

CATALYSIS WITH COORDINATE NON-SATURATED METAL COMPLEXES

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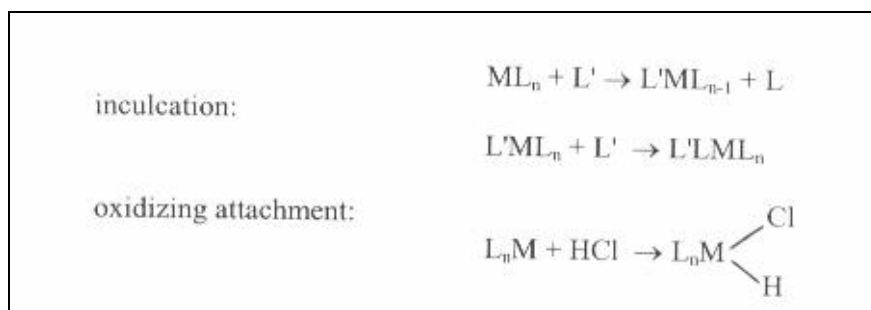
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At First There Were Facts

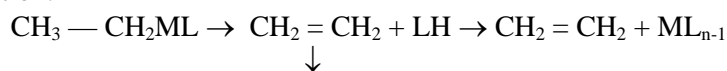
The 1950s of our century were known for their abrupt development of coordinate catalyst chemistry. The interest in coordinate catalysis, first of all, was stimulated by the inculcation of industrial processes which were catalyzed with complex catalysts.

Within a comparatively short period (10-15 years) the production of aldehydes out of olefins via the method of oxide-synthesis with the use of carbonyls of cobalt, the oxidation of ethylene up to acetaldehyde with the use of chloride palladium as a catalyst, and the polymerization of olefins and dyads with the use of complex weighed catalysts of the Tsigler – Natta ??? type (i.e., chloride-titanium + aluminum-alkyl).

The success of the wide and productive inculcation of these processes caused great interest in the study of the coordinate catalysis mechanism. A detailed study of these processes has caused great interest in the study of the mechanism of coordinate catalysis. A detailed study of reactions catalyzed by metal complexes, has revealed a number of common intermediate products and a number of common conformities. Thus, in [1] ??? it was found that the key reactions were substitution reactions:



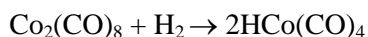
and the reverse chip-off substitution reaction, and also the elimination reaction:



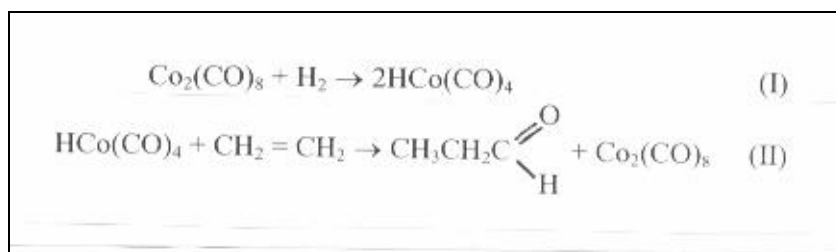


The procedure of a number of key reactions was experimentally proven in the course of the catalytic act on the example of the hydroformylation reaction [2].

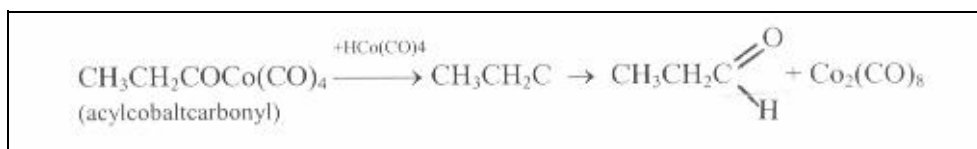
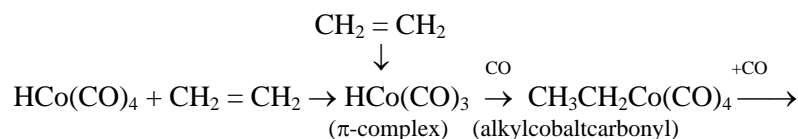
In the first studies of this mechanism, various compounds of cobalt were used in the capacity of catalysts (salts, complex compounds, metal cobalt). It was proven that under conditions of industrial catalytic processes (150°, p = 300 atm.) the inculcation of practically any forms of cobalt with oxidized carbon and hydrogen are transformed into dicobaltcarbonyl and hydrocarbonyl cobalt $HCo(CO)_4$. Then it was found that hydrocarbonyl readily reacts with olefin at room temperature and at normal pressure and reacts with olefin thereby forming aldehydes and dicobaltcarbonyl $Co_2(CO)_8$. The following reaction proceeds under conditions of the catalytic synthesis:



Catalytic hydroformylation includes two main reactions:



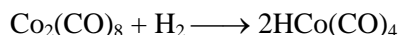
When studying the stoichiometric hydroformylation reaction II, it was found that the reaction proceeded with an intermediate formation during the reaction of the π -complex, the alkyl, and the acylcobaltcarbonyl along the following scheme:



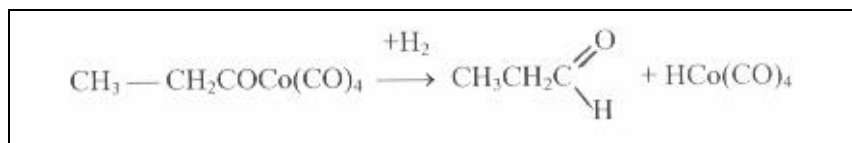
While studying the kinetics of the processes catalyzed by complex compounds, it was found that the reaction speed decreases with the increase of the ligand concentration in the reaction mixture. Various

mechanisms were offered in each concrete case to observe the influence of the ligands on the mechanism speed of various stages. Thus, for example, most often a negative influence of the ligand was noticed during the transition of the equilibrium in substitution reactions.

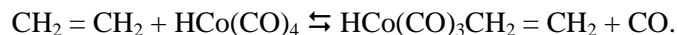
The negative influence of the carbon oxide concentration increase on the reaction speed during catalytic hydroformylation, is explained (experimentally) by the slow-down (braking) of the reaction that produces the hydrocarbonyl cobalt out of the dicobalt-carbonyl:



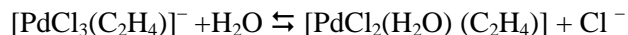
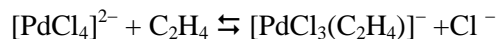
and this is also explained by the experimentally installed brakes for the transition reaction from acylcobaltcarbonyl to aldehyde:



Besides, there was a supposition that carbon oxide has influence because of the transition of the reverse reaction of the π -complex to the left:



The negative influence of the concentration increase of chlorine ions on the reaction speed of chlorine palladium oxidation, was explained by the reaction speed's influence on the equilibrium of the two substitution reactions [1]:

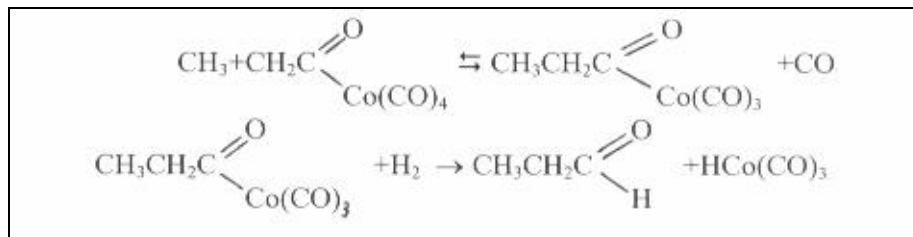


If the explanation concerning the influence of the ligand on the reaction speed (i.e., transition of the equilibrium reaction) did not require additional hypotheses, this explanation relative to the reaction speed of one of the main stages require additional hypotheses; thereby the ligand causes a slow-down on this reaction's speed.

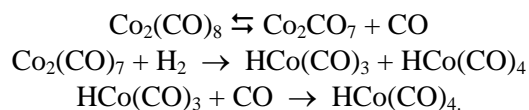
It was found that the ligand has influence not only on the reaction speed during the transition of dicobaltoctacarbonyl into hydrocarbonyl, and acylcobaltcarbonyl into aldehyde, but also on the transition speed of the π -complex into alkylcarbonyl, and alkylcarbonyl into acylcarbonyl.

The commonness of this phenomenon served as a basis for the supposition that it is not the initial coordinate bonds that enter the reaction, but it is the coordinate unsaturated compounds that are in equilibrium with them. [2].

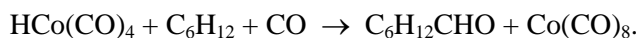
According to the given hypothesis, for example, the transition reaction of acylcobalttetracarbonyl into aldehyde via the action of hydrogen was as follows:



Here it was supposed that cobaltacetyltetracarbonyl is incapable of reacting. The slow-down (braking) of the formation of hydrocarbonyl cobalt out of dicobaltoctacarbonyl when the pressure of the oxide carbon increased is analogously explained as follows:



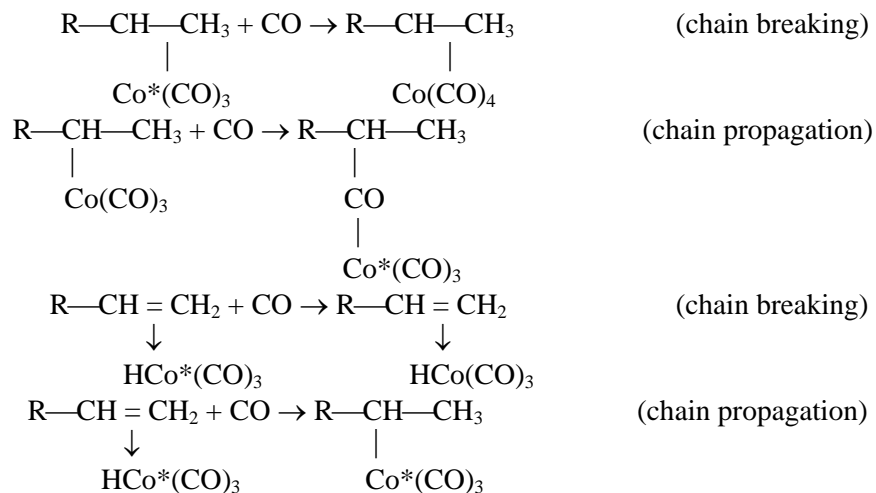
But when studying hydrocarbonyl cobalt reactions with olefin, we get:



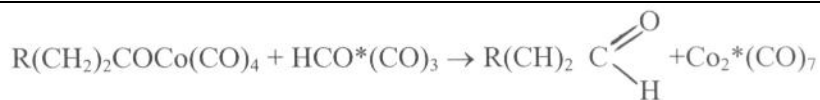
In the presence of carbon oxide, it was found that the reaction proceeds with auto-acceleration. This was confirmed by the fact that the induction period was deleted when the trial product was introduced at the beginning of the reaction (~ 3%) and taken in the developed period of the reaction. The activating influence of the sample, taken at the end of the reaction, was practically not present. This fact indicates that it is the intermediate product that has the activation property.

In the course of a systematic study, it was found that with the increase of the exposure time, the samples in the carbon oxide atmosphere, that accelerates the effect of the next inculcation of the given sample, decreases abruptly. It was supposed that the active compounds are the coordinate unsaturated compounds with carbon oxide, and that their formation proceeds along a chain mechanism.

In order to check this supposition, an attempt was made at receiving coordinate unsaturated compounds out of various metal carbonyls. For



The formation of aldehydes is accomplished via reaction:



This mechanism explains all the above-described experimental data.

Compared with the previously given explanatory variants concerning the slowing down feature of the ligand in processes catalyzed by complex compounds, this mechanism is more general, since the above-mentioned hypotheses can be regarded as individual and taken out of the general chain mechanism. Thus, the influence via the equilibrium is possible if the speed of the breakage and origin of the chain are much greater than the speed of its continuation.

The similarity in the negative dependence of the homogenic-catalytic reaction speed on the ligand concentration allows us to suppose that there is a possibility of a chain conence mechanism in other homogenocatalytic reactions (and not only in stoichiometric hydroformylated reactions). Some stages of the stoichiometric hydroformylation are widely known reactions in coordinate ligand exchange chemistry (for example, the formation of the π -complex) and the inculcation reaction — the transition of alkylcarbonyls into acylcarbonyls.

Thus, it was of interest to examine the possibility of having a substitution and an inculcation reaction, as well as the substitution of an elimination reaction along the chain conence mechanism.

THEORY OF CONENCE REACTIONS

The main supposition in the theory of conence reactions is the supposition that, as a rule, coordinate compounds enter reaction in the form of conences, and the formation of conences occurs along the chain mechanism. Unlike usual theories, here there is no need for additional suppositions, and new conclusions can be made on the basis of systematization, generalization, and the widening of the boundaries for the use of the already experimentally found phenomena.

Such coordinate compounds are called *coordinate-unsaturated compounds*, and these have fewer than 18 electrons in the outermost shell of the metal, calculated via the old rules of the valence scheme.

The name itself — *coordinate unsaturated compound* — has long been used in chemical literature to indicate coordinate compounds with fewer ligands than in the coordinate-saturated compound. The inculcation of this contraction does not imply that the conence has introduced a new word into science; it is just a convenient combination — '*chain conence reactions*'.

The new term has an additional meaning since it singles out the types of reactions that differ by the character of the intermediate particles from ion ones to radical ones. The main mass of conences, besides the free orbitals in the outermost shell, also contains non-bonding electrons, that is, it is actually made up of acids and the Lewis Principle.

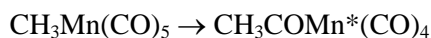
The logic of singling out conences into a separate class with a special name is defined not only by the specifics of the type of phenomena where conences play a role, but also by the wide variety of types (coordinate compound reactions, complex catalytic catalysts).

CONENCE FORMATION

Conences can be formed as a result of dissociation reactions:



inculcation



elimination

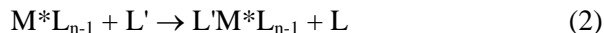


Conences can interact with ligands, with coordinate saturated compounds, and between themselves.

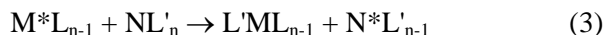
The interaction of a conence with a ligand can lead to the formation of a coordinate-saturated compound along the scheme:



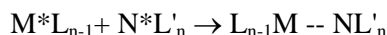
or it can lead to the substitution of the ligand at the expense of the energy discharged during the attachment of the entering ligand:



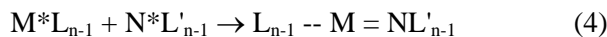
A conence interaction with a coordinate-saturated compound can proceed with the formation of another conence via the scheme:



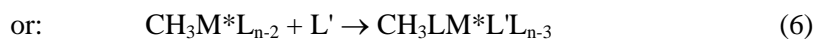
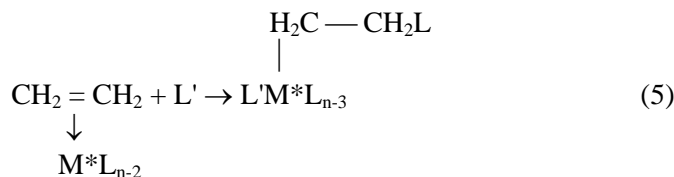
or with the formation of a cluster:



The interaction of two conences can also lead to cluster formation:



The interaction conence -- ligand can lead to an inculcation reaction:

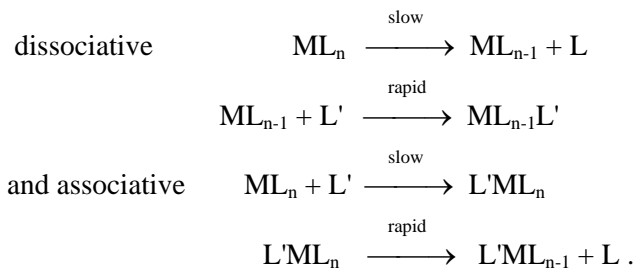


All the above-mentioned types of conence reactions are actually common coordinate compound reactions:

- 1.— the second stage in ligand substitution reactions, proceeding via the dissociation mechanism;
- 2.— the ligand substitution reaction, proceeding via the association mechanism. As a rule, the ligand substitution reaction in conences proceeds via the association mechanism (for example, the ligand substitution reaction in the flat square complexes);
3. — the ligand redistribution reaction. Many oxide-restoration reactions also proceed via this mechanism;
4. — reactions typical for many carbonyl complexes.

SUBSTITUTION AND LIGAND EXCHANGE REACTIONS

Substitution reactions (exchange of one ligand in the complex for another) and *ligand exchange reactions* (exchange of a ligand for an identical radioactive one) are among the most widely studied of the complex bonding reactions. To guarantee their kinetic regularities, two mechanisms have been suggested:



The dissociation mechanism describes reactions having the first order of magnitude relative to the complex, and the zero order relative to the ligand, while the association mechanism describes the reactions with the first order of magnitude regarding both — the complex bonding and the ligand. To explain the often observed great deviations in the orders of the reagents, a supposition was made to the effect that both of the above given mechanisms are extreme, and part of the reaction proceeds via a mixed mechanism where one of the mentioned routes is dominant.

Other suppositions did not explain any noticeable anomalies in the process of the substitution and the ligand exchange reactions [3].

For example:

1. The exchange speed constants CO in the row Ni(CO)₄, Fe(CO)₅, Cr(CO)₆, comprise $7,8 \cdot 10^{-4} \text{ c}^{-1}$ at 0°, 4 years (half-period exchange) at 25°, and $2 \cdot 10^{-5} \text{ c}^{-1}$ at 117° (the reaction proceeds along the dissociation mechanism, so the constants are calculated as those of the first order reactions) while bonding energy M–C decreases in this row.

2. The speed constants and the activation parameters of the substitution and exchange reactions CO in Ni(CO)₄, P(C₆H₅)₂ and ¹⁴CO are close in value since both reactions proceed along the dissociative mechanism. Quite unexpected are the results for the substitution reaction:

$k = 4 \cdot 10^{-4} \text{ c}^{-1}$ at 0° and $\Delta H = 85 \text{ k/J}$, $\Delta S = +2$ while for the exchange reaction $k = 8 \cdot 10^{-4} \text{ c}^{-1}$, $\Delta H = 49 \text{ k/J}$, $\Delta S = -26$.

Identical anomalies were found when comparing kinetic exchange and substitution parameters Hg [Co(CO)₄]₂ with other compounds.

3. From the viewpoint of kinetics the great exchange speed CO in $\text{Co}_2(\text{CO})_8$, in substitution reactions, as compared with the carbonyl in other metals, is unexplainable.

The enumerated anomalies point to the fact that the described reaction mechanisms for ligand substitution and exchange with the help of simple (dissociative and associative) schemes are not good enough.

The use of the Conence Reaction Theory for ligand substitution and exchange reactions in complex compounds, has allowed to propose the following mechanism for ligand substitution and exchange reactions:

1. $\text{ML}_n \rightleftharpoons \text{M}^*\text{L}_{n-1} + \text{L}$
2. $\text{M}^*\text{L}_{n-1} + \text{L}' \rightarrow \text{L}'\text{ML}_{n-1}$
3. $\text{M}^*\text{L}_{n-1} + \text{L}' \rightarrow \text{L}'\text{ML}_{n-2} + \text{L}$
4. $\text{ML}_n + \text{LM}^*\text{L}_{n-2} \rightarrow \text{M}^*\text{L}_{n-1} + \text{L}'\text{ML}_{n-1}$

According to the given mechanism, for the slow dissociative coordinate-saturated complex compounds, we should observe the first order of magnitude relative to the complex and the zero order relative to the ligand. For coordinate, non-saturated compounds, or when the equation for reaction 1 is significantly transited to the right (non-stable complex compounds) the first order relative to the complex and the first order relative to the entering ligand can be observed. Indeed, as a rule, the coordinate saturated compounds react along the dissociative mechanism, while the coordinate non-saturated compounds react along the associative mechanism.

As compared to the above-mentioned dissociative mechanism, the given mechanism has additional stages 3 and 4 whose possibilities have already been mentioned.

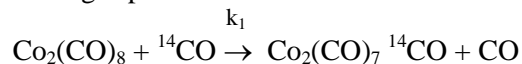
A mechanism that includes reactions 1, 2, and 3, can be regarded as a chain conence mechanism analogously to the chain radical mechanism. Here reaction 1 is the chain origin reaction, 3 is the continuation of the chain, 4 is the transition, and 2 is the breaking of the chain. The common dissociation scheme (routes 1, 2) is a special case.

In the general case, any non-chain mechanism can be regarded as a special case of a chain mechanism with a chain length equal to zero. From the energetic viewpoint, route 1, 2, 3 is more desirable than route 1, 2 because in this route there is one endothermic act accompanied by n acts of exchange proceeding via a reaction with exothermal (in case of substitution) or with a zero thermal effect in the case of an exchange reaction.

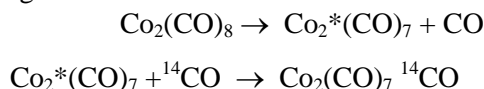
It was of interest to find the chain reactions of exchange experimentally, study the chip-off reactions and the reverse bonding of

carbon oxide in dicobaltoctacarbonyl, which has an anomalously great exchange speed.

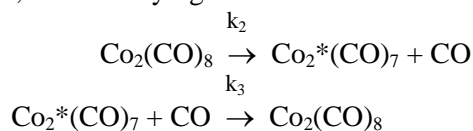
Thus, the exchange speed



has the following speed constant $k_1 = 1.5 \cdot 10^{-3} \text{ c}^{-1}$. If we use a common dissociation scheme, the mechanism of this reaction should include the following stages:



However, while studying the kinetics of reactions:



it was found that $k_2 = 2 \cdot 10^{-5} \text{ c}^{-1}$ while $k_3 = 1.1 \cdot 10^{-2} \text{ L/mol/sec}$. It is quite obvious that common comparison of the speed constant values in reactions 1, 2, and 3 allows us to exclude the use of the common dissociative scheme to describe the reaction's mechanism.

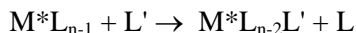
The use of conence chain reaction principles in this case, which is mainly an account of possible interactions of conences as coordinate saturated compounds and conences as ligands with the formation of new conences, leads to the following reaction mechanism:

1. $\text{Co}_2(\text{CO})_8 \rightarrow \text{Co}_2^*(\text{CO})_7 + \text{CO}$
2. $\text{Co}_2^*(\text{CO})_7 + {}^{14}\text{CO} \rightarrow \text{Co}_2^*(\text{CO})_6 {}^{14}\text{CO} + \text{CO}$
3. $\text{Co}_2(\text{CO})_8 + \text{Co}^*(\text{CO})_6 {}^{14}\text{CO} \rightarrow \text{Co}_2^*(\text{CO})_7 + \text{Co}_2(\text{CO})_7 {}^{14}\text{CO}$
4. $\text{Co}_2^*(\text{CO})_7 + {}^{14}\text{CO} \rightarrow \text{Co}_2(\text{CO})_8$

Since the reaction is of the first order of magnitude via $\text{Co}_2(\text{CO})_8$, it is obvious that the speed of stage 3 does not limit the process. Considering this fact, it was found that reaction 2 has a speed constant $k = 10 \text{ lit./mol} \cdot \text{sec}$. with an activation energy $E = 5 \text{ kcal/mol}$.

The much greater speed constant of reaction 2 as compared with that of reaction 4, and the much smaller activation energy when inserting carbon oxide with the simultaneous elimination of the ligand, is well explained by the fact that this reaction proceeds more readily than does a common saturation. That is, the speed of the given reaction is controlled by vast difficulties, but not by bonding energy M—L .

The chain mechanism and the main role of the reaction



proceeding practically with a zero thermal effect, are satisfactory and well explain the above mentioned anomalies.

The acceleration of the exchange speed CO in the carbonyl row: Ni(CO)₄, Fe(CO)₅, Cr(CO)₆, is explained by the systematic increase of the shielding of the central atom. The various reaction speeds during the exchange of ligands of various structure [for example, CO changes for ¹⁴CO more readily than CO changes for P(C₆H₅)₃ can be explained by the various sizes of the ligands, that is, the vast difficulties for the chain continuation reaction.

Besides carbonyl reactions, the chain mechanism is valuable, say, for photochemical ligand exchange reactions like PtCl₆²⁻ and PtBr₆²⁻ that were changed into marked Cl⁻ and Br⁻ [3]. It was supposed that PtCl₅²⁻ and PtBr₄²⁻ are carriers, though they are actually conences. The branched chain mechanism reaction well agrees with the high quantum discharge ($\phi \gg 1$).

When studying the ligand substitution reactions, it was found that, as a rule, such reactions in octahedron complexes proceed along the dissociative mechanism (SN1), while in flat-square complexes — along the associative one (SN2). But there are many exceptions to this rule.

Thus, for example, the ligand substitution reaction in octahedron halogen-like complexes Pt (IV) has the first order of magnitude via the complex and the ligand, which is characteristic of the associative mechanism. There are some complexes Pt (IV) where not only the second order reaction was found, but also — the dependence of the reaction's speed on the type of substitution ligand.

Complexes Pt (NH₃)₂Cl₃⁺ and Pt (en) (NH₃) (NO₂) ClBr (where **en** is the ethylene-diamine) react with pyridine along the reaction of the second order of magnitude. Pt (NH₃)₄ Cl₂²⁺ also reacts to the second order with ammoniac. Pyridine reacts with trans-Pt (H₃)₄ (NO₂) Cl₂²⁺ more readily than with ammonia. Exceptions from the substitution rules are known to occur among the carbonyl octahedron complexes.

For most of the metal carbonyls, the ligand substitution reaction has the first order in the complex and the zero order in the substituting ligand. However, for Co(NO) (CO)₃, Fe(NO)₂ (CO)₂, π -C₅H₅Pt(CO)₂ and some others, a summed up second order substitution reaction was observed. It was supposed that the indicated reactions proceeded along mechanism SN2.

The observed deviations and seeming contradictions in such cases, can be explained in the framework of the theory relative to more or less stability of these compounds, or of the existence of the stage:



Besides a qualitative explanation, one could have expected that in many a case the chain transition reaction could limit the speed of the process, which would be reflected in the kinetics of the process. Indeed, when studying the kinetics of the ligand exchange and substitution reactions, it was found that complexes Pt (IV), including Cl^- in $Pt(en)_2Cl^{2+}_2$ on radioactive Cl^- and NO^-_2 , [3], and that the speed of the exchange reaction in the darkness, corresponds to the equation:

$$r = k [Pt(II)] [Pt(IV)] [Cl]^-$$

while the substitution reaction speed corresponds to the equation:

$$r = k [Pt(II)] [Pt(IV)] [NO_2].$$

This coincides with the chain conence scheme of the reaction data [interaction of the coordinate non-saturated complexes Pt (II) with coordinated saturated complexes Pt (IV) as the limiting stage of the process].

When coordinate non-saturated compounds, or compounds that easily dissociate in the solvent, are put into the system, the substitution reaction proceeds along the scheme analogously to the associative mechanism. However, in this case, further dissociation of the complex is possible in accordance with the following equation:



The conception of conence substitution reactions includes:

- 1) It is based on chemical suppositions with no contradictions.
- 2) Each of the stages has serious experimental confirmation.
- 3) The whole chain mechanism has confirmation for carbonyl complex reactions and for non-carbonyl complexes.

This conception involves the following points:

A) The anomalies in substitution reactions, when explained before the association and dissociation scheme came into being and also various activating parameters and substitution reaction speeds proceeding along the dissociation mechanism;

B) Influence of the type of ligand substitution for certain types of reactions;

C) The second ligand order for a number of reactions.

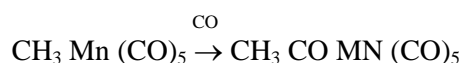
LIGAND INCULCATION REACTIONS

Ligand incultation reactions in complex compounds can be described by the following general scheme:



where $X = H^-, R^-, OR^-, NR_2^-, NR_3^-, OH^-, H_2O, Cl^-, Br^-, I^-$; $Y = CO$; olefin, acetylene, $RCHO$, RCN , SO_2 , O_2 or other non-saturated systems. Details on the specifics of this reaction are available from the book by Basolo and Pierson [3].

The first incultation reaction discovered was:



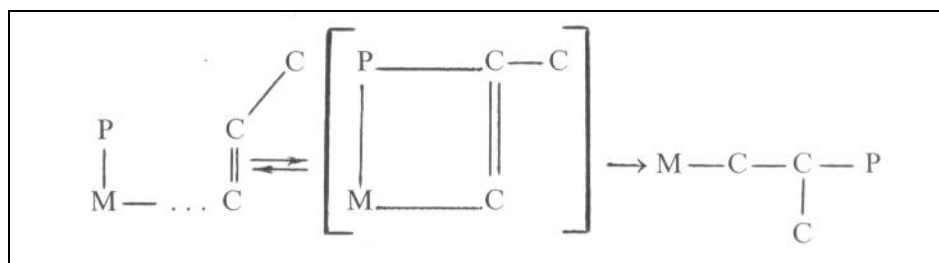
Several mechanisms of this reaction were offered. In this following one



Here we see a coincidence with kinetic regularity reactions. But this mechanism did not explain the low value of activation energy for this reaction [1]. For example, the activation energy comprised 62 kJ/mol^{-1} , while the strength of bond $M-C$ is equal to about $125-380 \text{ kJ/mol}^{-1}$.

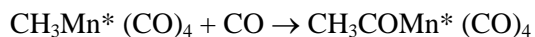
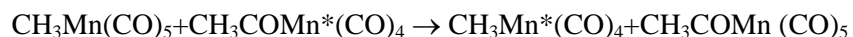
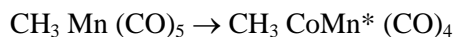
An analogous phenomenon was found when introducing ethylene was introduced in a bond *metal — carbon* in ethyl-rhodium. Here energy $E_a = 72 \text{ kJ/mol}^{-1}$, the strength of the coordinated bond rhodium — ethylene comprises about 130 kJ/mol^{-1} , while the opening of a carbon — carbon double bond requires 264 kJ/mol^{-1} .

To explain the small activation energy, it was supposed that the incultation reaction proceeds as agreed, that is, via a more or less polar, cyclic transitional state with a simultaneous breaking and bond formation. Thus, for example, for the ethylene incultation reaction via the metal — carbon bond, the ethyl-rhodium reaction mechanism is illustrated in the following scheme:



Such an idea about polar complexes is not at all convincing.

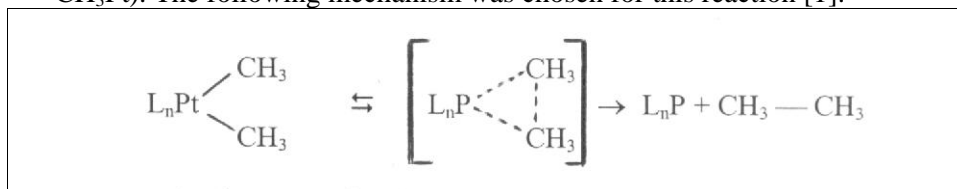
Unlike the given schemes in the framework of the conence reaction mechanism conception, say, for example, the CO incultation reaction in carbonyl manganese is realized as follows:



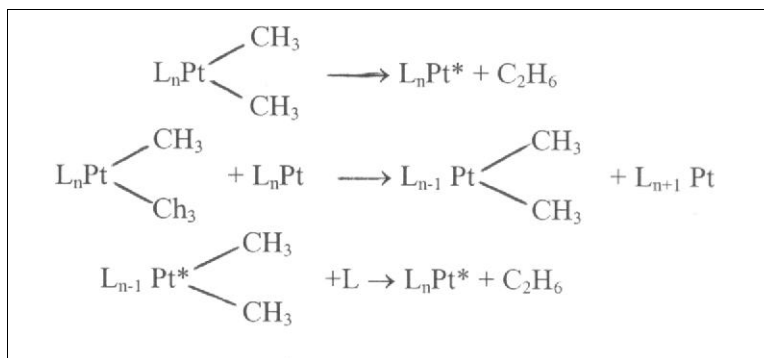
Here doubtful endothermic reactions serve only for beginning the chain.

ELIMINATION SUBSTITUTION REACTIONS

When studying the mechanism for ethane elimination substitution in complex $\text{PtX}(\text{CH}_3)_3$ ($\text{L} - \text{L}$), where $\text{X} = \text{Cl}, \text{Br}$ and $\text{L} - \text{L} = 1,2$ encore diphenylphosphine ethane, it was also found that the energy value of the elimination activation was 69 kJ/mol^{-1} (less than half of bonding energy CH_3Pt). The following mechanism was chosen for this reaction [1].

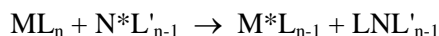


Analogous to the chain reaction, the incultation of the conence mechanism for this reaction can be represented as follows:



OXIDE SUBSTITUTION REACTIONS OF COMPLEX COMPOUNDS

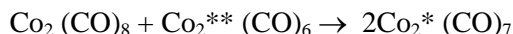
Oxide substitution reactions of complex compounds are described by the following equation:



that is, such reactions are examples of chain transition in a chain conence mechanism. For such a type of reaction, if the conences are singled out into a separate reaction group, it is characteristic to transmit the ligand with a charge.

This reaction group lies on the border between oxide-restoration reactions and conence ones. They belong to both categories.

In this chemical work, a reaction of the following type:



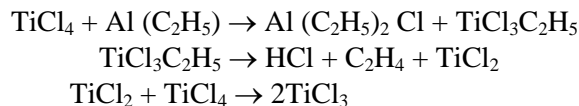
is regarded as belonging to the *chain conence propagation reactions*, while a reaction of the following type:



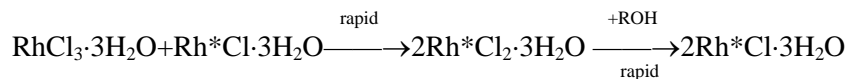
belongs to the chain inculcation type in oxide substitution reactions.

Generally, the existence of both types of reactions underlines the need to keep account of interaction mechanism reactions, that lead to the transition of the chain, or to its branching. The presence of chain oxide restoration reactions and conence chain reactions confirms the hypothesis of N.N.Semyonov about the widespread use of chain processes.

An example of the branched oxide restoration reaction can be seen in the formation reaction in the catalyst polymerization of olefins:

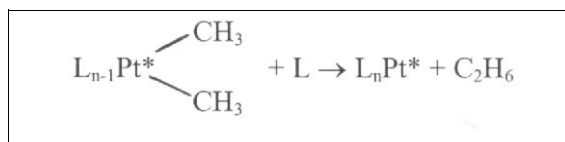
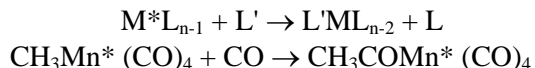


A reaction of this type is meant for explaining the autocatalytic character of reactions for the formation of single-valence rhodium — a catalyst for the isomerization and dimmerization of olefins.



Here the dual-valence rhodium is a conence-radical.

The observed mechanisms for substitution, incultation, and chip-off reactions include the following:



What is common for these reactions is that they proceed in the complex at the expense of the ligand's entrance energy to the conence, that is, very much like the reactions proceeding when two radicals collide. These reactions can be considered as chemically activated. The energy of chemical activation is received as a result of the interaction of a conence with a ligand.

The main method of conence formation in the cited cases is the dissociation of the initial complex or its interaction with another conence. Probably, in the general case, such interaction offers a much more rapid reaction, which allows to suppose an influence on the speed of the main conence reactions by introducing conences or labial coordinate non-saturated compounds. Cases of such use of conences or labial complex compounds have been described in literature.

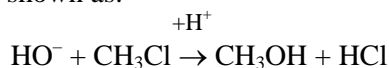
For example, Y.S.Varshavsky uses a stoichiometric addition of conences in a substitution reaction of stable complexes. The incultation of dual-valence cobalt $CoCl_2$ accelerates the exchange reaction of the carbonyl groups in carbonyls Cr, Mo, W into aliphatic iso-nitrile.

In the above given substitution, incultation, and elimination reactions, we can presuppose three main cases:

- 1) The reaction of the ligand's entrance precedes other reactions (the difference in time is smaller than the energy's dissipation time).
- 2) The reaction of the ligand's entrance proceeds simultaneously.
- 3) The reaction of the ligand's entrance comes in turn.

Of these variants, for the above mentioned reactions, the first variant seems most desirable, though there is no doubt that variants 2 and 3 can be used, especially if one intends to use quantum chemistry. Indeed, only in the first case is the energy of the light, exothermal, chemical bonding reaction utilized (even if in part) to guarantee difficult energetic reactions that lead to the breaking of the bond.

Generally, we can suppose that (in the 1st variant) chemical activation is the driving force of chemical reactions, while in the 2nd and 3rd variants there can be chemical activation only as an exception. When citing a classical example of nucleophil substitution reactions in a saturated carbon atom, the literature offers two main types of substitution which are generally shown as:



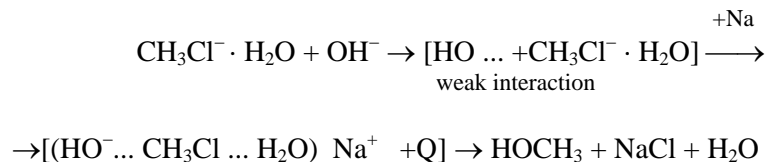
Without an analysis of the driving force and with the usual classical citing, the difficulty of the initial bonding of the hydroxyl group along the only free friable orbital that can be compared with the preliminary dissociation of the initial chlorous metal

However, even with further studies, we can still suspect chemical activation at the preliminary stages. Thus, dissociation halogen-substituted carbonated hydrogen takes place with the use of a solvent.

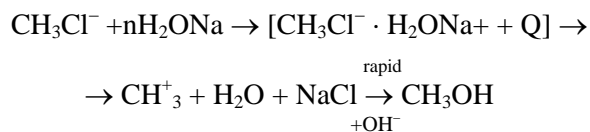
Of the three above-mentioned possible variants, literature is likely to offer us the 3rd because there is a conviction that solvents compensate for dissociation. More preferable is the supposition that — the preliminary exothermic interaction in dipoles of water or solvent of ion sodium with non-divided electronic pairs of chlorine in a molecule — helps the process of dissociation.

For an association mechanism, if we follow the logic of conception, we should presuppose that solvation, if there is any, is not enough to break the bond, though the bond might become weakened. Thus, the decisive point in chemical activation is either the interaction of the anion with the weakened bond, or, which is more likely, along the positive charge of molecule CH_3Cl with the formation of an ionic pair and with a discharge of energy capable of breaking the bond. A significant contribution can be made in both cases by the energy formed of the collision of the ion with its foe that is invariably in the solvent.

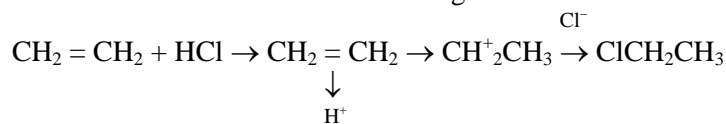
This can be illustrated for **associative reactions**:



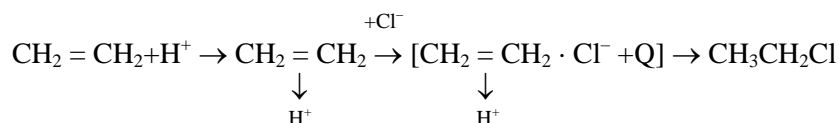
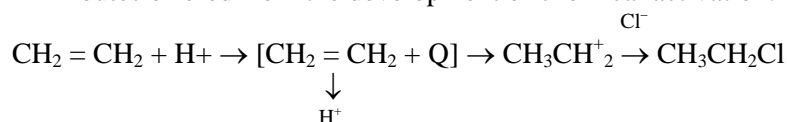
and for **dissociation reactions**:



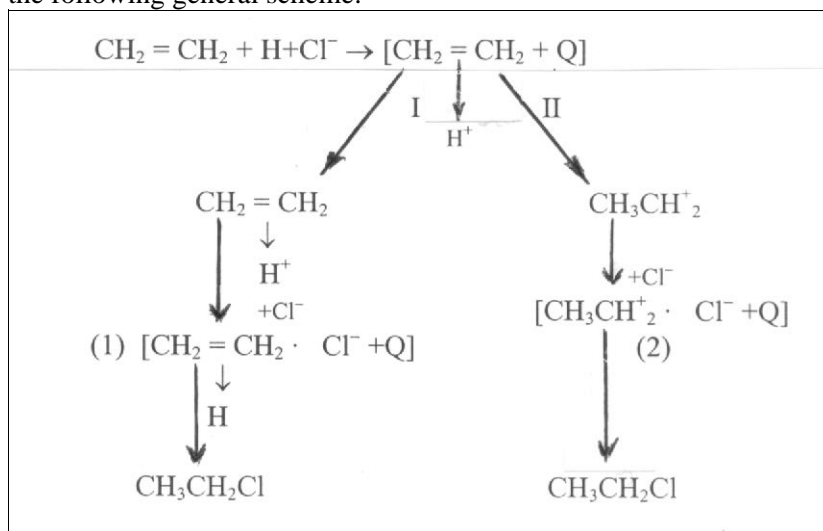
Thus, having looked through the alternative routes of electrophyl bonding via double bonding in concert with the above mentioned considerations (mainly energetic) the most logic routes appear to be routes 2 and 3. Now here is a route given in various chemistry papers:



Routes offered from the development of chemical activation:



The difference between the routes is defined by the comparison of the speed of energy dissipation and the reconstruction of the given activated compound, i.e., the comparison of speeds I and II as given in the following general scheme:



The great energy of the formed ionic pairs 1 and 2 well explains the isomerization of the carbonated hydrogen during formation in the course of the carbocationic reaction. In turn, the presence of isomerization can serve as circumstantial evidence in favor of route II, since isomerization is observed in carbocation and also when there is no preliminary formation of the π -complex. This is why, without excluding the

possibilities of route I, we can suppose that, nevertheless, the most preferable route is II because this route first switches on (includes) the weak chemical interaction, and then the strong one.

In general, chemical reactions, as chemically activated processes, allow us to explain the driving force of chemical processes.

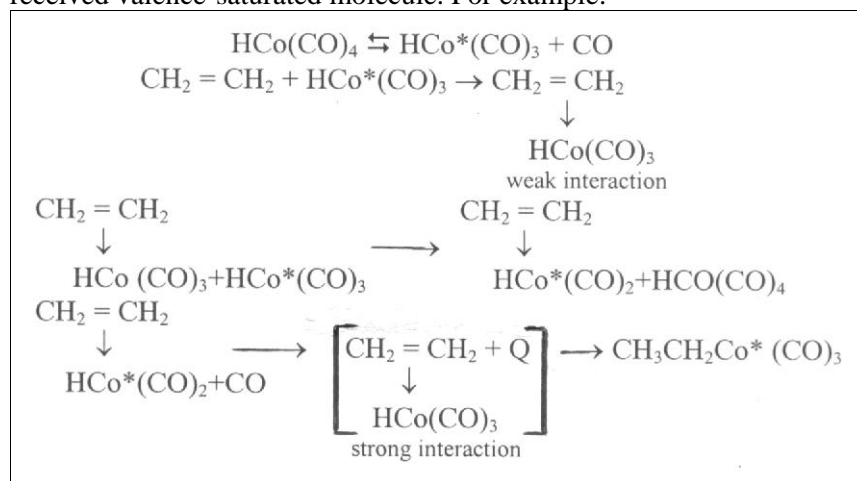
The acceleration of chemical reactions during catalysis is well explained by chemical activation, which is aided by the catalyst during the reaction.

Generally, this is offered in the following manner. The catalyst produces chemically active valence-non-saturated compounds (conences, ions, radicals, acids, and bases), which, together with reagents, enter interaction sequentially. As a rule, at the beginning we should expect weak chemical activation (interaction), and then comes the rapid one.

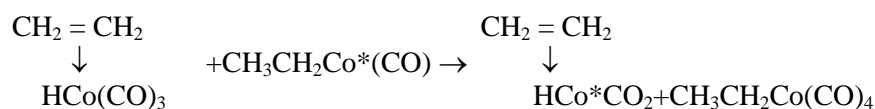
There are two kinds of weak interactions:

- 1) weak interaction does away with valence non-saturation;
- 2) weak interaction does not do away with valence non-saturation or the degree of molecule polarization, like, for example, the formation of the π -complex out of a proton or olefin.

If, during the reaction, via the second variant, the action of the catalyst on the second stage leads to chemical activation reaction because of a collision with an anti-ion or radical (second of the particles into which the catalyst broke up), then, during the reaction via the first variant, the catalyst forms a valence-unsaturated molecule out of the received valence-saturated molecule. For example:



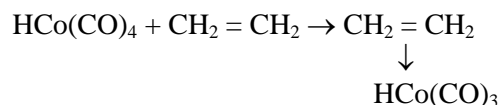
We expect a chain route in the reaction along the following scheme:



That is, the catalyst initiates the chain and supports it during the catalytic reaction. A mechanism that well explains the experimental data, presupposes that a reaction includes both substitution and incultation reactions that proceed along chain conence mechanisms, in which the initiation of the chain is initiated by $\text{HCo}^*(\text{CO})_3$.

The example of a hydroformylation reaction also vividly shows the role of the catalyst that united two reagents on one center; for example, alkyl and carbon-oxide, and putting them into interaction at the expense of the energy meant for bonding the ligand to the conence.

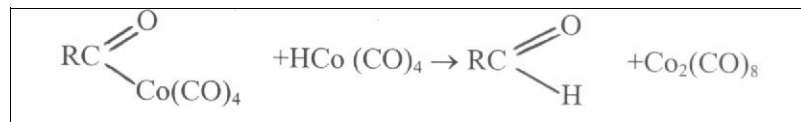
The above-given mechanism, besides the previously explained specifics of hydroformylation reactions (negative influence of carbon-oxide, auto-accelerated character of stoichiometric hydroformylation, smaller speeds at the initial stages) as compared with the total speed of the process, allowed to explain the fact that formerly this was regarded as an exception from the main supposition relative to the theory of conence theories. Thus, the induction period in stoichiometric hydroformylation did not depend on the time of preliminary exposure of hydrocarbonyl cobalt, which allowed presupposing this reaction:



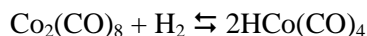
The above-mentioned mechanism explains the need for the supposition that the π -complex is formed along the chain mechanism reaching equilibrium during the induction period. When this period ends, the reaction proceeds along the common chain mechanism from the transition stage of the π -complex in alkyl and then in acylcarbonyl.

True, it was found experimentally that the π -complex is formed during the time comprising less than 1/3 of the reaction's induction period, and limits (defines) the induction period for the transition of the π -complex into alkylcobaltcarbonyl.

Studying the kinetics stages of the hydroformylation reaction mechanism, we found that the speed of the acylcobaltcarbonyl transition into aldehyde via the hydrogen was less than the total speed of hydroformylation. To explain this, a supposition was introduced to the effect that during the catalytic reaction, the breaking of the acylcobaltcarbonyl occurs under the influence of the hydrocarbonyl cobalt along the scheme:

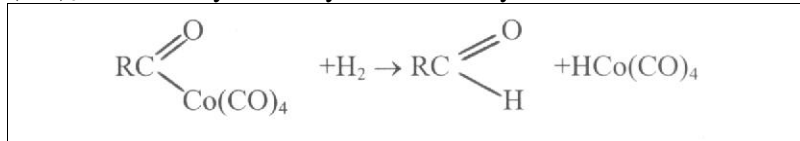


Under the influence of the hydrogen, $\text{Co}_2(\text{CO})_8$ transforms into $\text{HCo}(\text{CO})_4$. The analysis concerning the comparative amount of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ in the course of the reaction confirmed a great possibility for such a route. The concentration of $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$ in the course of a catalytic synthesis is much greater than the equilibrium in the given conditions for the well know reaction:



Studying the kinetic transition from $\text{Co}_2(\text{CO})_8$ into $\text{HCo}(\text{CO})_4$ it was found that the speed of this reaction was also much smaller than that of hydroformylation.

This inconsistency is explained by the fact that under conditions of catalyst hydroformylating hydrocarbonyl, cobalt comes not from $\text{Co}_2(\text{CO})_8$, but directly from acylcobaltcarbonyl via this reaction



However, this explanation, too, could not be confirmed by experiments. The chain conence mechanism, in this case, well explains the inconsistency, and this explanation has a more general meaning. The theory of intermediate connections in catalysis is generally recognized, though the widely known efforts at its kinetic confirmation offered a reverse result. Thus, the transition speed of iron nitride into ammonia was smaller than the ammonia synthesis speed on the iron catalysts.

When studying the oxidation process of hydrogen, many metals showed a phenomenon that was identical to the hydroformylation reaction, that is, the final product production speed of the supposed intermediate compounds, was smaller than the speed of the total reaction, which, if it did not negate the theory of intermediate compounds itself (it is difficult to negate a perfectly logic supposition to the effect that the action of the catalyst is obviously in the formation of some kind of compounds with a substratum) then it forced one to suppose that, at least, the studied compounds are not intermediate. The non-contradictory and experimentally confirmed explanation of this phenomenon for the hydroformylation reaction allows to say that, generally speaking, the catalysis takes place via intermediate reaction-unsaturated compounds and their formation takes place along the chain mechanism.

In 1936 N.N.Semyonov wrote that the reaction's acceleration during catalyst inculcation, was due to its proceeding along a chain reaction, which was energetically more possible than a non-chain route. Since the

only known chemical particles that led chain routes at that time were radicals, to confirm Semyonov's hypothesis, efforts were made to find some radicals in the heterogeneous catalytic reactions. The fact that the first successes, connected with the discovery of radicals in catalytic reactions, proved to be artifacts, caused difficulty in the development of the catalysis conception of the chain theory,

Unsuccessful, also were other attempts at finding radicals in the capacity of characteristic intermediate particles in hetero-gene-catalytic reactions. The conception itself, which explains catalysis as a chain process, where the thermal effect of the reaction is used to initiate the chains, or, in general, to overcome the activation energy in the limiting stage, was also criticized, because this did not explain the acceleration of reactions that proceeded with a zero thermal or endothermic effect.

Besides this, it seemed hardly worthwhile to expect a change in the reaction's mechanism close to the equilibrium, when the heat that is absorbed by its reverse endothermic reaction compensates the heat-discharge of the exothermic reaction.

The supposition that radicals in chain catalytic processes are intermediate particles, did not agree with the selectivity of the catalytic reaction.

Unlike the radical chain routes, the conence chain routes are actually catalytic chain routes. That is, the realization of conence chain routes in the catalysis is a serious proof of N.N.Semyonov's hypothesis about the chain mechanism of the catalysis.

The conence chain catalysis also cancels those objections that were motioned against the basics of the chain catalysis concept (procedure of the reaction with a zero thermal effect) since the chain route was realized and was more desirable energy-wise than the non-chain route, and even in reactions proceeding with zero thermal effect. Probably it would be more proper to say that the chain route, conditioned by the insertion of the catalyst, guarantees the procedure of the reaction along a route more advantageous energy-wise.

The chain conence mechanism, unlike the chain radical one, allows explaining the high selectivity of catalytic processes. On the other hand, the presence of a specific conence catalyst besides a chain one, gives us to understand that the confirmation of the existence of the catalyst does not exclude the existence of other methods of reaction acceleration. Moreover, the difference in the types of catalysts can depend on the type of substances entering the reaction, and on the conditions of its realization, since, after all, what is being defines is the relation of the constant of separate elementary stages.

Translated from Russian by Alexander P. Rogach

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