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Reactivity of Coordinated Substances

I. The Oxidation of EDTA Bound in the Cr(III)EDTA Complex by Permanganate Ion

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Earlier observations showed that free EDTA is oxidised by permanganate ion in acidic solution. Addition of Bi(III) in excess to EDTA results in a marked decrease of the reaction rate: the complex formation with Bi(III) protects the EDTA [1] against the oxidising effect of MnO_4^-.

This qualitative result suggests that it is possible to decide by a direct chemical method between the different types of coordination of EDTA to different metal ions. For this purpose we compared the oxidation of EDTA in the presence of excess Bi(III) and that of the inert Cr(III) EDTA complex by MnO_4^-. The reaction was studied in perchloric acid medium at $20 \pm 1-2°C$ by means of spectrophotometric investigations.

As is shown in Fig. 1, the Bi(III)EDTA complex is oxidised very slowly (curve 1), while the oxidation of Cr(III)EDTA takes place much faster (curve 2). Under similar conditions the reduction of MnO_4^- by free EDTA is completed within 30 sec. 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.* the pentadentate nature of EDTA in this complex [2].

If Bi(III) is added to the Cr(III)EDTA the oxidation rate decreases (curve 3). This effect can be interpreted by an interaction of free Bi(III) and Cr(III)EDTA. It must be mentioned, however, that so far this interaction could not be demonstrated by other methods.

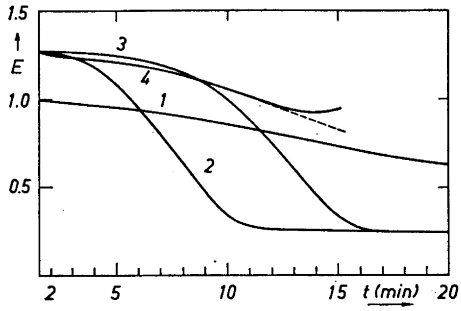

Fig. 1. Change of extinction (E) with time (t) of the following solutions: Curve 1. 2×10^{-3} M Bi(III), 10^{-3} M EDTA, 2.12×10^{-4} M MnO_4^-, 0.23 M $HClO_4$. Curve 2. 10^{-3} M Cr(III)EDTA, 2.12×10^{-4} M MnO_4^-, 0.23 M $HClO_4$. Curve 3. 10^{-3} M Cr(III)EDTA, 2×10^{-3} M Bi(III), 2.12×10^{-4} M MnO_4^-, 0.23 M $HClO_4$. Curve 4. 10^{-3} M Cr(III)EDTA, 2.12×10^{-3} M Mn(II), 2.12×10^{-4} M MnO_4^-, 0.23 M $HClO_4$. Wavelength 525 mμ, cell length 2 cm.

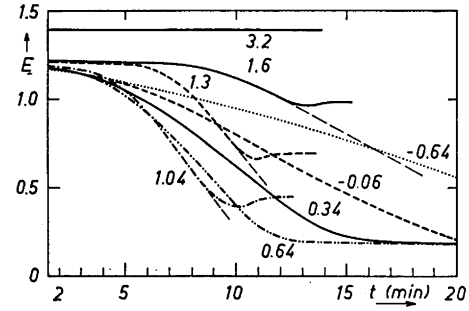

Fig. 2. The effect of pH on the reduction of MnO_4^- by Cr(III)EDTA complex. Numbers indicate pH values of solutions: 10^{-3} M Cr(III)EDTA, 2.12×10^{-4} M MnO_4^-. Wavelength 525 mμ, cell length 2 cm.

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The shape of the curves shown in Fig. 1 is typical for autocatalytic processes, evidently due to the effect of Mn(II) formed during the reaction. Studying the influence of a large excess of Mn(II) it was observed that the reaction rate also decreases (curve 4). The Mn(II) ions have a double role, an accelerating one and a retarding one, the latter being presumably effected by an interaction with Cr(III) EDTA similar to that in the Bi(III) case.

It does not seem likely that the observed decrease of the reaction rates after addition of Bi(III) or Mn(II) is due only to a salt effect (cf. Ref.[3]). Any comparison with the permanganate-oxalate reaction is of course a very conditional one, it is found, however, that the influence of the ionic strength on the reaction rate may be either positive or negative [4]. Corresponding spectrophotometric investigations at 525 mμ made by Malcolm and Noyes [5] give the same qualitative shape of the curves as is shown in Figs. 1 and 2. They observed an increase of the reaction rate with increasing initial Mn(II) concentration. The permanganate-citrate oxidation [6,7] lead in the cases mentioned to opposite conclusions about the direction of the influence of added Mn(II). In any case, however, irrespective of the mechanism discussed, a direct association with the substance to be oxidised is proposed. Further investigations in this field will have to take account of these interferences.

The influence of hydrogen ion concentration on the oxidation of Cr(III)EDTA is shown in Fig. 2. Due to the complicated mechanism of the overall reaction it is difficult to find a definite measure of the reaction rate. But using either halftime or slope in the inflection point of the different curves the velocity of oxidation as a function of pH shows in every case a maximum at about pH 1. This sort of influence by hydrogen ions can hardly be explained otherwise than by the assumption that Cr(III)EDTA exists in acidic medium in two species of different reactivity. Although nothing is known about the molecularity of the oxidation reaction studied, it is very probable that the nonprotonated species is oxidised faster. Therefore on the basis of the results of the foregoing experiments, the following definite qualitative conclusions may be drawn:

The oxidation of complex bound EDTA by MnO_4^- depends primarily on the structure of the complex. The free functional groups are the most vulnerable.

Both protons and metal ions protect these groups against oxidation, the protective effect of the latter being greater.

Experimental. H[Cr EDTA (H_2O)] was prepared following Hamm [8] and three times recrystallised, the last recrystallisation under addition of HCl. The product proved to be free of Cl^-.

The extinction measurements were made in a 2 cm cell using an air thermostated CARY Spectrophotometer Model 11MS-50 at 525 mμ, *i.e.* the absorption maximum of MnO_4^- ion.

The solutions were made from stock solutions of 10^{-2} M H[Cr EDTA (H_2O)], 2.12×10^{-3} M MnO_4^-, 2.3 M $HClO_4$, and 10^{-2} M $Bi(NO_3)_3 \cdot 5H_2O$ in 10^{-1} M $HClO_4$.

The measurements of absorbancy were started 90 sec. after addition of MnO_4^-. At lower acidities (pH > 1) it was impossible to follow the reaction to completion, due to the transient formation of MnO_2 as it is indicated by a reincrease of extinction.

pH-Values were determined by means of a pH-Meter 3 (Radiometer, Copenhagen) or calculated with sufficient accuracy from the amount added of perchloric acid, using the pK-values given for H[Cr EDTA (H_2O)] by Furlani [2].

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