

EFFECT OF COMPLEX FORMATION ON REACTIVITY¹

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The different reactions in which reactivity is altered by complex formation are systematized. The manifold relations between the equilibrium and kinetic studies are treated. On the basis of the detailed investigation of several particular reactions general conclusions are made on the mechanism of complex reactions, especially on that of the complex catalysed ones. Several analytical applications are mentioned.

The expression "reactivity" is used quite frequently, but in most of the cases its sense is not exactly defined. We can speak of reactivity in *thermodynamical* and *kinetical* senses. Reactivity means thermodynamically the possibility of a reaction to take place — *i. e.* it is accompanied by a decrease in free enthalpy; kinetically the word indicates the rate of the process, *i. e.* the magnitude of activation energy and of activation entropy.

Complex formation influences reactivity both in kinetical and thermodynamical senses. The effect of complex formation on reactivity in this respect involves several types of reactions and almost innumerable particular reactions. The aim of the present paper is to systematize the corresponding reaction types and to make deductions in general sense from the detailed study of some processes, to establish interdependences and to clarify the manysided connections of equilibrium and kinetical studies.

Systematization of the Processes

It is obvious to differentiate in the systems processes affecting the central ion and the ligands. In case of several reactions, however, the process involves both components of the complex ion: central ion and ligands in the coordination sphere. Concerning the central ion there are only two possible types of reactions where changes in the coordination sphere do not occur. These are:

- 1,1 Changes in charge of the central ion
- 1,2 Changes in the quality of the central ion.

Any change in the charge of the central ion is a redox process, the way and possibility of its occurrence is the most closely connected with coordination. Thermo-

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dynamically the complex formation either makes possible or inhibits the reaction with a given reaction partner by shift of the redox potential, and the complex formation is kinetically important since the electron transfer occurs through ligands bound in the coordination sphere. Changes in the quality of the central ion, *i. e.* in case of substitution reactions of the central ion although there are no changes in the coordination sphere, it is obvious that the properties of ligands play an important part in the mechanism of the reaction, and *transiently* there are changes in the coordination sphere of the partners.

From point of view of the reaction of the ligand the following types can be distinguished:

- 2,1 Substitution reaction of the ligand
- 2,2 Reactions of the coordinated group(s) of the ligand
- 2,3 Reactions of parts of the ligand molecule, which do not play a direct part in the coordination

Naturally the reaction of the non-coordinated part of the ligand affect the electron distribution of the donor group bound to the central ion, — frequently to a negligible extent only — thus there is not a sharp boundary between reactions of groups 2,2 and 2,3, the transition is smooth and continuous.

From point of view of both theory and practice, the different catalytic reactions, closely connected with the reactions of the central ion and the ligand, are of extreme importance. Catalytic phenomena of coordination chemistry can be divided into two groups:

3. Catalysis of complex formation reactions
4. Catalytic effect of complexes.

Complex formation reactions catalyzed by complexes are between the two extreme cases. As for the catalysis of complex formation reactions [1] it is purposeful to distinguish the following cases:

- 3,1 Coordination catalysis
- 3,2 Induced complex formation
- 3,3 Electron transfer catalysis
- 3,4 Heterogeneous catalysis

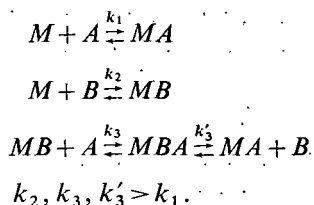
In case of coordination catalysis the complex formation is preceded by the formation of another transitional complex. Coordination catalysis is connected with the opening of the coordination sphere, what may happen² either by means of a ligand or the central ions. Depending on this we distinguish

- 3,1.1 Ligand catalysis
- 3,1.2 Metal ion catalysis.

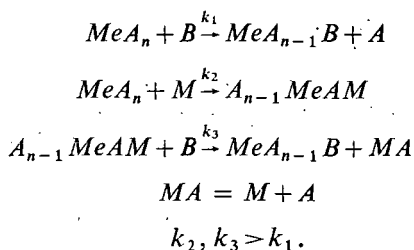
If M central ion reacts only slowly with ligand A and rapidly with ligand D — forming with this latter a thermodynamically less stable complex — and complex

² In course of our recent investigations [2] — after the completion of the dissertation — a new type of coordination catalysis was found: the catalytic effect of the solvent. The $\text{Hg}(\text{CN})_2 + \text{HgCl}_2 = 2\text{HgClCN}$ reaction in aqueous medium takes place instantaneously, but in dioxane only very slowly. The rate of the process in dioxane is markedly increased by small amounts of water. This type of reaction can be regarded as a special case of ligand catalysis.

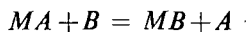
MB reacts also rapidly with ligand A , then ligand D catalyzes the formation of the MA complex. Schematically



The catalytic effect of cations appears through the formation of a binuclear transitional complex:



In case of induced complex formation the process is accelerated by a simultaneous redox reaction. We can speak of electron transfer catalysis when the following substitution reaction



— where ion M is in a higher oxidation state — is accelerated by M ions in lower oxidation state.

Heterogeneous catalysis, having been applied for a longer time in preparation of different complex compounds can be interpreted so that, owing to the adsorption of the complex ion, the coordination sphere is getting loose, *i. e.* the collision of the adsorbed complex with a ligand forming a thermodynamically more stable complex is more effective than a collision in the bulk of the solution.

Classification of complex catalyzed processes can be done according to the type of the catalyzed process.

Kinetical importance of equilibrium studies

The way and extent of a chemical reaction taking place is determined by the quality and quantity of the partners. Thus equilibrium studies are of utmost importance for complex reactions as here we get information about the composition and concentration of ionic species of the given system. Those investigations of equilibria, are of special importance, where the protonation of complexes, formation of polynuclear, mixed and outer-sphere complexes is treated. Namely each chemical reaction requires the interaction of partners, and this may happen just by the reaction types described above.

Protonation of Complexes

Ligands are LEWIS bases, thus, as a rule, competition between the proton and the complex forming metal ion has to be considered. It is reasonable to distinguish complexes of monodentate ligands and chelate complexes. In the protonation of monodentate ligands there are two possibilities: the protonated ligand loses its donor ability, the ligand-metal ion bond breaks, or the protonated ligand is coordinated to the central ion as a dipole. In protonation of hydroxy complexes the corresponding aquocomplexes are formed. Naturally the protonation of polydentate ligands can be various and in its course generally the gradual opening of rings occurs. The kinetical importance of protonation is, that some of the coordination places, occupied by functional groups of the bound ligand they block, become free for interaction with a reaction partner. The method developed by us for determination of stability constants of protonated-complexes [3] — in contrast to earlier ones — is applicable even when the protonation takes place at low pH values. The essence of the method is that in case of given central ion and ligand concentrations the extent of decomposition following the increase of hydrogen ion concentration is determined. Corresponding equilibrium constants are obtained by a simple mathematical analysis of the function defined by considering the complex equilibria. The method has been applied for the study of the protonation of Fe(III)-ethylenediamine-tetraacetic acid [4] and Fe(III)-1,2-diaminocyclohexanetetraacetic acid [3, 4] complexes.

Formation of mixed complexes

In the coordination sphere of mixed complexes there are at least two different ligands. The number of mixed complexes is very great, especially considering that the coordination sphere of metal ions is saturated even in case of small ligand concentration, partly by the ligand in question and partly by water or other solvent-molecules, resp. The kinetical importance of mixed complexes is obvious, especially for the catalytic effect of the complexes. Namely in these cases besides activator ligand(s) (A) the molecule of the substrate (S) is present also in the coordination sphere of the central ion, that is the formation of an activator-substrate mixed complex (MeA_nS_m) is to be considered. The mole fraction of the mixed complex necessarily changes according to a maximum curve both with changes in concentration of A and S . From this immediately follows that as a rule catalytic activity changes with the concentration of the activator ligand according to a maximum curve. In connection with mixed complexes one of the most important questions is the clearing up of factors influencing the formation and stability of mixed complexes, that is, the connection between stability constants of mixed complexes and "parent complexes" of homogeneous coordination sphere. Partly from data in literature and partly from our own investigations the following two rules can be deduced:

1. If the ratio between stability constants³ of complexes of a metal ion formed

$$\begin{aligned}
 K_{MY} &= \frac{[MY]}{[M][Y]}; & K_{MX} &= \frac{[MX]}{[M][X]} \\
 K_{MYA} &= \frac{[MYA]}{[MY][A]}; & K_{MXA} &= \frac{[MXA]}{[MX][A]}
 \end{aligned}$$

with different polydentate ligands (X and Y) is

$$K_{MY} > K_{MX}$$

then the ratio between stability constants of mixed complexes formed with ligand A is

$$K_{MYA} < K_{MXA}$$

2. The value of equilibrium constant characterizing the stability of $MA_{n/2}B_{n/2}$

$$K = \frac{[MA_{n/2}B_{n/2}]^2}{[MA_n][MB_n]}$$

is greater, the greater the difference between stability constants of the corresponding mother complexes (MA_n and MB_n).

We refer here that the first rule is of general validity, while the validity of the second is markedly influenced by quality of ligands A and B . It was to be valid e. g. in case of mercury(II)-cyanide-halide [5] mixed complexes.

In connection with formation of mixed complexes it was pointed out that tetracyano-nickel(II) complex forms with different halide ions pentacoordinated complexes of very slight stability [6]. Nickel(II)-aminopolycarboxylic acid complexes form mixed complexes with cyanide ions [7], and Fe(III)-aminopolycarboxylic acid complexes with hydrogen peroxide [8]. The former rule is valid in respect to their stability, too.

Complexes of outer sphere type

Complexes with saturated coordination sphere may coordinate further ligands in the so called outer coordination sphere. Since changes frequently happen in different redox processes affecting the central ion without even a transient change in the structure of the coordination sphere, it must be supposed that in these cases the electron is conducted by the ligand. From among outer sphere complexes kinetically the most important are those where the ligands bound in the inner sphere contain mobile electrons. Stability constants of such complexes [9] were first time rendered by our experiments, as stability constants of outer sphere complexes of tris (phenantroline)-iron(II) with iodide ions [9] were determined.

Deduction of equilibrium data from kinetical measurements

Rate of chemical reactions is proportional with some powers of the concentration of the partners. Therefore values of velocity — in case of well chosen experimental conditions — may furnish information about the concentration of the particular ionic species, and from this we can calculate equilibrium constants. Kinetical methods formally are similar to spectrophotometric methods, the factor corresponding to the molar extinction coefficient is the rate constant of the particular reaction ways. A marked difference is that in case of optical measurements the concentration is always on the first power what is not always so in kinetical experiments. Constants of the reaction rate change much more sensitively with temperature than extinction coefficients.

Especially in case of catalytic reactions it must be considered that ions present in the system only in small equilibrium concentration and having small thermodynamical stability may markedly influence the experienced rate, since it can be expected that just the intensive factor, the rate constant, will have a great value. In this connection we may refer to investigations described later, in the course of which it became possible to point out the existence of a so far unknown binuclear complex from the kinetical measurements. To determine the stability constants either the increase of activity on the effect of some activator ligands, [10], or in case of a catalytically already active system the decrease of activity on the effect of some inhibitors [11] was measured. From the changes of the rate we make deductions on the concentration of ionic species present in the given system and calculations on the value of stability constants.

Summary of kinetical experiments

Mechanism of redox processes involving the central ion. In this respect the reduction of Cr(VI) was studied. Observing the reduction in presence of ethylenediaminetetraacetic acid [12] it appeared that the cause of the instantaneous complex formation and increase of the rate of reduction is that Cr(VI) forms a complex with EDTA and this complex is reduced more quickly than chromate ion and the reaction results in the formation of an inert Cr(III) EDTA complex. The twofold role of complex formation is very interesting in the reduction of Cr(VI) by Co(II)-aminopolycarbonic acid complexes. The reduction is thermodynamically made possible by complex formation: Cr(VI) oxidizes Co(II) complexes of different aminopolycarboxylic acids but not the Co(II) aquocomplex. But the applied aminopolycarboxylic acids do not contain electrons, thus, if all the coordination places of Co(II) are occupied by functional groups of the ligand, the complex formation prevents the transfer of electron to the oxidizing agent, *i. e.* the coordinated aminopolycarboxylic acid plays the role of an insulator. A condition of the redox process is that water molecule(s) get into the coordination sphere instead of a part of the functional group of the ligand. This is made possible by protonation of the complexes. The necessity of protonation is exhibited by the fact that the rate of reaction, as a function of pH, changes according to a maximum curve. Namely, in case of very low pH values the complexes completely decompose thus the reaction is thermodynamically impossible. At higher pH, where normal non-protonated complexes exist, the mentioned steric inhibitions hinder the interaction of the partners. At intermediate pH values where protonated complexes exist the redox process becomes both thermodynamically and kinetically possible.

The reduction of Cr(VI) takes place in several steps and spectrophotometric investigation unequivocally prove the existence of at least one intermediate. In case of reduction of Cr(VI) by Co(II) EDTA complex [13] the intermediate is relatively stable and its study and the reaction kinetical data show that it is a heteronuclear complex containing Co(III) and Cr(IV) central ions.

Reaction of the ligand. Our investigations aimed to make suppositions on the structure of the complex from changes in the reactivity of the ligand. In acidified medium free EDTA is rapidly oxidized by permanganate and — under favourable conditions — the reaction can be applied to determine EDTA permanganometri-

cally, too [14]. In the course of these experiments it has been also pointed out that in presence of Bi(III) of equivalent or excess amount, EDTA is not oxidized, that is complex formation defends the ligand against the oxidizing effect of permanganate. This phenomenon can be usefully applied in different analytical methods, and at the same time it suggests that in the Bi(III) EDTA complex all the function groups are coordinated to the central ions, *i. e.* there is no protonation even at relatively great acidity. For sake of comparison experiments were done with the oxidation of Cr(III) EDTA complex by permanganate [15]. As it is known, this complex is substitution inert, so free EDTA does not get into the solution during the experiment, and as it is proved by a lot of experiments, EDTA occupies in this complex only 5 coordination places. Therefore it can be expected that now the oxidation of the ligand will be more rapid. This expectation had been proved by our experiments, where the decrease in the permanganate concentration was followed by measuring the light absorption. It was also observed that the rate changes with the pH according to a maximum curve. This hardly can be interpreted otherwise than with the existence of Cr(III) EDTA in acidified medium in two forms having different reactivity, and of these the non-protonated ionic species oxidizes more rapidly.

Catalytic decomposition of hydrogen peroxide is the most thoroughly studied process of the reactions catalyzed by complexes. Fe(III)-triethylenetetramine complex is the most effective catalyst of the decomposition of hydrogen peroxide. It has been pointed out [16] that parallel to the catalytic decomposition of hydrogen peroxide, the oxidation of triethylenetetramine by hydrogen peroxide, being present in great excess to Fe(III), also takes place, and this process is also catalyzed by the triethylenetetramine-Fe(III) complex. The rate-decrease in time of the catalytic reaction can also be ascribed to this process. On the basis of our experiments the great catalytic activity of triethylenetetramine-Fe(III) complex is the result of the following factors:

1. The stability of the complex is much greater than that of ethylenediamine-Fe(III) or diethylenetriamine-Fe(III) complexes, and makes possible to reach relatively great complex concentration even about $\text{pH} = 10$.

2. The direct source of catalytic activity is the common effect exerted on bound hydrogen peroxide of the central ion and hydroxide ion ligand bound at the fifth coordination place. So the catalytic ineffectivity of tetraethylenepentamine-Fe(III) complex, although it is more stable than triethylenetetramine-Fe(III), can be interpreted.

3. In the formation of catalytic activity a decisive factor is that the electrically neutral ligand does not screen considerably the positive charge of the central ion, thus its electron withdrawing effect is greater what results in weakening of the O—O bond.

Our investigations supported the experience that the common Fe(III) aminopolycarboxylic acid complexes are catalytically ineffective for the decomposition of hydrogen peroxide. It was also observed [17] that in acidified medium the rate of decomposition of hydrogen peroxide catalyzed by Fe(III) changes with the concentration of EDTA according to a maximum curve, *i. e.* it must be considered by all means that in this system, owing to the Fe(III) EDTA interactions besides the inactive normal complex another with great catalytic activity is formed. This is probably a binuclear complex, in which the source of the increase of activity is the concerted effect of the two central ions on the same substrate molecule.

Catalytic effect of oxygen carrying complexes. It has been established, that the autoxidation of ascorbic acid is catalyzed both by Co(II)-glycylglycine [18] and Co(II)-histidine complexes [19], but the mechanism of the process is different in the two cases. In case of Co(II)-glycylglycine complex the formation of the oxygen-carrying complex is catalyzed by ascorbic acid, and decreases the rate of irreversible oxidation leading to Co(III). In case of Co(II)-histidine complex, however, the rate of irreversible oxidation increases in presence of ascorbic acid. Further difference, that while in case of Co(II)-glycylglycine the catalytic activity completely ceases following the irreversible oxidation, there is only a decrease in activity at the Co(II)-histidine complex.

Activation of molecular hydrogen. From earlier investigations it is known that reduction processes with molecular hydrogen are catalyzed by some metal ions and complexes, resp. Starting from theoretical considerations, the effect of fluoride ions on the reaction of silver(I)-ion with molecular hydrogen was studied [9]. The rate of the process can be described by the following equation:

$$\frac{d(\text{H}_2)}{dt} = \frac{1}{2} \frac{d(\text{Ag}^+)}{dt} = \frac{kC_{\text{Ag}}C_{\text{F}}(\text{H}_2)}{1 + k'C_{\text{F}}}$$

The empirical rate equation can be interpreted so that the reduction of the less stable monofluoro-silver(I) complex takes place at about ten thousand times more rapidly than that of the silver(I) aquocomplex. The experiments rendered possible the determination of both the rate constant and the stability constant of the complex. The great activation effect of fluoride ion undoubtedly is the result of the concerted effect of central silver(I) ion and coordinated fluoride ion. Considering the steric conditions it must be supposed that the polarizing effect of fluoride ion appears by means of a water molecule through a hydrogen bridge bond.

As to catalyzed complex formation reactions we have found the first instance of specific ligand catalysis and of induced complex formation. Namely, it has been pointed out, that the formation of thiocyanato-Cr(III)-complexes is catalyzed by carbonate ion [1], and — as it had already been pointed out in connection with the catalytic effect of oxygen-carrying complexes — that the autoxidation of ascorbic acid accelerates the formation of oxygen carrying Co(II)-glycylglycine complex [18]. In connection with catalysis of the aquotization processes by metal ions we gave a direct experimental proof that this catalytic effect appears through the transient formation of a binuclear complex [20]. In the course of aqutation of hexacyano-Fe(II) complex, catalyzed by mercury(II), it was cleared up which ionic species are catalytically effective, and it was established that the effect of different cations and anions can be interpreted by complex and ionic pair formation, respectively [21].

Analytical Applications

The effect of complex formation on the reaction rate is the basis of several analytical methods. The fact, that on the effect of excess of cyanide ion Ni(II) EDTA transforms to tetracyano-Ni(II) complex instantaneously while Ni(II) DCTA only slowly, makes possible the simple spectrophotometric determination of DCTA in presence of great amounts of EDTA [8].

On the basis of the inhibiting effect of complex formation on the oxidation of ligands, the permanganometric determination of chromium(III) [22], bismuth(III)

and iron(III) has been elaborated, and it was found, that permanganometric determinations can be carried out in presence of EDTA, if EDTA is transformed into complex by bismuth(III) [14].

The extreme effectivity of the triethylenetetramine Fe(III) complex on the decomposition of hydrogen peroxide made possible the elaboration of a simple permanganometric method [23] for the determination of ultramicro amount of iron (0,03—1,2 μ g).

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ВЛИЯНИЕ ОФОРМЛЕНИЯ КОМПЛЕКСОВ НА РЕАКЦИОННУЮ СПОСОБНОСТЬ

М. Т. Бек

Автором дается классификация типов реакций, где оформление комплексов ведет к изменению реакционной способности. Далее он трактует многостороннюю связь равновесных и кинетических экспериментов, и исходя из тщательного изучения некоторых процессов, даются общие сведения о механизме комплексных реакций, особенно о механизме реакций катализованных комплексом. Автор также указывает на несколько аналитические применения.

References*

- [1] Beck, M. T.: Inorg. Nucl. Chem. **15**, 250 (1960).
- [2] Beck, M., F. Gaizer: Magy. Kém. Folyóirat **69**, 560 (1963).
- [3] Beck, M., S. Görög: Magy. Kém. Folyóirat **65**, 413 (1959); J. Inorg. Nucl. Chem. **12**, 353 (1960).
- [4] Beck, M., S. Görög: MTA Kém. Tud. Oszt. Közl. **12**, 256 (1959); Acta Chim. Hung. **22**, 159 (1960).
- [5] Beck, M., F. Gaizer: Magy. Kém. Folyóirat **69**, 555 (1963).
- [6] Beck, M. T., J. Bjerrum: Acta Chem. Scand. **16**, 2050 (1962).
- [7] Beck, M., J. Bjerrum: Unpublished results.
- [8] Beck, M., Csiszár: Magy. Kém. Folyóirat **66**, 259 (1960); Acta Chim. Hung. **32**, 1 (1962).
- [9] Beck, M., V. Nikolasev: Magy. Kém. Folyóirat, in press.
- [10] Beck, M., I. Gimesi: Magy. Kém. Folyóirat **69**, 552 (1963).
- [11] Beck, M., S. Görög: Magy. Kém. Folyóirat **65**, 60 (1959); Acta. Phys. Chem. Szeged **4**, 59 (1958).
- [12] Beck, M., I. Bárdi: Magy. Kém. Folyóirat **69**, 60 (1963); Acta Chim. Hung. **29**, 283 (1961).
- [13] Beck, M. T., I. Seres, I. Bárdi: Proc. 7 I. C. C. C. 1962. p 278.
- [14] Beck, M. T.: Chemist Analyst **50**, 14 (1961).
- [15] Beck, M. T., O. Kling: Acta Chem. Scand. **15**, 453 (1961).
- [16] Beck, M. T., S. Görög: Magy. Kém. Folyóirat **64**, 432 (1958); Acta Chim. Hung. **20**, 17 (1959).
- [17] Beck, M., S. Görög, Z. Kiss: Magy. Kém. Folyóirat **69**, 550 (1963).
- [18] Beck, M., S. Görög: Magy. Kém. Folyóirat **69**, 56 (1963); Acta Chim. Hung. **29**, 401 (1961).
- [19] Beck, M., Z. Kiss: Unpublished results.
- [20] Beck, M.: Magy. Kém. Folyóirat, in press.
- [21] Beck, M., J. Farkas: Magy. Kém. Folyóirat, in press.
- [22] Beck, M. T., I. Seres: Chemist Analyst **50**, 48 (1961).
- [23] Beck, M., S. Görög: Magy. Kém. Folyóirat **65**, 201 (1959); Acta Chim. Hung. **29**, 291 (1961).

* References only include papers of the author. For further references see the quoted papers.