributing the received results on any degree of transformation of initial products.

Side Reactions During Aldehyde Hydrogenation on Nickel-Chromic Catalysts

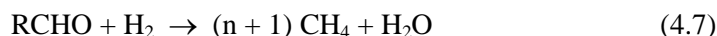
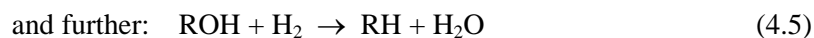
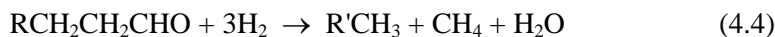
The hydrogenation of lower aldehydes (propionic, isobutyl, and butyl) in the steam phase on a nickel-chromic catalyst under optimal conditions proceeds with extremely high selectivity.

During the hydrogenation of isobutylaldehyde on a nickel-chromic catalyst, even after 5,000 hours of nonstop work (catalyst aging) the reaction selectivity was higher than 99 % (table 4.6).

It is known that nickel contacts are capable of catalyzing numerous side reactions of aldehydes and alcohols, for example:



which can be summed up into one total equation:



**TABLE 4.6 Product composition of steam-phase hydrogenation
relative to isobutyl aldehydes on a nickel-chromic catalyst**
Conditions: temperature 150°-170°C; pressure 0.25 MPa.

C o m p o n e n t	Initial raw material, % (mass.)	Hydrogenization, % (mass.)	
		1	2
Propionic aldehyde	0.64	-----	-----
Propylene alcohol	-----	0.67	0.67
Butyl aldehyde	0.60	-----	-----
Butyl alcohol	0.01	0.52	0.62
Isobutyl aldehyde	97.12	0.29	5.44
Isobutyl alcohol	0.02	96.29	90.71
Deisobutyl ether	-----	0.02	-----
Deisobutylacetyl isobutyl aldehyde	-----	0.20	-----
Water	1.52	1.90	1.90
Other foreign objects	0.09	0.11	0.66

A thermal-dynamic analysis of these reactions, relative to the butyl aldehyde, has shown that in the interval of 130° - 430° C, the equilibrium of all these reactions are almost completely shifted to the right, and all of them proceed with a great big exothermal effect.

The reaction's equilibrium constants and heat effects are calculated as follows:

$$\lg K_p = \sum_{i=1}^i a_i \lg K_{p_i} - \sum_{j=1}^j a_j \lg K_{p_j}$$

$$\Delta H = \sum_{i=1}^i a_i \Delta H_i - \sum_{j=1}^j a_j \Delta H_j$$

where **ai** and **aj** — stoichiometric coefficients; **i** and **j** — indexes relative to initial and final substances (see tables 4.7 and 4.8).

Therefore, if the procedure of these reactions, under conditions of an industrial reactor, seem to be not only thermodynamically possible, but also kinetically realistic, they will affect the thermal stability of the reactor. This aspect is more important under conditions of industrial technology, than, say, the loss of products via the nonselective reaction.

Studying kinetic side reactions that proceed during the hydrogenation of butyl aldehyde on a nickel-chromic catalyst [272, 273], it became obvious that at a temperature higher than 180° C, reactions (4.1) to (4.3) begin playing quite an active role, and reactions (4.5) and (4.6) start activating as well.

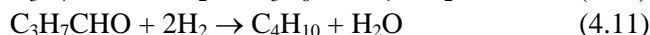
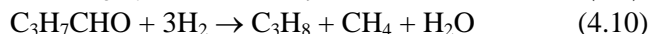
TABLE 4.7 Reactions' Equilibrium Constants

Reaction	lg Kr			
	400 K	500 K	600 K	700 K
$C_3H_7CHO + 3H_2 \rightarrow C_3H_8 + CH_4 + H_2O$	22.85	17.14	13.26	10.46
$C_4H_9OH + 2H_2 \rightarrow C_4H_{10} + H_2O$	26.46	16.53	9.79	4.91
$C_4H_9OH + 2H_2 \rightarrow C_3H_8 + CH_4 + H_2O$	19.98	16.10	13.46	11.54
$C_3H_7CHO + 5H_2 \rightarrow 4CH_4 + H_2O$	39.97	31.03	24.91	20.47
$C_4H_9OH + 4H_2 \rightarrow 4CH_4 + H_2O$	37.10	29.99	25.11	21.55

TABLE 4.8 Reactions' Thermal Effects

Reaction	ΔH , kJ/mol ⁻¹			
	400 K	500 K	600 K	700 K
$C_3H_7CHO + 3H_2 \rightarrow C_3H_8 + CH_4 + H_2O$	216.87	220.90	224.37	227.56
$C_4H_9OH + 2H_2 \rightarrow C_4H_{10} + H_2O$	93.69	94.53	95.29	96.08
$C_4H_9OH + 2H_2 \rightarrow C_3H_8 + CH_4 + H_2O$	148.12	150.71	153.19	155.53
$C_3H_7CHO + 5H_2 \rightarrow 4CH_4 + H_2O$	340.61	347.77	354.31	360.42
$C_4H_9OH + 4H_2 \rightarrow 4CH_4 + H_2O$	271.85	277.59	283.12	288.40

Macro-kinetic data helped define the amount of butyl aldehydes entering the reaction in directions expressed by these equations:



The mechanism of that leads to the formation of the final products of reactions (4.9) to (4.11) has not been studied. Neither was the reaction for forming such side products as de-butylether, butylbutyrate, iso-octylalcohol, etc., since the portion of all these reactions in the total process amounted to less than 3 % - 4 %. It turned out that at 180°C (fig. 4.13) only 90 % of the butyl aldehyde transforms into butyl alcohol according to reaction (4.9) on a newly reconstructed catalyst. When the temperature rises, the speed of the side reactions at once increases, and at 240°C only about 4% of the aldehydes transform into alcohol.

The main reaction of 'nonselective' hydrogenation is the process that leads to the formation of methane, propane, and water. To a much smaller degree does the hydrogenation reaction occur before the butane and water. If we compare the speeds of product accumulation in the hydrogenation system for butyl aldehyde and butyl alcohol (compare fig. 4.13 & 4.14), we can conclude that the formation of hydrogenation products proceeds mainly at the expense of aldehyde itself, and not at the expense of the intermediately formed alcohol.

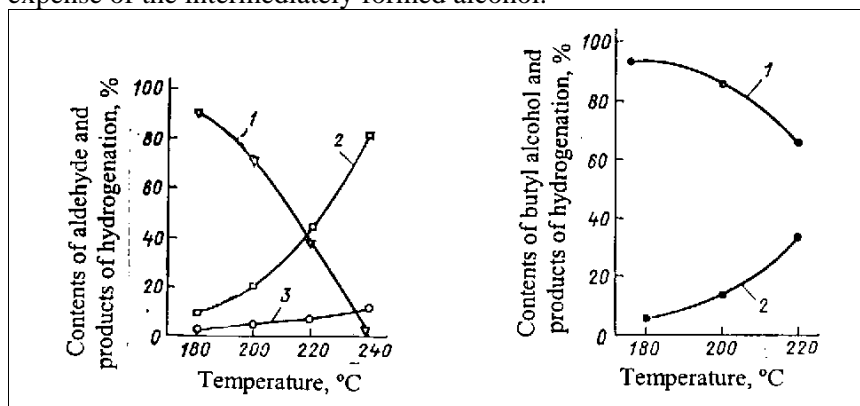


Fig. 4.13 Dependence of product forming speed during hydrogenation of butyl aldehyde in nickel-chromic catalyst on the temperature:
1 — butyl alcohol; 2 — methane and water; 3 — butane and water.

Fig. 4.14 Dependence of product forming speed during hydrogenation of butyl alcohol in a nickel-chromic catalyst on the temperature:
1 — butyl alcohol; 2 — products of hydrogenation.

When calculating and constructing a hydrogenation reactor for oxosynthesis of products on a nickel-chromic catalyst, one must keep in mind the effective and reliable thermal heat liquidator that guarantees the optimal temperature regime with Δt not more than $10^{\circ} - 15^{\circ}\text{C}$

Hydrogenating Aldehydes on Zinc-Chromic Catalysts; Side Reactions During Liquid-Phase Hydrogenation

The reaction for the hydrogenation of aldehydes in the presence of zinc-chromic catalysts with accepted speeds can be accomplished only on high pressures [274]. Table 4.9 gives the data on the influence of pressure on the hydrogenation speed of aldehydes $\text{C}_7\text{—C}_9$, which were received during the hydroformylation of olefins that were kept in fraction $55^{\circ}\text{—}125^{\circ}\text{C}$ of thermal-cracking benzene. Here we see that to accomplish this reaction we need a pressure of more than 20 MPa.

In many cases the use of zinc-chromic catalysts during the hydrogenation oxosynthesis process can be desirable. This is especially true in cases of hydroformylation of higher olefins and olefin fractions, since the zinc-chromic catalysts are very stable relative to catalytic poisons and have a high mechanic strength and work with stability in either the liquid or mixed phase.

TABLE 4.9

Dependence of the reaction speed for hydrogenating aldehydes $\text{C}_7 - \text{C}_9$ with a zinc-chromic catalyst on the pressure.

Conditions: temp. 320°C ; voluminous speed for feeding raw material 2.2 hours^{-1} ; correlation of hydrogen : raw material $1,600 \text{ lit.} \times \text{lit}^{-1}$.

Pressure in MPa	C o n t e n t s , % (mass.)				Transfor- mation degree of aldehyde in %	Output of alco- hols, % of transformed aldehydes and alcohols, put into the initial raw material.
	in the raw material		in the hydrogenator			
	alde- hydes	alco- hols	alde- hydes	alco- hls		
5	38.2	5.3	31.9	11.6	16.1	100
10	38.2	5.3	22.9	20.6	40.0	99.0
15	41.4	6.2	15.2	32.4	63.2	99.0
20	38.2	5.3	3.7	39.8	90.2	99.0
25	41.4	6.2	2.5	45.1	94.0	99.0
30	41.4	6.2	2.6	45.0	93.9	99.0

When hydrogenating aldehyde mixtures received during hydroformylation of olefin-containing fractions, common kinetic regularities play a secondary role since the kinetic regularities of aldehyde hydrogenation depends on the origin of the olefin raw material, i.e., on the presence of various macro-admixtures. Indeed, in the case of hydrogenating aldehydes C_7 — C_{10} the greatest reaction speed was observed during the restoration of the aldehydes received by hydroformylation of the propylene's trimmer. Aldehydes from olefin fractions of paraffin and thermal cracking have a small hydrogenation speed, while the speed is still smaller for aldehydes of olefins from catalytic cracking (table 4.10).

Aldehyde hydrogenation on the zinc-chromic catalyst has a zero order of magnitude relative to aldehyde and a pseudo-zero order relative to hydrogen, since under the pressure of 20 MPa and higher, the change of the hydrogen concentration in the system is very small. An analogous conclusion was made when studying the reaction for hydrogenating butyl aldehydes on an aluminum-zinc-chromic catalyst [245].

The activation energy of the butyl aldehyde hydrogenation reaction is as follows: $E = 65.4 \text{ kJ/mol}^{-1}$.

At high temperatures, besides the main hydrogenation reaction, side hydrogenation reactions, like dehydration, etc. also proceed, catalyzed by zinc-chromic catalysts. When hydrogenating butyl aldehydes on an alum.-zinc-chromic catalyst [246] up to 320° - 330° C , the heterogenous-catalytic side reactions practically do not proceed, and 99 % of the butyl aldehydes transform into butyl alcohol (table 4.11).

TABLE 4.10 Hydrogenation of Aldehydes C_7 — C_{10} Received from Various Kinds of Raw Materials on Zinc-Chromic Catalysts

Conditions: pressure 30 MPa; temp. 320°C ; voluminous speed for feeding raw material 2.0 hrs^{-1} ; ratio of hydrogen : raw mat. $2,000 \text{ lit. x kg}^{-1}$.

Raw material	Contents in % (mass.)				Degree aldehyd. transf. in %
	in raw material		in hydrogenizate		
	aldehydes	alcohols	aldehydes	alcohols	

Products carbonylized by fraction

55° - 125°C , separated from benzenes of the catalytic cracking

and thermal cracking	27.8	5.4	2.4	30.8	91.1
Oils of Grozny	29.0	----	1.5	27.5	94.9
Oils of Ufa	30.3	3.9	1.3	32.9	95.6
Paraffin cracking	54.4	6.8	1.2	6.0	97.8
Propylene trimmer	34.2	3.5	0.2	37.5	99.4

TABLE 4.11

Dependence of Final & Side Product Output when Hydrogenating Butyl Aldehydes on Alum.-Zinc-Chromic Catalyst on Temperature

Product	Output of products, mol x 100 mol, of transformed aldehyde			
	280°C	340°C	380°C	460°C
Butyl alcohol	99.00	83.50	62.50	6.00
Water	0.70	6.90	23.60	73.00
Methane	----	0.20	0.90	6.83
Ethane	Traces	Traces	0.50	5.90
Propane	----	3.02	3.36	30.20
Propylene	----	----	0.37	1.69
Butane	0.60	----	6.10	25.00
Butylene	----	----	4.20	6.45
Other hydrocarbons	----	----	8.15	19.60
Carbon dioxide	Traces	Traces	Traces	7.60

At temperatures higher than 350°C the reaction products reveal butane, butylene, propane, carbon-hydrogen C₅—C₈; at temperatures above 400°C — methane, ethane, propylene, and carbon dioxide.

When hydrogenating aldehydes at high pressures, in the liquid or mixed phase (some are in steam) a great role is played by the side condensation reactions that are not catalyzed by the hydrogenous contacts, but proceed inside the volume. This is relative to aldehyde hydrogenation on zinc-chromic catalysts and other liquid-phase hydrogenation variations. If the aldehyde hydrogenation reaction in the liquid phase often has the zero order relative to the carbonyl component, then the condensation reaction has the order from the first to the second; their speed depends on the aldehyde concentration in the liquid raw material. A solvent is used to lower the aldehyde concentration in the initial product.

In table 4.12 is given the data on the influence of butyl aldehyde concentration on the formation of compact products in the course of the liquid phase of the hydrogenation reaction. It is necessary to note that the deciphering of the kinetics of side reactions on the basis of this data is impossible because of the absence of the necessary information about the phase equilibriums in the system (number of liquid phases), data on the 'reverse' hydrogenation reactions for making products more compact, like complex ethers, etc. However, the general picture of the influence of the aldehyde concentration on the formation of side oxygen-containing products is clear enough.

TABLE 4.12

**Dependence of Compact Product Formation Speed During
Hydrogenation Reaction on Contents of Butyl Aldehydes in Raw
Materials**

Conditions: **Serial 1** - pressure 5 MPa, temp. 160 C, voluminous raw material feeding speed 1.0 hrs⁻¹; **Serial 2** - pressure 30 MPa, temp. 160 C, voluminous raw material feeding speed 2.0 hrs⁻¹.

C o n t e n t s, % (mass.)					Degree of aldehyde transfor- mation; %
in raw material		in hydrogenation products			
Aldehydes	compact products	aldehydes	alcohols	compact	
Serial 1					
31.9	6.0	0.1	34.4	4.5	99.9
45.0	4.5	0.3	45.0	4.5	99.3
52.7	6.0	0.7	52.0	4.0	98.7
60.0	3.0	0.8	60.0	2.1	98.6
75.0	3.0	1.0	69.5	8.5	98.0
Serial 2					
48.0	7.4	0.9	47.1	7.4	98.1
59.0	7.5	1.0	58.0	7.5	98.3
75.1	7.3	1.5	70.9	10.5	98.1
82.5	7.6	2.0	72.3	15.8	97.5

In order to lower the aldehyde concentration in the initial raw material, we can use toluol, pentane-hexane fraction, alcohol proper, etc., (received in the process) as solvents.

The data on the influence of the solvent and voluminous raw material feeding speed on the formation of side oxygen-containing products for some cases are given in figures 4.15 and 4.16.

However, it is also necessary to consider the influence of the chosen solvent on the aldehyde hydrogenation reaction proper. In the case of liquid phase reactions, the solvent can offer a very noticeable influence on the reaction speed. In some cases the solvent influences the speed without changing the mechanism.

Thus, the dielectric penetration of the medium can influence the electrostatic forces between the reacting particles. The viscosity of the solvent can influence the reacting sub-stances' diffusion speed, and therefore, on the speed of the heterogenous-catalytic reaction. The capability of the solvent to be adsorbed on the surface of the catalyst can also significantly influence the reaction speed.

Other properties of the solvent (capacity for reagent solvation, nucleophilicity, electrophylity, etc.) can also influence the reaction's mechanism thereby changing the reaction speed.

In table 4.13 are given the data on the influence of the solvent on the butyl aldehyde hydrogenation reaction speed making use of the aluminum-zinc-chromic catalyst [245].

It has been thus shown that the hydrogenation reaction speed in the presence of aliphatic hydrocarbons (pentane-hexane fraction) is greater than in the case of an aromatic solvent like toluol.

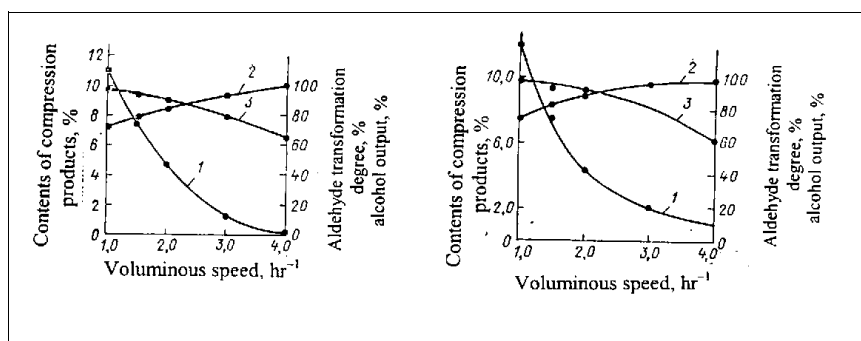


Fig. 4.15 Dependence of reaction speed for the formation of condensation and compact products on the voluminous speed for feeding raw material during the hydrogenation of propylene aldehyde solution in toluol:

1 – contents of compact products in hydrogenation products; 2 – degree of aldehyde transformation; 3 – output of alcohol from the transformed aldehyde.

Fig. 4.16 Dependence of condensation reaction speed on voluminous speed for feeding raw mat. when hydrogenating butyl aldehydes in butyl alcohol:

1 – contents of compact products in hydrogenation products; 2 – degree of aldehyde transformation; 3 – output of alcohol from the transformed aldehyde.

TABLE 4.13

**Dependence of Liquid Phase Butyl Aldehyde Hydrogenation
Reaction Speed in Aluminum-Zinc-Chromic Catalyst on Type of
Solvent**

Solvent: temper- ature in °C	Voluminous speed for feeding raw mat. (hrs ⁻¹)	Contents of alde- hyde in liqu. raw mat., % (mass.)	Reaction speed of hydrogenation, grams butyl alco- hol (liters cata- lyst x hrs) ⁻¹
Toluol; 258° C	2.2	22.1	390
	2.2	33.4	388
	2.2	48.7	393
Penthane-hexane	2.1	33.2	515
fraction; 259° C	1.7	55.0	540
	2.0	70.1	540

**More Information Relative to the
Aldehyde Hydrogenation Reaction Mechanism**

Anderson and MacNaughton conducted a research of a liquid-phase hydrogenation mechanism of some carbonyl compounds (acetaldehyde, butyl aldehydes, acetone, and others) using the method of restoring deuterium-hydrogen compound on nickel, platinum, and chromic copper [275]. They have found that at a temperature of about 25°C the bonding of deuterium to the carbonyl group takes place, while at higher temperatures (150 - 250C) the bonding of deuterium to the α -hydrocarbon takes place, which can be regarded as the preliminary enolization of the carbonyl compounds with the ensuing bonding of the hydrogen to the dual bond carbon — carbon.

On the basis of the received experimental data, two reaction mechanisms were suggested. For example, the following was suggested for the butyl aldehyde at a low temperature:

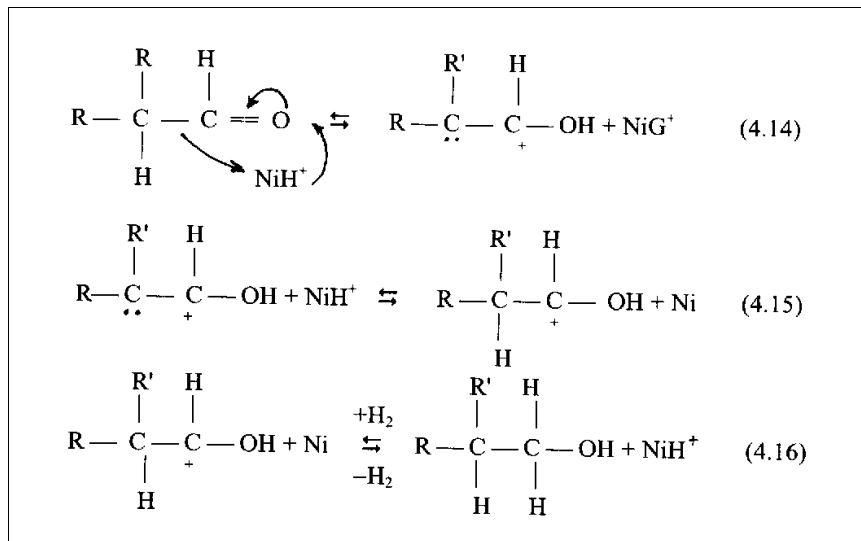


and at a high temperature: (4.13)



A conclusion was also made [276] to the effect that when hydrogenating aldehydes on nickel at high temperatures, independent of where the hydrogenation is in process -- in a liquid or steam phase, the reaction takes place with the carbon atom, a neighbor in the carbonyl group. Optically active 2-ethyl-propylene was used in this work as a site for research. The authors made some suppositions to the effect that metallic nickel, saturated with hydrogen, is capable of catalyzing

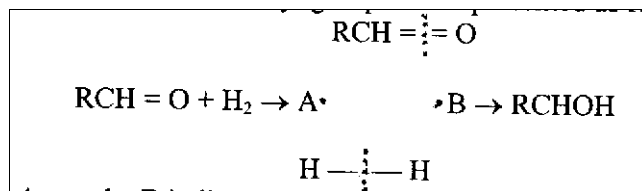
enolization very well and so suggested the following reaction mechanism for the hydrogenation of aldehydes on nickel:



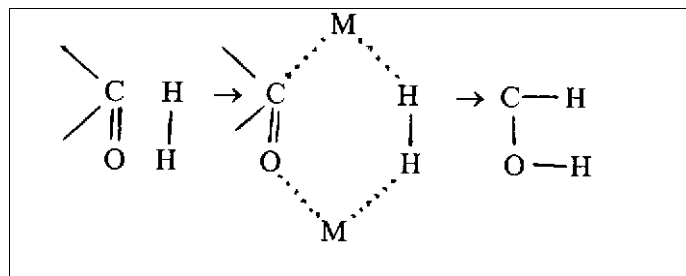
The mechanism expressed by equations (4.14) – (4.16) differs from mechanism (4.13) mainly in writing which is an effort to reflect the role of the heterogenous catalyst in the mechanism of the reaction.

Direct deuterium bonding to the carbonyl group during the low-temperature (25°C) was discovered later [277] when the acetone hydrogenation steam-phase reaction was researched.

Some works attempted to interpret the aldehyde hydrogenation reaction mechanism as being based on Balandin's multiplet theory. In the framework of the terminology of this theory, the mechanism for the hydrogenation of the carbonyl group can be presented as follows:



where A· and ·B indicate the active centers of the catalyst taking part in the reaction. Freidlin and his colleagues offered this mechanism for hydrogenating carbonyl compounds on zinc and cadmium [278, 279]:



4.2 TECHNOLOGICAL PRINCIPLES OF THE HYDROGENATION STAGE

As seen from the previous material, the reaction for product hydrogenation of olefin (aldehyde) hydroformylation in alcohol can be achieved in the wide interval of conditions via the common pressure and temperature, in the liquid and steam phases with the use of a great number of heterogenous catalysts.

In connection with this, the technological features of the hydrogenation stage, like the choice of pressure, which in many respects, defines the whole of the technological scheme of the stage, depend on many factors, including the general technical scheme of the oxosynthesis process, concrete economical logic, connected with the space for the equipment, the availability of resources in various catalysts, etc.

It is impossible to foresee all the possible combinations of the defining factors that will dictate the proper technological decisions for this or that industrial oxosynthesis installation. This is why it is logic to dwell upon only the general features of the apparatuses of the reaction's assembly of the hydrogenation stage, and the main technological principles of choosing the proper catalysts.

4.2.1 CHOOSING INDUSTRIAL REACTORS FOR HYDROGENATION

A high economic effect of the heavy industry's process can be accomplished only where there is no interruption.

From the point of view of the peculiarities in technological mounting of heterogenous-catalytic processes, conditionally, there can be three main groups: 1) with a stationary (immovable) layer of the catalyst; 2) with a movable suspended catalyst; 3) with a weighed catalyst (so-called *boiling* or *pseudo-liquid* layer).

The simplest, from the viewpoint of constructive mounting, are the processes accomplished on the stationary layer of the catalyst. In this case, the stream of reagents, being in the steam, liquid, or mixed phase, transits through the catalyst's layer, most often, along the scheme, from top to bottom. It is this variant that is accepted worldwide.

There is a lot of chemical literature that describes the various types of reactors for various processes, their particularities, their merits and demerits. Below we will try to throw light upon such problems making use of the most fundamental information [161, 162, 280 - 283], considering their importance for the problem as a whole.

An industrial reactor should be chosen with consideration for the following main parameters of the process: 1) the necessary time for the raw material to be in the contact zone; 2) the optimal temperature and pressure in the zone of the reaction; 3) the optimal conditions for mass- and thermal-exchange. The apparatus should be simple in construction, and convenient for exploitation. But, practically, it is quite difficult to construct an apparatus that would include all these requirements.

Indeed, it seems the first problem can be easily implemented. Reactors with an immovable layer of grains in the catalyst are related to the so-called *reactors of ideal displacement*, that is, apparatuses where all the elements of the volume move along the top of the apparatus parallel to the other elements without mixing with them.

The time for molecules of reacting substances to remain in such an apparatus is the same for all molecules and is equal to: $\tau_f = V/v$ (where V — volume of the reactor's zone; v — voluminous speed for feeding the raw material; τ_f — fictional contact time).

The so-called *fictional contact time* is always greater than the real time because when the former is defined, the filling of the reactor's zone with the mass of the catalyst is not considered.

By using the correlation: $\tau_r = \tau_f / \varepsilon$ (where ε — degree of uniformity of the layer; τ_r — real contact time). We can thus switch from the fictional contact time to the real time.

However, the ideal displacement regime is realized only during the laminar stream in the reactor.

In practice, not all the molecules that make up the reactor stream, stay in the reaction zone equally long. Various parts of the turbulent stream in the reactor have various speeds; therefore, the time for the substance to remain in the reaction zone is an incidental value, characterized by a certain distribution function whose form is defined by the hydrodynamic regime of the reactor.

Thus, the character of function $f = n(\tau)$ (where n is the number of molecules; τ is the time the molecules remained in the reaction zone) depends on the diameter of the reactor. The smaller the diameter of the reactor, the more molecules will have time to stay there close to τ_{med} .

A small diameter of the reaction layer is kept in tube-type reactors, though it is practically impossible to guarantee a constant hydraulic resistance for each tube, as the streams in the tubes will have different linear speeds, which will lead, again to a certain incidental distribution of molecules in accordance with their length of staying time.

To calculate reactors with immovable catalysts, nevertheless, kinetic equations of ideal displacement are used (with certain errors). The equation taken for defining the time of contact in the reactor for an irreversible reaction, runs as follows:

$$\tau = C \int_0^x dx / KC_A^n = C_{A_0} \int_0^x dx / KC_A^n (1-x)^n$$

where x — degree of reacting substance transformation; C_{A_0} and C_A — initial and current concentration of the main substance; K — reaction speed constant; n — order of reaction relative to the main substance.

Keeping up a constant pressure in the apparatus is also practically impossible because of the presence of a hydrodynamic resistance layer in the catalyst there can be a fall of pressure in the reactor in the course of the raw material feeding. To decrease the influence of this factor one must optimize the construction of the apparatus or optimize the size of the grains used in the catalyst.

The hydrodynamic resistance of the grained layer in the catalyst of the reactor depends on the size of the particles. The smaller they are, the more hydraulic resistance will this layer have. However, the increase of the size of the catalyst's tablets increases the inner-diffusion braking (slow-down) of the reaction speed.

The intensity of the mass-transition and thermal transition, as a whole, are but indirectly connected with reactor construction. The mass- and thermal-exchange between streams of reacting products and the layer's grains in the catalyst, can offer a significant influence on the speed and selectivity of the chemical reaction.

For the mass-transition of distribution of concentrated substance defusing from the stream onto the hard surface, can be defined by solving the equation of convection diffusion:

$$u_x(dc/dx) + u_y(dc/dy) + u_z(dc/dz) = D_M(d^2c/dx^2)$$

where u_x , u_y , and u_z are components of the speed vectors of coordinate functions x , y , and z ; D_M is the coefficient of molecular diffusion.

In the case of the substance transition from the stream to particles of complex configuration, this equation is practically impossible to solve. Therefore, in cases when we have a grain layer, the following mass-transition coefficient:

$$B = D_M/\delta$$

(where δ is the effective thickness of the diffusion layer) can be defined only experimentally.

Experimental data can be represented by criteria, stretch-sized dependencies that we see here:

$$\begin{aligned} \text{Nu}_M &= Bl/D_M = 1/\delta \\ \text{Pr}_M &= \nu/D_M \\ \text{Re} &= ul/\nu \end{aligned}$$

where Nu_M — Nuselt's diffusion criterion; Pr_M — Prandtle's diffusion criterion; Re — Reynold's criterion; l — characteristic linear measurement of the particle; ν — kinematical viscose substances.

In the case of a grain catalyst, the characteristic linear measurement is the diameter of the tablet, i.e., $l = d$.

The thermal-exchange between the stream of reacting substance and the grain layer is characterized by the following dependence [284]:

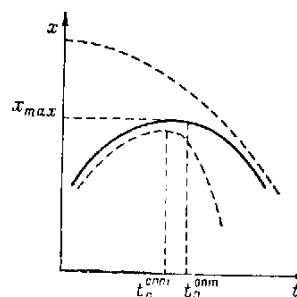
$$\text{Nu} = f(\text{Re}, \text{Pr})$$

$$\text{and:} \quad \text{Nu} = \alpha d/\lambda; \quad \text{Re} = u d \rho/\eta; \quad \text{Pr} = c_p/\lambda$$

where α — thermal output coefficient from the layer to the surface; d — diameter of the particles in the catalyst; λ — thermal conductivity of substance; u — linear speed of stream; ρ — condensation of the substance; c_p — heat capacity of the substance.

Fig. 4.17 Dependence of the product output of the exothermal reaction on the temperature.

Conditions: x_0 — output of products for the equilibrium reaction without side processes; x_s — output of products during the appearance of side processes.



Only the linear speed of the stream is defined, to a certain degree, by the constructive peculiarities of the reactor.

It is important to keep the so-called *optimal temperature profile* in the reactor zone. In the case of exothermal reactions, with a big thermal effect, this problem often disappears to be the main one.

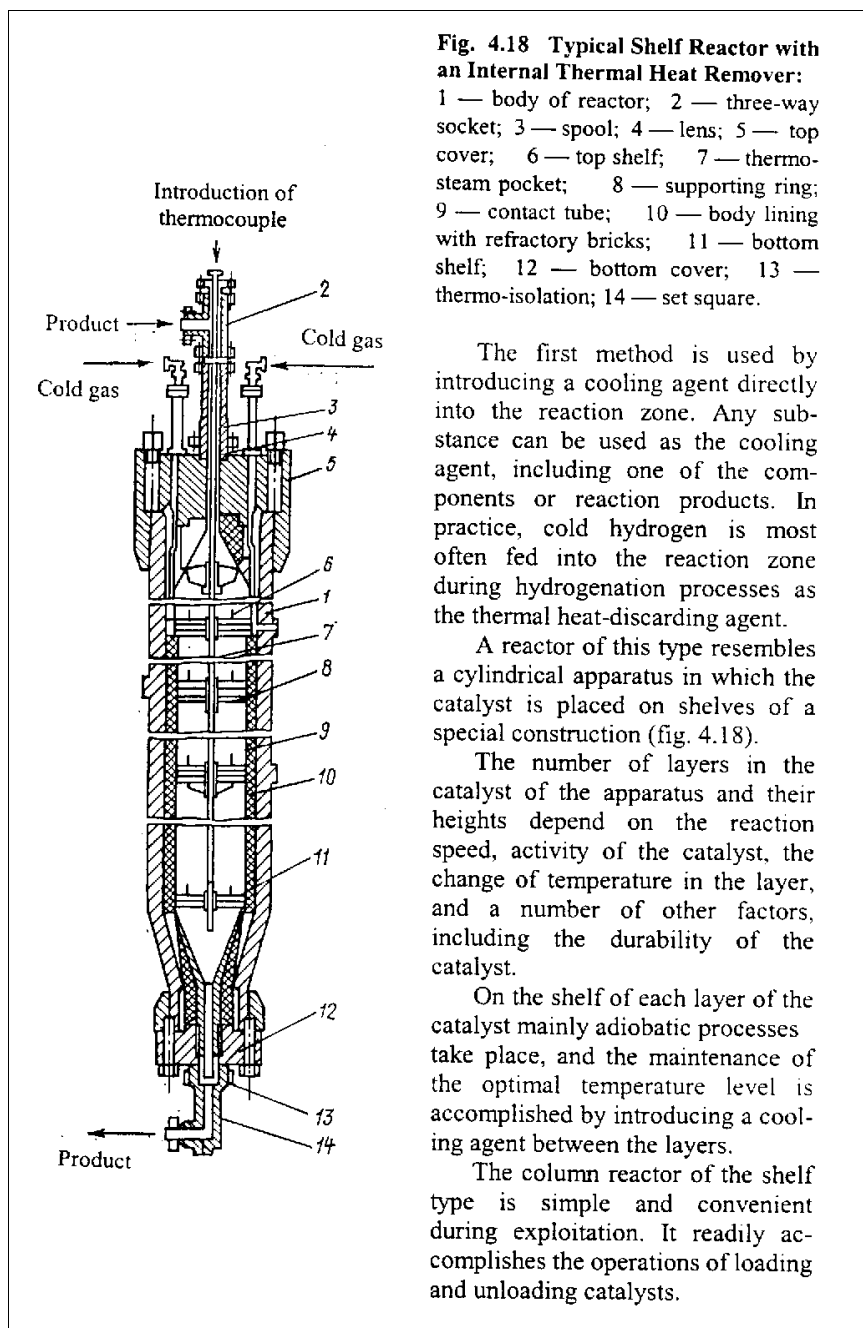
The output of exothermal reaction products with the increase of temperature proceeds via the maximum (fig. 4.17). For reverse exothermic reactions, the decrease of the output at high temperatures is conditioned by moving the equilibrium.

For the aldehyde hydrogenation reaction most important is the fact that when the temperature rises above the optimum, very active exothermal side processes begin.

If the increase of the optimal temperature profile, which influences the equilibrium constant, causes only a decrease of the final product, this will lead to the worsening of the parameters of the process, but will not have any effect on its working ability.

In our case, when the increase of the optimal temperature profile causes the appearance of exothermal side processes, this can completely disrupt the work of the reactor because of its thermal instability.

For reactors with stationary catalysts there are two main methods for taking away heat from exothermal reactions and regulating temperature regime in the reaction zone.



It most readily withstands all the necessary strict conditions if the reactions, proceeding on the catalyst, extremely sensible to temperatures. If it happens to be too high, then providing a stable regime of the process in such a reactor becomes extremely difficult.

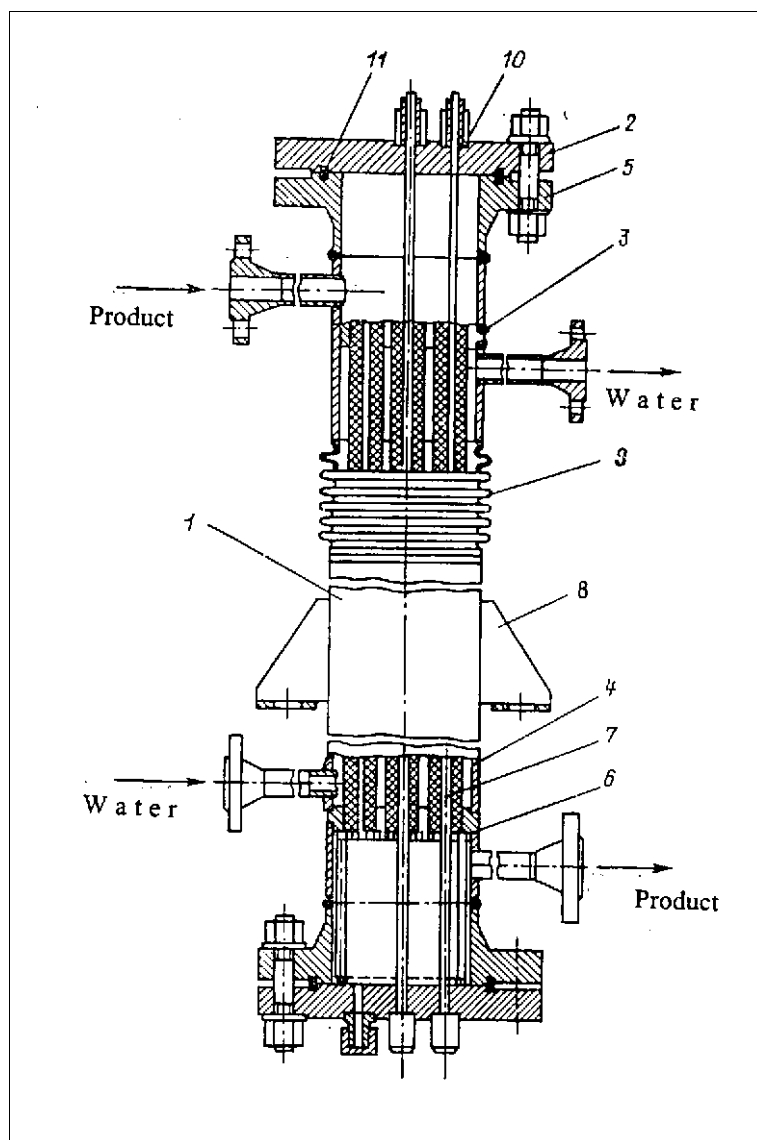


Fig. 4.19 Experimental Industrial Tube-Like Reactor for Hydrogenating Aldehydes of Oxosynthesis:

1 — body of reactor; 2 — cover; 3 — tube-like board; 4 — reaction tube; 5 — flange; 6 — grating; 7 — shell of the thermo-steam; 8 — support; 9 — compensator; 10, 11 — paddings.

As indicated above, the thermal regime of each layer of the catalyst in such a reactor approaches the adiabatic regime. This is why, in the case of exothermic reactions that are characteristic for the process being cited, the average temperature of the reaction's mixture, relative to the height of the layer, increases in the direction of the movement of the reactor's stream.

Having properly chosen the necessary number of shelves (layers), one can manage to get the average temperature at the end of each shelf not higher than by Δt of the initial temperature. If it is obvious that in the range of temperatures from t_0 to $t_1 = t_0 + \Delta t$, there are no side reactions with a noticeable discharge of heat, then the problem can be regarded as solved. But one should also be sure of the fact that as a result of the change of temperature, in the cross section of the reactor it is never higher than Δt , which is hard to believe.

Because of the uneven distribution of material streams along the cross-cut sections of the reactor and the lack of intensity in mixing the cold hydrogen with the reaction's mixture, the local temperature deviations from the usual one, can greatly surpass the calculated value of Δt . Out of this, a conclusion can be made to the effect that reactors of the shelf type can be used in the hydrogenation stage of the oxosynthesis process only if the catalyst in use, during the regime's deviation from the temperature profile by a value noticeably greater than the calculation of Δt in the layer, does not cause the appearance of side exothermic reactions. The catalysts for hydrogenating aldehydes are, for example: zinc chromic, and copper-chromic ones.

A second way of diverting the heat of exothermic reactions and regulating the temperature in the reaction zone is to remove it through the wall. In this case the process is accomplished in reactors of the tube-like type of various construction (fig. 4.19). A tube-like reactor has a much more complicated construction than a shelf reactor, especially when we need to perform a process at a high pressure. Undoubtedly, it is more complicated to perform the loading and unloading of the catalyst on this type of reactor. It is next to impossible to get identical layer resistance from each of the reactions' tubes (of which there are several thousand in one reactor) — an extremely difficult job!

However, tube reactors allow accomplishing a very effective thermal diversion in an exothermal reaction, first of all at the expense of the great ratio of the heat exchange of the surface to the volume of the reactor's space. Besides this, the comparatively small diameter of the tubes allows to get only a very few changes in temperature relative to the cross-sections of the tubes.

It is more difficult to observe the optimal temperature profile in the tubes along the top of the catalyst's layer. In most of the cases the temperature of the cooling agent in the space between the reactor's tubes, is constant, while the thermal discharge decreases during the feeding of the raw material.

For hydrogenating aldehydes, boiling water under pressure is most often used as a cooling agent in tube-containing reactors, though organic liquids can also be used.

On the whole, we must consider that the use of tube-containing reactors on the hydrogenation stage of the oxosynthesis process is desirable when accomplishing hydrogenation reactions at low pressure on a highly active catalyst, like the nickel-chromic one.

4.2.2 PRINCIPLES FOR CONSIDERING REACTORS FOR THE HYDROGENATION STAGE

Column reactors of the shelf type with a zonal introduction of a cooling agent for taking off heat in an exothermic reaction, in spite of the seemingly simple calculations when projecting the apparatus, this hardly conforms with the strict mathematical modeling, especially during the passing of a multi-phase raw material stream. The cause of this should be clear from the above-mentioned material.

However, the great flexibility in running the process of thermal heat removing, the possibility of operative redistribution of the amount of introduced cooling agent among the thermal heat removing zones, make the exploitation of these reactors simple and reliable in cases when the change of temperature in the layer is noticeably smaller than the change between the optimal temperature profile and the border exothermic side reactions.

Only for systems with single-phase raw material streams [273] the calculation of a reactor of this type can be made via collaboration in solving these equations:

$$\begin{aligned} u \, dC_i / dx &= r_i (C_i T) \\ \gamma u \, dT / dx &= r_T (C_i T) - q (T T_c) \end{aligned}$$

where x — longitudinal coordinate; r_i — formation speed of substance i ; r_T — speed of heat discharge in unit volume of reactor; γ — heat capacity of reacting solution; q — speed of thermal heat remover relative to a unit of the reactor zone, depending on temperature T in the reaction zone, and on the temperature of the cooling agent T_c ; C — substance concentration in the reaction zone.

The speed of the thermal-exchange between the reacting mixture and the heat-carrier can be expressed by the equation:

$$q = (K_T/R_h) (T - T_c)$$

where K_T — coefficient of thermal transition; R_h — hydrolyzed radius of the reactor.

The single-measurement quasi-homogenous model of the tube type reactor with an outer thermal heat remover (through the wall) can be used for hydrogenation in the steam phase, as a calculation model for thermo- and mass-transition processes. Such an approach appears to be sufficient relative to the comparative smallness of the diameter of the tubes and the prevailing role of the surface effects of the exchange.

The non-consideration of the diffusion in the process and its non-stationary aspect, being close to the outer-diffusion regime, does not negatively effect the calculation, but offers additional thermal stability. Such a calculation is made in the case of a steam phase hydrogenation of butyl aldehydes in a tube-type reactor with the use of water as a cooling agent on the basis of the data on the kinetics of this process.

The main equations of the model can be written in the non-measurement form as follows:

$$\begin{aligned} d\varepsilon/\Delta\tau &= -e^{\theta}f(\varepsilon) \\ d\theta/d\tau &= \Lambda e^{\theta}f(\varepsilon) - \mu\theta \\ f(\varepsilon) &= \varepsilon(x + \varepsilon)/[1 + b(x + \varepsilon)]^2 \end{aligned}$$

where ε — non-measurement current aldehyde concentration; θ — non-measurement current temperature in the tube; μ — non-measurement parameter of the thermal heat remover; b — adsorption coefficient; Λ — non-measurement parameter of thermal discharge.

Suppose that: $\tau = 0$; $\varepsilon = 1$; $\theta = \theta_0$.

$$\begin{aligned}
\varepsilon &= C_a/C_{a0} \\
\theta &= \varepsilon (T - T_x)/RT_x^2 \\
\tau &= tK^* \\
K^* &= C_{a0} \\
b &= b_{H_2}C_{a0} \\
x &= C_{H_20}/C_{a0} - 1 \\
\Lambda &= qC_{a0}/c_p\gamma \cdot E/RT_x^2 \\
\mu &= 4\alpha/d_T K^* c_p \gamma
\end{aligned}$$

Here C_a — current aldehyde concentration; C_{a0} — aldehyde concentration at exit; C_{H_2O} — hydrogen concentration at exit; t — conditional contact time; b_{H_2} — hydrogen adsorption coefficient; q — reaction thermal effect; c_p — heat capacity of mixture; γ — gas density; d_T — inner diameter of tube; K^* — reaction speed constant; E — activation energy.

The conditional time of contact t , the initial mol concentration C , the density of the reaction mixture at the entrance to the reactor γ , and the average mass heat capacity of the mixture at the exit of the reactor c_p , are defined by the following correlation:

$$t = l(1 - \varepsilon)/(u_0 - \varepsilon)$$

where l — tube length; ε — layer variety; u_0 — linear speed of gas at exit of tube. The rest of the members of these equations can be found in the following formulas:

$$\begin{aligned}
C_{a0} &= 0,045 \frac{P_0}{P_H} \cdot \frac{T_H}{T_0} \cdot \frac{1}{1 + A_0 + B_0} \\
\gamma_0 &= 0,045 \frac{P_0}{P_H} \cdot \frac{T_H}{T_0} \cdot \frac{M_a M_{H_2} A_0 M_c B_0}{1 + A_0 + B_0} \\
c_{p0} &= \frac{M_a c_{p_a0} + M_{H_2} A_0 c_{p_{H_20}} + M_c B_0 c_{p_{c0}}}{M_a + M_{H_2} A_0 + M_c B_0} \\
\frac{C_{a0}}{c_p \gamma_0} &= \frac{1}{M_a c_{p_a0} + M_{H_2} A_0 c_{p_{H_20}} + M_c B_0 c_{p_{c0}}}
\end{aligned}$$

Here C_{a0} , C_{H_20} , C_{c0} — mole concentrations of aldehydes, hydrogen, and alcohol at the entrance to the reactor; M_a , M_{H_2} , M_c — molecular masses of aldehydes, hydrogen and alcohol; P_0 and T_0 — pressure and temperature at entrance to reactor (at $x = 0$)

$$\mathbf{A}_0 = C_{H_2O}/C_{a0}; \quad \mathbf{B}_0 = C_c/C_{a0}; \quad \mathbf{P}_H = 0.1 \text{ MPa}; \quad \mathbf{T}_H = 273 \text{ K}$$

The current time for the mixture to remain in the reaction zone is defined by the correlation:

$$\tau' = V_k/V_0$$

$$V_k = Na(\pi\delta^2/4)h$$

where V_k — grain volume in reactor's catalyst; N — number of tablets; δ — tablet's diameter; h — thickness of tablet; V_0 — voluminous feeding of reaction mixture at entrance to reactor.

For each tube from $x = 0$ to the current x :

$$V_x^n = (\pi/4) d_T^2 x (1 - \varepsilon)$$

$$V_0^n = (\pi/4) d_T^2 \varepsilon u_0$$

Here $x = L$ which defines the general length of the tube; and d_T — diameter of the tube.

The pressure change along the reaction tube is defined by the following correlation:

$$p = p_L + \Delta p (1 - xL)$$

$$\text{therefore:} \quad \Delta p = (a/Re + a_2)\gamma_0 u_0 S \alpha / g \quad (4.VII)$$

$$Re_0 = \gamma_0 u_0 / \mu_0 g S \quad (4.VIII)$$

$$S = (4/\delta + 2/h) [(1 - \varepsilon)/\varepsilon] \quad (4.IX)$$

According to data [284], $\varepsilon = 0.4$; $a \approx 5 \times 10^{-4}$ and $a_2 \approx 0.3 \times 10^{-4}$. In expression (4.VIII) dynamic viscosity μ_0 is defined via μ_i ($i = 1, 2, 3$) relative to (4.VI).

The total coefficient of thermal transition α from the cooling stream to the cooling agent is defined from the correlation:

$$\alpha = 1 / \left(\frac{1}{\alpha_x \varepsilon_x} + \frac{\Delta w}{\lambda_w} + \frac{1}{\alpha_r} \right) \approx \alpha_T$$

The coefficient of internal thermal output α_T is defined by the sum:

$$\alpha_T = \Delta\alpha_T + \alpha_T^K$$

Note that $\Delta\alpha_T$ defines the contribution to the thermal output of the conduction and radiation coefficients, while α_T^K defines the effects of the convection.

According to [285], for the cited conditions $\Delta\alpha_T = 10^{-2}$ we get:

$$\alpha_T^K = 0.062 \lambda Sp_2^{1/3} Re^{0.8}$$

When calculating a reactor via a described model, besides the already mentioned digital and kinetic characteristics of the process, the following parameters should be given as well:

- a) the temp. of reaction mixture at the entrance to the reactor T_o ;
- b) the mol relations of the *hydrogen : aldehyde* and *alcohol : aldehyde* at the entrance to the reactor A_o and B_o ;
- c) the linear speed of the mixture at entrance to the reactor u_o ;
- d) the temperature of cooling agent in space between tubes T_x ;
- e) the pressure at the exit of the reactor p_L ;
- f) the degree of aldehyde transformation at exit of reactor $1 - \varepsilon_i$;
- g) the diameters of the reactor's tubes d_T ;
- h) the physical characteristics of the mixture components at the entrance to the reactor;
- i) the total feeding of aldehydes to the reactor $G_{a.o.}^e$.

When dealing with these parameters, however, there are two types of limitations. The chosen specter of parameter values should guarantee a reliable thermal stability in the work of the reactor. The essence of the first type of limitation is that value μ received from the given parameters, should satisfy the condition $\mu > \mu_{kr}$; where μ_{kr} — value, at which the reactor loses its thermal stability and transits from the quasi-isothermal to the quasi-adiabatic regime. An approximate value of μ_{kr} can be defined by the following equation:

$$\mu_{kp}^* = Aef(\varepsilon_x) \left[1 - \sqrt{\frac{1}{A} \frac{f'(\varepsilon_x)}{f(\varepsilon_x)}} \right]$$

where $\varepsilon_x = 1 - (1 - \theta_o)/A$

The second type of limitations mainly deals with the regime peculiarities of the process and with general technological requirements.

4.2.3 REQUIREMENTS FOR CATALYSTS IN THE HYDROGENATION STAGE

The exploitation of industrial reactors in heterogenous-catalytic processes puts forth many specific requirements relative to catalysts that are defined as chemical, technological, and economical problems.

Catalysts should be active and selective. But a high catalytic activity and selectivity in hard bodies relative to accomplishing reactions, yet does not give enough ground to think that the catalyst, on the basis of this substance, will be good enough for an industrial multi-ton process.

The most important property of an industrial catalyst is its capability to work non-stop with good results. Hydrogenation catalysts, used in the oxosynthesis process, practically do not regenerate. Because of this, the requirement for stability in catalysts in this case, is very high.

The stability of heterogenous catalysts, used in stationary layers, is defined by a number of factors: sensibility towards poisoning and overheating, mechanical durability, etc. Nowadays, only that catalyst can be regarded as good, which has been at work for at least half a year. The life span for the best heterogenous catalysts is equal to several years.

The most valuable property of a tablet-using heterogenous catalyst, working in a stationary layer, is its porous structure, which defines the contribution of the inner-diffusion braking factor.

The diffusion braking is usually accompanied by a troublesome heat diversion from the grain of the catalyst which leads to the appearance of a temperature gradient on the grain, and therefore, to the possibility to develop side processes.

The transition of substances into the pores of a catalyst is accomplished by molecular diffusion. In conditions of a large-pore structure in the catalyst, the moving molecules bump into each other more often than with the walls of the pores. Under such conditions, the transition speed for carrying the substance along the pores, relative to one unit of its crosscut section, can be defined by Fick's Law:

$$q = -D_M dC/dx$$

The molecular diffusion coefficient D_M is proportional to the average length of the free race of molecule λ :

$$D_M = \frac{1}{3} v \lambda$$

where v — average speed of the molecule.

If the catalyst has a small-pore structure, the collisions of the molecules with the walls of the pores play a great role. In cases when the size of the pores is much smaller than the length of the free run of the molecule, the diffusion coefficient is then proportional not to the length of the free run, but to the diameter of the pore d_n :

$$D_{Kn} = \frac{1}{3} v d_n$$

This expression was suggested by Knudsen, and the value of D_{En} had become known as the *Knudsen diffusion coefficient*.

Therefore, the porous structure of the catalyst can have the most serious influence on the catalytic process. Of course, the real porous structure of the catalyst is actually a complex system of pores of various sizes. However, as a rule, the pore-distributing curve, radius-wise, has one or two maximums that characterize the prevailing size of the pores.

The complex structure of the pores in the grain hinders the study the macro-kinetics of chemical reactions dealing with a concrete structure. Because of this, it is customary to regard the catalyst grain as a quasi-homogenous media, characterized by an effective diffusion coefficient D_{ef} , which is connected with realistic diffusion coefficients (molecular and that of Knudsen) via the correlation:

$$D_{ef} = aD_M$$

where $a < 1$ — multiplier that depends on the grain structure.

The role of the porous structure of the catalyst for hydrogenating the oxosynthesis process is illustrated by the butyl aldehyde hydrogenation reaction on a nickel-chromic catalyst. It was shown that when hydrogenating butyl aldehydes on a standard industrial nickel-chromic catalyst (OCT 6-03-314 — 76) at temperatures over 220°C, side hydrogenation reactions increase. This process was conducted at an increased pressure to avoid the reverse reaction of dehydrogenation.

The structure of a nickel-chromic catalyst greatly depends on the conditions of the preliminary restoration. The preliminary treatment of a nickel-chromic catalyst in a current of hydrogen before exploitation is conducted to restore a passive film of nickel oxide, originally put upon tablet-using catalysts at the mill of origin, to be able to take off the pyrophoric properties and enlighten the further transportation and loading of the recently made catalyst.

For this operation, it is enough to accomplish the treatment of the catalyst with hydrogen at 150° - 180°C. However, the temperature for the restoration of the catalyst can be artificially increased.

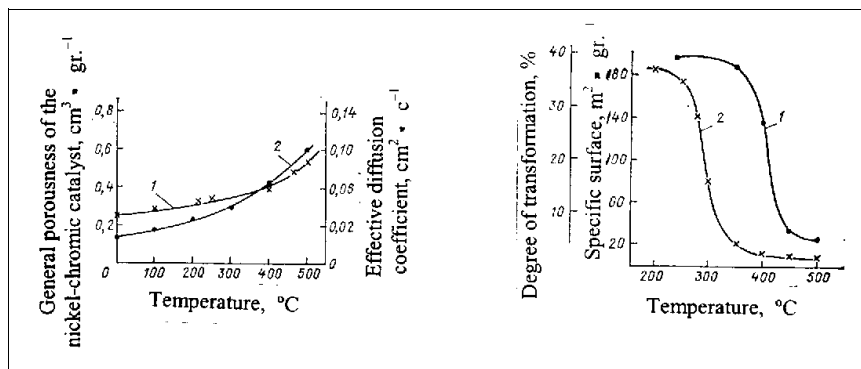


Fig. 4.20 Dependence of the general porousness of a nickel-chromic catalyst (1) and effective diffusion coefficient in the catalyst's grain (2) on the temperature for the restoration of a catalyst

Fig. 4.21 Dependence of the general specific surface of a nickel chromic catalyst (1) and its selectivity in a butyl aldehyde hydrogenation reaction (2) on the temperature for the restoration of a catalyst.

In fig. 4.20 and 4.21 are given data showing the dependence of general porousness of a nickel-chromic catalyst and effective diffusion coefficient in grain, and the whole specific surface of the catalyst on the temperature for the replacement of the catalyst in the stream of hydrogen.

With the increase of the restoration temperature, the general porousness and the effective diffusion coefficient of the catalyst also increase. At the same time there is a significant growth of part of the larger pores in the common porous structure at the expense of the disappearance and enlargement of the smaller pores.

Thanks to this redistribution with the increase of the reconstruction temperature, the common specific surface of the catalyst becomes smaller in spite of the increase of the porousness.

Simultaneously the selectivity of the catalyst increases. The curve that characterizes the output of hydrogenated products during the butyl aldehyde hydrogenation (curve 2, fig. 4.21) is like the curve that characterizes the decrease of the specific surface of the catalyst (curve 1, fig. 4.21). Thus, the change of the porous nickel-chromic structure of the catalyst allows changing its selectivity within a wide range.

When using the catalyst for work in a stable layer, a great role is played by the size and form of the catalyst's tablets. On the one hand, these large tablets, when loaded into the reactor, offer a layer with a smaller hydro resistance, i.e., they simplify the exploitation of reactors. But the increase of the size of the tablets simultaneously causes the increase of inter-diffusion difficulties.

Therefore, there exists a problem connected with the choice of optimal sized tablets for the catalyst. As a rule, catalyst tablets of sizes from 5 x 5 mm to 10 x 10 mm are used in hydrogenation reactors in the oxosynthesis process.

4.3 HOMOGENOUS CATALYTIC HYDROGENATION OF ALDEHYDES WITH COBALT CARBONYLS

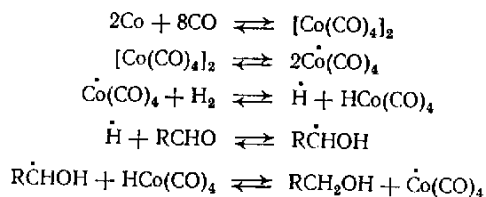
The capability of cobalt carbonyl to catalyze hydrogenation reactions was discovered during the research of the hydroformylation of the croton aldehyde [286]. It was shown that even at 125°C half of the croton aldehyde turns into butyl aldehyde. Later it was shown that the increase of the temperature up to 175° - 185°C leads to the fact that the croton aldehyde completely hydrogenates into butyl alcohol [287, 288].

Wender and his colleagues have shown that aldehyde hydrogenation in the presence of cobalt carbonyls bears a homogenous catalytic character. To prove this, the butyl aldehyde was hydrogenated at 185°C at a pressure of 14 MPa in a solution of cyclohexane on a newly restored metallic cobalt catalyst. Then carbon oxide was added to the hydrogen via the ratio $H_2 : CO = 7 : 1$.

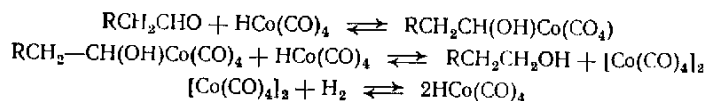
As a result, the hydrogenation reaction stopped in spite of the fact that the temperature remained the same and the pressure rose to 16 MPa because of the poisoning of the surface of the metallic cobalt with carbon oxide. However, the increase of the carbon oxide concentration to the ratio of $H_2 : CO = 2 : 1$ allowed to completely restore the butyl aldehyde into butinol at 185°C. In this case the partial pressure of the carbon oxide was enough for the formation of cobalt carbonyls having served as a hydrogenation catalyst.

Thus, it was proven that cobalt carbonyls can catalyze not only the hydroformylation reaction, but the hydrogenation reaction as well. The hydrogenation of a double bond proceeds at 120° - 125°C; while that of a carbonyl group — at 180° - 185°C.

A free-radical mechanism of this reaction was offered [289]:

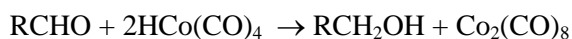


Somewhat later another reaction mechanism for hydrogenation in the presence of cobalt hydrocarbonyl was offered [290].

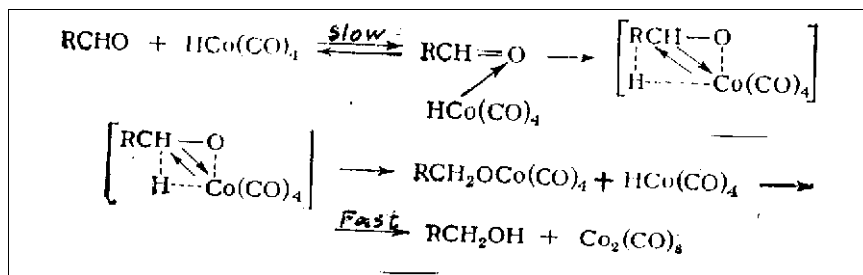


The catalytic activity of cobalt hydrocarbonyl, in part, in hydrogenation reactions of various compounds, was confirmed when studying reactions of stoichiometric interaction of $\text{HCo}(\text{CO})_4$ with aldehydes, with non-saturated aldehydes, with ketones, ethers, nitrils, olefins at room temperature and normal pressure [47, 89, 291 – 299].

It was shown that the stoichiometric restoration of saturated aldehydes [297] is a reaction of the first order via cobalt carbonyl:



The following mechanism for this reaction was suggested:



Hungarian chemists [133, 136, 300, 301] researched the homogenous-catalytic hydrogenation of aldehydes with cobalt carbonyls studying the influence of substrate structure on the reaction speed.

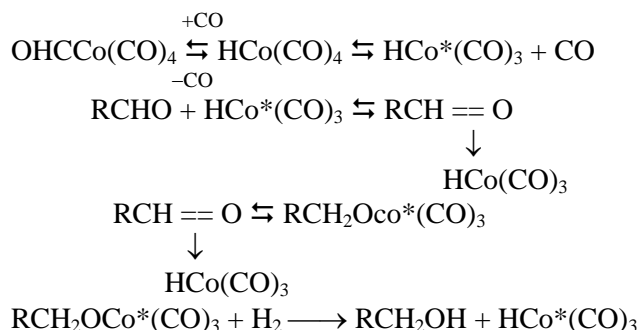
When studying the kinetics of the hydrogenation reaction of propionic aldehyde in a toluol solution up to propylene alcohol at 150°C, it was found that the maximal reaction speeds are observed at low partial pressure of carbon oxide. In the carbon oxide pressure intervals of 3.5 to 20 MPa, the hydrogenation reaction speed is counter proportional to the square of the carbon oxide's concentration, that is, the reaction speed R is expressed by this equation:

$$R = K \cdot C_a C_{Co} p_{H_2} \div p_{CO}^2 \quad (4.X)$$

where C_a and C_{Co} — aldehyde concentration in cobalt; p_{H_2} and p_{CO} — partial pressures of H_2 and CO .

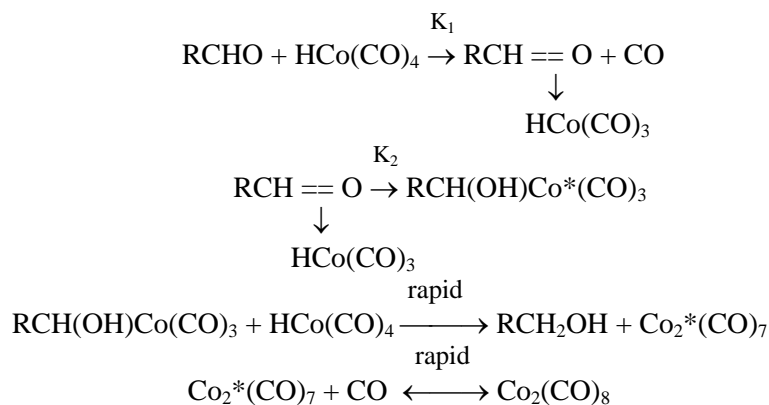
The dependence of the hydrogenation reaction speed on p_{CO} was settled at $p_{H_2} = 9.5$ MPa. Under such conditions when $p_{CO} < 3.2$ MPa, the stability of the carbonyls influences the reaction speed.

Considering the reverse dependence of the second order of magnitude of the reaction speed on the carbon oxide concentration, Marko [301] suggested the following reaction mechanism scheme:



According to this mechanism, the negative second order of magnitude for the carbon oxide reaction, is explained by the fact that cobalt, during the reaction, is in the form of OHCCo(CO)_4 , with 2 mols of CO more than the active coordinate-unsaturated form $\text{HCo}^*(\text{CO})_3$.

Unlike Marko's data, work [302] states that the hydrogenation reaction speed is reversely proportional to the concentration of CO. The reaction speed has half an order of magnitude, relative to hydrogen, up to the partial hydrogen pressure of about 0.7 MPa, and further approaches the zero order. Thus the authors offered the following mechanism:



The reaction speed equation is resembled as follows:

$$R = K_1 K_2 C_{\text{Co}} / p_{\text{CO}}$$

The designations are the same as in (4.X)

The reaction mechanism for aldehyde homogenous hydrogenation in the presence of cobalt carbonyls, on the level of modern notions of this process (theory of conence reactions, etc.) detailed in section 2.7 and described via reactions in (2.88) to (2.100).

Since hydrogenation with cobalt carbonyls proceeds at higher temperatures than hydroformylation, attempts were made to contrive a technology for the oxosynthesis process with homogenous-catalytic hydrogenation of the received aldehydes. A method was suggested [211] for direct production of alcohol from olefins and synthesis gas. According to this patent, at 130° – 160°C and 15 MPa, the received aldehydes hydrogenate in alcohol at temperatures of 160° – 220°C.

The homogenous-catalytic hydrogenation of oxosynthesis products is also described in a number of other patents [303], however, there is no information concerning the realization of such a variant on an industrial scale.

This in no way is related to the technological schemes of oxosynthesis with modified cobalt-phosphine and rhodium catalysts.

5 TECHNOLOGICAL SCHEMES FOR OXOSYNTHESIS PROCESSES

5.1 OLEFIN HYDROFORMYLATION AT LOW CONCENTRATIONS OF COBALT CATALYSTS

During industrial accomplishment of the oxosynthesis process, frequent technological difficulties arise, not necessarily on the hydroformylation reaction stage proper, but on the stage where the extraction of the cobalt from the catalyst and its recirculation take place in the process. In connection with this, of great interest are the attempts to accomplish the oxosynthesis process at low concentrations of the catalyst (cobalt carbonyls) in the reaction zone.

For example, during cobalt concentration in a product less than 0.01% (mass.) the oxosynthesis could be accomplished without any cobalt regeneration and recirculating since only one *secondary* problem would remain — to clear the hydroformylation products of cobalt. The economic indexes of the process, the losses of cobalt in such small quantities are practically unnoticed. The clearing of the hydrogenation product from cobalt can be accomplished with the help of thermal decobaltization, or, for example, merged with the hydrogenation stage.

The cobalt concentration decrease in the reaction zone is compensated by increasing the temperature. However, the possibility of increasing the temperature of the process is limited by the stability of the

cobalt carbonyls. It is known that stable concentrations of the catalyst in a solution are defined by the equation:

$$\text{Co}_2(\text{CO})_8 \rightleftharpoons 2\text{Co} + 8\text{CO} \quad (5.1)$$

therefore: $K_p = C_{\text{Co}_2(\text{CO})_8} / P_{\text{CO}}^8$

The minimal partial pressure of carbon oxide for the equilibrium concentration can be defined from the equation:

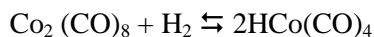
$$\text{Lg } P_{\text{CO}} = 7.94 - 2,160 / T$$

where T is the temperature in K units.

The close correlation between the temperature and partial pressure of the carbon oxide were received not only on the basis of the studies of the equilibrium of reaction (5.1), but also when studying the dependence of the hydroformylation reaction speed on the temperature. The linear dependence of the logarithm of the speed constant on the reverse absolute temperature was violated in the area of temperatures calculated via equation (5.1), that correspond to the shift of the equilibrium to the left of reaction (5.1).

Calculations made via equation (5.1) have shown that when $P_{\text{CO}} = 12$ MPa (normal conditions for the process of hydroformylation) the increase of temperature from $180^\circ - 220^\circ\text{C}$ decreased the equilibrium concentration of cobalt in the solution from 0.2 to 0.00004% (mass.). At such a catalyst concentration the reaction speed of hydroformylation is extremely low.

However, experimentally it was confirmed [19] that the hydroformylation of propylene can be accomplished at temperatures that are significantly higher than those of the thermal stability area of decobaltoctacarbonyl — up to 260°C . An explanation for the observed phenomenon was found when researching the equilibrium between the octa- and hydro-carbonyls:



Here we see that when decreasing the concentration of cobalt carbonyls in a solution, a greater part of which, in accordance with the Le-Shatelye principle, exists in the form of hydrocarbonyls.

It was found [121] that with the decrease of the cobalt concentration from 1.4% to 0.146% the correlation in the solution between cobalt hydrocarbonyl and decobaltoctacarbonyl increased by 3 times (see table 5.1).

If the partial pressure of carbon oxide changes from 3 to 10 MPa (decobaltoctacarbonyl contents comprises 0.105 - 0.116 mol x lit.⁻¹), the cobalt hydrocarbonyl contents practically does not change and remains within the limits of 0.0165 - 0.0185 mol x lit.⁻¹ (table 5.2).

The partial pressure of hydrogen has great influence on the equilibrium concentration of cobalt hydrocarbonyl (table 5.3).

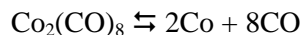
With the increase of the general pressure, the equilibrium of reaction (5.1) shifts towards the cobalt hydrocarbonyl at the expense of the increase of the hydrogen's partial pressure. [The partial pressure of carbon oxide, as already said, does not influence the contents of cobalt hydrocarbonyl.] Thus, with a small portion of cobalt carbonyls in the solution — 0.005 % - 0.01 % (mass.) calculated relative to the metallic cobalt — most of them are in the form of hydrocarbonyl.

Thus, under usual conditions of the oxosynthesis process ($p_{H_2} = 15$ MPa) in accordance with the value of the equilibrium constant and the contents of cobalt solution being equal to 0.01 % (mass.), this is already more than 90 % bonded to cobalt hydrocarbonyl. At smaller contents of carbonyls, the portion of octacarbonyls is extremely small.

At high temperatures (over 190°C) the equilibrium cobalt carbonyl concentrations in a solution, as a result of their thorough thermal breakup, are very small (less than 0.01 %). The equilibrium between metallic cobalt and carbonyls is defined via the following stoichiometric equation:



while for low temperatures and high concentrations of cobalt carbonyls, we have the following equation:



Thus, at a low cobalt carbonyl concentration, the latter is proportional to the fourth degree of P_{CO} and depends on $P_{H_2}^{0.5}$, while at a high concentration, it is proportional to the 8th degree of P_{CO} and does not depend on P_{H_2} .

With the increase of temperature, the equilibrium between octa- and hydro-carbonyl shifts towards the latter (table 5.4). This data can be expressed by the following equation:

$$K_r = 1,365 - 1,900/T$$

where K_r — conditional value of equilibrium constant; T — absolute temperature K.

The concentration of cobalt carbonyls under conditions of equilibrium, according to data [121], can be expressed thus:

$$\lg C_{\text{Co}} = -24.38 + 6,400/T + 4 \lg P_{\text{CO}} + \frac{1}{2} \lg P_{\text{H}_2} \quad (5.II)$$

C_{Co} — carbonyl concentration calculated for metallic cobalt, % (mass.).

Experiments on carbonylizing propylene at various partial pressures of carbon oxide (table 5.5) and various temperatures (table 5.6) have shown that the concentration of cobalt in exited products is close to that of the calculation via equation (5.II). Thus, at $200^\circ - 210^\circ\text{C}$ and $P_{\text{CO}} = 10.8 \text{ MPa}$ the equilibrium of the concentration of cobalt carbonyls comprises 0.025 % and 0.0135 % (mass.). The experimental values under these conditions are 0.019 %- 0.025 % and 0.012 %- 0.015 % (mass.).

It has been shown that the hydroformylation process during cobalt concentration in products less than 0.02 % (mass.) can take place at high temperatures that are not limited by the stability of decobaltoctacarbonyl, unlike the classical parameters of the oxosynthesis hydroformylation stage — about 30 MPa, $100^\circ - 150^\circ\text{C}$, cobalt concentration of about 0.2 % (mass.).

In small concentrations cobalt exists in the system mainly in the form of a more stable hydrocarbonyl. The accomplishment of the hydroformylation process at small cobalt concentrations significantly permits to raise the temperature and maintain the accepted speed values.

When accomplishing hydroformylation with a concentration smaller than 0.02 % (mass.) cobalt regeneration is abruptly simplified.

TABLE 5.1

Dependence of Equilibrium Cobalt Carbonyl Concentration on Total Cobalt Carbonyl Concentration in Solution

Conditions: temperature 130°C ; carbon oxide partial pressure 4.5 MPa; hydrogen — 5.6 MPa; solvent — toluol.

Total concentration of cobalt carbonyl in % (mass.)	Equilibrium concentration (calculated relative to met. cobalt)			
	$\text{Co}_2(\text{CO})_8$		$\text{HCo}(\text{CO})_4$	
	% (mass.)	mol. portion	% (mass.)	mol. portion
1.403	0.945	0.066	0.458	0.450
0.760	0.500	0.034	0.260	0.035
0.353	0.203	0.0137	0.150	0.0204
0.146	0.064	0.00435	0.0820	0.0112

TABLE 5.2

Dependence of Equilibrium Cobalt Carbonyl Concentration on Carbon Oxide Partial Pressure

Conditions: temperature 130° C; partial pressure of hydrogen 0.5 MPa; solvent — toluol.

Partial pressure of carbon oxide in MPa	Equilibrium concentration; mol x lit. ⁻¹		Partial pressure of hydrocarbonyl in gas phase; MPa
	Co ₂ (CO) ₈	HCo(CO) ₄	
3	0.0116	0.0173	0.0080
4	0.0092	0.0186	0.0085
5	0.0116	0.0184	0.0085
5.9	0.0063	0.013	0.0060
6.5	0.12	0.0196	0.0090
7	0.0092	0.0153	0.007
8	0.0106	0.017	0.008
9	0.0076	0.014	0.0065
10	0.0105	0.0165	0.0080

TABLE 5.3

Dependence of Equilibrium Cobalt Carbonyl Concentration on Hydrogen Partial Pressure

Conditions: temperature 150° C; partial pressure of carbon oxide 6 MPa; solvent — toluol.

Partial pressure of Hydrogen in MPa	Equilibrium concentration in mol x lit. ⁻¹	
	Co ₂ (CO) ₈	HCo(CO) ₄
2.5	0.0082	0.0140
4	0.0068	0.0145
6	0.0053	0.015
10	0.0043	0.019
14	0.003	0.017
16	0.0023	0.019
18	0.0032	0.02

TABLE 5.4 Dependence of Equilibrium Cobalt Carbonyl Concentrations on Temperature

Condition: solvent — toluol.

Temperature; K	Hydrogen partial pressure; MPa	Equilibrium concentration			
		Co ₂ (CO) ₈		HCo(CO) ₄	
		% (mass.)	Mol. Portion	% (mass.)	mol. portion
383	5.6	0.25	0.017	0.116	0.0157
393	6.6	0.112	0.0075	0.094	0.0127
403	4.8	0.092	0.0062	0.09	0.0122
423	6.1	0.087	0.0059	0.114	0.0154
433	5.9	0.06	0.004	0.105	0.0142
433	4.6	0.089	0.006	0.125	0.0169
433	4.5	0.88	0.00596	0.136	0.0184
453	5.1	0.066	0.00446	0.131	0.1777

TABLE 5.5 Dependence of Cobalt Carbonyl Stability During Propylene Hydroformylation on Carbon Oxide Partial Pressure

Condition: initial cobalt concentration 0.0170 % (mass.).

Temperature, °C	Partial pressure of carbon oxide, MPa	Cobalt concentration in catalyst, % (mass.)
202	7.5	0.0065
202	10	0.0101
204	13	0.0170

TABLE 5.6 Dependence of Cobalt Concentration at Reactor Exit on Temperature

Conditions: pressure 27 MPa; portion of carbon oxide in synthesis gas 40 % of the volume; cobalt concentration (calculated for metallic cobalt) in raw material 0.03 % (mass.).

Temperature, °C	Feeding liquid raw material, hr ⁻¹	Concentration of cobalt carbonyls in product (calculated for metallic cobalt), % (mass.)
200	0.35	0.019
200	0.52	0.025
200	0.66	0.019
210	0.50	0.012
210	0.70	0.015
220	0.50	0.009
240	0.50	0.002

5.2 NAPHTHENE EVAPORATION SCHEME (NES) FOR OXOSYNTHESIS

The naphthene evaporation scheme (NES) of the oxosynthesis process is, at present, one of the best as far as the technical and economic indexes are concerned. After the 'workout' of its technical aspect, in the Soviet Union [205 - 208] at the All Union Scientific Research Institute of Oil Chemistry and at the Leuna Werke (German Democratic Republic) a joint technology was elaborated [103], which was tried on large experimental installations. The process of getting butyl aldehydes and butyl alcohol via this scheme is accomplished on a number of large industrial installations with one capacity of 60,000 tons a year via propylene each.

5.2.1 PRINCIPLES FOR ACCOMPLISHING THE NES

In the naphthene evaporation scheme of the oxosynthesis process, cobalt was introduced into the system in the form of salt diluted in a hydrocarbon solvent. It is most desirable to use salts of the higher organic acids that are less corrosion-active. It is also desirable to use acids with a branched chain, since these dilute better in organic products.

It is desirable to use hydrocarbons as a solvent for cobalt salts and for ensuring the success of the hydroformylation process. It is best to use the highest hydrocarbons (with a boiling point over 160°C), since this eases the division of the products on the rectification stage. Aromatic hydrocarbons (like toluol) can also be used.

Carbonyl-formation should be accomplished in a special reactor. This offers the following advantages:

1) reception of more concentrated (relative to cobalt) solutions of the catalyst, which is profitable, in part, because of the auto-catalytic character of the carbonyl-forming reaction out of salts, whose speed, therefore, increases with the increase of the cobalt concentration;

2) introduction of the carbonyl-formation reaction at sufficiently high temperatures (over 160°C); if the carbonyl-formation and hydroformylation reactions were merged into one reactor, too many iso-structure products would be formed.

To sum up the above, we can draw the conclusion that by accomplishing the carbonyl-formation reaction in a separate apparatus, the necessary total reaction volume is decreased.

Hydroformylation is best accomplished when the cobalt concentration in the system amounts to 0.1% - 0.2% (mass.). The increase of this concentration over 0.2 % causes an increase in the losses

of the final product. [Three mols of aldehydes are used per one mol of cobalt on the decobaltization oxidizing stage.]

The optimal temperature of the hydroformylation process is 120°–130°C. The increase of temperature and the reaction speed, and consequently — the production of the reactor's block, have a negatively influence on the isomer correlation of the products (i.e., increase of the iso-structured products). A decrease of the temperature to 120°C and lower has hardly any influence on the isomer distribution, but it does decrease the productivity of the reactors.

In spite of the fact that the intensive mixing in the transition reaction of cobalt carbonyls into salt proceeds in the diffusion area, it is obvious that the use of mixers on the decobaltization oxidation stage is not advisable. The reaction speed in the diffusion area is high enough to guarantee a high production process (up to 5 hr⁻¹) on the Scrubber apparatus.

If we consider that the decobaltization process in the NES is accomplished at normal pressure, the irrationality of the complex construction of the reactor becomes quite obvious. The optimal temperature for decobaltization is about 50°C. At a higher temperature there can be a thermal breakup of the cobalt carbonyls.

The separation of the cobalt salt solution from the propylene hydroformylation products can be accomplished by evaporation. During the incomplete elaboration of the olefin on the propylene hydroformylation stage (the dependence of the output of side hydroformylation products on the degree of olefin transformation has already been cited in this book) the few formed side products of the 'first generation' is readily separated from the solution of cobalt naphthene via distillation.

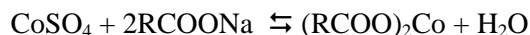
During hydroformylation with a deep 'workout' of propylene, part of the formed heavy side products (over 90%) gets into the circulating solution of the catalyst (cobalt naphthene) and causes the need to shift part of the solution to the regeneration process to get rid of the cobalt and avoid the accumulation of side products in the cycle.

5.2.2 PRODUCTION OF COBALT NAPHTHENE

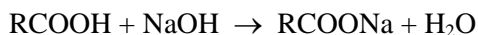
Strictly speaking, getting cobalt salt of fatty (butyl) acid like that of naphthene, in the form of which cobalt is introduced to the oxo-process in the naphthene-evaporation scheme (NES), has nothing to do with the oxosynthesis technology. However, such salts are not produced on the industrial scale, which causes the need to prepare them directly on the oxosynthesis installations. With plenty of such installations around that make use of the NES, it is wise to organize a separate shop for the

preparation of cobalt salts (II) and naphthene acids that could satisfy the needs of all the oxosynthesis installations with their product.

Naphthene cobalt is produced with the help of an exchange reaction between cobalt sulfate and sodium naphthene:



In turn, sodium naphthene can readily be received from naphthene acid and alkaline:



Thus, caustic soda, cobalt sulfate, and naphthene acids (products produced on a wide scale) are used as initial raw materials for producing cobalt naphthene.

5.2.3 STAGES OF CARBONYL FORMATION AND HYDROFORMYLATION

Since, according to the naphthene evaporation scheme (NES) of oxosynthesis the processes of carbonyl formation and hydroformylation proper are accomplished at the same pressure of about 30 MPa, these processes are combined into one technological chain that is commonly called the *hydroformylation stage* thereby omitting the mention about the carbonyl formation as a separate process (fig. 5.1). The processes of carbonyl formation and hydroformylation are conducted as follows:

The solution of cobalt naphthene in a solvent with a concentration of salt 7 - 8 % (mass.) enters volume 11. The solvent used for preparing a fresh solution of cobalt naphthene is toluol.

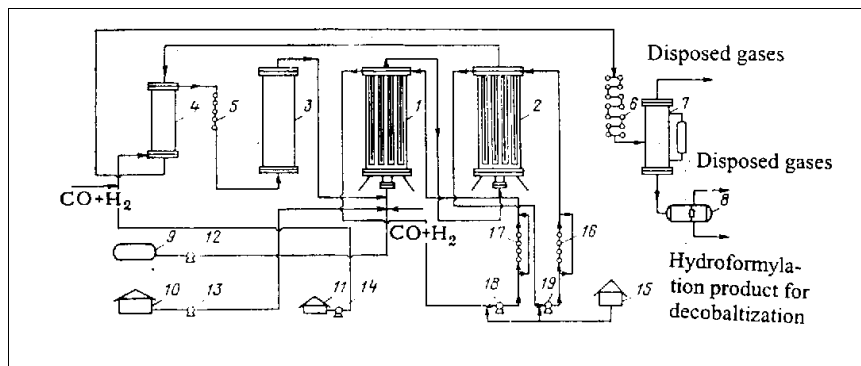


Fig. 5.1 Technological Hydroformylation Stage in the Naphthene Evaporation Scheme of the Process:

1, 2- hydroformylation reactors; 3 - carbonyl formation reactor;
 4 - heat changer; 5 - heater; 6 - refrigerator; 7 - high pressure separator;
 8 - low pressure separator; 9 - volume for propylene; 10 - volume for solvent;
 11 - volume for cobalt naphthene solution; 12, 13, 14, 18, 19, - pumps;
 15 - volume for steam condenser; 16, 17 - refrigerators.

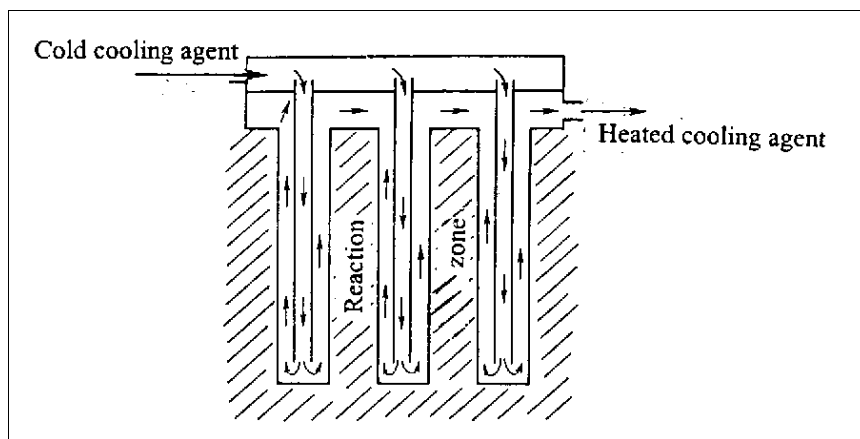


Figure 5.2 Scheme of Thermal Heat Remover with Field Tubes.

When starting the work of the installation, there is a solution of cobalt naphthene in the toluol. The same kind of solution is used when substituting for lost cobalt during the nonstop exploitation of the installation. To guarantee cobalt circulation in the system, the solvent used is a mixture of high boiling side oxygen-containing products of hydroformylation, the so-called *boiler leftovers*.

The cobalt naphthene solution is taken out of volume 11 with pump 14 and passed on to be mixed with synthesis gas, then the received liquid gas mixture goes through thermal exchange device 4, steam heater 5, then goes into carbonyl forming reactor 3. In thermal exchange device 4, the cold mixture of the cobalt naphthene solution and synthesis gas heats up at the expense of the heat of the products of hydroformylation that are discharged from the reactor. The heated mixture is then heated again in the steam heater up to the working temperature. The carbonyl formation process is completed in reactor 3 at 170°C and at about 30 MPa. The reactor is a hollow column-type apparatus with high pressure.

The received cobalt carbonyl solution enters hydroformylation reactor 1. Then, the propylene, synthesis gas, and the solvent (toluol)

appear. For better results, the hydroformylation is accomplished in two consecutively connected reactors. Hydroformylation reactors are actually apparatuses of the column type with high pressure and built-in gadgets for withdrawing heat of the exothermic reaction.

Hydroformylation is accomplished at 120° - 130°C and at about 30 MPa. The heat collecting in the reactors is done with the help of *Field tubes* or *double tubes* (fig. 5.2) in which the cooling agent (steam condensate) keeps recirculating.

The heated steam condensate exiting from the hydroformylation reactor with the help of pumps 18 and 19 (fig. 5.1) proceeds through refrigerators 16 and 17, where it gives up its heat to the reactor and later returns to the reactor to take off another portion of heat. Note that part of the cooling agent enters the refrigerator, and the other part passes by and enters the reactor.

Thus, the change of the cooling agent's temperature at the entrance to the hydroformylation reactor is gained by changing the correlation of the streams of the steam condensate that proceeds through the refrigerator and passes by it. This allows to automatically maintain the necessary temperature regime in the hydroformylation reactor.

The hydroformylation product, leaving the reactor, passes some of its heat on to heat exchanger 4, a product that is proceeding to the carbonyl formation reactor, there it cools down in refrigerator 6 to its normal temperature and gets to high pressure separator 7. The gas that separated from the liquid in the separator (mainly a mixture of carbon oxide and hydrogen) is throttled and discarded. By removing the gas from the high-pressure separators, this pressure can be regulated to about 30 MPa in the system of hydroformylation and carbonyl formation.

Liquid products from the high-pressure separator throttle to low-pressure separator 8. From here also runs the gas that was separated from the liquid; the liquid products enter the oxidation decobaltization system. A constant level of liquid is maintained in the separators of high and low pressure automatically with the help of a regulator.

5.2.4 THE OXIDIZING DECOBALTIZATION STAGE

The transfer of cobalt carbonyls to a thermally stable form (naphthene cobalt) for subsequent extraction of cobalt and recirculating it into the process of naphthene evaporation oxosynthesis scheme is accomplished with the help of cobalt carbonyl oxidizing via oxygen from the air and further bonding the separated cobalt with naphthene acid into salt. See (3.14) to (3.16).

The technological scheme for the oxidizing decobaltization stage in the naphthene-evaporation scheme (NES) is shown in figure 5.3. Products of hydroformylation that contain cobalt carbonyls and free naphthene acids, travel from a low pressure separator of the hydroformylation stage and pass into heater 2 where they get heated up to 50° C. This temperature is regulated by feeding steam condensate into the heater that circulates in the heat carrier. The heated product then goes on to oxidizing decobaltization reactor 1. This reactor gets some air whose oxygen is actually the oxidizer of the cobalt carbonyls. In order to guarantee a complete transition of the cobalt into naphthene cobalt, a small amount of fresh naphthene acids is also fed into the reactor.

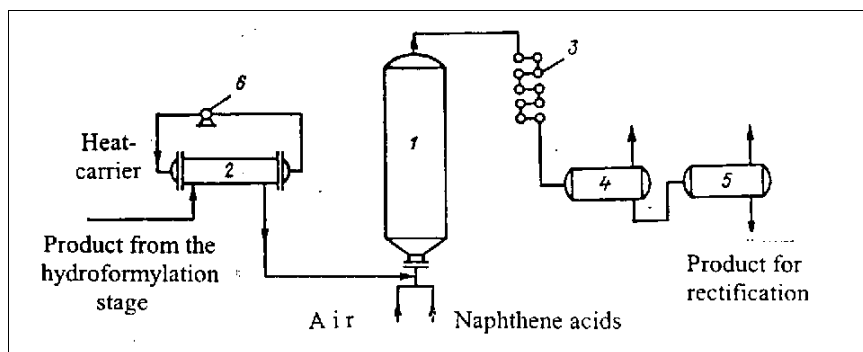


Fig. 5.3 Technological scheme of the oxidizing decobaltization stage:
1 – reactor for this stage; 2 – heater; 3 – refrigerator;
4, 5 – separators; 6 – pump.

The oxidizing decobaltization process is conducted at 0.3 - 0.5 MPa and at a temperature of 40° - 50°C.

When the hydroformylated product, with cobalt in the form of naphthene salts, exits the reactor, it goes to refrigerator 3, then it frees itself of the gas-like products in separators 4 and 5; under normal pressure, it enters the stage for rectification of aldehyde products, where the received products are divided; part of the naphthene cobalt is separated in the form of a solution in high-boiling side oxygen-containing products that are returned to the process on the carbonyl-formation stage.

5.2.5 SEPARATION OF HYDROFORMYLATED FINAL PRODUCTS; COBALT RECIRCULATION AND REGENERATION

After cobalt-carbonyl oxidation and its transfer to naphthene cobalt, the hydroformylated products enter the division stage, which is supplied with atmospheric and vacuum rectification columns.

The scheme of the rectification stage for aldehyde-containing hydroformylation products, used to separate aldehydes and naphthene-cobalt solutions returned to hydroformylation stage, is given in fig. 5.4.

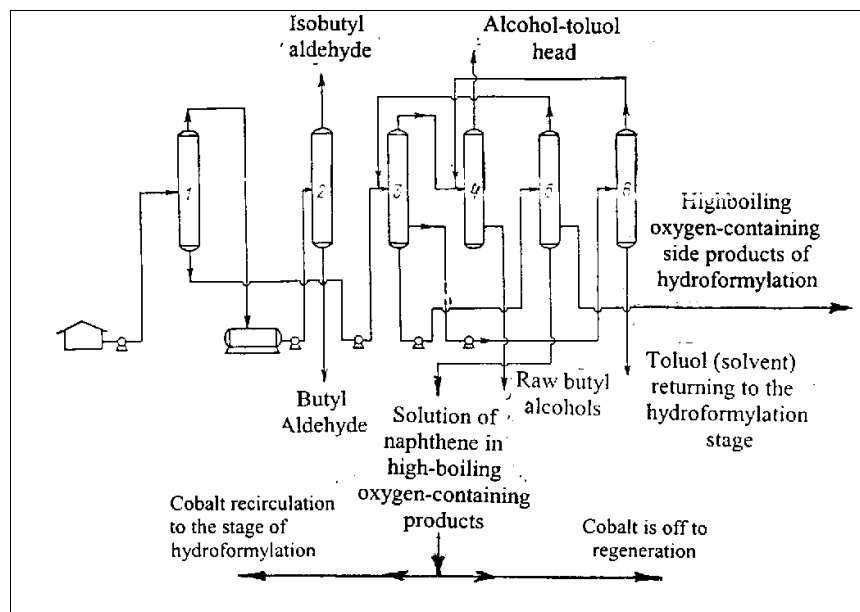


Fig. 5.4 Technological Scheme for the Rectification of Aldehyde Products and the Recirculation of the Catalyst into the Process

In column 1 butyl aldehydes are singled out (according to the product's moving order) in the form of distillate from hydroformylated products and directed straight for hydrogenation in alcohol. However, the NES, during propylene hydroformylation, is especially effective in cases when the oxosynthesis installation is working in complex with an installation for producing 2-ethylhexane out of butyl aldehyde.

These aldehydes are directed to column 2 where they are divided into butyl and isobutyl aldehydes. Butyl aldehydes serve as initial raw material for producing 2-ethylhexane, and the isobutyl ones are directed to the hydrogenation stage so as to get isobutyl alcohol out of it.

The boiler product of column 1, containing toluol, cobalt naphthene and oxygen-containing products formed on the hydroformylation stage, including butyl alcohol, is directed to column 3. Through the top of this column the mixture of butyl alcohol and toluol (so-called alcotoluol head) is exited, and the toluol is exited in the form of a side distillate.

The alcotoluol head is divided in column 4 into an isotrope of isobutyl alcohol and toluol (taken from the top of the column) and raw butyl alcohol (boiler of column 4). Raw butyl alcohols are mixed with isobutyl aldehydes while on their way to hydrogenation. Such a summed up processing simplifies getting butyl alcohol of a very high quality.

The toluol received at column 3 is additionally cleared of admixtures from butyl alcohol in column 6. The butyl alcohol, purified in this way, is returned to column 4, while the cleared toluol is returned to the hydroformylation stage in the capacity of a solvent.

The boiler product of column 3 enters column 5 where, through the top, are taken away the remains of the butyl alcohol and toluol that pass to the feeding line of column 3. In the capacity of side distills, from column 5, are taken the high-boiling side oxygen-containing products of hydroformylation which can be subject to further processing to extract the valuable products out of them, like octyl alcohol or sent off to be burned.

The cobalt naphthene solution, in high-boiling side products, exits from the boiler of column 5 and is returned to the process of the cobalt carbonyl formation stage. Thus, the recirculation of the cobalt catalyst in the NES is complete.

To avoid the accumulation of cobalt tar-like high-boiling products in the circulation cycle, part of the cobalt naphthene solution introduced to column 5, is sent off to regeneration. A water solution, for example, H_2SO_4 , is extracted out of the cobalt solution, while the organic part of the product is taken away and burned.

5.2.6 ALDEHYDE FINAL PRODUCT HYDROGENATION

Since the oxosynthesis in the NES, during propylene hydroformylation, the butyl aldehyde is extracted in the capacity of the final product, the isobutyl aldehyde approaches the hydrogenation stage. Besides, this stage can be approached by raw butyl alcohol that was separated in the form alcohol fraction on the rectification stage of the aldehyde hydroformylation product.

This is explained by the fact that the raw butyl alcohol, having passed through the hydrogenation catalyst, allows to produce butyl alcohol of a much higher quality. Thus, the product, entering the hydrogenation stage, usually contains about 70 % isobutyl aldehyde and about 30 % of butyl alcohol.

At present there are two main variants of technological installations for the hydrogenation stage.

The **first variant** (fig. 5.5) for the hydrogenation of aldehyde products is accomplished in the liquid phase under high pressure (≈ 30 MPa). The aldehyde raw material is pumped out of volume 1 by high powered pump 2 and is mixed with the circulating hydrogen, then the aldehyde-hydrogen mixture enters heat-exchanger 3, where it heats up at the expense of the heat of the products exiting from hydrogenation reactor 5. Then the preliminarily heated raw material mixture is heated to the working temperature in heater 4 and enters hydrogenation reactor 5.

The hydrogenation reactor is actually a column apparatus of high pressure, equipped with special plate-like gadgets for the placement of the catalyst. The hydrogenation reactor with a height of 12 to 15 meters is usually divided with the help of these plates into 5 or 6 separate sections. These plates have two main functions.

Firstly, they ease the loading of the catalyst, which is done separately in each sector, and they decrease the mechanical load on the lower tablets of the catalyst.

Secondly, they serve as distribution gadgets for the mixing of the hot raw material stream with the cold hydrogen that is fed to the reactor to draw away the heat of the exothermic hydrogenation reaction

The drawing away of the reaction heat and the regulation of the temperature regime in the reactor are accomplished by feeding cold hydrogen at the entrance of the reactor (temperature control of the entering raw material) and at several points along its top.

The reactor is loaded with tablet-shaped catalysts of hydrogenation, for example, with thermally modified nickel-chromic catalysts.

The products of hydrogenation, leaving the reactor and giving part of their heat to the fresh raw material in heat-exchange device 3, get cooled in refrigerator 6 and go on to high-pressure separator 7 where the hydrogen separates from the liquid products. The separated hydrogen is then sucked up by circular gas pump 9 and goes on further to the path of the circulatory gas area.

In order to avoid the accumulation of inert substances and dangerous foreign particles in the circulatory system, part of the hydrogen that leaves the high-pressure separator, is thrown into the net for fuel gas. From high-pressure separator 7 the hydride enters low-pressure separator 8 where the diluted gases are singled out, thrown into the fuel gas net, and then passed on to rectification for the withdrawal of the final products.

The **second variant** for the hydrogenation of aldehyde products is accomplished in the steam phase at a low surplus pressure (0.03 - 0.3 MPa). In this case the hydrogenation process proceeds in a tube-type reactor with an outer heat-remover, and is accomplished most often with the help of circulating water in the area between the tubes of the reactor.

The hydrogenation can occur via the correlation *hydrogen : aldehyde*, close to that of stoichiometry, that is, without the circulation of hydrogen, as a rule, on nickel catalysts.

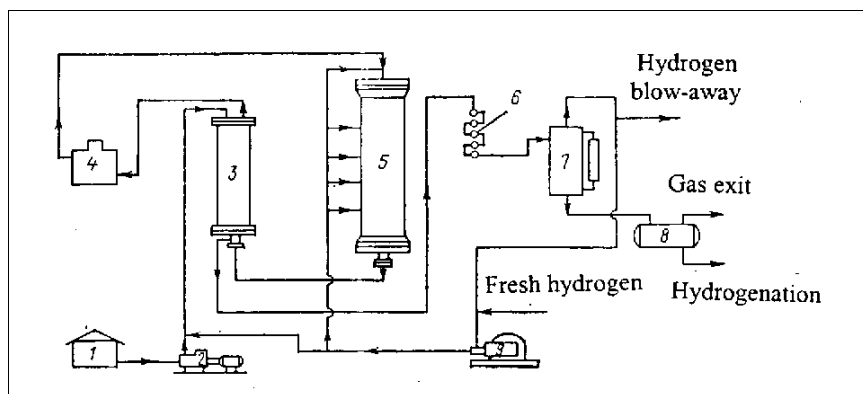
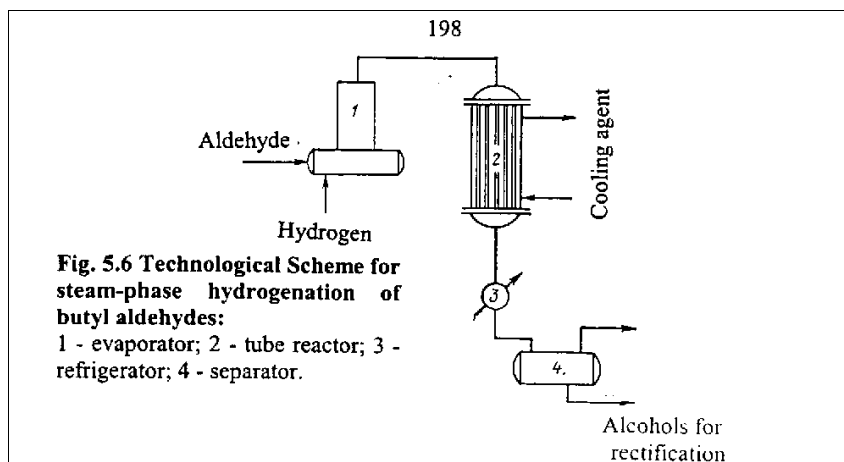


Fig. 5.5 Technological Scheme for the Hydrogenation of the Aldehyde Product at High Pressure:

1 - volume for aldehyde product; 2 - pump for feeding liquid product; 3 - heat exchanger; 4 - heating stove; 5 - hydrogenation reactor; 6 - refrigerator; 7 - high pressure separator; 8 - low pressure separator; 9 - circulatory gas pump.



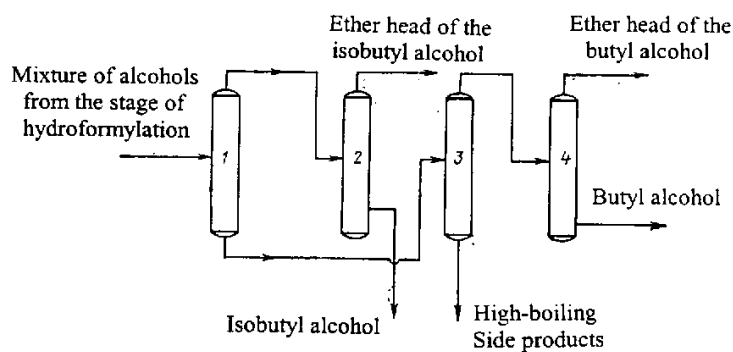
The process of steam-phase hydrogenation of lower aldehydes at stoichiometric quantities of hydrogen (fig. 5.6) is very economical since it differs with its very low capital and exploitation expenditures.

5.2.7 BUTYL ALCOHOL RECTIFICATION

The separation of alcohols received after the hydrogenation of aldehyde products is done with the help of rectification (fig. 5.7).

Hydrogenation products containing a mixture of butyl alcohols of normal structure and iso-structure, and foreign substances of simple and complex ethers, aldehydes, and high boiling side products, enter column 1, where they break up into fractions of isobutyl alcohol (which exits at the top of the column) and butyl alcohol (which exits at the bottom). Raw isobutyl alcohol enters the top of column 2 for cleaning, where, in the form of a complex mixture of double and triple isotopes of water with butyl aldehydes, ethers, and isobutyl alcohols, the foreign particles are removed, while from the bottom part of the column exits the final isobutyl alcohol. The raw butyl alcohol enters column 3 to be cleared of the foreign particles of high-boiling products, and goes to column 4 where it is cleared of light foreign particles.

Fig. 5.7 Technological Scheme for the Rectification of Butyl Alcohols



5.2.8 NES WITH OLEFIN RECIRCULATION

The development of the naphthene-evaporation scheme (NES) of oxosynthesis for producing butyl aldehydes and butyl alcohols via propylene hydroformylation is obvious from the so-called *naphthene-evaporation scheme with propylene recirculation*.

The main theoretical precondition, when constructing this scheme, was the fact that all the reactions for the formation of side oxygen-containing products during olefin hydroformylation are successive as compared with the main reaction for aldehyde formation.

The use of the data on the kinetics of the propylene hydroformylation reaction allowed concluding that by lowering the propylene transformation degree from 90-95% to 50-70% we can decrease the number of side oxygen-containing products formed during the reaction from 12-20% to 1.5-4.5%.

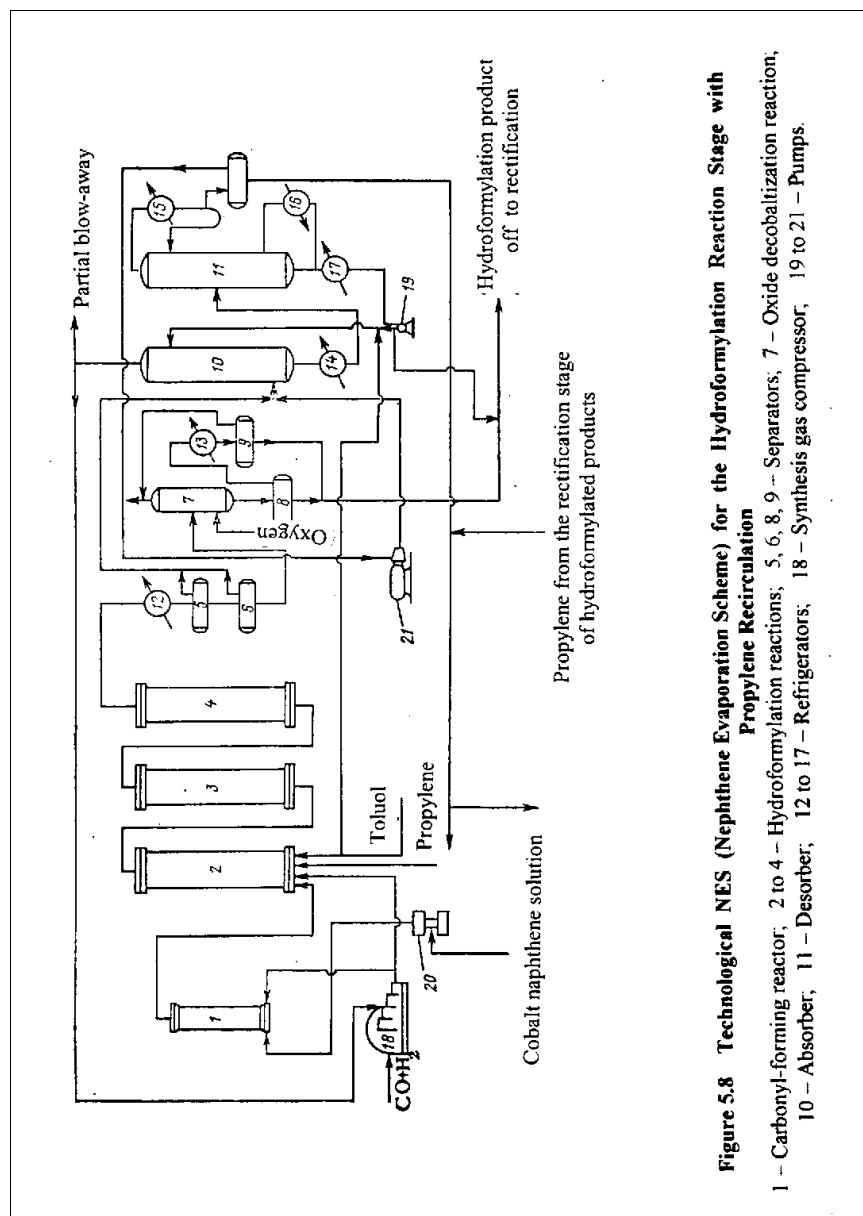
Therefore, the accomplishment of the process with an incomplete transformation of the initial olefin, its separation from the reaction products and recirculating into the process, allows to significantly cur down costs of the initial raw material at the expense of increasing the selectivity of the process, as well as to simplify the scheme for dividing the products and single out the final products at comparatively small costs relative to organizing the recirculation.

Carbonyl formation in the oxoprocess with recirculating propylene (fig. 5.8) is accomplished in a high-pressure column apparatus. The preliminarily heated solution of cobalt salts in high boiling carbon-hydrogen solvent, which is meant to organize the recirculation of the cobalt catalyst, is fed to the carbonyl former 1, with synthesis gas following. In the carbonyl former at 150° – 170°C and at about 30 MPa, cobalt salts change into carbonyls.

The hydroformylation process is accomplished in the cascade of reactors with complete mixing at 120° - 130°C and 30 MPa. The number of reactors in the cascade depends on the power of the installation and the method of organizing the heat collector. If the power of the installation is 150,000 tons of propylene per year, and the heat collector is of the Field tube type, the cascade should consist of three reactors.

The solution of cobalt carbonyls in heavy solvent goes into the first hydroformylation reactor (2) with propylene, synthesis gas, and solvent (toluol). The hydroformylation products exit from the last reactor of cascade 4, they are cooled in fridge 12 and moved on through separator 6, where the pressure amounts to about 2.5 MPa. The liquid products of hydroformylation run out of separator 6 and go into the oxide decobaltization reactor 7, into which oxygen is fed. After the interaction

of cobalt carbonyls with oxygen, and their transfer to a thermally stable form of salt, the decobaltized product enters separator 8 where the pressure is maintained at about 0.1 MPa. The gas stream from separator 8



is cooled in fridge 13 down to minus 10° - minus 6°C and goes to separator 9 for an additional separation from the liquid products (toluol, aldehydes, etc.) that broke away when the gas stream cooled down. Then

the gas stream from separator 9 is merged with those of separators 5 and 6 and all this goes to absorber 10, where irrigation by toluol takes place.

Here the separation of propylene and leftovers of aldehydes from the synthesis gas takes place as well. The old synthesis gas is sent off to be mixed with fresh synthesis gas that had entered the process. Part of the synthesis gas, separated in the absorber, is blown away to avoid accumulation of inert substances in the system. The toluol with absorbed propylene passes on to desorber 11. Then the propylene exits from the top of the desorber in a liquid form. The toluol, being free of propylene, enters the absorber for irrigation. The liquid product of hydroformylation leaves separator 8 simultaneously with the liquid product from separator 9 and they go to the first column of the rectification stage. This column also accepts part of the reverse toluol to avoid the accumulation of aldehydes in the toluol that circulates in the absorber-desorber system.

The head of the rectification products of hydroformylation from the first rectification column, which is actually a concentrate of propylene, enters to mix with fresh propylene and the circulating propylene from the desorber. In order to avoid the accumulation of propane in the system, part of the circulating propylene is shifted to the gas-fractionalizing installation that is included in the system of producing initial propylene. Otherwise, the scheme for the rectification of hydroformylation products is analogous to the previously described in this chapter. The technological scheme of the hydrogenation stage is also analogous to the described one.

The NES of the oxosynthesis process with the recirculation of propylene allows the successful solving of many problems of technological and economical nature. An abrupt decrease in the exit of side products (by a whole order of magnitude) and the absence of hydroformylation products of high-boiling side products of the 'second generation', not only improves the economical characteristics of the process, but also allows to simplify the scheme for the return of the catalyst that declined the acid cobalt regeneration stage.

5.3 OXOSYNTHESIS WITH COBALT CATALYSTS FOR HYDROFORMYLATION OF MODIFIED PHOSPHINES

The first mentioning of the use of cobalt catalysts in the hydroformylation reaction modified by organic phosphines appeared in chemical literature in the 1960s [104, 304, 305] and belonged to a group of workers of the firm 'Shell'.

Complexes of cobalt with organic phosphines differ from pure cobalt carbonyls by their activity * in the hydroformylation reaction at a much smaller pressure (2 MPa) and offer a greater output of products that bond to the final olefin atom, that is, an increased output of aldehydes of normal structure.

The influence of the kind of the organic phosphine modifier on the output of straight chain products during hydroformylation has been studied by Tucci [306 - 308] (table 5.7).

TABLE 5.7

Dependence of the Isomer Contents of Aldehydes on the Basics of Modifying Phosphine During Hydroformylation of 1-Hexane

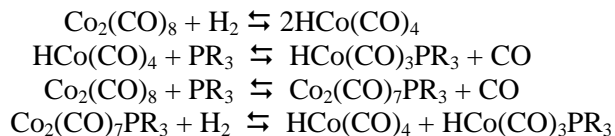
Conditions: temp. 160° C; pressure 7 MPa; ratio H₂ : CO = 1.2 : 1.

Trialkyl phosphine	Acidity, pHa	Exit of product with straight chain, %
(iso-C ₃ H ₇) ₃ P	9.4	85.0
(C ₂ H ₅) ₃ P	8.7	89.6
(C ₃ H ₇) ₃	8.6	89.5
(C ₄ H ₉) ₃ P	8.4	89.6
(C ₈ H ₁₇) ₃ P	8.4	90.2
(C ₂ H ₅) ₂ C ₆ H ₅ P	6.3	84.6
(C ₂ H ₅ (C ₆ H ₅) ₂ P	4.9	71.7
(C ₆ H ₅) ₃ P	2.7	62.4

* The activity of the phosphine complex is smaller than that of pure carbonyls. However, the phosphine complex's thermal stability allows accomplishing the process at higher speeds and at lower pressures.

Since the industry's need for oxygen-containing products of normal structure exceeds the need for aldehydes, alcohols, iso-structural acids, the information of a much greater production of straight-chained products of hydroformylation with the use of cobalt-phosphine complexes stimulated a wide research of this variant of oxosynthesis.

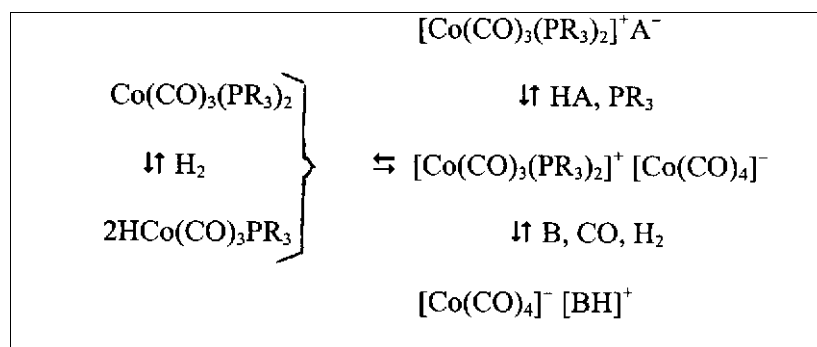
It was found that during the interaction of decobaltoctacarbonyl with phosphine in conditions close to those of hydroformylation, mixed phosphine-carbonyl complexes are formed, for example [309. 310]:



where **R** is equal to C₄H₉ (or any other alkyl radical).

The catalyst for the hydroformylation is complex $\text{HCo}(\text{CO})_3\text{PR}_3$ [305, 306, 311].

Depending on the polarity of the solvent being used, a complex equilibrium of phosphine-carbonyl complexes of the covalent and ionic type [312] can take place:



where **HA** is the acid, **B** is the organic basis.

In non-polar solvents the equilibrium is shifted towards the covalent complexes, while in polar ones — towards the ionic complexes.

The polarity of the solvent influences the final products of the hydroformylation reaction. Aldehydes are mainly formed in polar solvents, while alcohols are formed in the non-polar ones [305, 308, 316, 317]. An analogous effect (producing alcohols as a final product of the reaction) can also be gained by raising the temperature of the process.

The explanation about the influence of cobalt catalyst modification with phosphines on the isomer distribution of hydroformylation products was first offered by Imyanitov [318]. It was his idea that cobalt hydrocarbonyl, being a powerful acid, bonds to olefin in accordance with the Markovnikov rule thereby producing aldehydes of iso-structure.

Phosphine-substituted hydrocarbonyl is a weak acid and bonds to the olefin in accordance with the Markovnikov rule to a smaller extent. The decrease of the acidity during transition, say, from $\text{HCo}(\text{CO})_4$ to $\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$ is explained by the fact that in the second bonding, the electron-acceptor group CO is substituted by the electron-donor group $\text{P}(\text{C}_4\text{H}_9)_3$. Thus, the change of acidity in the catalyst defines the isomer contents of the received products (see table 5,7).

Also, there were suppositions to the effect that the increase of the product output of normal structure during the hydroformylation of olefins in the presence of cobalt-phosphine catalysts is the result of the

lesser isomerization of the olefins with a final double bond before hydroformylation.

It was supposed that the increase of electronic density on the cobalt atom during the introduction of PR_3 into the carbonyl group, there is a decrease in the olefin isomerization speed [306, 308, 319]. However, when studying the isomerization of 1-octane, there was no braking reaction found during the modification of cobalt hydro-carbonyl tricyclohexylphosphine [320, 321].

The same conclusion was made after studying reactions for the hydroformylation of 1- and 2-octanes, as well as 1- and 2-hexanes on a cobalt catalyst modified by tributylphosphine [322, 323].

The output increase of normally structured products by feeding phosphines into the catalytic complex can be explained by the influence of phosphine on the speed of the acylcobaltcarbonyl isomerization stage as compared with its influence on the speed of the acyl-cobalt-carbonyl transition stage into aldehyde along the scheme (2.87).

Note that when hydroformylating on a usual cobalt catalyst or when using cobalt-phosphine complexes, there is a certain limited correlation of isomers in the hydroformylated product (about 4:1 for *classical* oxosynthesis and about 10:1 for the *phosphine* variant).

Most likely, this can be explained by the fact that above a certain limit, the influence of a corresponding parameter (partial pressure of carbon oxide, phosphine concentration) and isomer product correlation are defined not by kinetic factors [speed correlation of the acylcobaltcarbonyl isomerization stage and the transition of the acylcobaltcarbonyl into aldehyde via scheme (2.87)] but by thermodynamic factors — the equilibrium between acylcobaltcarbonyl and iso-acylcobaltcarbonyl.

The kinetics of the propylene hydroformylation reaction in the presence of cobalt catalyst, modified by tributylphosphine, was studied in work [324]. It was shown that the reaction speed is proportional to the propylene concentration and cobalt carbonyls (table 5.8).

The hydroformylation reaction speed increases with the increase of the hydrogen's partial pressure (the order of magnitude via hydrogen is 0.7) and slows down a bit with the increase of the carbon oxide's partial pressure (the order of magnitude for the carbon oxide reaction is 0.3)

TABLE 5.8

Dependence of the Hydroformylation Reaction Speed and Product Contents on the Propylene Concentration and Cobalt Carbonyl
 Cond: CO partial pressure 5 MPa; H₂ pressure 5 MPa; temp. 160°C

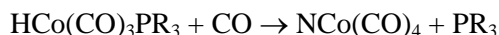
Initial concentration		Contents of product in % (mol.)			Ratio of product in H : iso	Initial reaction speed after fall of pressure in MPa x min ⁻¹
Co ₂ (CO) ₈ mmol	C ₃ H ₆ mol	Sum of aldehydes & Alcohols	Alcohols	Propane		
0.39	0.30	92	11	5.8	9.5	0.022
0.79	0.30	93	11	4.4	9.0	0.037
1.58	0.30	93	9.6	4.6	10.0	0.091
0.79	0.15	94	11	4.0	9.0	0.019
0.79	0.30	93	11	4.4	9.0	0.037
0.79	0.60	94	9.0	4.0	9.3	0.077

TABLE 5.9

Dependence of Propylene Hydroformylation Reaction Speed via Cobalt-Phosphine Catalyst on Partial Pressures of CO and H₂

Partial Pressure in MPa		Contents of product in % (mol.)			Ratio of product H : iso	Initial reaction speed (defined after fall of pressure) MPa x min ⁻¹
CO	H ₂	Sum of aldehydes & alcohols	Alcohols	Propane		
1	5	86	16	14.0	9.0	0.068
2	5	91	12	8.0	9.0	0.053
5	5	93	11	4.4	9.0	0.037
10	5	97	10	3.5	9.2	0.032
20	5	96	8	3.7	7.3	0.019
30	5	98	4	1.9	3.2	0.020
5	1	98	9	1.8	7.6	0.011
5	2	98	11	1.8	8.7	0.019
5	5	93	11	4.4	9.0	0.037
5	10	90	10	7.9	9.9	0.072
5	20	80	6	16.0	10.1	0.095
5	30	72	4	23.0	10.5	0.120

However, at P_{co} > 20 MPa, a tendency has been noticed towards the increase of the reaction with an increase of the carbon oxide pressure (table 5.9). Such a phenomenon has never before been observed in metal carbonyl catalysis. The authors explain this fact that the pressure increase squeezes the tri-alkyl-phosphine out of the complex by reaction:



Non-substituted cobalt hydrocarbonyl has much more activity in hydroformylation reactions (≈ 200 times). The comparative concentrations of hydrocarbonyl and cobalt phosphine-hydrocarbonyl in the system are defined by the correlation of the carbon oxide and tri-alkylphosphine concentrations:

$$\frac{[\text{HCo}(\text{CO})_4]}{[\text{HCo}(\text{CO})_3\text{PR}_3]} = K_p \frac{[\text{CO}]}{[\text{PR}_3]}$$

Therefore, the increase of the carbon oxide partial pressure can lead to the shift of the reaction's equilibrium and to the appearance of cobalt carbonyls in the system, thereby increasing the reaction speed at the expense of greater activity on the part of the hydrocarbonyls.

Work [324] includes an interesting comparison of the main kinetic regularities of the hydroformylation reaction in the presence of the classical catalyst $\text{HCo}(\text{CO})_4$ and the modified tributylphosphine catalyst $\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$ (table 5.10).

This data shows that during hydroformylation in the presence of cobalt-phosphine catalyst, a role is beginning to be played by the olefin hydrogenation reaction. Slaugh announced that the hydrogenation degree is increasing with the increase of the temperature and the branching of the olefin [305].

Imyanitov [324] failed to see the increase of the degree of propylene hydrogenation in propane during hydroformylation in the presence of $\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$ in a temperature of $160^\circ - 200^\circ\text{C}$, but noted that the degree of olefin hydrogenation increases at high pressures of hydrogen and at low pressures of carbon oxide.

In general, cobalt phosphine-hydrocarbonyls are good catalysts for hydrogenation; that is why the aldehyde hydroformylation formed in the reaction hydrogenates in alcohol to a great extent. At $\approx 200^\circ\text{C}$ only alcohols actually get the oxoprocess as the final product.

The hydrogenation of aldehydes in alcohol on complexes $\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$, $\text{HCo}(\text{CO})_2[\text{P}(\text{C}_4\text{H}_9)_3]_2$ and $\text{HCo}(\text{CO})[\text{P}(\text{C}_4\text{H}_9)_3]_3$ under conditions of hydroformylation is described, in part, in works [325, 326].

TABLE 5.10

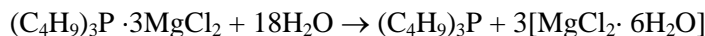
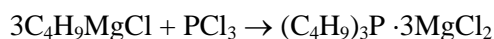
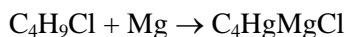
**Principle Kinetic Regularities of Hydroformylation Reaction in
the Presence of $\text{HCo}(\text{CO})_4$ and $\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$**

Catalyst	Reaction speed	Reaction order relative to				Degree of hydrogenation of olefin, %	Ratio of product H : iso
		catalyst	olefin	carbon oxide	hydrogen		
$\text{HCo}(\text{CO})_4$		1	1	-1	1	0.2	(1÷4):1
$\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$ 0.004 – 0.006		1	1	-0.3	0.7	2 – 23	(8÷10):1

When using triphenylphosphine in the capacity of a ligand, the transformation of aldehydes into alcohol is hardly noticeable even at high temperatures [327], this is why such a catalyst can be recommended for the process of producing aldehydes. A low hydrogenation activity is also characteristic of cobalt-carbonyl complexes with P_2Ph_4 ; Ph_2PCl ; R_2PCl ; and $\text{P}(\text{OCH}_2)_3\text{CR}$ [328].

From the viewpoint of technological installations, the process of oxosynthesis with modified cobalt-phosphine catalyst hardly differs from the classical oxosynthesis.

The stage for receiving modified additions of tri-alkyl-phosphine (for example, tributylphosphine) is based, as a rule, on these reactions:



The stage for getting hydroformylation catalyst proper — of the trialkylphosphinecobaltcarbonyl complex — is analogous to the cobaltization stage of the usual oxoprocess.

The technological specifics of using modified catalyst on the hydroformylation stage are connected with the specifics of kinetic reactions that proceed on the hydroformylation stage with the thermal stability of the catalytic complex; that is, mainly with the possibility of accomplishing the hydroformylation reaction under lower pressures and higher temperatures than in the usual variant of the oxoprocess.

The trialkylphosphinecobaltcarbonyl complex is less active in the hydroformylation reaction than cobalt hydrocarbonyl, but it is much

more stable thermally. Therefore, it is possible to conduct the reaction of hydroformylation at $\approx 200^\circ\text{C}$ and $p_{\text{co}} \leq 5 \text{ MPa}$, i.e., in places inaccessible to the usual oxoprocess because of the breaking of the cobalt hydrocarbonyl. By lowering the working pressure of the process, we can decrease the volume of capital investments to a good extent.

The great hydrogenous activity of the carbonylphosphine complexes allows to manage without the hydrogenation stage in the process, or to have only the stage of finishing off the hydrogenation job with a minimal volume of reaction apparatuses.

Thanks to the high hydrogenation activity of the carbonylphosphine complexes, the aldehyde concentration in the reactor's product during the reaction is comparatively low. This is why the final product contains very few high-boiling side products of the second aldehyde transformation. [See section 2.6 for details.]

Since the aldehyde homogenous hydrogenation reaction on cobalt carbonyls (and carbonylphosphine complexes) is accompanied by the formation of formyls (details in section 4.3), the products of hydroformylation, in this variant of the process, contain a great amount of formyls (up to 8 %). This causes the need to separate the formyls and to treat them, for example, with saponification.

Increased hydrogenation activity of carbonylphosphine complexes causes the need to take measures that would avoid aldehyde hydrogenation. In order to lower the degree of hydrogenation, it is sometimes wise to work with an increased amount of carbon oxide [329].

The use of carbonylphosphine complexes in the capacity of catalysts for hydroformylation requires a very thorough cleaning of the initial raw material, including that of synthesis gas from oxygen, since olefins oxidize quite easily, and oxides are not modifiers. This is why the oxoprocess on carbonylphosphine complexes includes a stage for the cleaning of the raw material from oxygen.

5.4 HYDROFORMYLATION WITH RHODIUM CARBONYLS

The hydroformylation reaction was first accomplished when cobalt carbonyl was used in the capacity of a catalyst. Later this invention was described in patents and used as a catalyst for the hydroformylation of a large number of various metals [11] including sodium, calcium, magnesium, and zinc, that is, even metals that do not form carbonyls.

The most detailed researches of the catalytic activity of various metals were conducted by Imyanitov and Rudkovsky [330 - 334]. In

these works it was found that there was high activity in the rhodium carbonyl hydroformylation reaction [329] (table 5.11).

TABLE 5.11

Catalytic Activity of Metallic Carbonyls of Group VIII

R e a c t i o n	Fe	Co	Ni	Rh	Ir
Hydroformylation	10^{-6}	1	$<10^{-6}$	$10^2 \div 10^3$	10^{-2}
Hydrocarbonxylenation	$\leq 10^{-7}$	1 (0.01)*	$<10^{-7}$	10^{-3}	10^{-5}
hydrocarbonmetoxylenation	$<10^{-5}$	1(0.001)*	$<10^{-5}$	10^{-2}	$<10^{-4}$

* In brackets is the ratio of the given reaction speed relative to the reaction speed of hydroformylation in the case when both reactions are conducted in the presence of identical amounts of cobalt carbonyls.

The direction for increasing the activity of metals in the VIII group, according to works [332, 333], can be offered as follows:

Period	Metal
IV	Fe \rightarrow Co \leftarrow Ni
	$\downarrow \quad \downarrow \quad \downarrow$
V	Ru \rightarrow Rh \leftarrow Pd
	$\uparrow \quad \uparrow \quad \uparrow$
VI	Os \rightarrow Ir \leftarrow Pt

There is an increase in the catalytic activity during transition from the IV and VI periods to the V. The metal carbonyls are placed in a row relative to their activity in the hydroformylation reaction as follows:

<u>Ni, Cr, Mo, W</u>	$<$	Fe	$<$	Mn	$<$	Os	$<$	Ru	$<$	Ir	$<$	Co	$<$	Rh
0		10^{-6}		10^{-4}		10^{-3}		10^{-2}		10^{-1}		1		10^3

This data was later confirmed in works [335 - 340].

Imyanitov [329] found the correlation between catalyst activity and oxidation of metal hydrocarbonyls (table 5.12).

To explain the discovered correlation, a supposition was made to the effect that the reaction speed of catalytic hydroformylation is defined by the affinity of the metal-carbonyl group to the electron, the second property of which is the acidity of the hydrocarbonyl metals.

TABLE 5.12

Acidity and Catalytic Activity of Metallic Hydrocarbonyls

Hydrocarbonyl	A c i d i t y		Catalytic activity in hydroformylation reaction
	Dissociation constant (in water)	Qualitative characteristics	
H ₂ Rh ₄ (CO) ₁₁	—	Strong acid, stronger than HCo(CO) ₄	10 ³
HCo(CO) ₄	1	Strong acid (just like Nitrogen)	1
H ₂ Ru(CO) ₄	—	Weaker than HCo(CO) ₄	3 · 10 ⁻²
H ₂ Fe(CO) ₄	4 · 10 ⁻⁵	Weak acid (just like vinegar)	10 ⁻⁶
H ₂ Os(CO) ₄	10 ⁻⁵ — 10 ⁻⁶	Weak acid	4 · 10 ⁻³
HCo(CO) ₃ PR ₃	1.08 · 10 ⁻⁷ *	Very weak acid	4 — 6 · 10 ⁻³
HMn(CO) ₅	0.8 · 10 ⁻⁷	D i t t o	10 ⁻⁴
HRe(CO) ₅	—	Extremely weak acid	0
H ₂ Ni ₂ (CO) ₆	—	This is not an acid	0
H ₂ Fe ₃ (CO) ₁₁	—	Strong acid	High **
H ₂ SO ₄ (for comparison)	—	Very strong acid	High ***

* For $R = C_6H_5$;

** In alcohol synthesis according to Reppe;

*** In acid synthesis according to Koch [11] when getting complex ethers according to Eidus and Puzitsky [341].

The electrophyl influence of the metal-carbonyl group is explained by the speed increase as the formation alkyl-cobalt-carbonyls and the breaking of the resulting acylcobaltcarbonyls during the increase of the electrophyl qualities of the metal-carbonyl group.

As already said, rhodium has the greatest catalytic activity. The first publication on the use of rhodium as a hydroformylation catalyst belongs to Imyanitov and Rudkovsky [334] who claim that the great activity of the rhodium carbonyls is caused by the formed clusters that increased electron-acceptor properties [342, 343]; and the transition to clusters is regarded as a universal method for increasing catalyst activity because of their great capability to bond and to break off electrons [344].

5.4.1 INFLUENCE OF OLEFIN HYDROFORMYLATION REACTIONS ON RHODIUM CARBONYL

The influence of synthesis gas, partial pressures of hydrogen and carbon oxide, temperature, solvent, catalyst concentration, initial olefin concentration, and various additions relative to the reaction speed of the hydroformylation of 1-hexane were studied [105, 345, 346]. A comparison of reaction speeds for hydroformylation of olefins was also made.

If the pressure of synthesis gas ($H_2 : CO = 1 : 1$) is up to 20 MPa the reaction speed on the rhodium carbonyls increases proportionally to the pressure, further pressure increase does not effect the reaction speed (fig. 5.9). The increase of carbon oxide partial pressure causes a reaction speed increase in the hydroformylation of 1-hexane. At 150°C the limit is at 9 MPa (hydrogen pressure: 10MPa). A further increase in carbon oxide partial pressure leads to a slowdown of the reaction (fig. 5.10).

During constant carbon oxide pressure, the increase of the hydrogen's partial pressure leads to the increase of the reaction speed of hydroformylation. When this partial pressure exceeds 6 MPa (carbon oxide's partial pressure is 10 MPa) the reaction's acceleration is directly proportional to the increase of the hydrogen's partial pressure (fig. 5.11).

The slight influence of synthesis gas ($H_2 : CO = 1 : 1$) on the reaction speed in an area above 20 MPa is explained by the practically equal, but with an opposite sign to show the influence of the partial pressures of hydrogen and carbon oxide.

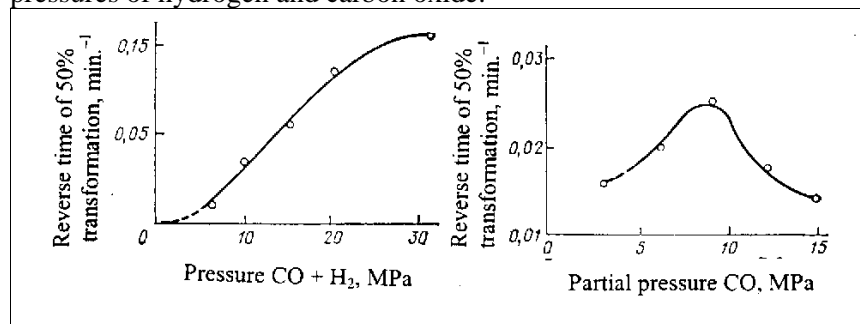


Fig. 5.9 Dependence of Reaction Speed for Hydroformylation of 1-Hexane with Rhodium Carbonyls on the Synthesis gas Pressure

Conditions: temperature 140°C; initial olefin concentration 40% (mass.); rhodium concentration in reaction mixture 0.0005 % (mass.); solvent -- toluol.

Fig. 5.10 Same — but on the Partial Pressure of Carbon Oxide
Conditions: temp. 150°C; hydrogen partial pres. 10 MPa; olefin initial concentr. 40 %; rhodium concentr. in reaction mixture 0.0005 % (mass.); solvent -- toluol.

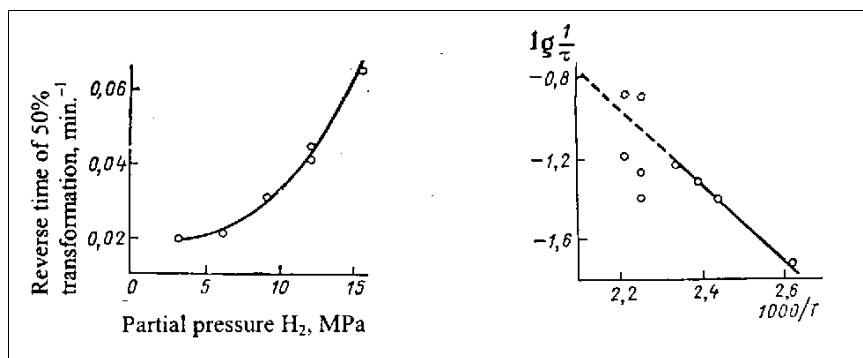


Fig. 5.11 Dependence of Reaction Speed for Hydroformylation of 1-Hexane on the Partial Pressure of Hydrogen

Conditions: temperature 150°C; carbon oxide partial pressure 10MPa; initial olefin concentration 40 % (mass.); rhodium concentration in reactor mixture 0.0005 % (mass.); solvent — toluol.

Fig. 5.12 Dependence of Reaction Speed for Hydroformylation of 1-Hexane on the temperature.

T — temp. K; τ — time for 50% of olefin transformation, minutes; synthesis gas pressure 15 MPa; initial olefin concentration 40% (mass.); rhodium concentr. in reaction mixture 0.0005% (mass.); solvent— toluol.

The reaction speed of hydroformylation on rhodium carbonyls increases with the increase of temperature. Just as in the case of cobalt carbonyls, up to a certain temperature a direct dependence is observed between the logarithm of the speed constant and the reverse temperature (fig. 5.12). The activation energy, calculated for temperature 110° to 165°C, at 15 MPa of general pressure, comprised 28.5 kJ/mol⁻¹ (for cobalt 96.4 kJ/mol⁻¹). When the temperature rises beyond a certain point, the hydroformylation reaction speed does not increase and there is a dispersion of the results (fig. 5.12). Most likely, analogously to cobalt, this is explained by the breakup of the rhodium carbonyls.

Just as in the case of cobalt carbonyls, in the case of rhodium carbonyls, each definite partial pressure of carbon oxide corresponds to its own temperature limit up to which is observed an increase of hydroformylation reaction speed with an increase of temperature. The thermal stability of rhodium carbonyls and cobalt are connected with the partial pressure of carbon oxide via direct logarithm dependence (fig. 5.13). However, the increase of thermal stability and that of pressure for rhodium carbonyls is of less significance than for cobalt carbonyls.

Toluol, dioxide, acetone, ethyl and iso-octanol alcohols, based on rhodium carbonyls, were tried as solvents for the hydroformylation

reaction of 1-hexane. It was found that the reaction speed decreases depending on the solvent as follows (table 5.13):

dioxide > iso-octanol > toluol > acetone > ethanol

The reaction speed of hydroformylation on cobalt carbonyls is directly proportional to the catalyst concentration, while on a rhodium catalyst the rhodium concentration is equal to from 0.0005 to 0.005 % (mass.). For 1-hexane it is proportional to the rhodium concentration to the degree of 0.4 (5.14).

The reaction speed for the hydroformylation of 1-hexane on rhodium carbonyl at a concentration of 0.0005 % (mass.) is reached under the same conditions on cobalt carbonyls only at a 0.2 % concentration (mass.).

It turns out that the 50% transformation of 1-hexane increases proportionally with the increase of its initial concentration (table 5.14), i.e., the order of magnitude relative to olefin is equal to zero.

A study was made relative to the influence of butylene and pyridine additions on olefin, and it was found that the presence of dyen compounds in the reaction mixture originates an induction period.

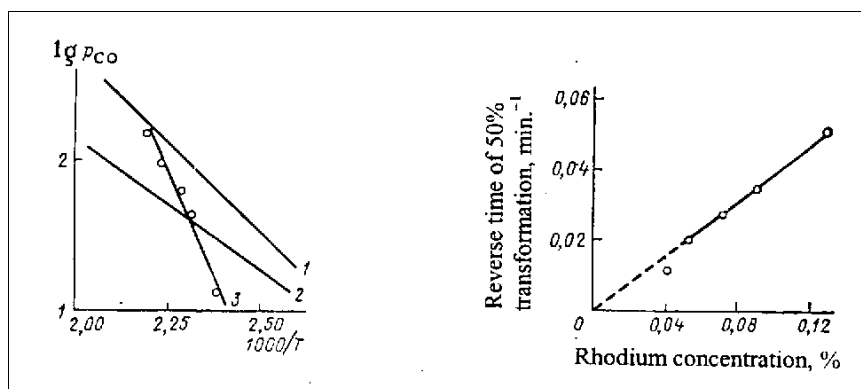


Fig. 5.13 Dependence of Rhodium Carbonyl and Cobalt Thermal Stability on Synthesis gas Pressure

Conditions: T — temperature, K; P_{CO} — partial pressure of carbon oxide 1 — decobaltoctacarbonyl; 2 — cobalt hydrocarbonyl; 3 — rhodium carbonyls.

Fig. 5.14 Dependence of Reaction Speed for Hydroformylation of 1-Hexane on Rhodium Concentration in Reaction Mixture

Conditions: temperature 110°C; synthesis gas pressure 15 MPa; initial concentration of olefin 40 % (mass.); solvent — toluol.

An addition of 250 mol of butylene to the reaction mixture per 1 mol of rhodium caused the appearance of the induction period that lasted about 90 minutes, during which the hydroformylation reaction did not proceed. After this time elapsed, the hydroformylation continued with the same speed without the butylene (table 5.15). During the butylene concentration, the reaction mixture contained 1,250 mols per 1 mol of rhodium, and the induction period already comprised over 200 minutes.

From this data it is obvious that during hydroformylation on rhodium carbonyls, if the catalyst is of a very low concentration -- 0.0005 % (mass.) a high degree of cleaning the raw material is required from the dyadic compounds.

TABLE 5.13

Dependence of Reaction Speed for Hydroformylation of 1-Hexane on Properties of Solvent

Conditions: synthesis gas pressure 15 MPa; temperature 110° C; rhodium concentr. 0.0005 % (mass.); initial olefin concentration 40 % (mass.).

S o l v e n t	Time for 50% of transformation, in min.	Dielectric solvent constant
T o l u o l	54	2.38
	53	2.38
D i o x a n	50	2.21
	46	2.21
E t h y l a l c o h o l	124	25.20
A c e t o n e	95	20.74
Iso-octyl alcohol	53	9.85
	47	9.85

TABLE 5.14

Dependence of Reaction Speed for Hydroformylation of 1-Hexane on initial olefin concentration

Conditions: synthesis gas pressure 15 MPa; temperature 110° C; rhodium concentration 0.0005 % (mass.).

Initial olefin concentration, %	Degree of olefin transformation, %	Aldehyde exit, % (on transformed olefin)	Time for 50 % transformation, minutes
25	80	100	7
80	98	100	19
100	91	92	29

An addition of pyridine in a wide range of concentrations — to 75 mols per 1 mol of rhodium — does not influence the reaction speed of the hydroformylation of 1-hexane. The further increase of the pyridine concentration causes a proportional slowdown of the reaction speed (see table 5.16. When studying the influence of olefin structure on the reaction speed of rhodium carbonyl hydroformylation, it was found that 1-hexane, isobutylene, and cyclohexane hydroformylate had almost identical speeds (table 5.17). It is worth noting that the cobalt carbonyls have a hydroformylation reaction speed for linear olefins equal to one order of magnitude higher than the speed of branched and cyclic ones.

TABLE 5.15

Dependence of length of induction period and reaction speed for hydroformylation of 1-hexane on the addition of butadiene

Conditions: synthesis gas pressure 15 MPa; temperature 110°C; rhodium concentration 0.0005% (mass.); initial olefin concentration 40% (mass.).

Amount of butadiene, mol x (mol rhodium) ⁻¹	Length of induction period, minutes	Time for 50 % trans- formation after induc- tion period, minutes
0	0	54
250	90	52
1250	200	—

TABLE 5.16

Dependence of reaction speed for hydroformylation of 1-hexane on the addition of pyridine

Conditions: synthesis gas pressure 15 MPa; temperature 110°C; rhodium concentration 0.0005% (mass.); initial olefin concentration 40% (mass.).

Amount of pyridine, mol x (mol rhodium) ⁻¹	Degree of olefin transformation, %	Time for 50 % trans- formation, minutes
0	96	54
75	90	58
150	93	109
300	47	183

TABLE 5.17

Reaction speed for hydroformylation of various olefins on rhodium carbonyls

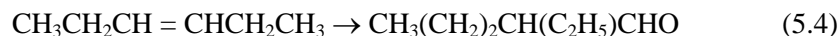
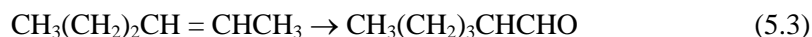
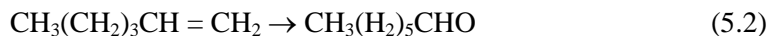
Conditions: synthesis gas pressure 15 MPa; temp. 150°C; rhodium concentration 0.0005% (mass.); initial olefin concentr. 40.5% (mass.); solvent -- toluol.

Olefin s	Degree of olefin transformation, %	Aldehyde exit, % (transformed olefin)	Time for 50% Transform., min.
1-Hexane	93	92	15
Isobutylene	60	95	20
Cyclohexane	75	100	16

5.4.2 PRODUCTS OF HYDROFORMYLATION REACTIONS

In works [345; 346] the contents of hydroformylation reaction products have been studied in respect to 1-hexane and iso-butylene depending on the reaction conditions. The exit of aldehydes onto the reacting olefin on rhodium carbonyls is higher than on the cobalt carbonyls, comprising usually 93% to 100% (table 5.17) thanks to the decreased role of the condensation and hydrogenation reactions.

When hydroformylating 1-hexane at the expense of the isomerization of double bonds, enantic (5.2), α -methylcapron (5.3), and α -ethylvalerian (5.4) aldehydes can be formed:



With the increase of the degree of transformation, the output of branched aldehydes also increases (5.3), (5.4) and the output of linear aldehydes decreases (table 5.18). This is why, when studying the influence of various factors on the isomer contents of aldehydes, the olefin transformation degree was kept practically unchanged (85 - 90 %).

The contents of aldehydes C_7 in the mixture of hexane hydroformylation, on rhodium carbonyls (relative to the number of aldehydes) depending on the conditions, was changed within the limits: α -ethylvalerian 8 % - 18 %, α -methylcapronic 38 % - 53 %, and enantic 32 % - 53 % (fig. 5.15).

TABLE 5.18**Dependence of Aldehyde Isomer Contents in Reaction Products for Hydroformylation of 1-Hexane on Degree of Olefin Transformation**

Conditions: synthesis gas pressure 15 MPa; temp. 150° C; rhodium concentration 0.0005 % (mass.); solvent -- toluol.

Degree of olefin transformation, %	Isomer contents of aldehydes, %		
	α -ethyl-valerian	α -methyl-kapronic	Enantic
47	0	26.2	73.8
60	0	30.7	69.3
67	3.7	44.7	51.6
77	14.1	48.4	37.5
89.5	16.8	49.3	33.9
100	17.4	50.5	32.1

The reaction's temperature increase leads to an increased output of aldehydes via reactions 95.2) and (5.3) at various synthesis gas pressures to a certain level, characteristic of each synthesis gas. Above this temperature, the output of branched aldehydes somewhat diminishes.

The temperature, at which there is an increased output of branched aldehydes, coincides with the limit of thermal rhodium carbonyl stability at the given pressure for each of the synthesis gases (fig. 5.16).

The increase of the synthesis gas pressure to 15 MPa at various temperatures causes a somewhat increased output of branched aldehydes; a further increase of pressure causes the reverse effect (fig. 5.17).

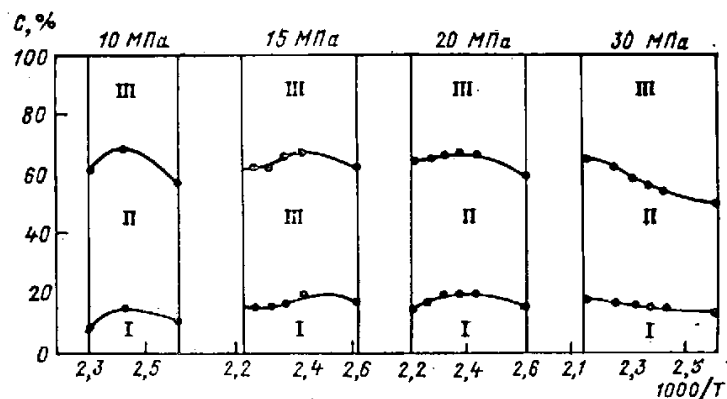


Fig. 5.15 Dependence of the Isomer Contents of Aldehydes in Products of Hydroformylation of 1-Hexane in the Presence of Rhodium Carbonyls on the Reaction Temperature at Various Pressures of Synthesis gas:

T — reaction temperature, K; C — contents of individual aldehydes in mixture.

Aldehydes: I — α -ethylvalerian; II — α -methylkapronic; III — enantic.

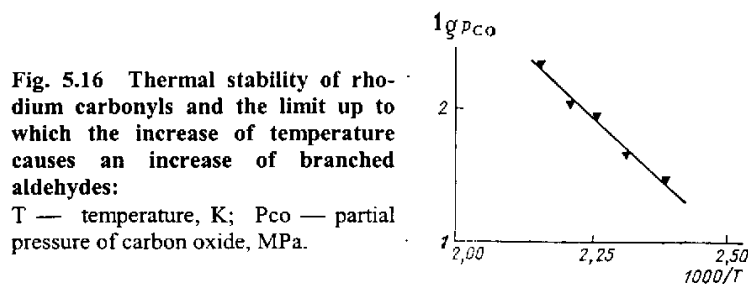


Fig. 5.16 Thermal stability of rhodium carbonyls and the limit up to which the increase of temperature causes an increase of branched aldehydes:

T — temperature, K; p_{CO} — partial pressure of carbon oxide, MPa.

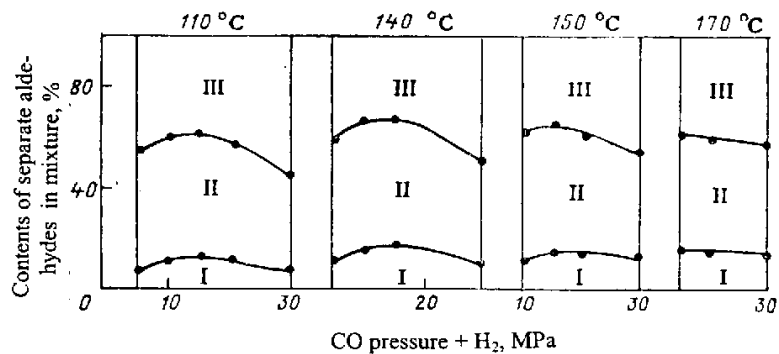


Fig. 5.17 Dependence of isomer contents of aldehydes in products of hydroformylation of 1-hexane in the presence of rhodium carbonyls on the pressures of synthesis gas at various reaction temperatures

Aldehydes: I — α -ethyl-valerian; II — α -methyl-kapronic; III — enantic.

The change of the hydrogen's partial pressure from 3 to 15 MPa (constant CO partial pressure at 10 MPa) hardly influences the isomer contents of aldehydes in the products of the hydroformylation reaction of 1-hexane on rhodium carbonyls (fig. 5.18).

The isomer correlations of aldehydes in reaction products during the hydroformylation of 1-hexane on rhodium carbonyls and cobalt, during their mutual presence in a reaction mixture, have been studied [105]. It was found that the contents of cobalt in the reaction mixture was 200 times greater than the contents of rhodium, which did not have any serious influence on the isomer correlation of the aldehydes, which is defined by the action of the rhodium carbonyls. Only when the correlation amounts to $\text{Co} : \text{Rh} > 200$ does the action of the cobalt carbonyls become obvious, and the isomer contents of the aldehydes changes in favor of increasing the output of normally structured aldehydes (fig.5.19).

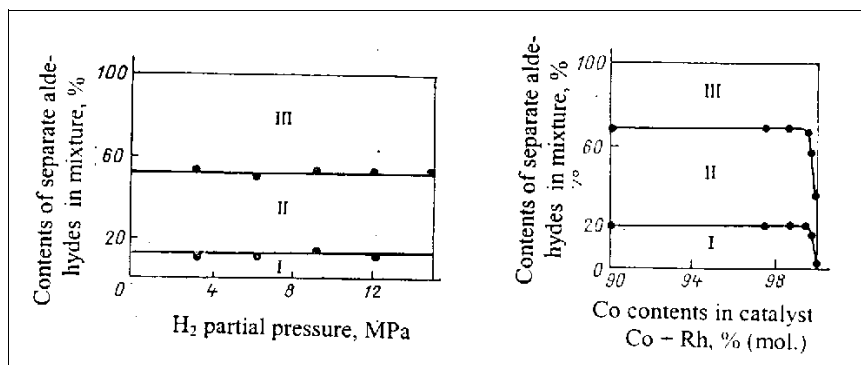


Fig. 5.18 Dependence of aldehyde isomer contents in hydroform. products of 1-hexane in presence of rhodium carbonyls on hydrogen partial pressure

Condition: partial pressure of carbon oxide 10 MPa;

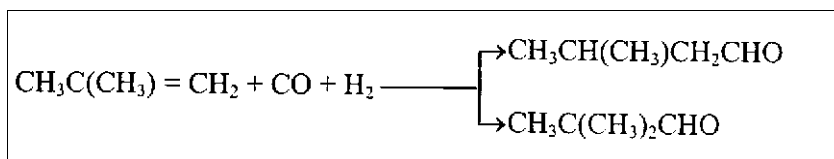
Aldehydes: I — α -ethyl-valerian; II — α -methyl-kapronic; III — enantic.

Fig. 5.19 SAME — on the correlation of cobalt and rhodium carbonyls during their mutual presence in the reaction mixture

Aldehydes: I — α -ethyl-valerian; II — α -methyl-kapronic; III — enantic.

This very well agrees with the data [329], according to which the rhodium carbonyls, just as the catalyst of the hydroformylation reaction, are 100 to 1,000 times more active than cobalt carbonyls.

The hydroformylation of isobutylene can produce α -methyl-butyl and pivalov aldehydes according to the following scheme:



Neither the rhodium concentration nor the partial pressure of the hydrogen or that of carbon oxide have any significant influence on the correlation of the reaction products. The main reaction product is the α -methyl-butyl aldehyde (table 5.19). Only the reaction temperature offers some influence; with its increase there is an increase in the output of pivalic aldehyde (table 5.20).

It is of interest to compare the possibility of using rhodium catalysts in the oxosynthesis process as compared with the widely used nowadays cobalt catalysts. The main technological priorities of rhodium catalysts are as follows:

- 1) much more activity that allows to accomplish the process by concentrating rhodium from 0.0005% to 0.001% (mass.);
- 2) independence of the hydroformylation speed from the structure of the olefins;
- 3) greater selectivity (the exit of aldehydes on the rhodium catalyst is close to the quantitative exit with the degree of olefin transformation equal to 90% - 95%).

TABLE 5.19

Dependence of Isomer Contents of Aldehydes in Products of Isobutylene Hydroformylation Reactions on Catalyst Concentration and Partial Pressures of Carbon Oxide and Hydrogen
 Conditions: temperature 150°C; initial isobutylene concentration 25% (mass.); solvent — toluol.

Rhodium concentration in reaction mixture, % (mass.)	Partial pressure, MPa		Aldehyde isomer contents	
	Carbon oxide	Hydrogen	Pivalic	α -methyl-butyl
0.0002	10	10	0.6	99.4
0.0005	10	10	0.8	99.2
0.0010	10	10	0.8	99.2
0.0005	5	5	1.0	99.0
0.0005	6	10	0.5	99.5
0.0005	12	10	0.6	99.4
0.0005	15	10	1.1	99.9
0.0005	15	15	1.0	99.0

The use of lower concentrations of the catalyst — 0.0005 % to 0.001 % (mass.) — radically simplifies the further stages of processing the aldehyde product. However, the use of the rhodium catalyst is possible only on thoroughly cleaned raw material. [The world output of rhodium comprises only about 6 tons.]

TABLE 5.20

Dependence of Isomer Contents of Aldehydes in Products of Isobutylene Hydroformylation Reactions on the Temperature

Synthesis gas pressure 30 MPa; rhodium concentration in reaction mixture 0.0005% (mass.); initial isobutylene concentr. 25% mass.); solvent -- toluol.

Temperature, °C	Isomer contents of aldehydes, %	
	pivalev	α -methyl-butyl
110	0.6	99.4
150	1.0	99.0
170	2.6	97.4

Thus, the use of rhodium is most desirable for hydroformylating thickly branched olefins (isobutylene, de-isobutylene, trimmer of propylene) relative to comparatively small industries.

In this case, the priority of a rhodium catalyst is quite obvious: out of isobutylene, you get but one aldehyde isomer, and the hydroformylation speed is 1,000 times higher than that on cobalt.

Besides this, it is of interest that the hydroformylation on a rhodium catalyst deals with raw materials containing a mixture of olefins of various structures, in this case the raw materials, are completely used up, unlike the case with a cobalt catalyst.

When using a cobalt catalyst, the optimal degree of transforming olefin mixtures of iso- and normal structure is close to 70 %, since during the further procedure of the reaction, the speed decreases (the olefins of normal structure are exhausted and the olefins of isostructure are beginning their hydroformylation) and the output of side products increases.

The use of a rhodium catalyst is, obviously, advisable when hydroformylating various product fractions of secondary oil treatment after their purification and concentration.

5.4.3 RHODIUM CARBONYL-PHOSPHINE COMPLEXES USED AS HYDROFORMYLATION CATALYSTS

In 1975 the first commercial advertisements appeared about the industrial realization of the oxosynthesis process on a modified tri-phenyl-phosphine or tributylphosphine rhodium catalyst.

According to these announcements, the use of this modified rhodium catalyst allows to lower the pressure on the hydroformylation stage to about 2 MPa and to lower or practically exclude side reactions of aldehyde hydrogenation in alcohol.

In 1976 the Union Carbide firm began the exploitation of an industrial oxosynthesis installation for hydroformylating propylene thereby producing butyl aldehydes with a capacity of 136,000 tons a year [352]. The process is accomplished at the low pressure of 0.7 - 2.5 MPa, and at a temperature of about 100°C and allows to vary the correlations of the received isomers of butyl aldehydes (of normal and of isonormal structure) in the limits from 8 : 1 to 16 : 1.

The advertisements did not offer sufficient information about the oxosynthesis process with the use of modified phosphines in a rhodium catalyst, and one cannot very well evaluate the process.

However, the unquestionable value of this process is in the fact that it is conducted at a low pressure and a moderate temperature, which decreases the capital investments. According to some sources [353], the capital expenditures, when using the modified rhodium catalyst, is about 20 % less than for the usual oxoprocess.

The process of propylene hydroformylation on a rhodium catalyst modified by phosphine (the LPO-process) is accomplished by recirculated inactive olefins (i.e., they used the principle described in detail in section 5.2.8), which allows minimizing the high boiling side products. This is also aided by the low temperature of the process.

The scheme of the LPO-process includes a stage of preliminary thorough cleaning of the propylene and the synthesis gas with the help of hard adsorbents from foreign particles of sulfur (mainly sulfur oxide) the compounds of which are catalytic nuclei. The process is accomplished at a low concentration of rhodium (hundreds of 1 %) with a surplus of modification (tri-phenyl-phosphine), the concentration of which is equal to several percent relative to the mass.

An important technological feature of the process is the method of separation of the catalyst from the hydroformylation product; the product is blown through after the reaction by circulating gas [354].

The question regarding the exit of the final products in their isomer contents is a complex one. According to data, also from a commercial ad, the output of aldehydes when hydroformylating ethylene and propylene on a rhodium-phosphine catalyst is almost quantitative [355]. More reliable is the data given in review [5] according to which the output of aldehydes of normal structure, calculated like transformed olefin comprises about 75%. in this case, judging by the output of products, the process on the rhodium-phosphine catalyst hardly differs from the best variants of classical oxosynthesis schemes.

Suggestions have been made to use a lot of carbonyl-phosphine complexes of rhodium as catalysts for hydroformylation. The most active among them are $\text{Ph}(\text{PR}_3)_2(\text{CO})\text{Cl}$ [356-358] and $\text{HRh}(\text{CO})[\text{P}(\text{C}_6\text{H}_5)_3]_3$ [357, 359, 360]. The use of modified rhodium catalysts increase the stability of the catalyst.

Catalyst $\text{HRh}(\text{CO})(\text{PR}_3)_3$, according to [315, 361], is active in the hydroformylation reaction even at room temperature and atmospheric pressure. The reaction speed during catalyst concentration is $6 \text{ mmols} \times \text{mol}^{-1}$, is directly proportional to the concentration of the catalyst, and it grows with the increase of olefin concentration and the increase of temperature, and decreases with the increase of the pressure. The increase of the partial pressure of the hydrogen helps to form aldehydes of normal structure.

Of great interest is the information [362] to the effect that the reaction speed for hydroformylation on $\text{HPh}(\text{CO})(\text{PR}_3)_3$ is increased in the presence of diens and acetylenes. Rhodium carboxylate complexes $\text{Rh}(\text{PR}_3)_2(\text{CO})(\text{C}_2\text{H}_5\text{COO})$ [363] are also active in atmospheric pressure .

5.5 COMPARISON OF DIRECTIONS IN OXOSYNTHESIS DEVELOPMENT

In order to orient oneself in the labyrinth of elaborated and exploiting technological schemes of oxosynthesis, it is wise to try analyzing them and compare their merits and demerits.

Of course, a detailed analysis is impossible in view of the fact that the lack of many of the technological characteristics are unavailable, especially those connected with patents, licenses, and know-how.

However, in modern chemical and oil-chemical technology, the most important index of the effectiveness of a process is its selectivity, that is, the output of the final product per mass unit of utilized raw material. What's more, the role of this factor, in total-economic evaluation of processes, is constantly increasing.

Neither capital expenditure on installations, nor exploitative expenditure for this or that variant of technological designing of the process, will, as a rule, effectively improve the indexes as selectivity will. Expenditure begins playing its role only when selectivity is introduced into the process. It is wise to make attempts at equalizing the potential possibilities of the main directions in the development of the oxoprocess along this most important index on the level of the available theoretical knowledge. Such an analysis is quite possible.

At present the oxosynthesis process is developing in the following three main directions:

- 1) the classical oxosynthesis variant with catalyst $\text{HCo}(\text{CO})_4$;
- 2) the cobalt-phosphine variant of oxosynthesis with catalyst $\text{HCo}(\text{CO})_3\text{PAlk}_3$;
- 3) the rhodium-phosphine variant of oxosynthesis with catalyst $\text{HRh}(\text{CO})(\text{PAr}_3)_3$.

Losses relative to selectivity in the process of oxosynthesis can be due to two types of side reactions (as mentioned in section 2.7):

- a) parallel reactions (hydrogenation of the initial olefin);
- b) successive reactions (a whole lot of reactions for further transformation of final aldehydes in products of greater molecular mass).

The catalyst for classical oxosynthesis, $\text{HCo}(\text{CO})_4$, in optimal conditions of the process ($120^\circ - 130^\circ\text{C}$, $P_{\text{CO}} \approx 15 \text{ MPa}$) practically does not catalyze the olefin hydrogenation reaction.

According to literature, the fact that the cobaltphosphine oxosynthesis catalyst $\text{HCo}(\text{CO})_3\text{Alk}_3$, having an increased hydrogenation capability,* notably catalyzes the olefin hydrogenation reaction. Under usual conditions of the oxoprocess ($P_{\text{CO}} \approx P_{\text{H}_2}$) the degree of olefin hydrogenation on such a catalyst is greater than 10%. By varying the conditions ($P_{\text{CO}} \approx 5P_{\text{H}_2}$), it is possible to decrease the hydrogenation of initial olefin, but not to do away completely from this side reaction.

* Strictly speaking, this interpretation is not precise. The introduction of the modified phosphine ligand into the cobalt hydrocarbonyl does not increase its hydrogenation capabilities, but slightly lowers the activity of the complex in the hydrogenation reaction as compared with the activity in the hydroformylation reaction. By compensating the lowering of the complex's activity relative to the hydroformylation for increasing the temperature of the process (the complex is stable and does not fall apart!), it becomes necessary to increase the speed of the olefin hydrogenation reaction (and aldehydes) non-proportionally.

In the rhodium-phosphine variant of the process are also observed losses of raw materials because of the partial hydrogenation of the olefin since the activity of $\text{HRh}(\text{CO})(\text{PAr}_3)_3$ in the hydrogenation reaction is higher than that of $\text{HCo}(\text{CO})_4$.

Therefore, the losses of selectivity at the expense of the parallel olefin hydrogenation reaction are minimal in the classical oxoprocess as compared with the cobalt- or rhodium-phosphine variants.

The losses at the expense of further side reactions are the second reason for the lowering of selectivity.

In the classical variant of the oxoprocess, these losses can be brought to a minimum at the expense of work with partial olefin transformation and its recirculation into the process. This point is touched upon in sections 2.7 and 5.2.8).

In the cobalt-phosphine variant of the process, losses connected with the formation of larger molecular masses than those of the final product relative to the subsequent side reactions because of the decrease of the aldehyde concentration in the reaction zone at the expense of their hydrogenation in alcohol. Because of this the cobaltphosphine catalyst is used in the processes of alcohol production, and not aldehydes.

The effect of decreasing the output of high-boiling side products, formed of aldehydes, is, most likely, also connected with the decrease of acidity of the cobalt hydro-carbonyl when introducing the modifying phosphine ligand into it. [See section 2.7.3 about the mechanism for the influence of acidity on the output of side products.]

It is worth noting that when producing alcohol with the help of a cobalt-phosphine catalyst with the subsequent use of a homogenous-catalytic aldehyde hydrogenation reaction, the formation of a noticeable amount of such side products as formyl is inevitable. [See sections 2.88 – 2.100 about the mechanism for the formation of formyl during hydrogenation.] Unlike most side products, formyls can be easily transformed into alcohol via saponification, but this operation requires additional technological design.

A much greater total selectivity, relative to the final product, can be gained in the classical variant of the oxoprocess. In table 5.21 we see the data that allow comparing the main technical-economic indexes of oxo-synthesis schemes with the use of various catalysts for propylene hydroformylation. If, according to the naphthene evaporation scheme, we get a total selectivity of 95% with propylene recirculation — the schemes with phosphine catalysts offer 86 to 90%.

Now let's take another important point, namely — the isomer contents of the received products, i.e., the so-called *correlation of normal*

products relative to iso-normal ones ($n : iso$) in different variants of the oxoprocess. In many cases oxygen-containing compounds (including alcohols) of normal structure, are valued much higher than the same compounds of iso-structure.

It is because of this that for many years, when comparing the indexes of various technological oxosynthesis schemes, the main feature was the gaining of the important correlation $n : iso$. Of course, this increase of correlation from $(2-2.5) : 1$ in old schemes for the propylene hydroformylation process to $\approx 4 : 1$ in modern industrial processes (schemes of firms like BASF, Mitsubishi, Ruhrchemie, Kuhlmann, and the naphthene-evaporation Scientific Oil and Chemical Works — Leuna Werke) indicates an increase in the output of butyl aldehydes from ≈ 55 % on reactive propylene to ≈ 70 %.

However, the transition from the naphthene-evaporation scheme with propylene recirculation, which offers a correlation of butyl and isobutyl aldehydes equal to $4 : 1$, to the scheme with a rhodium-phosphine catalyst (LPO-process) offering the correlation of $n : iso \approx (11 \div 12) : 1$, allows increasing the output of normally structured products only from 76 – 78 %, thereby decreasing the output of the final product (total isomers) by 9% (see table 5.21), which cannot be regarded as economically advantageous.

It is obvious that during the hydroformylation of lower olefins (ethylene, propylene) the technological schemes of the classical oxoprocess are capable of challenging any of the modified schemes.

A different situation arises in the case of producing higher alcohols (say, C_{10} — C_{20}) on the basis of the oxoprocess. To divide the higher alcohols into products of normal and isonormal structure is practically impossible. Besides, the foreign particles in the isostructured alcohol of the products used, for example, as components of laundering means, actually lower the quality of the alcohol quite significantly.

By using oxosynthesis catalysts modified by phosphine to entice the increase of the output of normally structured products, it is possible to raise the production and quality of consumer goods up to the indexes that were never imagined in the classical variant of the oxoprocess.

Various countries are buying licenses for processes elaborated by Union Carbide, Davy Powergas, and Johnson Matthey LPO-process. Mills in Sweden, Poland, China, and Germany are putting into operation installations for production along the oxoprocess variant.

Obviously, the decisive role here is played by the knowledge that with the decrease of capital expenditures for the construction of such installations with comparatively low pressures, which is typical for this variant, have long been mentioned in chemical literature.

TABLE 5.21

Tech-Economic Indexes of Processes for Producing Butyl Aldehydes and Butyl Alcohols via Propylene Hydroformylation

Indexes	Nephthene-Evaporation Schemes		Scheme with a cobalt-phosphine catalyst	Scheme with a rhodium-phosphine catalyst (LPOprocess)
	Sc. Oil & Chem. Works; Leuna Werke	With recirculation of olefin; Sc. Oil & Chem. Works		
1) Catalyst	$\text{HCo}(\text{CO})_4$	$\text{HCo}(\text{CO})_4$	$\text{HCo}(\text{CO})_3\text{P}(\text{C}_4\text{H}_9)_3$	$\text{HRh}(\text{CO}) \cdot [\text{P}(\text{C}_6\text{H}_5)_3]_3$
2) Temp. °C	120 – 160	120 – 130	160 – 200	60 – 120
3) Pressure; MPa	20 – 35	20 – 35	5 – 10	1 – 5
4) Catalyst concentration; % (mass.)	0.1 – 0.5	0.1 – 0.3	0.6	0.01 – 0.1
5) Olefin hydrogenation during process	Low	Low	High	High
6) Reaction's products	Aldehydes & alcohols	Aldehydes	Alcohols	Aldehydes
7) Correlation of products <i>n</i> : <i>iso</i>	80 : 20	80 : 20	88 : 12	92 : 8
8) Number of products produced per 1 ton of propylene; in kilograms:				
a) mixture of butyl aldehyde + butyl alcohol	1,185	1,310	1,390	1,330
b) isobutyl alcohol	305	320	150	140
9) Selectivity of process; % (of theoret.) relative to normally structured products	69	76	81	78
10) Total final product	87	95	90	86

6 NEW DIRECTIONS IN OXOSYNTHESIS DEVELOPMENT

Since the discovery of the hydroformylation reaction and the introduction of the first industrial oxosynthesis installations, scientific and applied researches in this field developed not only along the path of improving the olefin hydroformylation process.

Another direction was the search and elaboration of a technology for producing various products (besides aldehydes and alcohols) via reactions with various compounds and with carbon oxide and hydrogen, or with hydrogen donors, catalyzed by carbonyls of metals of the VIII group (mainly cobalt, and in latter years – rhodium).

Naturally, such directions went crisscross with analogous reactions whose catalyses were based upon different principles and compounds for example, the hydrocarbalcoxylation of olefins catalyzed by cobalt carbonyls and other metals; and the same reaction catalyzed by nickel chloride or palladium compounds. It is worth mentioning that in many cases, the insufficient studies of this or that reaction mechanism do not allow to negate with assurance the possible role of metal carbonyls as a worthy catalyst of the reaction.

In concert with the profile and conception of this book, we will touch upon only those directions in the development of the new syntheses with the participation of carbon oxide where metal carbonyls are compulsory components in the capacity of catalysts.

The possibility of increasing the number reactions that we are interested in, depends on:

1) the change of the hydrogen donor type: molecular H_2 (hydroformylation), H_2O (hydrocarboxylation), ROH (hydrocarbalcoxylation), organic acids, amines, thiols, hydrogen halogens;

2) the change of the substratum type: olefins, diolefins, alcohols, simple and complex ethers, non-saturated aldehydes, acids and their ethers, nitriles, etc.

Most of the reaction variants received, when combining various hydrogen donors and substrata, are described, more or less, in Falbe's well-known monographs [11] and in those of Nefedov [315].

Therefore, we will touch upon only those new directions of the development of the oxosynthesis process, that are of the most practical significance, and are insufficiently reflected in chemical literature and, finally, which are closer to the topic of our research.

6.1 PRODUCTION OF 3-METHYLHEXANOLE

One of the most important directions with the use of aliphatic alcohols is the production of plasticizers on their foundation. The best plasticizers are received on the basis of individual initial alcohols of the C_7 — C_{12} type. The most widely used plasticizers of polyvinylchloride pitch (as an alcohol component) is the 2-ethyl-hexanole, received out of acet-aldehyde or out of butyl aldehyde.

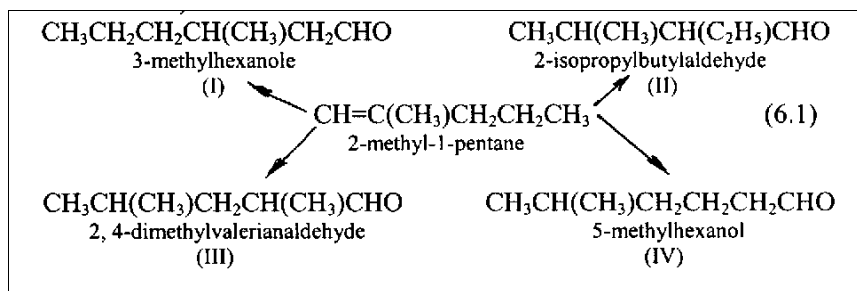
The prevailing role of the 2-ethyl-hexanole in the production of complex ether plasticizers is explained not only by the high plasticizing qualities of its phthalates, but also by the comparative simplicity in producing alcohol with a high grade of purity.

But when producing 2-ethylhexanole from oxosynthesis butyl aldehyde (this method is developing at present) it was found that there was no way of utilizing the simultaneously received isobutyl aldehyde

It goes without saying that the most radical solution of the problem would be to receive individual alcohol with sufficient molecular mass on the basis of the oxosynthesis process. Such an opportunity arises when hydrogenating olefins with a screened double bond on the rhodium carbonyls, since in this case we get only one of the possible isomer aldehydes, and thus — individual alcohol after hydrogenation.

During the hydroformylation of 2-methyl-1-pentane (product of propylene dimerization) in the presence of rhodium carbonyls, there can be a great output of 3-methyl-hexanole that hydrogenates into 3-methyl-hexanole [364]. Phthalates prepared out of it, have the same plasticizer properties as the di-iso-octyl-phthalates received out of 2-ethyl-hexanole.

Four isomer aldehydes are formed during hydroformylation of 2-methyl-1-pentane (relative to the isomerization of initial olefin):



When studying the influence of the main parameters of the process on the correlation of isomers of aldehyde C_7 in the product of a 2-methyl-1-pentane hydroformylation on rhodium carbonyls, it was found that the maximal output of 3-methylhexanole is guaranteed when the partial pressure of the carbon oxide is higher than 7 MPa. Its further

increase practically does not change the correlation of the isomers in the products of hydroformylation (fig. 6.1). The temperature causes an influence on the isomer contents of the received products (fig. 6.2).

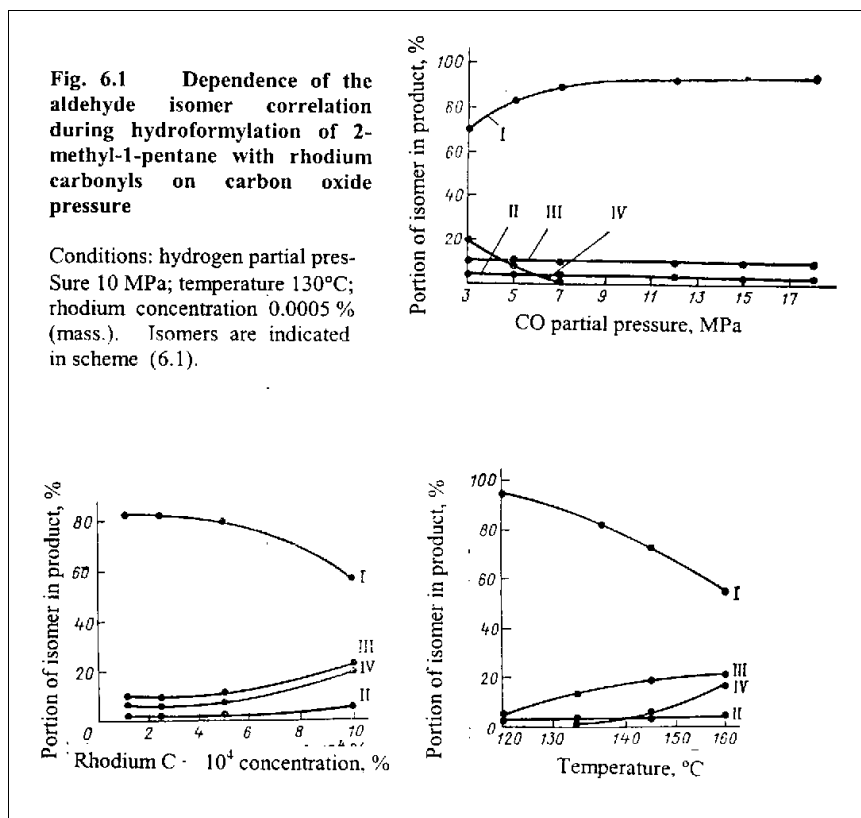


Fig. 6.2 Dependence of aldehyde isomer correlation during hydroformylation of 2-methyl-1-pentane with rhodium carbonyls on the temperature

Conditions: hydrogen partial pressure 15 MPa; carbon oxide 12 MPa; rhodium concentration 0.0005 % (mass.). Isomers are indicated in scheme (6.1).

Fig. 6.3 Dependence of aldehyde isomer correlation during hydroformylation of 2-methyl-1-pentane on rhodium concentration

Conditions: hydrogen partial pressure 10 MPa; carbon oxide 7 MPa; temperature 130°C. Isomers are indicated in scheme (6.1).

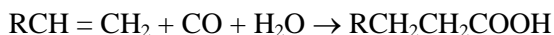
The increase of temperature from 120° to 165°C leads to the lowering the portion of 3-methylhexane from 95.5 to 58%. The change of the rhodium concentration from 0.0001% to 0.0005% (mass.) practically has no influence on the contents of the 3-methylhexanole in

the mixture of the received aldehydes (fig. 6.3). The further increase of the rhodium concentration leads to a noticeable acceleration of olefin isomerization and a relative decrease in the output of 3-methylhexanole.

The maximal output of 3-methylhexanole during the hydroformylation of 2-methyl-1-pentane comprises $\approx 95\%$ and is possible at a temperature lower than 130°C , at a partial pressure of carbon oxide above 7 MPa (the general pressure is greater than 17 MPa) and a concentration is up to 0.0005 % (mass.).

6.2 OLEFIN HYDROCARBOXYLATION

A reaction where olefins interact with carbon oxide and water, thereby forming acids, is called a hydrocarboxylation reaction:



This reaction proceeds, in part, via the action of mineral acids [365], but under very severe conditions (temperature up to 350°C , pressure up to 100 MPa). Koch and his colleagues [366, 367] have found that this reaction can be accomplished under pleasing conditions if it is conducted in two stages.

In the first stage the olefin interacts with carbon oxide and an acid with no water, conducted at a pressure of 0.1 — 10 MPa, and a temperature of 20° to 80°C . On the second stage, the formed product is broken up by water, producing acid; the pressure is atmospheric. This reaction came to be known as the *Koch reaction*.

Reppe discovered that the olefin hydrocarbonxylene reaction, just like the hydroformylation reaction, is catalyzed by carbonyls of metals from the VIII group.

Just as in the case of hydrocarboxylation, further we will deal only with this method of accomplishing hydrocarboxylation..

The hydrocarboxylation of mono-olefins in the presence of metal carbonyls proceeds under conditions close to those of hydroformylation (20 – 30 MPa, 120° – 250°C). Carbonyls of cobalt and nickel are the most active in this reaction [368], though carbonyls of ruthenium can also be used [369]. The hydrocarboxylation reaction greatly accelerates when adding I_2 , HI, CH_3I , KI to the reaction's system [315].

α -olefins of normal structure enter reactions most readily. Just as in the case of hydroformylation and hydrocarboxylation, during the hydrocarboxylation of non-symmetric olefins, there forms a mixture of acids of normal- and iso-structure. The relation of the isomers in the

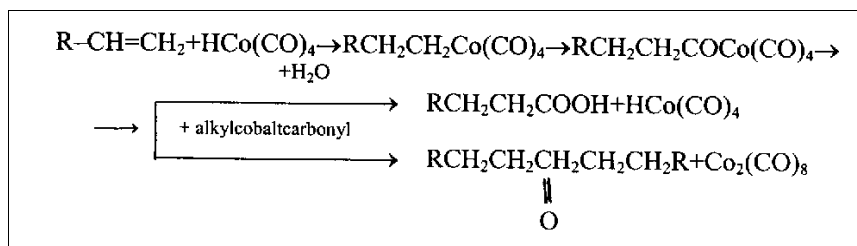
process of hydrocarboxylation in the presence of cobalt carbonyls amounts to about 3 : 1.

An effective promoter, during hydrocarboxylation, is pyridine [370 – 373], which increases not only the speed of the reaction, but also – the output of acids of normal structure.

TABLE 6.1 Dependence of exiting and isomer contents of acids during the butane hydrocarboxylation reaction

Olefin	Reaction Media	Output of acids		Correlation n : iso
		Valerian	Methylethyl-vinegar	
1-Butane	Pyridine	56.5	9.5	6
	Dioxide	25	15	1.7
2-Butane	Pyridine	51	17	3
	Dioxide	24	13	1.8

Some of the data concerning the influence of pyridine on the hydrocarboxylation reaction are given in table 6.1 [374]. The action of pyridine in this case, obviously, is due to the acceleration of the hydrolysis stage of the acylcobaltcarbonyl:



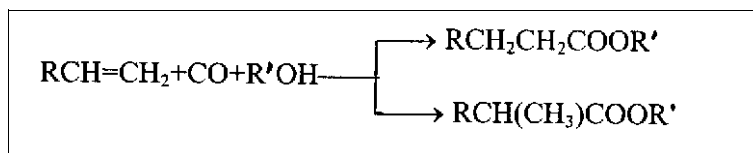
If there is no pyridine, a challenging reaction takes place where the alkylcobaltcarbonyls interact with the acylcobaltcarbonyls that leads to ketone formation.

Pyridine accelerates one of the stages of a complex reaction that is catalyzed by metal hydrocarbonyl — the hydrolysis stage for acylmetalcarbonyl. According to Imyanitov's terminology, the pyridine here *plays the role of a second-rank catalyst*.

The hydrocarboxylation speed increases also with small amounts of hydrogen [375]. For example, an addition of 5 – 10 % of hydrogen to carbon oxide increases the hydrocarboxylation speed in the presence of cobalt carbonyls by 3 times. This is probably explained by the more rapid formation of cobalt hydrocarbonyl in the presence of hydrogen.

6.3 OLEFIN HYDROCARBALCOXYLATION

The reaction for forming ethers from olefins, carbon oxide, and alcohols was discovered before the hydroformylation reaction was [376]:

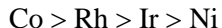


Later it was found that the reaction was catalyzed by cobalt-carbonyl, sometimes by cobalt, but the reaction was extremely slow and caused doubts about its practical use. Indeed, at 140° C, with a carbon oxide pressure of 30 MPa, and a catalyst concentration of 2 % (mass.), the 90 % transformation of olefin took more than 15 hours [377].

After Imyanitov and Rudkovsky [370] found that pyridine was an effective promoter for reactions with carbonyls, and that the reaction speed increases in the presence of small quantities of hydrogen [378, 379] which, most likely, helped the formation of hydrocarbonyl, these reactions were regarded as being of greater practical use [380, 381].

6.3.1 HYDROCARBALCOXYLATION CATALYSTS

Olefin hydrocarbalcoxylation reactions are catalyzed by nickel halogenides [382, 383]. Considering that compounds of palladium are the most active catalysts [382 – 386]; carbonyls of metals from group VIII, relative to their activity in the reaction, can be placed in a row thus:



The reaction speed of propylene hydrocarbmethoxylation catalyzed by cobalt carbonyls in an inert solvent is proportional to the concentration of the catalyst to the degree of 0.5 (fig. 6.4a). In the presence of pyridine, the reaction speed is directly proportional to the concentration of the catalyst (fig. 6.4b).

The speed correlation in the final and side reactions with cobalt carbonyls practically does not change when the cobalt concentration changes in the presence of pyridine or without it (table 6.2).

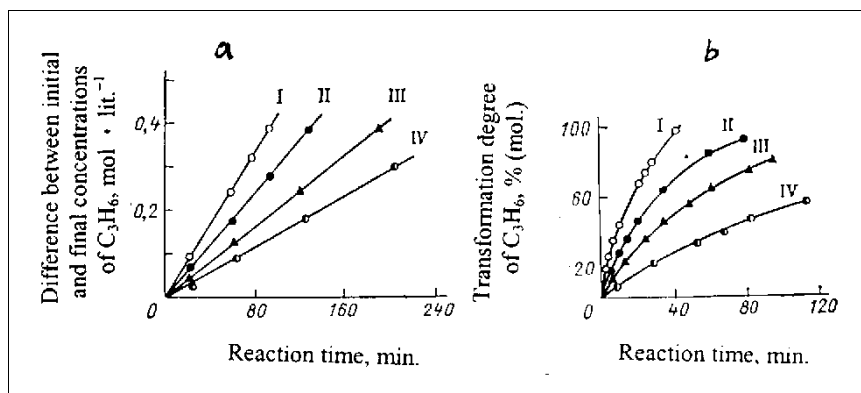


Fig. 6.4 Dependence of reaction speeds of propylene hydrocarbmetoxylation on the concentration of dicobaltoctacarbonyl:

a) without pyridine; b) with 10 % (mass.) pyridine.

Cobalt concentr. – 10 % (mass.) I – 1; II – 0.5; III – 0.25; IV – 0.12.

TABLE 6.2

Dependence of the output of the final and side products during propylene hydrocarbmetoxylation on cobalt carbonyls on cobalt concentration

Conditions: initial amount of propylene 0.5 mol; correlation – methyl alcohol : propylene 5 mol x mol⁻¹; partial carbon oxide pressure – 30 MPa; temp. 180°C.

Cobalt concentration in % (mass.)	Contents of products in the reaction, % (mass.)			
	Methyl alcohol of butyl acids	Side products	Methyl ethers of butyl acids	Side products
	Without pyridine		With 0.12 mol of pyridine	
0.12	80.8	19.2	98.0	2.0
0.25	80.0	20.0	99.0	1.0
0.50	80.1	19.9	98.8	1.2
1.00	81.0	19.0	98.5	1.5

Considering the specifics of this book, further, all the attention will be turned to information about the procedure of the hydrocarbalcoxylation reaction, catalyzed by cobalt carbonyls.

6.3.2 INFLUENCE OF PYRIDINE ON REACTION SPEED AND SELECTIVITY

It was found that additions of pyridine increase the speed and selectivity of the olefin hydrocarbalcoxylation reaction [370, 380]. The curve showing the dependence of the reaction speed on the pyridine concentration, passes through the maximum; the value of this threshold concentration increases with the increase of the temperature (fig. 6.5). In the presence of pyridine, the temperature increase causes an increase in the selectivity of the reaction to such amounts that guarantee the stability of the catalyst.

The dependence selectivity (output of complex ethers) on pyridine concentration and on the temperature is illustrated herewith (fig. 6.6). Besides pyridine, other organic bases have been tried as promoters that can serve as additions to cobalt carbonyls. The data about the influence of some promoters on the hydrocarbalcoxylation reaction speed is given in table 6.3.

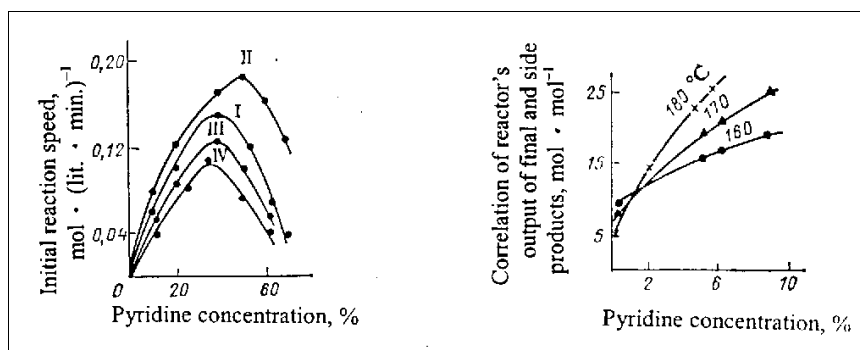


Fig. 6.5 Dependence of reaction speed during 1-hexane hydrocarbmethoxylation on the pyridine concentration:

I – $P_{CO} = 20 \text{ MPa}$, $t = 190^\circ\text{C}$; II – $P_{CO} = 30 \text{ MPa}$, $t = 190^\circ\text{C}$;
 III – $P_{CO} = 30 \text{ MPa}$, $t = 175^\circ\text{C}$; IV – $P_{CO} = 20 \text{ MPa}$, $t = 175^\circ\text{C}$.

Fig. 6.6 Dependence of selectivity of the propylene hydrocarbmethoxylation reaction on the pyridine concentration and temperature:
 $P_{CO} = 20 \text{ MPa}$.

TABLE 6.3

Dependence of Reaction Speed During 1-hexane Hydrocarbmethoxylation on the Character of Organic Bases:

Basis (promoter)	pKa of the basis	Promoter concentration; % (mass.)	Degree of Hexane transformation; % (mol)	Contents of methyl ethers, enantio acids in reaction prod.; %mol (mol)
No promoter	—	—	29	62.4
Pyridine	5.23	10	91	85.4
α -Picoline	5.97	10	51	85.1
β -Picoline	5.68	10	69	85.1
γ -Picoline	6.01	10	78	84.9
Quinoline	4.97	10	47	84.2
Ethylamine	10.67	2	28	63.0
Diethylamine	10.93	2	27	62.1
Triethylamine	10.87	2	0	—
Piperidine	11.12	1.5	3.5	Not found
Pirrolidine	11.27	1.5	8	Not found
Pyrimidine	1.30	1.5	8	Not found
Morpholine	1.10	1.5	0	—
<i>o</i> -phenantroline	2.10	10	0	—

6.3.3 INFLUENCE OF PARAMETERS ON HYDROCARBALCOXYLATION REACTION SPEED CATALYZED BY COBALT CARBONYL

With the absence of pyridine, the propylene hydrocarbmethoxylation reaction has a zero order of magnitude relative to olefin, and the first order – relative to alcohol. An analogous dependence was found for hydrocarbalcoxylation of cyclohexane [388]. In the presence of pyridine, the propylene hydrocarbmethoxylation reaction proceeds with the first order relative to the olefin, but has the zero order relative to methanol.

The data on the dependence of the reaction speed of propylene hydrocarbmethoxylation on olefin concentration is given in table 6.4. The influence of the temperature on the reaction speed is well described by the Arrhenius equation:

a) without pyridine: $\lg(1/\tau_{0.5}) = 5.33 - 3390/T$

b) in the presence of pyridine: $\lg(1/\tau_{0.5}) = 13.33 - 6660/T$

where $\tau_{0.5}$ is the time of the 50 % transformation in minutes.

TABLE 6.4

Dependence of reaction speed of propylene hydrocarbmetoxylation on olefin concentration

Conditions: partial pressure of carbon oxide 30 MPa; temp. 180°C; cobalt concentration 0.35 % (mass.).

Propylene concentration in initial reaction mixture; % (mass.)	Initial reaction speed in mol x (lit. x min.) ⁻¹	
	without pyridine	with 10 % (mass.) pyridine
10	0.0045	0.016
20	0.0040	0.031
30	0.0048	0.044
40	0.0042	0.057

TABLE 6.5

Dependence of final and side products output of propylene hydrocarbmetoxylation reaction on carbon oxide partial pressure

Conditions: initial amount of propylene 0.5 mol; ratio of methyl alcohol: propylene 5 mol x mol⁻¹; cobalt concentr. 0.35 % (mass.); temp. 170°C.

Carbon oxide partial pressure; MPa	Contents of reaction's products; % (mass.)			
	methyl ethers of butyl acids	side products	methyl ethers of butyl acids	side products
	without pyridine		with 0.12 mol of pyridine	
10	64.3	35.7	81.0	19.0
15	70.9	29.1	85.7	14.3
20	81.9	18.1	94.5	5.5
25	82.7	17.3	94.5	5.5
30	83.0	17.0	95.0	5.0

The increase of the carbon oxide pressure from 20 to 30 MPa practically does not influence the speed or the selectivity of the reactions, though at smaller pressures, especially lower than 15 MPa, the output of side products significantly increases (table 6.5).

6.3.4 INFLUENCE OF OLIFIN STRUCTURE ON HYDROCARBALCOXYLATION REACTION SPEED CATALYZED BY COBALT CARBONYL

During the hydrocarbalcoxylation of normally structured olefins with dual bonds at the end of the chain, the reaction speed slightly decreases with the increase of the length of the chain. An analogous picture is observed when the cobalt catalyst is modified by pyridine.

The presence of substitutes in dual bonds abruptly decreases the reaction speed. Thus, the reaction speed for the hydrocarbmetoxylation of 2-methyl-1-pentane in the presence of cobalt carbonyls promoted by pyridine, are about 5 times smaller than for 1-hexane. Under the same conditions, the reaction speed of diisobutylene hydrocarbmetoxylation is about 6 times smaller than that of 1-hexane. It is impossible to measure the speed of these reactions without modification by pyridine because the values are extremely small.

Cyclic olefins react slower than direct-chain ones. The hydrocarbmetoxylation of cyclohexane in the presence of pyridine proceeds 4.5 times slower than that of 1-hexane.

Olefins with dual bonds in the middle of the chain enter the hydrocarbalcoxylation reaction slower than such olefins do at the end of the chain. Thus, the hydrocarbalcoxylation reaction speed for 1-hexane is 1.5 times higher than that for 2-hexane. When modifying a catalyst with pyridine, the difference in the hydrocarbmetoxylation speeds of the 1-hexane and 2-hexane increases by 4.5 times. The data on the speeds of olefin hydrocarbmetoxylation of various structures are given in table 6.6.

The acceleration degree of the hydrocarbalcoxylation reaction, that promotes the addition of pyridine, depends on the structure of the olefin. The hydrocarbmetoxylation of olefins whose migration of dual bonds, does not cause a change in the structure of propylene, isobutylene, or cyclohexane, causes acceleration in the presence of pyridine by 2.5 – 3.5 times. The addition of pyridine slows down the speed of the dual bond's migration. This explains the difference in the speed of olefin hydrocarbmetoxylation with the inner and end situations of the dual bond in the absence of pyridine (table 6.7). Most likely, in this case, at the very start of the reaction, the isomerization of the olefins takes place.

The position of the dual bond in the olefin molecule has influence on the reaction speed, but is hardly noticeable in the correlation of the isomers received during olefin hydrocarbalcoxylation (tables 6.7 & 6.8) both with pyridine and without it.

TABLE 6.6

Dependence of the Hydrocarbmetoxylation Reaction Speed on the Structure of the Olefin

Conditions: carbon oxide partial pressure 30 MPa; temperature 180°C;
Cobal concentration 0,35 % (mass.).

Olefin	Relative reaction speed	
	without pyridine	with 20 % (mass.) pyridine
Propylene	0.33	1.12
1-Hexane	0.082	1.00
2-Hexane	0.055	0.23
1-Heptane	0.070	0.91
1-Octane	0.069	0.83
1-Ditsen	0.059	0.77
Isobutylene	0.077	0.24
Diisobutylene	—	0.16
2-methyl-1-pentane	—	0.19
2-methyl-2-pentane	—	0.08
Cyclohexane	0.065	0.22

TABLE 6.7

Dependence of reaction speed for hexane hydrocarbmet-oxylation and isomer contents of the received product on the situation of dual bonds in a hexane molecule

Conditions: pressure 20 MPa; temperature 175°C.

Contained in raw material; % (mass.)			Transformation time; minutes		Total reaction time in minutes	Contents of reaction Product, % (mass.) methyl ether acids		
1-hex-ane	2-hex-ane	3-hex-ane	30 %	50 %		α -ethyl-valer-ian	α -methyl capron	enan-tic
4.5	22.4	73.1	290	—	320	13.2	23.4	63.4
99.8	0.2	—	173	—	235	13.1	22.4	64.5

20 % (mass.) toluol without pyridine

4.5	22.4	73.1	290	—	320	13.2	23.4	63.4
99.8	0.2	—	173	—	235	13.1	22.4	64.5

20 % (mass.) pyridine

4.5	22.4	73.1	7	26	71	4.1	13.8	82.1
99.8	0.2	—	2	11	55	3.6	12.0	84.4

The contents of normally structured ether in the product of hydrocarbmethoxylation, a mixture of hexanes with a main portion of 3-hexane, is practically the same as in the product of 1-hexane hydrocarbmethoxylation. Obviously, this is explained by the fact that the migration of the dual bond in the olefin under conditions of hydrocarbalcoxylation proceeds at great speeds while the hydrocarbalcoxylation speed at the end of the dual bond is much greater than that on the inside.

This is of great significance since it guarantees a greater output of ethers of normal structure in the process of hydrocarbalcoxylation of olefins with an inside position of dual bond, and not only α -olefins.

TABLE 6.8

**Dependence of Isomer Contents of the Hydrocarbalcoxylation
Reaction Products on Olefin Structure**

Olefins	Contents of ether of normal structure in reaction Products; % (mass.)	
	without pyridine	25% (mass.) pyridine
A) Propylene	80	75
B) 1-Hexane	83	62
C) Hexane mixture, % (mass.)		
1-Hexane – 4.5;		
2-Hexane – 22.4;		
3-Hexane – 73.1.	82	60
D) 1-Heptane	81	62
E) 2-Heptane	80	61
F) 1-Octane	82	—
G) 1-Detsane	79	58
H) Isobutylene	99	99

**6.3.5 ISOMER CONTENTS OF PRODUCTS DURING
HYDROCARBALCOXYLATION AND ITS DEFINING
FACTORS**

When hydrocarbalcoxylation of olefins (besides symmetric ones) we get an isomer mixture of complex ethers. The general scheme for the formation of ethers of various structures, relative to 1-hexane hydrocarbmethoxylation, can be represented as follows:

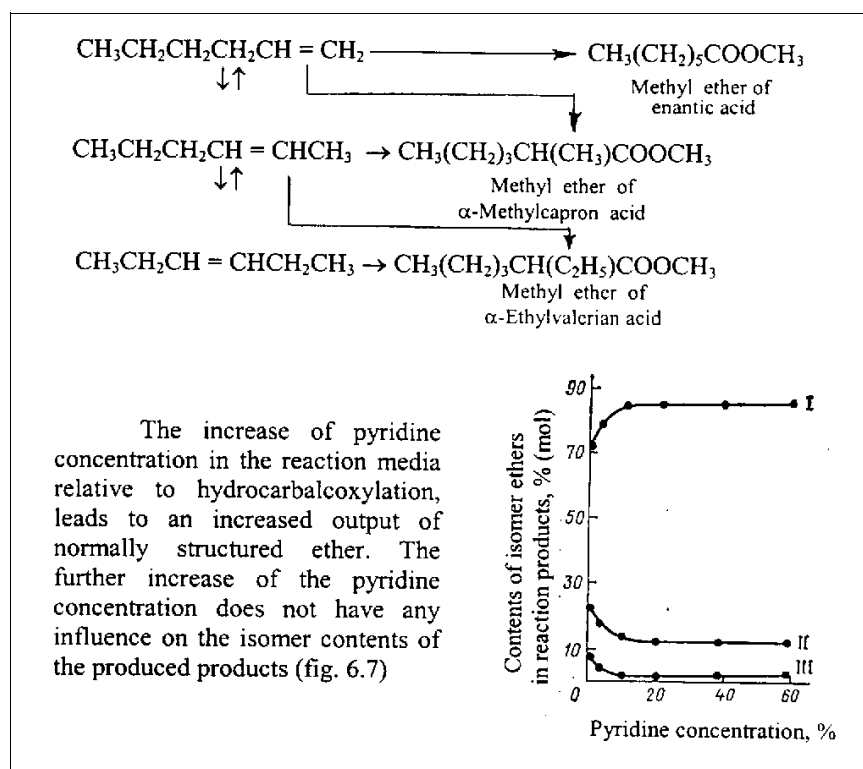


Fig. 6.7 Dependence of isomer contents of 1-hexane hydrocarbmetoxylation products on pyridine concentration:

Methyl ethers: I – enanthic acid; II – α -Methyl-kapron acid;
 III – α -Ethyl-valerian acid

With the rise of the temperature, the output of straight-chain ethers decreases. During the 1-hexane hydrocarbmetoxylation and an increase of temperature from 160 to 175 and 190 °C, the output of methyl ether of enanthic acid decreases to 70%, 65%, and 60% respectively.

The catalyst concentration and mol correlation *alcohol : olefin* practically do not influence the isomer contents of the hydrocarbalcoxylation products no matter – with or without pyridine (table 6.9)

As already stated previously, the conditions of the dual bond in an olefin molecule practically have no influence on the isomer contents of the final product.

TABLE 6.9 Isomer contents of products from 1-hexane hydrocarbmetoxy-lation reaction

Conditions: carbon oxide partial pressure 30 MPa; temperature 175°C; cobalt concentration 0.35 % (mass.).

Ratio – methyl alcohol : 1-hexane, mol x mol ⁻¹	Contents of methyl ether acids in reaction products, % (mol)		
	Enantic	α-methyl-kapron	α-ethyl-valerian

20 % (mass.) toluol (without pyridine)

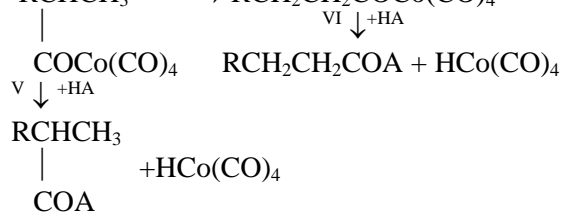
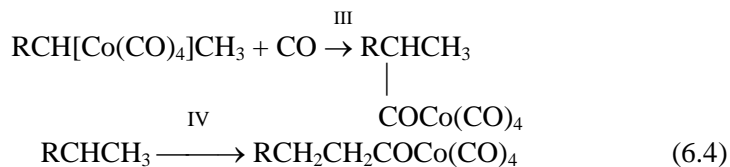
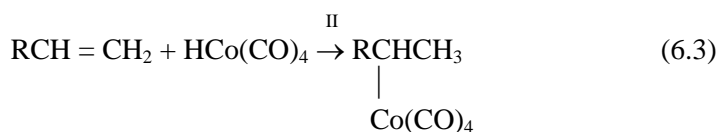
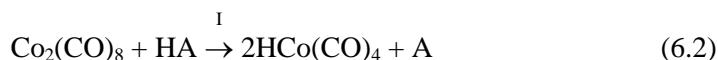
1.9	63.2	24.5	12.3
3.8	64.0	23.6	12.4
5.7	63.0	25.0	12.0
8.6	64.0	23.2	12.8

20 % (mass.) pyridine

1.9	85.0	13.0	2.0
3.8	84.5	13.0	2.5
5.7	85.1	12.9	2.0
8.6	85.0	13.0	2.0

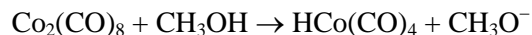
6.3.6 THE HYDROCARBALCOXYLATION MECHANISM; INFLUENCE OF BASES ON REACTION SPEED

Analogously to the reaction mechanism of hydroformylation, the hydrocarbalcoxylation mechanism can generally be presented thus:



where A = OR or OH, NH₂, NHR'.

The formation of cobalt carbonyl out of dicobaltoctacarbonyl and alcohol, based on an example of interaction is shown in fig. 6.8:



The breaking of the acylcobaltcarbonyls with methanol — see stages V and VI in schemes (6.2) to (6.4) — is shown in work [389].

The main kinetic regularities of the hydrocarbalcoxylation reaction are well explained on the basis of mechanisms (6.2) – (6.4) analogously to that of the hydrocarboxylation [390], offered by Imyanitov and his colleagues:

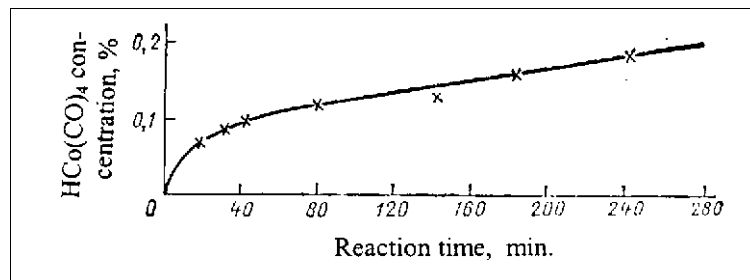
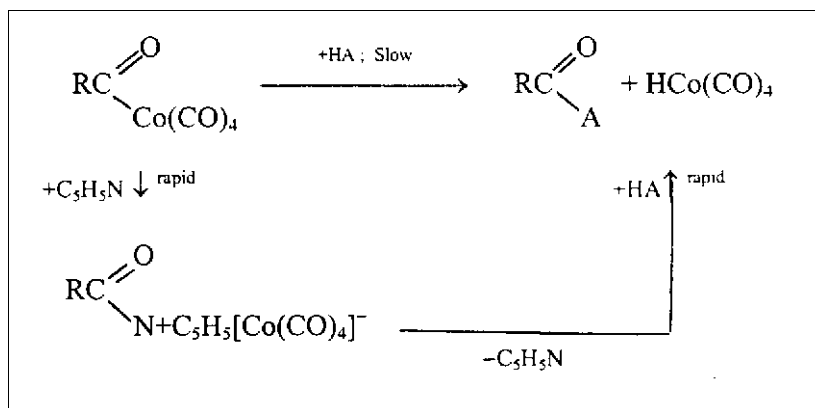


Fig. 6.8 Kinetic curve showing the formation of cobalt hydrocarbonyl out of dicobaltoctacarbonyl and methyl alcohol.
Concentration HCo(CO)₄ calculated on Co.

In the absence of pyridine, the slowest is the stage for breaking the acylcobaltcarbonyls — stages V and VI, schemes (6.2) to (6.4) — which agrees with the zero order of magnitude relative to the olefin reaction and the first order of magnitude relative to methanol. The introduction of pyridine accelerates the acylcobaltcarbonyl breaking stage. Simultaneously, the reaction order of magnitude, relative to alcohol, becomes equal to zero, and olefin gets the first order.

To explain the mechanism for the acceleration of the breakup of the acylcobaltcarbonyls in the presence of pyridine, the following scheme is suggested [371]:



The influence of pyridine on the increase of normally structured products is due to the fact that pyridine hastens the breakup of the acylcobaltcarbonyls of normal structure more readily than that of isoacylcobaltcarbonyls. Such a supposition is well based. Indeed, it was found [391] that the α -picoline practically has no influence on the reaction speed of hydrocarboxylation, while the actions of β -picoline and γ -picoline are close to those of pyridine. This is explained by the fact that the presence of the methyl group in the base of the α -position hinders the formation of the co-planned complex of pyridine with acylcobaltcarbonyls. Most likely, the branching of the chain in the carbonyl group of the isoacylcobaltcarbonyls also hinders the formation of the complex pyridine — acylcobaltcarbonyl because of steric hindrance.

TABLE 6.10

Correlation of the isomers of alacylcobaltcarbonyls and ethers in the course of the 1-hexane hydrocarbmetoxylation reaction

Conditions: carbon oxide partial pressure 30 MPa; temperature 140°C.

Degree of transformation of 1-hexane, % mol	Contained in the reaction product, % (mol.)					
	acylcobaltcarbonyls, offering methyl ether acids			methyl ether acids		
	enantiatic	α -methylkapron	α -ethylvalerian	enantiatic	α -methylkapron	α -ethylkapron

20 % (mass.) toluol (without pyridine)

5	69.8	24.2	6.0	71.4	21.3	7.3
20	71.6	21.5	6.9	71.2	21.3	7.5
33	71.4	21.3	7.3	71.9	20.9	7.2
47	72.0	21.0	7.0	73.1	20.3	6.6

CONTINUED

Degree of trans- formation of 1-hex- ane,%mol	Contained in the reaction product, % (mol.)					
	acylcobaltcarbonyls, offering methyl ether acids			methyl ether acids		
	enan- tic	α -methyl- kapron	α -ethyl- valerian	enan- tic	α -methyl- kapron	α -ethyl- kapron

20 % (mass.) with pyridine

16	62.9	30.4	6.7	79.8	17.6	2.6
27	69.4	24.9	5.7	80.4	16.1	3.5
35	70.2	22.8	7.0	79.6	17.9	2.5
52	70.1	22.2	7.0	78.9	19.0	2.1

The above-mentioned supposition is confirmed, in part, by the data on the isomer distribution of acylcobaltcarbonyls and ethers in products of the 1-hexane hydrocarbmetoxylation reaction (table 6.10). If in the presence of pyridine, the correlation of the acylcobaltcarbonyl isomers is close to that of the ether, then, in the presence of pyridine, the portion of normally structured ether in the product is greater than that in the normal acylcobaltcarbonyl in the mixture of acyls.

6.3.7 DIRECTIVES ON THE PRACTICAL USE OF OLEFIN HYDROCARBALCOXYLATION REACTIONS

Complex ethers of organic acids are widely used in modern industries as solvents, components of plasticizers, intermediate products for organic syntheses.

Thus, in the lacquer-paint industry, the most widely used solvent is butylacetate, which is received via a rather complex and multi-stage method, if we consider the stages of producing vinegar acid and butyl alcohol, which are intermediate products in the butylacetate synthesis. Effective substitutes for butylacetate are methylbutyrate and ethylbutyrate, which are received by hydrocarbalcoxylation of propylene.

Hydrocarbmetoxylation of propylene is accomplished at partial pressure of carbon oxide equal to 15 – 20 MPa, that of hydrogen — 0.1 – 1 MPa, at a temperature of 140°–170°C, at a mol correlation equal to methanol : propylene 5 – 5, with a cobalt catalyst concentration of 0.3 – 0.5 % (mass.), and a concentration of promoter (pyridine) 1 – 5 % (mass.). Under these conditions within about one hour the transformation of propylene amounts to 95 – 98 % relative to the output of ethers onto the transformed propylene up to 96% with a correlation of methyl-

butyrate : methylisobutyrate = 82 : 18. The process of producing ethylbutyrate has about the same values.

Many works have been devoted to the methods of producing methyl ethers of high acids [392 – 394]. If we consider the fact that, in accordance with some of these works, we can produce such ethers with the help of a catalyst complex like *pyridine — cobaltcarbonyls* and this can be accomplished at a pressure of 1 MPa and a temperature of 80°C, and also that the process of hydrogenating high butyl acid methyl ethers, up to the corresponding alcohols, proceeds with a high output, and is widely used in industry, such a path may turn out to be quite effective for the production of the highest of alcohols.

When hydrocarbalcoxylation unsaturated acids or ethers, ethers of dicarbonic acids can be received [395]. The raw materials for the hydrocarbalcoxylation process can be acrylicmethyl [396], acrylonitrile [397], with the production of corresponding ethers.

Olefins (plus diens – see section 6.4) and ethers (plus diethers) produced via hydrocarbalcoxylation, serve as raw materials for producing respective carbonyl (or dicarbonyl) acids, since the hydrolysis of complex ethers does not contain any technological complications.

6.4 DIOLEFIN HYDROCARBOXYLATION

One of the most interesting directions of the further development of industrial oxoprocess is the hydrocarboxylation of the diolefins with the production of dicarbonic acids.

The direct bonding of two carboxyl groups to the olefin was first accomplished by Imyanitov and Rudkovsky when hydrocarboxylizing butadiene [398]. For a long time attempts to get bifunctional products out of olefins via the oxosynthesis method failed to give positive results because in the conditions of hydroformylation a joined dual bond does not hydroformylate, it hydrogenates [399].

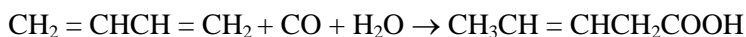
The transition of a dual bond in an initial diolefin causes the formation of a joint diene and further hydrogenation to a mono-olefin. Analogously, migration of a dual bond in an unsaturated aldehyde causes its joining and hydrogenation sooner than its hydroformylation. Even the exclusion of hydrogen from the reaction's system, that is, the exclusion of the hydrogenation reaction did not help.

Thus, during the interaction of diolefins with carbon oxide and water in the presence of cobalt carbonyls it was not products of hydrocarboxylation that were formed, but cyclic ketones [400]. During

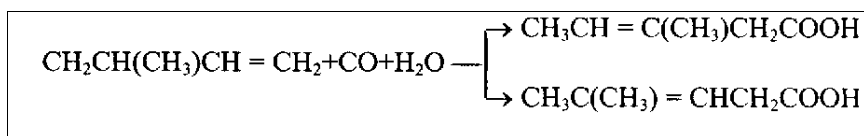
the reaction of butadiene with carbon oxide and water in the presence of rhodium carbonyls, instead of the expected bifunctional derivatives, we got amyl alcohol and valerian acid [401].

Even when hydrocarboxylating butadiene at 300 MPa, we got only mono-carbon acid [402]. Imyanitov and Rudkovsky thus demonstrated an important fact: the hydrocarboxylation of diolefins with dicarbonyl acids can be accomplished in the presence of pyridine.

The study of chemical transformations in the course of diolefin hydrocarboxylation [398, 403 – 405] allowed to conclude that the process proceeds as if in two stages. On the first stage occurs the 1,4-bonding with getting the β , γ -unsaturated acids. Thus, out of butadiene we get the trans-3-pentane acid:



from the isoprene mixture 3-metyl-3-pentane and 4-metyl-3-pentane acid we get the following:

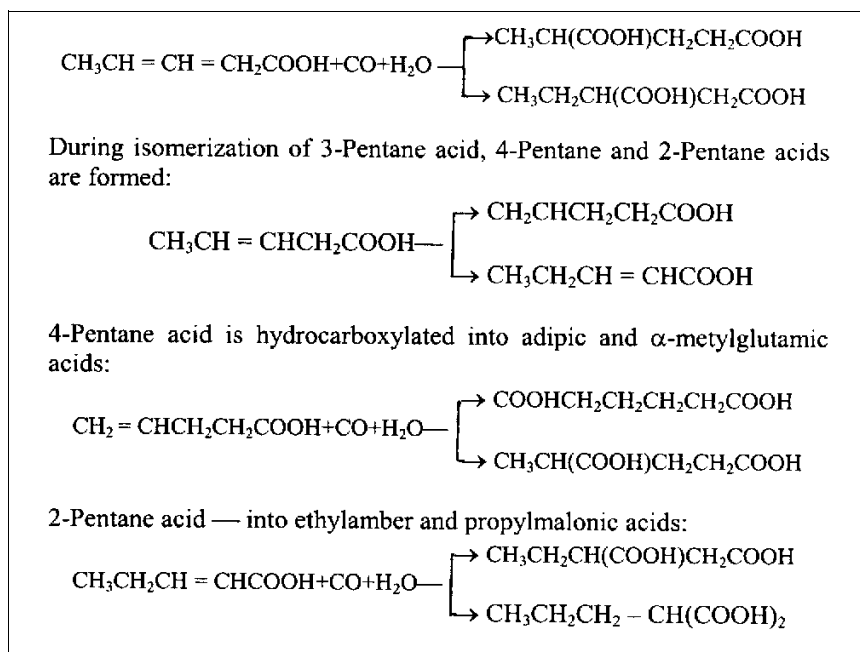


Non-saturated acids are formed at 30 – 40 MPa and at $\approx 160^\circ\text{C}$. Being less reaction-capable than initial diolefins, under such conditions they are not subject to further transformations and can be yielded with a good output.

The increase of reaction temperature by about 50°C allows accomplishing the second stage of hydrocarboxylation with the production of dicarbonic acids. Now, out of 3-pentane acid (product of the first stage of the butadiene hydrocarboxylation) we get α -methylglutamic, ethylamber, adipic acids, and valerian acids.

Imyanitov [329] offers the following schematic explanation regarding the mechanism of the formation of these products.

When 3-Pentane acid is hydrocarboxylated, it gives α -methylglutaric and ethylamber acids:



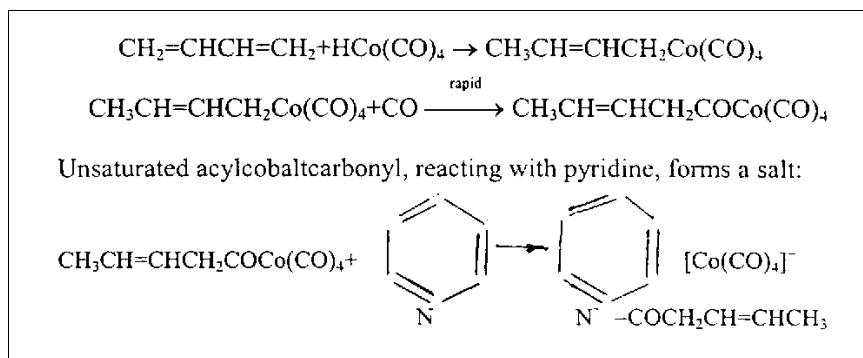
The propylmalonic acid, being unstable under conditions of the reaction, is dicarboxylated into valerian acid:



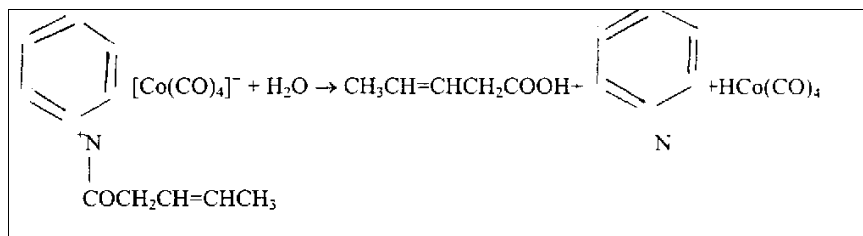
This scheme, according to the authors, is a simplified one, since, indeed, in the course of the reaction, it is not the 3-pentane acid that is isomerized, but the initial interacting products of this acid with cobalt hydrocarbonyls; however, this allows to very well imagine the methods forming the products of butadiene hydrocarboxylation.

In the case of hydrocarboxylating butadiene at a pressure of 40 MPa and a temperature of 210°C, the following final products were received within an hour (in % of theoretical output relative to loaded butadiene): adipic acid 16%, α -methylglutaric acid 7.5%, ethylamber — 25.5%, valerian — 20%.

The mechanism of pyridine influence on the diolefin hydrocarboxylation reaction can be represented as follows. During the interaction of diene with cobalt hydrocarbonyl via the mechanism of 1.4-bonding, alkencobaltcarbonyl is formed, which is rapidly transformed into unsaturated acylcobaltcarbonyl under the influence of carbon oxide:



The rapid reaction of pyridine with unsaturated acylcobaltcarbonyl hinders the formation of cyclic ketone, which, in turn, hinders the formation of hydrocarboxylation products in the absence of pyridine. The hydrolysis of the formed salt and water, in elementary conditions of hydrocarboxylation (temperature up to 160°C) leads to the production of unsaturated acid:



To confirm the mechanism for the promotable action of pyridine, the reaction for the interaction of acetylcobalttetracarbonyl with methyl alcohol was studied with the help of the IR-spectroscopy:

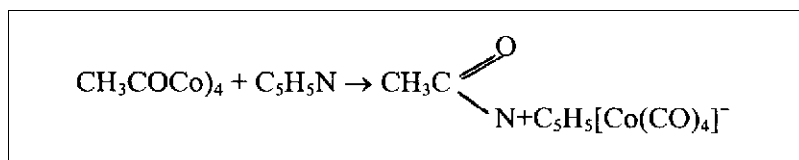


The reaction was conducted at room temperature in an atmosphere of carbon oxide that guaranteed stability of the acetylcobalttetracarbonyl. The reaction speed was controlled with the change of the intensity of the characteristic stripes showing the absorption of the acetylcobaltcarbonyl and metalacetate in the IR-specter.

It turned out that under such conditions the reaction proceeds within 6 to 7 % in 30 minutes. Even in 24 hours the acetylcobaltcarbonyl did not react to the full extent. When pyridine was added to the reaction's mixture, the formation of methylacetate was so rapid, that it was impossible to register the speed. An approximate evaluation has shown that when introducing pyridine, the reaction speed (6.5) increases by more than 400 times. These results very well prove what influence

pyridine has on the speed of the breakup stage of the acetylcobalt-carbonyls.

Also experimentally proven with the help of the IR (infra-red) spectra, was the formation of tetracarbonylcobalt N-acetylpyridine during the interaction of acetylcobalttetracarbonyl with pyridine:



This reaction proceeds at a high speed, ten times higher than that of the interaction of acylcobalttetracarbonyl with methyl alcohol.

Pyridine was not included in the coordinative sphere of cobalt in the described transformations; the interaction of pyridine with acylcobaltcarbonyl proceeded in the same manner as the reaction of pyridine with chlorine-anhydride or with anhydrides of carbon acids. The kinetic regularities of the butadiene hydrocarboxylation reaction [329, 406] are given in the form of a summary in table 6.11.

TABLE 6.11 Main kinetic regularities of the butadiene hydrocarboxylation reaction

Reaction for acid production	
3-pentane	Dicarbonic

Reaction order:

relative to water	from 0 to - 1	from 0 to - 1
relative to butadiene	1	—
relative to 3-pentane acid	—	1
relative to cobalt	1	1
Reaction's temperature coefficient	2.5 - 3	2.6
Carbon oxide partial pressure that guarantees the maximal reaction speed, MPa	30 - 35	10 - 15

Most of the observed kinetic regularities are clear enough from the given scheme of the macro-mechanism of the reaction, and needs no discussion. Most interesting is the influence of water on the reaction speed of hydrocarboxylation (the order of the reaction relative to water changes from zero to minus the first order or magnitude).

The change of the reaction order relative to water (0 - 1) is connected with the change of the correlation of the speeds of separate

stages of the mechanism depending on the conditions (in part, the pyridine concentration).

The influence of pyridine on diene hydrocarboxylation speed is like its influence on hydrocarbalcoxylation reactions — see section 6.3.

Studies were made on the influence of the diene structure on the hydrocarboxylation reaction speed [374, 407]. The reaction speed for the hydrocarboxylation of isoprene and butadiene were practically equal, but the reaction speed for the 2.3-dimethylbutadiene was very small.

Thus, if one substitute of the inner carbon atom in the system of joint dual bonds does not influence the hydrocarboxylation speed, the presence of substitutes in both inner carbon atoms abruptly lowers the reaction abilities of the diene, most likely, at the expense of decreasing the interaction speed of the branched diene cobalt hydrocarbonyls.

Piperilene is hydrocarboxylized with a smaller speed than butadiene, while the reaction speed for 2.4-hexadiene is equal to that of piperilene hydrocarboxylation. The unlinked 1.5-hexadiene hydrocarboxylates much slower than butadiene.

6.5 DIOLEFIN HYDROCARBALCOXYLATION

Just as hydrocarboxylation, hydrocarbalcoxylation of diolefins proceeds quite readily and with a good output in the presence of pyridine. The interaction of diolefins with carbon oxide and alcohol (or aniline) leads to the formation of complex ethers (or anilines) [329,408]. The pyridine action mechanism for these reactions is somewhat like the mechanism of its action hydrocarboxylating diolefins.

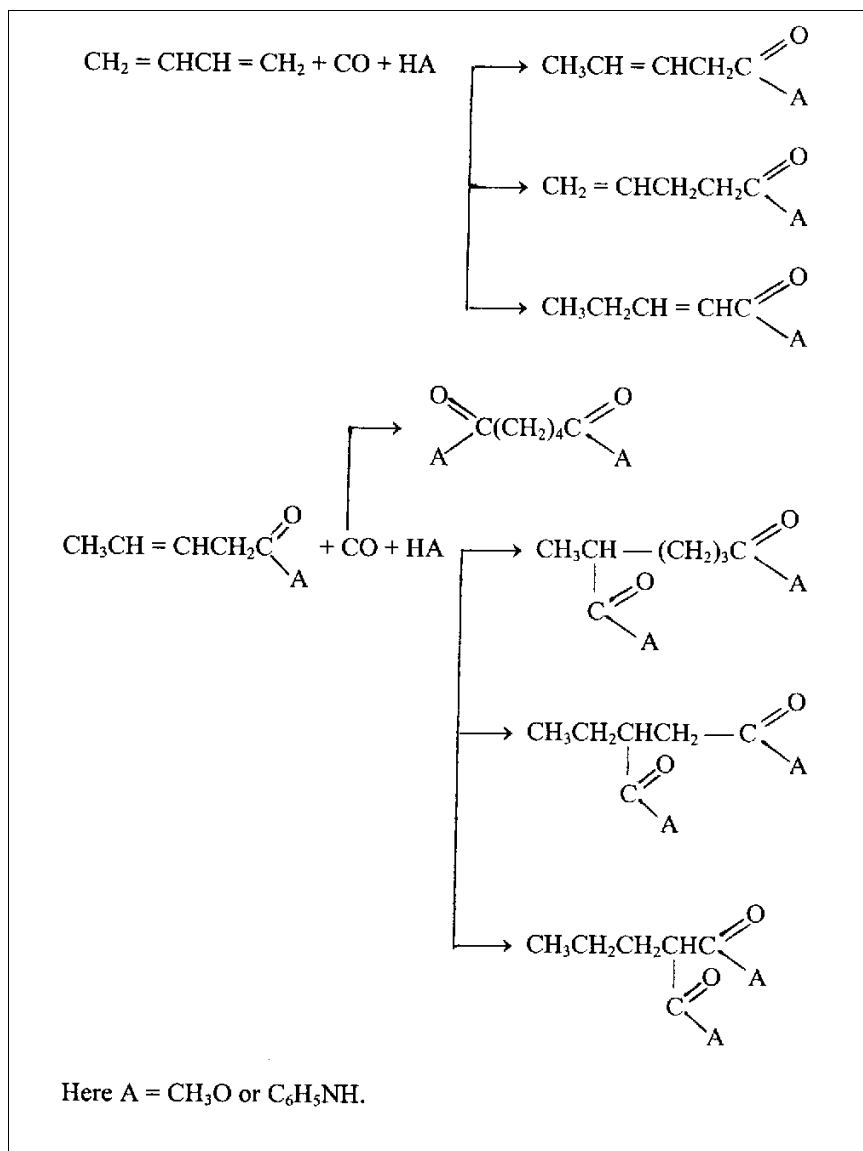
The interaction of diolefin with methyl alcohol or aniline is illustrated by table 6.12 which shows the data on the output of products that were received during the hydrocarbalcoxylation of butadiene.

TABLE 6.12 Output of Ethers (or Anilines) During Hydrocarbalcoxylation of Butadiene

Conditions: pressure 40 MPa; temperature 210° C

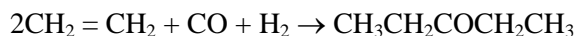
Alcoxyli- zing agent	Output, % of theoretical data on loaded butadiene, dimethyl Ethers (or dianilines) of acids				
	3-pentane	adipine	α -methyl- glutar	ethylene- tar	propyl- melone
Methyl Alcohol	23	43	7	3	0.1
Aniline	—	24	10	27	—

During the hydrocarbmetoxylation of butadiene the main product is dimethyl ether of adipic acid. This is a great advantage from the practical point of view since adipic acid is the most valuable of all the produced products.



6.6 PRODUCTION OF DIETHYLKETONE VIA HYDROFORMYLATION

The formation of ketone (diethylketone) during ethylene hydroformylation was first observed by Roelen. The reaction proceeds along the following equation:



The possibility of getting ketones out of olefins, considering their wide use in various fields, had attracted the attention of many researchers. However, the numerous attempts at producing diethylketone by hydroformylating ethylene and getting a high output, failed.

It was found that in order to get a noticeable output of diethylketone, the reaction should proceed at a comparatively low pressure (≈ 12 MPa) and with a big surplus of olefin. However, later it was found that a good output of diethylketone can be received at a pressure over 70 MPa. In all cases, nevertheless, the output of diethylketone did not exceed 20 % – 25 %. The results, characteristic for the synthesis of diethylketone out of ethylene and synthesis gas, are given in table 6.13 [409].

TABLE 6.13

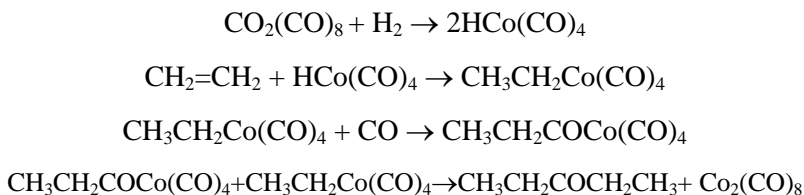
Output of Diethylketone during Ethylene Hydroformylation

Conditions: pressure 2 MPa; temperature 65°C.

Mol correlation of reagents			Output of liquid product gr. x m. ⁻³	Contents of liquid product, % (mass.)	
C ₂ H ₄	CO	H ₂		diethylketone	propionic aldehyde
1.0	1.0	1.1	430	24	16
1.5	1.0	1.0	555	53	5
2.4	1.0	1.0	635	78	3
3.8	1.0	1.0	460	80	2
5.7	1.0	0.9	267	82	2
1.0	1.0	1.9	495	20	22
1.8	1.0	1.8	646	42	11
2.9	1.0	2.1	524	62	9

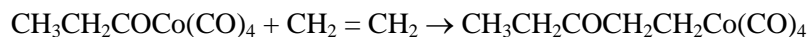
However, when hydroformylating other olefins, ketones practically do not form.

Bertrand and his colleagues [410] offered a mechanism for ketone formation where acylcobaltcarbonyl, being an intermediate product of hydroformylation, reacts not with hydrogen or hydrocarbonyl to form aldehyde, but with alkylcobaltcarbonyl thereby forming ketone:



This scheme reflects the *Brutto Mechanism* for ketone formation without singling out the separate stages.

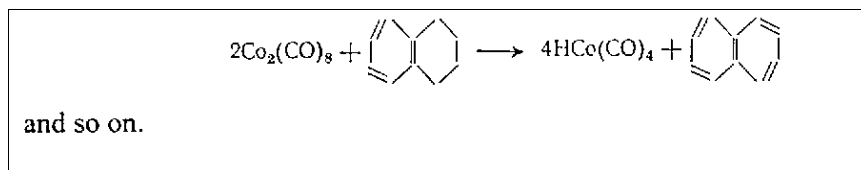
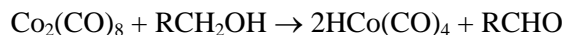
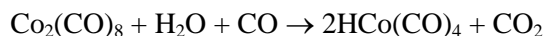
There is another mechanism relative to this reaction [411] where acylcobaltcarbonyl reacts with ethylene:



the formed compound, reacting with cobalt hydrocarbonyl, offers ketone:



Then it was found that the source of hydrogen for the reaction can be not only molecular hydrogen, but alcohol [412], water, tetrahydronaphthalene and other compounds [413], that serve as a hydrogen source for forming cobalt hydrocarbonyl according to these reactions:



Producing ketones by using water and hydrocarbon, as sources of hydrogen, never had any real effect from the viewpoint of improving the process. But when using alcohol, there were some interesting results.

Thus, when researching the reactions of ethylene with carbon oxide and isopropylene alcohol in the presence of cobalt carbonyls [414], it became known that the reaction could be directed towards the

formation of isopropyl-propionate (hydrocarbalcoxylation) and towards the formation of diethylketone.

A selective formation of diethylketone was observed during high concentrations of ethylene, small concentrations of isopropyl alcohol, and at high temperatures (table 6.14).

TABLE 6.14

The Production of Diethylketone in the Interaction between Ethylene, Carbon Oxide, and Isopropyl Alcohol

Temperature	Pressure	Time in Minutes	Concentration of cobalt in % (mass.)	Output in % of theoretical data	
				diethylketone	Isopropyl-Propionate
210	35	20	0,16	95	4
220	36	60	0.08	88	3
240	42	120	0.015	79	2
250	44	100	0.018	83	4

The very same work [414] offered information on the use of various alcohols as sources of hydrogen. It turned out that when using initial alcohols, the formation of diethylketone under definite conditions (pressure 38 MPa; temperature 220°C) proceeded as a main reaction, though with a smaller selectivity than with isopropyl alcohol:

Alcohol	Output of diethylketone % (from the theoretical)
Methyl	61
Ethyl	81
Propyl	84
Isopropyl	92

TABLE 6.15

Ketone production during interaction of various olefins with carbon oxide and alcohol

Olefin	Output of products, % (mol)		
	ketone	complex ether	aldehyde
Ethylene	57	21.5	5
Propylene	26	33.2	3
Isobutylene	traces	56.0	3

The transition from ethylene to higher molecular olefins decreases the output of ketones (table 6.15) [3].

On the whole, we can say that the method of receiving diethylketone out of ethylene can prove to be quite perspective.

6.7 HYDROCARBALCOXYLATION OF NON-SATURATED HIGH ACIDS AND THEIR ETHERS

The production of higher dicarbonic acids and their ethers can be accomplished with the help of the hydrocarbalcoxylation of non-limited higher acids (ethers) [415]. The reaction that is catalyzed by cobalt carbonyls, is conducted in the presence of pyridine.

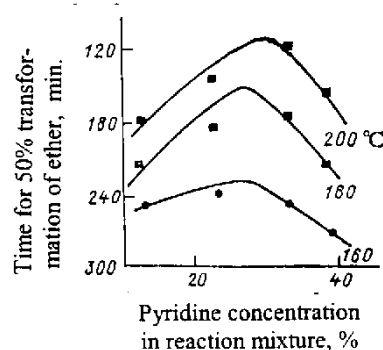
With the increase of the pyridine concentration up to about 30%, a linear increase in the reaction speed is observed; a further increase in the pyridine concentration will slow down the reaction speed — the value of the threshold pyridine concentration practically does not depend on the temperature of the reaction (fig. 6.9).

The hydrocarbmethoxylation reaction of methyl ether from undecylenic acid has the first order or magnitude relative to the substratum and to the catalyst, and a zero order of magnitude relative to the methyl alcohol.

The reaction speed depends on the position of the dual bond like in all related reactions. The greatest speed during double bonding is observed at the end of the hydrocarbon chain; the smallest speed is next to the carboxyl (or ether) group.

When placing the dual bond in the center of the molecule, the defining speed factor is the number of carbon atoms in the chain (viewpoint of the substratum's structure). When it is increased (all other conditions being equal) the reaction speed decreases.

Fig. 6.9 Dependence of reaction speed for hydrocarbmethoxylation of methyl ether of undecylenic acid on pyridine concentration



Unlike a number of related reactions, the correlation of isomers in the mixture of the produced dicarbonic acids or ethers, noticeably depends on the position of the dual bond in the molecule of the substratum (table 6.16).

When hydrocarbmetoxylating methyl ether with undecylenic acid, the relation of the output of dimethyl ether to the total number of isostructured diethers comprises, for the end position of the dual bond in initial mono-ether (methyl ether of 9-undecylenic acid) — about $1 \text{ mol} \times \text{mol}^{-1}$; for ether with a statistically distributed dual bond — about $0.5 \text{ mol} \times \text{mol}^{-1}$; and for ether with a dual bond, joined to the carboxyl group (methyl ether of α -disenic acid) — about $0.4 \text{ mol} \times \text{mol}^{-1}$.

The introduction of pyridine to the reaction's mixture noticeably increases the output of diethers of normal structure (for methyl ether of 9-undecylenic acid, for example, from 1 to $3 \text{ mol} \times \text{mol}^{-1}$).

TABLE 6.16

Dependence of diether isomer output on position of dual bond in ether of unlimited acid during hydrocarbmetoxylation

Conditions: carbon oxide partial pressure 30 MPa; temp. 180°C ; cobalt concentration 0.75 % (mass.); mol correlation $\text{CH}_3\text{OH} : \text{ether} = 5 : 1$.

Initial methyl ether	Correlation of dimethyl ether of normal structure to the sum of diethers of isostructure in the products of hydroarbmetylation, $\text{mol} \times \text{mol}^{-1}$	
	without pyridine	32 % (mass.) pyridine
α -Disenic acid	0.4	1
9-Undecylenic acid	1	3
9-Oleine acid	0.6	2
Undecylenic acid with statistic distribution of dual bonds	0.5	2
Tetradisenic acid	0.5	2
Pentadisenic acid	0.5	2
Dodecadisenic acid	0.5	2

7 OXOSYNTHESIS PRODUCTS; SCALE OF PRODUCTION AND FIELDS OF APPLICATION

In the modern chemical and oil-chemical industries, very few technological processes, based on concrete chemical reactions, can challenge with oxosynthesis relative to both the general volume of industrial production and the wide assortment of product output.

The total capacities of the world's industrial oxosynthesis installations nowadays (1980) amounts to over 5 million tons of various alcohols a year, and the increase of industrial power has been accelerating (table 7.1) until recently, when the acceleration slacked somewhat because of overproduction.

The assortment of alcohols, produced on the oxosynthesis installations, is a wide one — with more than a dozen items. Because of this, it is advisable to cite them separately, having divided them conditionally into several groups.

TABLE 7.1

Dynamics of Development of Oxosynthesis Capacity

	1968	1970	1974	1978
Worldwide (without the USSR):	1500	2600	4600	5200
Western Europe:	850	1300	2400	2600
United States:	520	600	1400	1700
Asia & Australia:	120	260	540	650

Besides, there are more than 10 large industrial installations in the world that are based on various oxosynthesis modifications. Their yearly output amounts to about 400 thousand tons of ethers of acrylic acid made of acetylene, and about 800 thousand tons of vinegar acid by carbonylizing methyl alcohol.

The process of carbonylizing methyl alcohol has been developing wildly the last few years. The BASF firm introduced the first industrial installation of this kind in 1964 in the city of Lyudvigshafen (FRG). Its initial capacity comprised 12,000 tons a year, and now it produces up to 40,000 tons a year. In 1970 the firm Monsanto Co. introduced a new technology for carbonylizing methyl alcohol into vinegar acid at a factory with a capacity of 136,000 tons a year in Texas

City (USA). By 1977 the capacity of such installations in the USA comprised 227,000 tons a year. At present installations with great capacities are being installed in England (350,000 tons a year), in Japan (200,000 tons a year) based on the technology of the Monsanto Co. Plants to this effect are being built in Canada and France. A plant with a capacity of 150,000 tons a year is under construction in the USSR. Thus, the total capacity of this process will soon reach one million tons a year!

There exist and are being built installations for producing propionic acid by hydrocarboxylating ethylene.

However, the main direction of the development of the oxosynthesis industry has been and will be the production of alcohols.

7.1 PROPYLIC ALCOHOL, PROPIONIC ALDEHYDE, AND PROPIONIC ACID

The scale of production of propylic alcohol, propionic aldehyde, and propionic acid, that is, the products of hydroformylation and hydrocarboxylation of ethylene so far are not very big.

The amount of propylic alcohol produced in the world with the help of oxoprocess, comprises about 10,000 tons a year. Propylic alcohol is mostly used as a solvent, for example, in the production of polyolefins.

Somewhat larger is the scale for the production of propionic aldehyde, which serves as the initial product when synthesizing medications, and is used as a modifier during emulsion polymerization of vinylacetate and for receiving propionic acid.

The main foreign producers of propylic alcohol and propionic aldehyde are the firms Union Carbide and Eastman Kodak, the USA.

Much wider are the scales of production of propionic acid that can be received either by oxidizing propionic aldehyde or by direct hydrocarboxylation of ethylene. It is known that the firm BASF (FRG) is running an industrial installation for producing propionic acid by hydrocarboxylating ethylene with a capacity of 30,000 tons a year. There are analogous industries in the USA, but we have no details about them.

The main areas where propionic acid is widely used are the food conserving industries where propionic calcium or sodium is used. Large quantities of propionic acid are used also for the production of chemical means of caring for plants and for the production of polymeric film coverings on the basis of vinyl-propionate.

7.2 BUTYL ALCOHOL AND BUTYL ALDEHYDE

The production of butyl alcohols and *n*-butyl aldehydes via hydroformylation of propylene is now, undoubtedly, a large-scale field for using the oxosynthesis process.

The first industrial installation for producing normal butyl and isobutyl alcohol by this method was accomplished in 1952 by BASF.

At present the world's volume of butyl alcohol production exceeds 1 million tons a year, and most of it is produced via the oxoprocess.

In table 7.2 are given the data on the volume of butyl alcohol production in the leading capitalist countries, while table 7.3 shows the relative portion of the main methods of producing *n*-butyl alcohol in the general production volume. The given data prove that out of all the challenging methods, oxosynthesis occupies the first place.

TABLE 7.2

Production volume of butyl alcohol in the leading capitalist countries of the world (in thousands of tons)

Country	1965	1970	1975	1976	1977
USA	22.1*	212.2	155.0	248.0	231
FRG*	129.7	268.0	329.0	—	—
Japan*	75.5	161.6	152.8	182.0	—
France	12.4	16.8	19.0	—	—
Italy	24.6	34.6	—	—	—
Spain	—	4.2	10.1	15.0	16

* Including butyl alcohol.

TABLE 7.3

Production of *n*-butyl alcohol in leading industrially developed countries (in %)

Method of production	USA		FRG		Japan		France	
	1970	1975	1970	1975	1970	1975	1970	1975
Oxosynthesis	50	88	100	100	21	60	100	100
Via acetaldehyde	43	12	—	—	49	20	—	—
Fermentation	7	—	—	—	—	—	—	—
The Reppe Method	—	—	—	—	30	20	—	—

Analyzing the data on the production volume of butyl alcohols, one must keep in mind that the statistical data often offers the total volume of the produced alcohol of normal and isostructure. It is known that in Japan, for example, the production of *n*-butyl alcohol comprised only 42.5% of the total output of butyl alcohol in 1976, and in the FRG the output also did not exceed 50 % of the total output.

Chemical literature, commonly, does not carry information about the output of butyl aldehyde with the help of the oxoprocess. This is probably explained by the fact that butyl aldehyde, as a rule, is not a commodity, and is immediately worked into 2-ethylhexanole. There are two ways of evaluating the production scale of butyl aldehyde made out of propylene with the help of the oxoprocess: judging by the production scale of 2-ethylhexanole, or by using the information about the scale of production of butyl alcohols.

It is also known that when hydroformylating propylene, a portion of normally structured products comprises 75 to 80%. Therefore, if in the total volume of the butyl alcohol production the portion of the *n*-butyl comprises only about 50%, then the volume of *n*-butyl aldehyde production, which is not transformed into butyl alcohol, but directed to the production of 2-ethylhexanole, is practically equal to the volume of butyl alcohol production.

This evaluation does not change even if we consider the fact that the propylene hydroformylation process in the presence of the carbonyl-cobalt complex (elaborated by the Shell Chemical Co.) allows to receive mainly products of normal structure because the portion of the *phosphine variant* of the oxoprocess, in the total volume of products of propylene hydroformylation, is comparatively not so big for the time being.

The volume correlation of butyl alcohol and butyl aldehyde production can soon change in favor of the latter if the new process of propylene hydroformylation in the presence of rhodium-phosphine catalyst, elaborated by Union Carbide, Davy Powergas, and Johnson Matthey is well developed. This process promises to produce mainly *n*-butyl aldehydes.

These firms have already tried their process on an installation in Puerto Rico with a capacity of about 140,000 tons of butyl aldehyde per year. In 1979 another such installation with a capacity of 100,000 tons a year is to be built by the Berol Kemi AB Company in Sweden. This will make Sweden a foremost producer of oxosynthesis products.

Nowadays more than 90% of all the industrial enterprises of the world that produce butyl alcohol and butyl aldehyde belong to three countries: USA, FRG, and Japan.

Among the foremost producers of butyl alcohols via the process of oxosynthesis are Shell Chemical Co., Union Carbide, Dow Badische Co., Eastman Kidak (all USA); BASF, Ruhrchemie AG, Chemische Werke Huls AG (all FRG); Kuhlmann, Oxochimie (both of France); Mitsubishi, Nissan Petrochem (both of Japan); and Montedison (Italy).

During the last years there has been a tendency to enlarge the manufacturing facilities for the production of butyl alcohol with the help of oxosynthesis. Thus, the capacity of BASF now comprises 120,000 tons per year, while the Union Carbide of Puerto Rico is calculated for a production of 140,000 to 150,000 tons per year.

The Soviet Union has also become a foremost producer of butyl alcohol and butyl aldehyde via oxosynthesis after a big plant was built in the city of Perm.

Butyl alcohols are used as solvents in paint factories, mainly in the production of celluloid varnish. Normal alcohol serves as raw material for producing butylacetate, which is also used as a solvent in industries involved with synthetic materials. A great consumer of the *n*-butyl alcohol is the enterprises that produce plasticizers.

In 1975 20% of the butyl alcohol in the USA was used as solvent, 29% was used on the productions of butylacrylate and butylacetate, 15% to receive glycol ethers, and 14% was used to produce complex-ether plasticizers.

The structure of *n*-butyl alcohol utilization in Japan is shown in the following table (7.4):

TABLE 7.4

Structure of *n*-butyl alcohol utilization in Japan

Field of utilization	1975		1976		1977	
	thous. tons	%	thous. tons	%	thous. tons	%
Plasticizers	12.4	19.6	15.4	20.8	15.5	20.5
Covering	12.5	19.7	14.0	19.0	15.0	20.0
Butylacrylate	10.5	16.6	13.7	18.5	13.7	18.1
Butylacetate	12.4	19.6	13.0	17.6	13.8	18.2
Butyl ethers of glycols	10.9	17.2	12.7	17.2	12.5	16.5
Stabilizers	1.0	1.6	1.1	1.5	1.2	1.6
Pharmaceutical preparation	0.1	0.2	0.2	0.3	0.2	0.3
Other	3.5	5.5	3.9	5.1	3.8	4.5
In all	63.3	100.0	74.0	100.0	75.7	100.0

In order to get a better idea about the series of products that is produced on the basis of *n*-butyl alcohol, we can make use of the data of the British firm Distillers Company:

Butylacetate. A solvent with a middle boiling point for natural and synthetic tar; an excellent softener with a hint of an evaporating smell; serves as the main solvent for the production of cellulose varnishes and other covering materials and glues; can extract solvent when purifying penicillin and other antibiotics.

Butyllactone. High-boiling solvent for natural and synthetic tars; used to make printing paint for paper and cloth.

Dibutyl ether. Used as an extracting solvent or reagent in many organic syntheses, for example, the Greenyar synthesis. This is often used instead of diethyl ether as a solvent when producing oils, fats, wax, alkaloids, vitamins, hormones, and other natural medical preparations.

Dibutylphthalate. Plasticizer for nitrocellulose, ethylcellulose, polyvinylchloride, vinylacetate, vinyl co-polymers, and many other tars.

Dibutylsebacic acid. An effective plasticizer for polyvinylchloride.

Dibutylacrylate. Used in the production of polyacrylates as a monomer and somonomer.

Dibutylmaliate This is widely used as somonomers and modifiers for polyvinylchloride, polyesterole, and polyacrylates, helping with the formation of tars, which have variegated characteristics. This is a valuable inner, non-migrating plasticizer in the production of emulsion polymers.

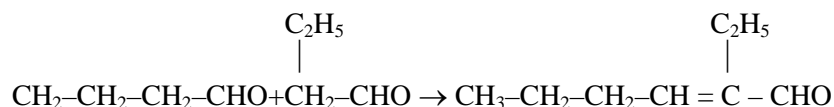
Dibutylfumarat is used for the same purposes.

Tributylecytrate. This is a special kind of plasticizer — for shellac and other natural tars that have hydroxyl groups in their structure. It improves the adhesion and flexibility of alcoholic varnishes and polishes; promotes brightness of acetylcellulose and nitrocellulose varnishes.

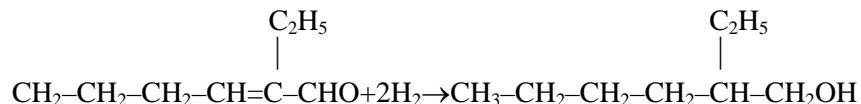
The main method of making use of *n*-butyl aldehyde, which is received by propylene hydroformylation, is by synthesis of 2-hexanole.

This synthesis consists of two stages.

The first stage is the alkali condensation at a temperature of 120° – 160°C and a pressure of 0.4 – 0.6 MPa; *n*-butyl aldehyde is in 2-ethylhexanal:



The second stage is the heterogeneous-catalytic hydrogenation of 2-ethylhexenals into 2-ethylhexanols:



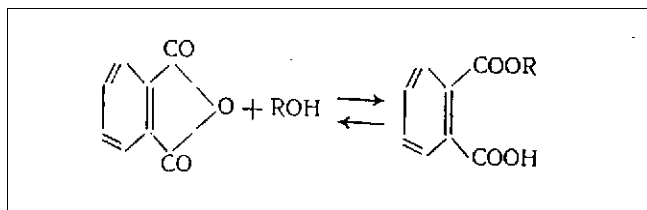
As a rule, enterprises producing 2-ethylhexanole out of *n*-butyl aldehyde are united into a one-unit industrial complex with oxosynthesis installations, which produce *n*-butyl aldehyde and butyl alcohol.

The main field for using 2-ethylhexanole is the synthesis of complex ether plasticizers, for example, di-2-ethylhexylphthalate. The utilization of 2-ethylhexanole in the USA, for example, can be characterized by the following figures (in %):

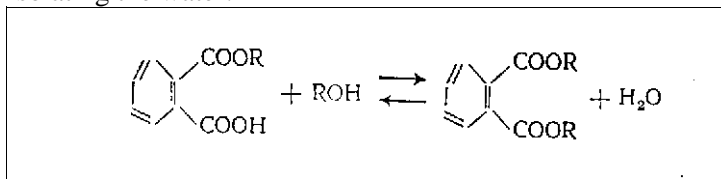
Di-2-ethylhexylphthalate	78
2-ethylhexylacrylate	10
Others	12

In 1972 in Japan made use of 123,800 tons of 2-ethylhexanole out of which 111,800 was used to produce di-2-ethylhexylphthalate.

The synthesis of di-2-ethylhexylphthalate made of phthalate anhydride and 2-ethylhexanole proceeds in two stages — 1) the formation of mono-ether via the interaction of anhydride and alcohol:



and 2) the condensation of mono-ether with the second alcohol molecule and isolating the water:



The speed of the homogenous reaction for the formation of mono-ether is very high, and at the dissolving temperature of phthalate anhydride in alcohol within the limits of the concentration of reagents, in practical use, the reaction proceeds almost simultaneously with the dissolving even if there is no catalyst.

The equilibrium constant of the mono-ether formation reaction within the concentration, used in factories (1 mol of phthalate anhydride per ≈ 2 mol alcohol), is moved to the right, and the transformation of the anhydride into mono-ether is over before a noticeable amount of diether is formed.

The transformation into diether proceeds slower than the formation of mono-ether. This is why the reaction is conducted in the presence of acidic catalysts and at a higher temperature.

The above said also goes for the production of other phthalate plasticators (dibutylphthalate and phthalates of higher alcohols). In general, the mentioned regularities are suitable also in cases where other dicarbonic acids are used as components of complex ether plasticators.

The greatest producers of 2-ethylhexanole on the basis of *n*-butyl aldehyde, received via oxosynthesis, are ICI (England); BASF, Ruhrchemie, Chemische Werke, Huls (FRG); Eastman, Enjay Chemical Co., Shell Chemical Co., Oxochemicals Enterprise, Dow Badische Chemical Corp., Union Carbide (USA).

The world's capacity in producing 2-ethylhexanole at present exceeds 1.5 million tons per year: Western Europe — 700,000 tons; America — 420,000 tons; Asia — 220,000 tons. The indicated capacities also include the working installations for producing 2-ethylhexanole out of acetaldehyde. There is no information concerning the structure of new enterprises of the same kind, but the old installations are still working.

Besides di-2-ethyl-hexyl-phthalate, an important plasticizer for poly-vinyl-chloride, the Distillers Company Limited, for example, produces the following products on the basis of the 2-ethylhexanole:

2-ethylhexylacetate. This is a stable, high-boiling ether, capable of forming decorative film on the basis of cellulose for textiles and leather; promoter of brilliance for cellulose varnishes.

Di-2-ethylhexyladipinate. Excellent plasticizer for polyvinylchloride and chlorine-vinyl-acetate co-polymers; forms compounds that are stable against heat, sunlight, and ultra-violet rays. Has dielectric properties necessary for producing high-quality isolation materials, like cable coverings.

Di-2-ethylhexylsebacynate. Occupies one of the first places among materials for the production of synthetic lubricating oils, including oils for reactive engines and precision instruments. Besides, it is a good plasticizer for polyvinyl polymers, in part, for the production of isolation materials and coverings for cables that carry electricity of the highest frequency.

TABLE 7.5**Quality of n-butyl alcohol produced via oxosynthesis**

I N D E X	Requirements of the firm or of the standards	
	ANSI/ASTM 304 – 15 USA	BS – 504 England

1) Contents of main substance, %, not less than:	—	—
2) Compactness at 20° C, gr. /cm. ³ :	0.810 – 0.813	0.810 - 0.812
3) Limits of boiling away, °C:	117.7 ± 1.5	—
4) Acidity calculated on vinegar acid, %, not more than:	0.005	0.007
5) Contents of carbonyl compounds calculated on butyl aldehyde, %, not more than:	—	0.2
6) Contents of water, %, not more than:	0.1	0.3
7) Color via platinum-cobalt scale, not more than:	10	—
8) Non-volatile leftovers, %, not more than:	0.005 gr./100 ml	0.01

TABLE 7.5 C O N T I N U E D

Requirements of the firm or of the standards				
Ruhrchemie (FRG)	Celanese (Switzerland)	Berol Kemi (Sweden)	Mitsubishi (Japan)	PC 4261 (CEA)**
1) 99	99.8	99.7	99.5	99.0
2) 0.814 *	0.810 – 0.811	0.810 – 0.811	0.809 – 0.810	—
3) —	—	117.8 ± 0.8	—	—
4) 0.005	0.005	—	0.0013	0.005
5) 0.06	—	—	0.05	0.08
6) 0.1	0.1	0.1	0.05	0.2
7) —	10	10	—	10
8) —	—	0.005	—	0.003

 Note: * At 15.5° C.

**Countries of Economic Aid.

Such a wide use of oxosynthesis products is well explained by the high quality of the manufactured products (see tables 7.5 & 7.6) that guarantees, in the long run, a high quality of plasticizers, solvents, lubricants, modifiers, co-polymers, etc.

TABLE 7.6

Quality characteristics of 2-ethylhexane produced by the oxosynthesis method. (* Acid digit, mg. KOH/gr.)

I N D E X	Requirements of the firm or of the standards			
	ICI (England)	Ruhrchemie (FRG)	STAS 9120 Rumania	Berol Kemi (Sweden)
1) Contents of main substance, in %, not less than:	99.5	99.0	99,5	99.7
2) Compactness at 20°C, gr./cm ³	0.833-0.835	0.831-0.833	0.832-0.833	0.832-0.833
3) Limits of boiling away:	180 – 186	183.5 – 185 (97%)	183 – 185	184.5 ± 1.5 (97%)
4) Contents of non-limited compounds recalculated for 2-ethylhexanole, %, not more than:	—	—	0.01	—
5) Contents of carbonyl compounds recalculated for 2-ethylhexanole, %, not more than:	—	0.045	0.05	0.05
6) Acidity calculated for vinegar acid, %, not more than:	—	0.1 *	0.01	0.01
7) Contents of water, %, not more than:	0.1	—	0.1	0.1
8) Color via platinum-cobalt scale, not more than:	5	10	—	5

7.3 HIGH ALIPHATIC ALCOHOLS

While studying the problems of production and utilization of high aliphatic alcohols, it is convenient to conditionally divide them into two groups: alcohols C₈ – C₁₃ and alcohols C₁₀ – C₁₈.

Practically, the only industrial method for the production of alcohol C₆ – C₁₃ in the developed capitalist countries, at present, is the oxoprocess. The most important alcohol representatives of this group, besides the mentioned 2-ethylhexanole, are as follows:

a) **Isooctyl alcohol** — received by hydroformylating co-polymer of propylene with butylene;

b) **Nonyl alcohol** — received by hydroformylating di-isobutylene thanks to which it contains only one of the possible isomers — 3,5,5-trimethylhexyl alcohol;

c) **Isodecyl alcohol** — received via hydroformylation of propylene trimer, resembles a mixture of alcohols, mainly those of the di-methyl-octyl and the tri-methyl-heptyl groups;

d) **Tridecyl alcohol** — received by hydroformylating propylene tetramer and resembles a complex mixture of isomer alcohols;

e) **Alcohol C₇ – C₉** — received by hydroformylating fractions of paraffin cracking, resembling mixtures of various molecular masses (like the ICI firm's alphanol 79, which contains three alcohols: 43 % heptyl, 45 % octyl, and 12 % nonyl).

f) **Alcohol C₆ – C₁₀** — received by hydroformylating olefins that are discharged from the products of the cracking.

In table 7.7 are given the data concerning the main foreign producers of high alcohols C₆ – C₁₃ via the oxosynthesis method; the capacities of their installations are also given.

The greatest producers of alcohol C₆ – C₁₃ are the USA and FRG. Each of these countries have a yearly output of more than 500 thousand tons of such alcohol, and most of this is produced via oxosynthesis. About 230,000 tons of C₆ – C₁₃ alcohol is annually produced in England. France produces about 100,000 tons a year.

The main aim in using high aliphatic alcohols like C₆ – C₁₃ is to satisfy the needs of plasticizer production. Alcohol and alcohol fractions of this group are also used for the synthesis of chemical means of defending plant life and some kinds of transplantation.

Here are some examples of products of this group:

Nonylacetate. High-boiling solvent of cellulose and other tars used for making coverings on the basis of simple and complex ethers of cellulose; a film-producing agent for intro-cellulose and emulsion dressing for leather and textile.

Alcohol adipinates C₇ – C₉. This is a plasticizer for poly-vinyl-chloride and vinyl chloride-vinyl acetate co-polymers; compatible with many natural and synthetic tars, including nitrocellulose, ethyl-cellulose, poly-stirole, and poly-acrylo-nitril.

TABLE 7.7 Main Foreign Producers of High Aliphatic Alcohols C₆ – C₁₃ via the Oxosynthesis Method

Firm; Country	Capacity of plant in thousands tons per year	Initial raw materials	Produced alcohols
Monsanto (USA)	68	oligomers of ethylene	heptyl , undecyl
Air Products	20	olefin mixtures	octyl, decyl, tridecyl
Enjay Chemical Co. (USA)	91	ditto	hexyl, octyl, nonyl, tridecyl
UCC Chem. Div. (USA)	40	ditto	octyl, decyl
Union Carbide (USA)	22	ditto	decyl, tridecyl
ICI (England)	150	co-polymers of propylene, diisobutylene, fractions of paraffin cracking	heptyl, octyl, nonyl, decyl, alcohol C ₇ – C ₉
Shell (England)	80	fraction of paraffin cracking	alcohols C ₇ – C ₁₅
Courrieres-Kuhlmann (France)	100*	products of paraffin cracking	octyl, nonyl, dicyl, dodecyl, and others
Ruhrchemie AG (FRG)	200*	co-polymers of propylene and butylene, diisobutylene and others	nonyl, decyl, and others.
BASF (FRG)	200*	ditto	octyl, nonyl, decyl, undecyl, dodecyl, tridecyl
Chemische Werke Huls (FRG)	120	butylene dimmers.....	nonyl
Mitsubishi (Japan)	98	fraction paraffin Cracking	heptyl, nonyl, undecyl, tridecyl, Alcohols C ₇ – C ₁₁

Note: * Together with 2-ethylhexanole.

Dinonylphthalate. Plasticizer for poly-vinyl-chloride and vinyl-chloride-vinyl-acetate co-polymers.

Diisodecylphthalate. Plasticizer for vinyl polymers; has better properties at low temperatures than phthalates of alcohols with a smaller molecular mass.

Diisooctylphthalate, & phthalates of alcohols $C_7 - C_9$. These are widely used as plasticizers in the production of cable and electric isolation.

Diisooctylsebacynate. Good plasticizer for vinyl polymers; has good properties under low temperatures, is used in the production of high-quality electro-isolation materials like coverings for high voltage cables.

In the production of aliphatic alcohols $C_{10} - C_{18}$ oxosynthesis is one of the most challenging of technological processes.

At the beginning of the 1960s, the production of alcohol $C_{10} - C_{18}$ was almost completely based on the treatment of vegetable and animal fats. However, from the middle of the 1960s, new technological processes for producing high aliphatic alcohols began developing via the Tsigler alum-organic synthesis and the oxosynthesis. The modern structure of $C_{10} - C_{18}$ alcohol production in the above mentioned capitalist countries, can be illustrated by the data in table 7.8.

The prospects of an increase in the production of high aliphatic alcohols $C_{10} - C_{18}$ on the basis of vegetable and animal fats are quite limited for comprehensible reasons. The Tsigler process (alum-organic synthesis) allows producing alcohols of a very high quality on the basis of readily accessible olefins. However, this process is very complicated from the technological viewpoint, therefore the capital investment and exploitation expenditures are very high.

The main shortcoming of the oxoprocess, relative to producing alcohols of this group, is that in spite of the fact all of them are initial alcohols, they are actually a mixture of normal and isonormal structure. Meanwhile, it became obvious that alcohol of normal structure was the best for most fields of activity.

This is why the production of alcohols $C_{10} - C_{18}$ via oxosynthesis started developing intensively after Shell's elaboration of the oxoprocess in the presence of a modified cobalt-phosphine catalyst, which allows to greatly increase the output of normally structured products (table 7.9).

An analysis of the technological and economical indexes of various methods of producing alcohols $C_{10} - C_{18}$ has shown that the

oxoprocess is most favored. The cost of manufacturing a ton of oxosynthesis alcohol is almost two times lower than the alcohols made via the Tsigler method.

The main target for the utilization of high fatty $C_{10} - C_{18}$ alcohols is the production of surface-active substances. For example, here is a utilization scheme for such alcohols produced in the USA (given in %):

Synthetic washing means	51.6
Washing liquids	6.7
Perfumery goods	16.7
Emulgents	4.2
Additions to oils	7.5
Others	13.3

About 80% of the product is spent on preparing the Surface Acting Substances. In the countries of Western Europe and in Japan, up to 75% of their $C_{10} - C_{18}$ alcohol is used for manufacturing synthetic laundering means.

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