Inorganica Chimica Acta, 100 (1985) 219–222

Solvent Influence on Rate and Mechanism of Oxidation of Ethylenediaminetetraacetatocobaltate(II) by Periodate

AHMED A. ABDEL-KHALEK* and MAHMOUD M. ELSEMONGY

Chemistry Department, Faculty of Science, Kuwait University, P.O. Box 5969, Kuwait

Received August 3, 1984

Abstract

The kinetics of the oxidation of $Co^{II}(EDTA)^{2-}$ by IO_4^- were studied in various ethanol + water mixtures covering the range 7.9 to 58.0 wt% ethanol, at five different temperatures in the range 15–35 °C. The effect of solvent on the rate and mechanism of the reaction was investigated. An inner-sphere mechanism for the reaction was proposed and supported by the calculated activation parameters.

Introduction

Although electron transfer reactions have been studied extensively, the influence of changes of solvent on such reactions has received comparatively little attention [1–7].

The oxidation of $Mo(CN)_8^{4-}$ [6] and of $Co^{II}(NTA)(H_2O)_2^-$ [7] (NTA = nitrilotriacetate) by periodate in ethanol + water mixtures has previously been studied in this laboratory. It was found that the rate of $Mo(CN)_8^{4-}$ oxidation passed through a maximum with increasing ethanol content [6], whereas the rate of oxidation of $Co^{II}(NTA)(H_2O)_2^-$ passed through a minimum [7] with increasing ethanol content. Mechanisms for these two reactions have been proposed [6, 7] which involve catalysis by H_3O^+ and by SH^+ (where S is an organic solvent molecule).

Here we report on the rate of oxidation of $Co^{II}(EDTA)^{2-}$ by periodate in ethanol + water mixtures. The reaction was previously studied [8] in aqueous solutions and an inner-sphere mechanism assigned. The evidence for an inner sphere mechanism included the rapid formation and slow decomposition of an initial Co(III) product. The rate law for this reaction is given by eqn. 1:

$$d[Co^{III}]/dt = k^{e.t.} \cdot K[Co^{II}(EDTA)^{2-}][IO_4^-]/(1 + K[IO_4^-]) \quad (1)$$

A fast equilibrium step precedes the slow intramolecular electron-transfer (e.t.) step [8].

Experimental

Analar ethanol (BDH) was used. Reagent grade of the other chemicals were used without further purification. Stock solutions of $NaIO_4$, wrapped in foil to avoid photochemical decomposition [9], EDTA (disodium salt), CH_3COONa and of $NaNO_3$ were made up by weight. Cobalt(II) nitrate solution was standardized volumetrically against EDTA [10]. Sodium acetate–acetic acid buffers of known concentrations were used. Ionic strength was adjusted with $NaNO_3$.

Stability of $Co^{II}(EDTA)^{2-}$ and $Co^{III}(EDTA)^-$ towards ethanol was checked, and no reaction was observed over the time taken for the measurements. It is known [11] that ethanol is stable towards periodate and this was verified experimentally for the solutions used.

The dielectric constants of ethanol + water solvent mixtures, used to study the dielectric constant effect on reaction rate, were obtained from the reported data [12].

Kinetic Procedure

The kinetic procedure was similar to that described for the $Co^{II}(EDTA)^{2-}/IO_4^-$ reaction in aqueous solutions [8]. The $Co^{II}(EDTA)^{2-}$ complex was made up in solution and contained about 20% excess of the ligand to ensure complete formation, as a precipitate occurred when the metal ion:ligand ratio was 1:1. The rate of formation of the initial cobalt(III) product was followed at 534 nm, where its absorption was maximal, on a Unicam SP 8000 spectrophotometer. Our studies covered the solvent composition 7.9–58.0 wt% ethanol. Attempts at measurements in solvents containing 63 wt% ethanol or more failed as precipitates occurred.

All measurements were made under pseudo first-order conditions of large excess of periodate concentration.

---

*Author to whom correspondence should be addressed.

0020-1693/85/$3.30

Results and Discussion

The stoichiometric equation of the reaction [8] is represented by

$$2CoEDTA^{2-} + IO_4^- \longrightarrow 2CoEDTA^- + IO_3^- \qquad (2)$$

As in the aqueous medium [8], oxidation of $Co^{II}(EDTA)^{2-}$ by IO_4^- proceeds *via* the formation of initial cobalt(III) product which was slowly converted to the hexadentate $Co^{III}(EDTA)^-$ product. This product was identified spectrophotometrically as indicated by its maxima and molar absorptivity [8]. The reaction proceeds with an apparent pseudo first-order rate constant k_{obs} determined from the slope of the straight lines obtained by plotting $\ln(A_\infty - A_t)$ *vs.* time, using a linear least-squares program. These plots were linear up to ≥85% of reaction.

The dependence of reaction rate on both $[Co^{II}(EDTA)^{2-}]$ and $[IO_4^-]$ was studied in 7.9, 31.6 and 58.0 wt% ethanol at 25 °C. The results, included in Table I, show that the reaction is first-order in both complex and periodate as found earlier in the aqueous medium [8], as shown in Fig. 1.

The variation of k_{obs} with $[IO_4^-]$ in ethanol + water solvent mixtures differs from that in aqueous solutions [8]. First-order rate constants k_{obs}, Table I, give a linear dependence on $[IO_4^-]$ which is represented by eqn. 3:

$$k_{obs} = k_2[IO_4^-] \qquad (3)$$

In order to check the dependence of reaction rate on hydrogen ion concentration in ethanol + water solvents, a number of runs were made in 31.6 wt% ethanol at 25 °C. The results, included in Table I, show that the reaction rate is not affected by variation of $[H^+]$ over the range 0.63×10^{-5}–7.94×10^{-5} M, as found earlier in aqueous solutions [8].

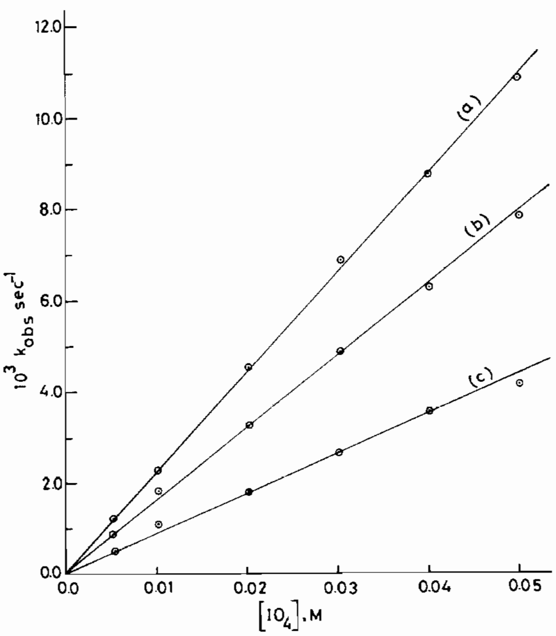

Fig. 1. Dependence of k_{obs} on $[IO_4^-]$ in (a) 7.9, (b) 31.6, (c) 58.0 wt% ethanol.

The rate law is thus expressed in the form:

$$Rate = k_2[Co^{II}(EDTA^{2-})][IO_4^-] \qquad (4)$$

Results included in Table II show that the reaction rate decreases gradually with increasing ethanol content in the solvent mixture, *i.e.* the reaction rate decreases with decreasing dielectric constant. Further, a plot of log k_{obs} as a function of the reciprocal of the dielectric constant D^{-1} of the medium gives a straight line, as shown in Fig. 2.

To study the effect of temperature, the reactions were carried out at five different temperatures in the range 15–35 ± 0.05 °C at constant $[H^+]$ and

TABLE I. Kinetic Data for the Oxidation of $Co^{II}EDTA^{2-}$ by IO_4^- at I = 0.25 M and 25 °C.[a]

$10^5\,[H^+]$ (M)	$10^2\,[IO_4^-]$ (M)	$10^3\,[Co^{II}EDTA^{2-}]$ (M)	$10^3\,k_{obs}\,s^{-1}$		
			7.9 wt%	31.6 wt%	58.0 wt% Ethanol
3.16	5.0	0.5	10.75	7.75	4.10
3.16	4.0	0.5	8.70	6.25	3.45
3.16	3.0	0.5	6.81	4.78	2.58
3.16	3.0	1.5	–	4.71	–
3.16	3.0	2.0	–	4.82	–
0.63	2.0	0.5	–	3.18	–
3.16	2.0	0.5	4.50	3.21	1.81
7.94	2.0	0.5	–	3.17	–
3.16	1.0	0.5	2.25	1.82	1.05
3.16	0.5	0.5	1.20	0.82	0.51

[a] Standard deviations in k_{obs} = 4%.

TABLE II. Kinetic Data for the Oxidation of Co^{II}EDTA^{2-} by IO$_4^-$ for Various Ethanol + Water Solvent Mixtures at [Co^{II}-EDTA^{2-}] = 5.0 × 10^{-4} M, [IO$_4^-$] = 3.0 × 10^{-2} M, I = 0.25 M and [H$^+$] = 3.16 × 10^{-5} M.[a]

Ethanol wt%	D at 25 °C	D at 30 °C	10 k_2 M^{-1} s^{-1}				
			15 °C	20 °C	25 °C	30 °C	35 °C
7.9	73.8	72.3	1.25	1.72	2.27	3.13	4.10
23.7	64.5	62.5	1.07	1.39	1.73	2.26	2.74
31.6	59.8	58.0	1.01	1.29	1.59	1.98	2.44
42.1	54.0	52.0	0.89	1.09	1.28	1.66	1.96
51.4	48.5	47.0	0.78	0.90	1.03	1.24	1.41
58.0	44.6	43.2	0.65	0.74	0.86	0.99	1.12

[a] Standard deviation in k_2 = 5%.

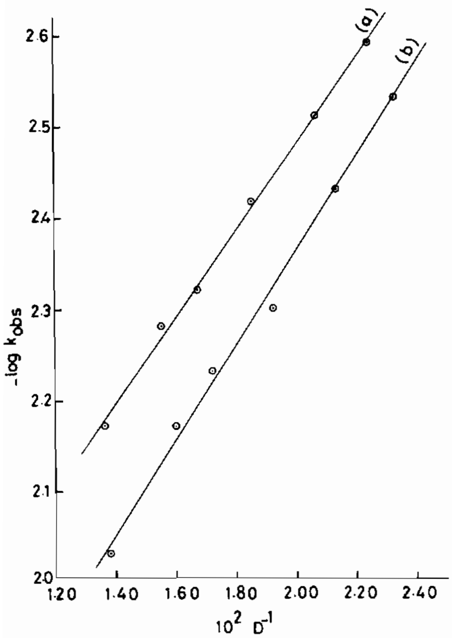

Fig. 2. Plots of log k_{obs} against D^{-1} at (a) 25.0, and (b) 30.0 °C.

TABLE III. Activation Parameters in Ethanol–Water Solvent Mixtures at 25 °C.

Ethanol wt%	ΔH^* kJ mol^{-1}	$-\Delta S^*$ J mol^{-1} K^{-1}	ΔG^* kJ mol^{-1}
7.9	42.3 ± 1.2	115.1 ± 5.1	76.6 ± 2.7
23.7	33.1 ± 1.1	148.2 ± 5.5	77.3 ± 2.7
31.6	30.8 ± 1.3	156.7 ± 4.9	77.5 ± 2.8
42.1	27.7 ± 1.2	168.8 ± 5.7	78.0 ± 2.9
51.4	20.1 ± 1.0	196.1 ± 5.6	78.5 ± 2.7
58.0	18.3 ± 1.1	204.0 ± 6.1	79.1 ± 2.9

ionic strength in various ethanol + water solvent mixtures, Table II. Enthalpy ΔH^* of activation associated with k_2 and the corresponding entropy, ΔS^*, and free energy, ΔG^*, of activation for various solvent compositions were calculated from a linear least-squares fit to the Eyring equation, Table III. The effect of solvent on the reaction rate can be examined in terms of changes in the activation parameters. These parameters are usually taken as a measure of the solvent effects. It is seen from Table III that ΔG^* increases gradually with increasing ethanol content. Some useful insight into the changes in the structural aspects of the solvents may be obtained from the changes in the enthalpy and entropy of activation which contain important structural contributions [13]. The enthalpy of activation, ΔH^*, decreases whereas the large negative value of ΔS^* increases gradually with progressive addition of ethanol, Table III.

From the kinetic results, as well as the observed rate law, an inner-sphere mechanism [8] for the oxidation of Co^{II}(EDTA)$^{2-}$ by periodate in ethanol + water solvent mixtures may be described by eqns. 5 and 6:

$$\mathrm{Co^{II}(EDTA)^{2-} + IO_4^-} \rightleftharpoons \mathrm{[(EDTA)Co^{II}{-}OIO_3]^{3-}} \quad K \qquad (5)$$

$$\mathrm{[(EDTA)Co^{II}{-}OIO_3]^{3-}} \longrightarrow \mathrm{[(EDTA)Co^{III}{-}OIO_3]^{2-}} \quad k^{\mathrm{e.t.}} \qquad (6)$$

The inital cobalt(III) product may be converted to a final product according to eqn. 7:

$$\mathrm{[(EDTA)Co^{III}{-}OIO_3]^{2-}} \longrightarrow \mathrm{Co^{III}(EDTA)^- + I^{VI}} \qquad (7)$$

$$\mathrm{2I^{VI}} \longrightarrow \mathrm{IO_4^- + IO_3^-} \qquad (8)$$

This mechanism is constant in all ethanol + water solvent mixtures, as shown by the range of activation parameter values.

References

1 M. J. Blandamer and J. Burgess, *Pure Appl. Chem., 51*, 2087 (1979).

2 K. Ohashi, T. Amano and K. Yamamoto, *Inorg. Chem., 16*, 3364 (1977).

3 M. Kimura and G. Wada, *Inorg. Chem., 17*, 2239 (1978).

4 D. Cohen, J. C. Sullivan, E. S. Amis and J. C. Hindman, *J. Am. Chem. Soc., 78*, 1543 (1956).

5 B. R. Baker, F. Basolo and H. M. Neumann, *J. Phys. Chem., 63*, 371 (1959).

6 A. A. Abdel-Khalek and M. M. Elsemongy, *Monatsh. Chem.* (1984) (in press).

7 A. A. Abdel-Khalek and M. M. Elsemongy, *Transition Met. Chem.* (1984), in press.

8 A. Y. Kasim and Y. Sulfab, *Inorg. Chim. Acta, 24*, 247 (1977).

9 F. S. H. Head and H. A. Standing, *J. Chem. Soc.*, 1457 (1952).

10 A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis, 3rd ed.', Longmans, London, 1961, p. 443.

11 G. J. Buist and S. M. Tabatabal, *J. Chem. Soc., Faraday Trans. 1, 75*, 631 (1979).

12 G. Akerlof, *J. Am. Chem. Soc., 54*, 4125 (1932).

13 W. L. Reynolds and R. W. Lumry, 'Mechanisms of Electron Transfers', Ronald, New York, 1966; E. S. Amis, 'Solvent Effect on Reaction Rates and Mechanisms', Academic Press, New York, 1966.