Inorganica Chimica Acta, 18 (1976) L17

Oxidation of Hydrazine by Chromium(VI). A Comment

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(Received January 19, 1976)

The kinetics of the oxidation of hydrazine by chromium(VI) in the absence and presence of complex-forming agents have been studied in some detail in the past few years. A recent paper by Ramanujam, Sundaram and Venkatesubramanian[1] reported some data which are in contradiction with our own previous findings[2-4] concerning the dependence of the rate on the concentration of EDTA. Since these data are of crucial importance as regards the mechanism of the reaction, we have reinvestigated the reaction and found that the reason of the contradiction is that the experiments of Ramanujam *et al.* were not always well-designed, and in some cases chemical meaning was attributed to experimental errors.

Ramanujam *et al.* found that the rate of the reduction of chromium(VI) changes in accordance with a fairly complicated function when the concentration of EDTA is increased at constant concentrations of chromium(VI) and hydrazine sulphate. First, there is an increase of rate to a maximum, and finally a decrease again. The first maximum occurs when the ratio EDTA:Cr(VI) = 1:2, and the second maximum at a ratio of 1:1. They found further that the absorbancy of the chromium(VI) changes in accordance with a strictly similar pattern as a function of EDTA concentration, confirming the formation of the two complexes of the above composition.

In the experiments of Ramanujam *et al.*, the results of which are listed in Table V of their paper, the hydrogen ion concentration was not kept constant. On reproducing their experiments, we found that there is a considerable change of pH, depending on the concentration of EDTA. The pH of the reaction mixtures and the rate of the reaction are plotted in Fig. 1.

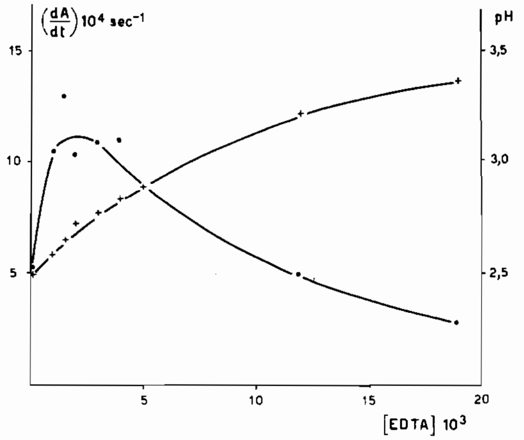

Fig. 1. Dependence of the rate of change of absorbance at 350 nm as a function of EDTA concentration. The change of the pH is also plotted. Initial concentration of the reaction mixture: $[N_2H_4 \cdot H_2SO_4] = 3.6 \times 10^{-3}$ mol dm^{-3}, $[CrO_3] = 3 \times 10^{-3}$ mol dm^{-3}. EDTA was added in the form of disodium salt. T = 25 °C.

Our finding concerning the rate of the reaction as a function of EDTA concentration is similar to the results of Ramanujam *et al.*, although the maximum rate-increasing effect of EDTA was found much smaller, just as in our former experiments. There is undoubtedly a rate maximum, which is evidently due to the fact that the rate-diminishing effect of the increasing pH overcompensates the rate-increasing effect of the EDTA. The change of pH greatly influences the molar absorbancy of chromium(VI), and therefore there is no simple, unequivocal connection between the rate of change of absorbancy and the reaction rate. The situation is further complicated by the fact that under the conditions applied by Ramanujam *et al.* there is a considerable change in the hydrogen ion concentration of the mixture *during* the reaction.

Complex formation between chromium(VI) and EDTA was assumed by us, but we could not obtain any direct experimental evidence for such an interaction. Besides spectrophotometric experiments, a great number of solubility measurements were performed, without any indication of formation of a chromium(VI)–EDTA complex. The data in Figure 5 of ref. 1 are far from convincing as regards complex formation. The measured absorbancies are very small, and at 350 nm the experimental error is too large. If the two maxima on the curve were real, the formation of as many as four stable chromium(VI)–EDTA species would necessarily have to be assumed. The only explanation is that the authors attributed chemical significance to absorbency changes within the experimental error.

References

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