

COMPLEX FORMATION AND REACTIVITY*

By M. T. BECK

Institute of Inorganic and Analytical Chemistry, The University, Szeged

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The paper deals with the factors which influence the change in reactivity on the effect of complex formation. Some analytical applications are indicated.

The term *reactivity*, frequently used but usually not exactly defined, has two different meanings: a thermodynamical and a kinetical one. Thermodynamically reactivity means whether a reaction is or is not possible; kinetically the reactivity denotes the velocity of a thermodynamically possible reaction; *i. e.* this term characterizes the mechanism of the reaction.

Complex formation alters reactivity in both senses of the term. For a systematic survey it would be desirable to classify the complex reactions, however, this is a very hard task. From a complex chemical point of view it is the most plausible to distinguish between reactions in which there is a change in the coordination and those in which this does not occur. The first group naturally includes the following reactions:

- i) processes in which the oxidation number of central ion changes;
- ii) ligand substitution reactions — this field is quite thoroughly studied and is beyond the scope of the present paper —,
- iii) reactions of the coordinated functional groups of ligand.

As a matter of course, the reactions, in which only the non-coordinated part of the ligand alters, belong to another group. However, any change in the bulk of the ligand affects the coordination, if at all, only in a negligible extent.

This means a practically continuous transition between the third subdivision of the first group and the second one. Further, we must evidently distinguish for example between the bromination of the aromatic ring of a ligand molecule and the reaction of a free functional group of a polydentate ligand which is potentially able to coordinate. Another difficulty of the classification is that the reactions belonging to different groups take place simultaneously.

The effect of a change in the non-coordinated part on the coordination is determined among other factors by the distance between the point of attack and the coordinated atom.

To illustrate this statement, it is enough to cite several recent papers. On the basis of halogenation of trichlorotriani-linechromium(III) and trichlorotripyridine-

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WANG [7] discovered the extremely great catalytic efficiency of the iron(III)-triethylenetetramine complex on the decomposition of hydrogen peroxide. According to him the HO_2^- ion acts as a bidentate ligand and the stretching of the O—O bond results in weakening, even in splitting it. The fact, that the iron(III)-tetraethylenepentamine complex is catalytically inactive, is regarded by WANG as a proof of this mechanism. However, it seems more probable that the HO_2^- occupies only

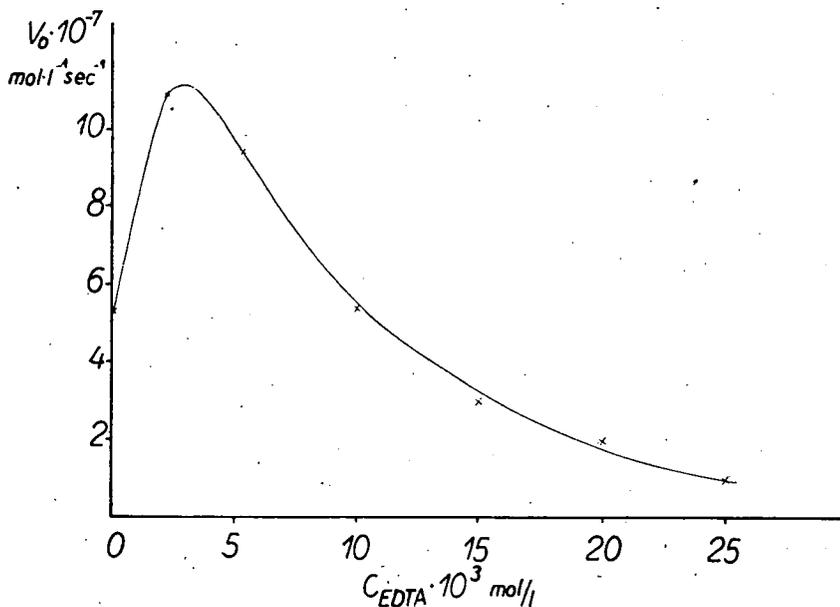


Fig. 1

one coordination site and is connected, to the adjacent coordinated hydroxide or fluoride ion by a hydrogen bridge. This picture would explain the experience that the fluoride ions do not inhibit the decomposition. Referring to this suggested mechanism I have to mention that YATSIMIRSKII explains the great catalytic activity of ThOH^{3+} complex on the decomposition of hydrogen peroxide by the formation of a mixed complex of similar structure, in which also a hydrogen bond makes possible the formation of the chelate ring [8].

The great catalytic effect of the complex allows the simple permanganometric determination of minute amounts of iron [9]. Namely, at pH 10 there is a linear relation between the concentration of iron and the amount of hydrogen peroxide decomposed during a given time. The buffer capacity of triethylenetetramine is enough to assure the constant pH. Three minutes of reaction time proved to be optimal. The amount of non-decomposed hydrogen peroxide is determined by a simple permanganometric titration. As little amounts as $0.03 \mu\text{g}$ iron can be determined by this method without instrumental equipment. Due to the specificity of this reaction — only the manganese(II) complex can catalyze the decomposition — the determination is not disturbed by a number of different ions.

The iron(II) and iron(III) ions themselves can catalyze the decomposition of hydrogen peroxide in acidic solution. This catalytic effect is inhibited by ethylenediaminetetraacetic acid (EDTA) which forms a catalytically inactive, stable complex with iron(III). It is interesting, however, that in dilute solution, if the concentration of EDTA is less than that of iron(III), the catalytic activity increases, *i. e.* the velocity *versus* EDTA concentration curve shows a definite maximum [10].

This interesting effect can be explained by the formation of a binuclear iron(II)-iron(III)-EDTA complex which is a more effective catalyst than either the iron(III) or iron(II) ions due to the decrease of *Franck-Condon* barrier, namely, the catalytic effect is connected with the change in valence state.

I have to deal with the role of pH at least in a few words. The amount and the decomposition of complexes depend on the pH. At lower pH protonated species, at higher pH hydroxo complexes form. The proton concentration may influence the structure and the reactivity of the reactants, too. The pH dependence of oxidation of histidine with persulphate ion influenced by copper(II) ion is worthy to mention. At about pH 6 the complex formation retards, in alkaline solution (pH 12—13) it promotes the oxidation [11].

Let us turn our attention to another aspect, namely to the oxidation of aminopolycarboxylic acids and their metal complexes [12]. The aminopolycarboxylic acids, for example EDTA, are easily oxidized by strong oxidizing agents. In acidic solution the oxidation with permanganate at 60° takes place smoothly, one molecule of EDTA consuming six equivalents of permanganate. The further oxidation takes place so slowly that a sharp endpoint can be observed. This reaction can be applied to the permanganometric determination of EDTA, however, this means that it is impossible to determine permanganometrically another substance in the presence of EDTA. It was observed, however, that in the presence of bismuth ions, which form complex in the relatively strong acidic medium necessary for the oxidation by permanganate, the EDTA cannot be oxidized, *i. e.* the complex formation protects the ligand against the oxidation. This protective effect renders possible on the one hand the permanganometric titrations in the presence of EDTA, and on the other hand the indirect permanganometric determination of bismuth and may be that of some other metal ions which form very stable complexes with EDTA. It is even possible to determine different metal ions in the presence of each other, with titrations performed at different *pH*. But the diethylenetriaminepentaacetic acid can be oxidized by permanganate in the presence of large excess of bismuth ions. This fact seems to prove the nonexistence of stable polynuclear bismuth (III)-diethylenetriaminepentaacetic acid complex.

The above results suggest that it is possible to decide by a direct chemical method between the different types of coordination of EDTA to different metal ions [13]. For this purpose we compared the oxidation of EDTA in the presence of excess bismuth and that of the inert Cr(III) EDTA complex by permanganate. The bismuth-(III) EDTA complex is oxidized very slowly, while the oxidation of Cr(III) EDTA proceeds much faster. Under similar conditions the reduction of permanganate by free EDTA is completed within 30 seconds. This characteristic behaviour may be explained most simply by the existence of at least one free functional group in the Cr(III) EDTA compound, *i. e.* by the pentadentate nature of EDTA in this complex. From the hydrogen ion concentration dependence of velocity it could be concluded that the protonation of this free carboxylic group also causes a less reactivity. The

photochemical oxidation of EDTA by methylene blue is also retarded by metal ions and this effect has been analytically applied [14].

FEIGL observed first the protective effect of complex formation against the oxidation of oxalate ion, applying molybdenum(VI) for complexation. In the case of chromium(III) the protective effect is much stronger owing to the inertness of the complex — one chromium(III) ion quantitatively protects two oxalate ions. On the basis of this behaviour, the indirect permanganometric determination of chromium(III) could be elaborated [15].

The oxalate ion can be reduced by chromium(II). It is surprising that TAUBE observed [16] the protective effect of complex formation with chromium(III) against the reduction, too. So it seems probable that the less reactivity is caused not only by the change in the electron distribution of ligand, but also by the fact that there is no possibility of forming an activated complex in the usual way, owing to the blocking of carboxylic groups by complex formation.

An extremely interesting feature of the oxidation of a free functional group of ligand was pointed out by TAUBE *et al.*: The oxidation of $\text{Co}(\text{NH}_3)_5\text{C}_2\text{O}_2^+$ [17] and $\text{Co}(\text{NH}_3)_5\text{OOCCH}_2\text{CHO}^{++}$ [18] complexes with one-electron oxidizing agents results in the reduction of central cobalt(III) ion, whereas it is not effected by two-electron oxidizing agents. The experiences with the latter complex reveal the electron conduction through the conjugated system.

Now I should like to deal with the oxidation of cobalt(II)-aminopolycarboxylic acid complexes by chromium(VI). Studying the cobalt(II)-EDTA-chromium(VI) system, GORO and KOBAYASHI [19] suggested spectrophotometric determination both of cobalt and chromium. They gave a rough estimation on the composition of the „double complex” formed: $(\text{Co-EDTA})_7\text{Cr}_2\text{O}_7$. On the basis of the comparative study of oxidation of different aminopolycarboxylic acid complexes by chromium(VI), perhaps we can understand somewhat more about the mechanism of these extremely complicated reactions.

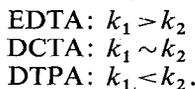
The reaction takes place in acidic medium (pH 1—2), where the cobalt(II) is only partially complexed by the applied aminopolycarboxylic acids, EDTA, diaminocyclohexanetetraacetic acid (DCTA) and diethylenetriaminepentaacetic acid (DTPA) and beside the hexa-coordinated complexes the different protonated species and cobalt(II) aquocomplex are present in considerable concentration.

The redox potential of the Co(III)—Co(II) system being greater than that of the Cr(VI)—Cr(III) one, only the complexed cobalt(II) can be oxidized. So in this case there is a change in the thermodynamical reactivity. The different aminopolycarboxylic acid-cobalt(II) complexes show characteristic behaviour. At 550 $m\mu$ a monotonic increase of absorbancy is found in all cases. In the case of DCTA and DTPA complexes the limiting values are the sums of absorbancies of Co(III)- and Cr(III)-aminopolycarboxylic acid complexes, while with EDTA the absorbancy is much greater than this sum. However, in the latter case there is a slow decrease of extinction and after some twenty hours the absorbancy becomes equal to the sum of the absorbancies of Co(III) EDTA and Cr(III) EDTA complexes. At 350 $m\mu$ wavelength the absorbancy first increases and reaches a limiting value, and then decreases very slowly in the case of EDTA, it shows a little increase, and then a relatively fast decrease with DCTA, while in the case of DTPA there is a fast, monotonic decrease. In considering this characteristic behaviour, one must bear in mind that the chromium(VI) has the greatest absorbancy among the reactants and end pro-

ducts at this wavelength. Consequently, in the case of EDTA there is a stable intermediate of so great absorbancy that the decrease of extinction due to the disappearance of chromium(VI) is overcompensated. This intermediate also appears in the case of DCTA, but it cannot be observed with DTPA. The reduction of chromium(VI) to chromium(III) takes place in two or more, probably in three steps. So the following schematic mechanism seems obvious:



Without making any statement on the stoichiometry of reaction and the structure of intermediate, it is plausible on the basis of the above spectrophotometric observations that the relation between k_1 and k_2 is as follows:



From the change of absorbancy as a function of cobalt(II) concentration, when the concentration of chromium(VI) was kept constant and from the change of absorbancy in the inverse case (constant cobalt(II) and varying chromium(VI) concentrations) it could be concluded that in each of the three cases the chromium(VI) is only partly reduced by cobalt(II). With the EDTA and DCTA complexes two electrons, with the DTPA complex only one electron comes from cobalt(II). Further reduction may occur at the expense of excess aminopolycarboxylic acids or the bound water. It is to be mentioned that the chromium(VI) oxidizes the water infinitesimally slowly and the aminopolycarboxylic acids very slowly, but the induced redox reaction can easily be imagined in both cases.

The experimental material at hand gives only limited possibilities to speculate on the structure of intermediate, that is on the fine mechanism of reaction. Nevertheless, it seems probable that it is not the polydentate ligand that sets up connection between the two central ions, namely between the cobalt(II) and chromium(VI), because, in lack of mobile electrons in the ligand, it would be hard to imagine the transition of an electron from cobalt(II) to chromium(VI). So there are only two real possibilities: either the chromium(VI) enters the coordination sphere of cobalt(II) by substituting a coordinated water molecule, or the coordinated water molecule itself plays the role of the bridge by hydrogen bond. After the rearrangement of electrons an intermediate forms in which the valence of chromium is five. In the case of EDTA and DCTA complexes the reduction of chromium(V) to chromium(IV) takes place by a second cobalt(II) complex according to the formerly mentioned mechanism. So the stable intermediate is probably a polynuclear complex with two cobalt(III) and one chromium(IV) central ion.

As a result of the fact that the EDTA and probably the DCTA incline to behave as pentadentate ligands — as it has been demonstrated formerly in this paper, — while it can be expected that the eight functional groups of DTPA tend to occupy all of the six coordination positions, the different behaviour of the aminopolycarboxylic acids can be understood.

The problem treated being manifold, it was impossible to deal with the whole field; nevertheless I hope the examples given suitably illustrate the importance of the subject from the point of view of theoretical and analytical chemistry.

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ОБРАЗОВАНИЕ КОМПЛЕКСОВ И РЕАКЦИОННАЯ СПОСОБНОСТЬ

M. T. Бек

Работа излагает факторы влияющие изменения в реакционной способности в следствии образования комплексов. Также описываются некоторые применения в аналитике.