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FUNDAMENTAL RESEARCH IN HOMOGENEOUS CATALYSIS AND ITS PERSPECTIVES IN INDUSTRIAL APPLICATIONS

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Catalysis, i.e. acceleration or realization of a chemical reaction by the presence of substances formally not involved in the overall stoechiometry of the reaction, has been long known and widely used in chemical processes.

The catalyst is either present in the same phase as other reactants (homogeneous catalysis) or forms an independent phase with the reaction taking place on the interphase (heterogeneous catalysis).

The physico-chemical principle of both types of catalyzed reaction is in its basis the same : the direct involvement of the catalyst in some step of the reaction sequence makes the kinetic or thermodynamic requirement of that step more favourable. Even the mechanism of the action of the catalyst seems to be, at least on the basis of our present knowledge, similar in both cases.

In the case of homogeneous catalysis the reactions take place on a molecular basis and it should thus be, at least in principle, possible to trace the mechanism of the action of the catalyst in more details than in the case of heterogeneous catalysis and to understand thus more deeply what properties of the catalyst are needed for a highly efficient catalytic action. Furthermore, on a molecular basis it is, or should be, possible, to change the properties of the catalyst by varying its structure and to find thus the highest efficiency and/or selectivity.

Homogeneous catalysis attracts in the last decades a lot of attention not only of chemists interested in the mechanism of reactions but also of those who search for new approaches in chemical industry. The reason for this tendency is to be seen in the feeling, substantiated by several successful studies, that the long neglected homogeneous catalysis might open quite new possibilities of very efficient and selective pathways in preparation of organic as well inorganic compounds. The oxo-synthesis, the Wacker process and polymerization of olefins can be quoted as examples of homogeneous catalysis brought to large scale industrial applications. However, there are still vast fields of reactions to be explored.

An empirical approach, which would be possible in principle, meets with great difficulties of picking up the proper combination of catalyst and reactants from the almost infinite number of possibilities. A fully rationalized approach, on the other hand, needs the understanding of the action of the catalyst (its molecular mode of interaction with reactants) and the tracing out of structural factors determining the activity and specifity of the catalyst.

The properties required for a homogeneous catalyst, e.g. wide range of variability of its structure, solubility, high reactivity with various substrates, are best met by coordination compounds of transition as well as of nontransition metals. All the present experience fully supports this conclusion. (It has to be noted that Nature works in its reactions in many cases with catalysts which are pure organic compounds or at most complicated organometallic compounds. Our present knowledge, however, does not enable us to follow or to copy Nature and we are limited to the use of much less sophisticated and simpler compounds which are by far less specific than the natural catalysts.) Coordination and organometallic compounds are widely studied from this point of view. The final goal of all these studies is to find out rules by the use of which it would be possible to "tailor" a catalyst which would bring a given substrate to the desired product.

In the first step, fundamental research is needed of those properties of coordination compounds which determine their ability to function as homogeneous catalysts. These properties are [1] :

1) The possibility of transitions between various redox states by various modes of molecular interaction (direct electron transfer, group transfer, redox addition etc.).
2) The ability to coordinate the molecule of substrate (or of its fragments) and to "store" ~~it~~ it for further reaction steps. This property is closely connected with the mobility of coordination sphere and the ability to change rapidly its composition by the reaction with the medium.
3) The possibility of reactions <u>within</u> the coordination sphere, including insertion reactions, changes of the donor atoms or direct reactions of bounded ligands.

The last two properties are highly specific for coordination compounds and predetermine them for the catalytic actions.

Fortunately enough, the intensive study of coordination chemistry has accumulated such an enormous amount of knowledge that the general theoretical as well as experimental basis is already available. What is needed, in some cases, is merely a reinvestigation of properties of several groups of compounds for specific requirement of homogeneous catalysis.

A further step in the fundamental research of homogeneous catalysis has to follow the mode of interaction between coordination compounds as catalysts and various types of substrates.

Such a research has to start with a working hypothesis or even theory, which would characterize fundamental types of catalytic action. One can think of various approaches to this problem (see e.g. [2]). One such an approach based on the mode of molecular interaction between the catalyst and the substrate has been worked out in The J.Heyrovský Institute of Polarography of the Czechoslovak Academy of Sciences [1]. In this hypothesis of catalytic action of complexes, four fundamental types of catalytic interaction are being distinguished :

1) The catalyst C functions as a <u>mediator</u> of transition of an electron or atomic group between the substrate S and second reactant X, the direct reaction of which does not proceed for kinetic reasons. This type of catalytic action operates in cases when the substrate requires, for the formation of the activated complex, such a mode of interaction which cannot be met by the reactant X. A compound able to react via different modes, one suitable for the substrate and another one for reactant X, would easily catalyze such a reaction.

This type of catalytic action can be described as

$$S + C \longrightarrow P + C_p$$

$$C_p + X \longrightarrow C$$

P being the products of the reaction and C_p the product formed from the catalyst.

As a typical example of such a mechanism the reduction of aromatic nitrocompounds by sodium borohydride catalyzed by Co $dipy_3^+$ can be quoted [3]. Aromatic nitrocompounds are easily reduced by electron transfer mechanism, other mechanisms of reduction are, on the other hand, rather difficult. Cobalt dipyridyl system is able to vary its oxidation states by various modes of interaction and is thus able to transfer the electron from borohydride to the organic molecule. As mentioned above, a group transfer is in principle possible to be catalyzed this way. Up to now, however, no unambiguou example can be quoted.

2) The catalyst generated the active form, free or bounded on the catalyst, by the reaction with the substrate or reactant X.

This group covers a very broad range of mechanisms by which the active form is generated :

2a) generation of the active form and its stabilization by coordination :

$$C + X - Y \longrightarrow C - X + Y'$$

$$C - X + S \longrightarrow S - X + C$$

This mechanism operates widely in such reactions where a σ-bond has to be broken and the substrate is unable to achieve this step. Furthermore, the fragment formed by bond rupture has to be shielded by coordination before unwanted reactions with the medium. Oxidation of hydrogen by ferric chloride, catalyzed by ruthenium (III) complexes can be quoted as a typical example [4].

2b) The catalyst generates a radical or a new oxidation state of the substrate :

$$\begin{tikzcd} S & + & C \arrow[r] & C_p \arrow[l, bend left, "Y"] & + & S^{*} \arrow[r, "X"] & P \end{tikzcd}$$

Reactions of this type are e.g. those which are strongly spin forbidden as direct ones. Autoxidations of many organic substances are a good example of these processes. Photosensitized reactions proceed in most cases via this type of mechanism (see [5,6] for review).

2c) In the reaction between the substrate and the catalyst the configuration of the substrate gets changed. In the simplest case this type of mechanism "opens" an active site on the molecule of the substrate, reactant X being unable to go through this vital step of reaction sequence :

$$S - Z + C \longrightarrow C - Z + S$$

$$S + X \longrightarrow P$$

A very frequent case of this sort of action is an abstraction of hydrogen from the molecule of an organic species. Another example is represented by polymerization of cyclic compounds resulting in linear polymers [7]. In this case a bond rupture is needed as the first step of the reaction sequence.

3) Change of reactivity of the substrate by coordination on the molecule of the catalyst.

This type or action is directly connected with changes in the distribution of electrons in the molecule of the organic ligand which effects the σ-system as well as the π-system of the ligand. These changes can be, depending upon the nature of the central atom and its active site, of various nature and it is possible to adjust them in a highly specific way.

Chlorination of ammonia in platinum complexes is one of many possible examples of this catalytic influence of coordination compounds [8]. Hydrolysis can serve as an example of mechanism in which the formation of a positive charge in a given point of the molecule is the vital step of the reaction (see e.g. [9]). When substrate is coordinated to a metal atom of high electrostatic influence a positive charge is induced in the molecule and this site is then attacted by highly nucleophillic agents, e.g. water or hydroxide ions.

Activation of small molecules (e.g. O_2, H_2, SO_2 etc.) by coordination to metals of d^8 (or d^{10}) group is a very important process in many homogeneous catalyzed reactions (see e.g. [10,11]). Activation of oxygen [10] represents one of the most remarkable examples of this type of process : Molecule of oxygen adds to a d^8 (or d^{10}) atom, mostly without the rupture of the O - O bond but the unpaired spins of the molecule disappear. This makes the reaction of oxygen with molecules in singlet states much easier. Many autoxidations of organic compounds are catalyzed in this way.

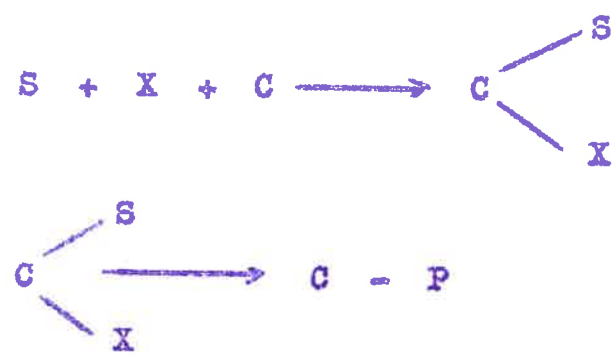
Many biological and enzyme catalyzed reactions belong also to this group of mechanism.

4) Reaction between the substrate and the second reactant (or its fragment) proceed within the coordination sphere. (Some types of reactions belonging to this group of mechanisms are sometimes denoted as "template reaction".)

The most important feature of this mechanism is the fixation of both reacting components in the coordination sphere and their subsequent reaction within it. In many cases a reaction of this type proceeds as a "chain" reaction, the position made free in one reaction step being occupied again by a new molecule of the substrate which reacts with the product of the preceding step still being hold to the molecule of the catalyst.

Steric fixation of reactants makes possible some stereospeciphic reactions and building up of makrocycles or chains. The differencies in the affinity of various parts of the molecule of the substrate to coordinate determines the steric arrangements and thus also the nature of the products.

The general scheme of this mechanism is :



Reactions within the coordination sphere proceed by a great variety of mechanisms. A simple one, formation of σ-bonds after opening of double or triple bonds, plays a rôle in several cyklization reactions, e.g. of acetylene to benzene using triphenyl chromium as the carrier [12].

Other, very widely found, mechanism is the insertion (see e.g. 5) which e.g. in combination with other intramolecular reactions forms a vital step in hydroformylation processes.

Isomerization and polymerization of olefins includes a conversion of the ligand bonded to the metal by its π-system to a ligand with a localized donor site bonded by a σ-bond. This process can repeat itself several times leading thus to shifts of π-bonds along the unsaturated chain.

Most of the homogeneous catalytic reactions proceed via one of the above mentioned mechanisms or by a combination and/or repetition of these. In solving the problem of finding the proper catalyst for a given reaction it is necessary to find out which of the possible mechanisms would be the proper one and which complex could meet the requirements of the mechanism for the given nature of the substrate and reactant.

The general philosophy of this "tailoring of the catalyst" is rather simple, needs, however great knowledge and understanding of the reactivity and its relations to the structure for all reacting components.

Having a reaction S + X giving a desired product P it is first necessary to find out all changes which have to take place within the molecules S and X during the transition to P and the pathways (usually several ones) along which these changes can be achieved.

The second step of the evaluation involves the detection of the reasons for hindering the direct uncatalyzed reactions and tracing out of the most crucial point of the reaction sequence in which the hindrance has to be overcome by the action of the catalyst.

Having reached this step possible catalyzed pathways can be proposed depending upon the nature of the hindrance. This proposal immediately specifies the requirements for the catalyst as reagrds its type of action and nature of its active site. Such a general specification of the type of catalyst does not of course mean that the catalyst is known. A stepwise readjustment of the catalyst is needed to achieve the proper activity of its active site towards the specific reactant. This is domm by changing the central metal atom and/or ligands in the coordination sphere. This point is rather a crucial one as the useful activity is in most cases limited to a very narrow range being critically dependent upon very small changes in the structure of the catalyst(cf e.g. the great differencies in the activity of otherwise identical rhodium (I) and iridium (I) planar complexes or the enormous influence exerted by substituents on phosphorus in various phosphine complexes).

As in many cases there is at least an intermediate with a bond between the catalyst and one of the reactants the properties of the catalyst have to be chosen in such a way as to make the bond under discussion not too strong (otherwise the bonded reactant would be inactivated or the eventual intermediate would not be recovered from the catalyst) but at the same time not too weak (the reactant would be only slightly influenced or held in the complex for a very short time). To meet all these requirements a gradual readjustment of the structure of the catalyst is needed before the optimum structure and conditions for the reaction are found. The above mentioned oxidation of hydrogen by ferric chloride demonstrates, when analyzed a posteriori, nicely all the above mentioned steps. The lastly mentioned problem of a "just right strength" of the bond has been investigated for a series of hydrogen carrying complexes [13] and it was possible to rationalize the properties of the metal hydrogen bond with respect to the ability of the complexes to store and transfer hydrogen in its hydridic form.

The last step in the investigation of a homogeneously catalyzed reaction is to find the pathway for regeneration of the active form of the catalyst. In some mechanisms (see case 1) the catalyst is immediately recovered by the reaction with the second component. In other cases (e.g. in the Wacker process) a special system has to be introduced to regenerate the catalyst. The most difficult situation arises in reactions where a bond between the catalyst and final product is formed and this compound has to be carefully decomposed to give the catalyst (or any of its forms from which it could be regenerated) and the product without destroying any one of them.

As mentioned above, the theoretical basis as well as the general philosophy of this "tailoring" of the catalyst are already available. However, the process of readjustment and refinement of the structure of the catalyst and of its regeneration is sometimes a tedious one even if fully understood.

Reaching successfully this stage we get a homogeneous catalytic cycle on a purely theoretical stage. It is usually not difficult to transfer it to a laboratory scale for carrying out reactions for preparative purposes. However, the problem of transferring such a system into large scale industrial applications opens new questions and their solving requires specific ingeneering studies. To make the process economic it is necessary to achieve such conditions under which the catalyst goes through as many cycles as possible without being destroyed to considerable extent. This needs to make the whole process continuous and to maintain the initial reaction conditions for as long as possible. The greatest problem is met by removal of the product from the reaction mixture which has to be done without stopping the reaction or irreversibly destroying the reaction mixture. This problem has proven in some cases to be so difficult that a heterogeneous reaction has been chosen even if less effective and specific. It seems, however, that this sort of difficulty is a temporarily one and that progress in chemical engineering is going to open many other reactions for large scale applications.

The industrial application of homogeneous catalysis has to overcome another difficulty even for reactions completely clear-cut on laboratory scale : The purity of chemicals used in large scale applications is usually much poorer than that in laboratory experiments. The traces of impurities might influence in a negative way the catalytic cycle and the system has to be readjusted to these conditions before its transfer to large scale operation.

The present state of knowledge of homogeneous catalysis promisses for the future many new approaches. It can be thought of to help the natural processes important for the man not be introducing chemicals in large quantities but merely by introducing catalysts to accelerate ot induce reactions in various systems (air and water polution, fertilizers etc.).

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