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Oxidation of Ethylenediaminetetraacetatocobaltate(II) by Periodate in Aqueous Acidic Solutions

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The kinetics of oxidation of $CoEDTA^{2-}$ by periodate follow the rate law (i)

$$Rate = \frac{k_3K_1[CoEDTA^{2-}][L^-]}{1 + K_1[L^-]}$$

Where $[L^-]$ is the total periodate concentration, k_3 is the rate constant for the electron-transfer process, and K_1 is the pre-equilibrium formation constant. Activation parameters are reported. An intermediate was identified spectrophotometrically which slowly forms hexadentate $CoEDTA^-$. The rate of this ring closure has been measured.

Introduction

Oxidation by periodate species seems to prefer an inner-sphere mechanism. In its oxidation of 1,2-diols formation of cyclic intermediates was proposed, and the form of the rate law lends support to this mechanism [1]. Its oxidation of iodide conforms with this mechanism as oxygen atom transfer was proposed [2]. Additional support for this hypothesis is obtained from reactions of this oxidant with some inorganic substrates. Thus it was observed that the labile aquametal ions V(IV) and Fe(II) and inert $Fe(CN)_6^{4-}$, with the cyano ligand capable of bridging, are rapidly oxidised [3–5], whereas the inert complex $Fe(phen)_3^{2+}$ (Phen = 1,10-Phenanthroline) is only slowly oxidised [6]. The product of oxidation by this oxidant is not the well known $Fe(Phen)_3^{3+}$ with its characteristic blue colour. The product of oxidation is probably a binuclear species, as observed in the inner-sphere oxidation of this reductant by ClO_2^- and Cl_2 [7]. The mechanism of oxidation of V(IV) has been assigned as inner-sphere mechanism by comparing its rate constant with that of Fe(II) under similar conditions using Rosseinsky's approach [3, 8]. An inner-sphere mechanism also seems to be operating in the oxidation of Fe(II) as the stopped-flow traces show a rapid formation and a slow decomposition of an intermediate with an induction period [4].

In this study we report our findings on the oxidation of the Co(II)–EDTA complex by periodate. The choice of this complex is relevant as it is labile and substitution into its inner-coordination sphere is likely prior to electron transfer. Some information on the mechanism of oxidation might also be inferred from the initial Co(III) product as Co(III) complexes are, usually, substitutionally inert.

Experimental

Materials

B.D.H. Analar grade sodium periodate, cobalt nitrate, disodium ethylenediaminetetracetate and acetic acid were used. Standard solutions were prepared by weight except that Co(II) nitrate solutions were standardised with EDTA volumetrically [9].

Kinetic Procedure

The two reactants were added each to one of the two compartments of an indented vessel containing the desired buffer. The Co(II)–EDTA complex contained a slight excess of EDTA to inhibit any catalysis by trace amounts of metal-ion impurities. Cu(II) ions have been shown to catalyse oxidations by periodate ions in acetate buffers [10]. After allowing 20–30 minutes for temperature equilibration, the reactants were thoroughly mixed and some of the reaction mixture quickly transferred to a 4 cm cell. The rate of the reaction was monitored as a function of time at 534 and 360 nm on a Unicam SP 700 spectrophotometer equipped with temperature cell-holders. The change in absorbance at 360 nm showed a relatively rapid increase and then a slow decrease with time indicating two reactions. The pH of the reaction solution was measured on a Radiometer digial pH meter model PHM 62. The spectrum of the product Co(III) was recorded on a Unicam SP 8000 spectrophotometer.

Pseudo first-order conditions were maintained in all runs by using a large excess of periodate concentration over that of the complex. The effect of varying the pH, ionic strength and temperature on the reaction rate was also investigated.

Results

Products and Stoichiometry

The nature of the primary product was determined spectrophotometrically. The spectrum of the Co(III) product was recorded as function of time. Figure 1 clearly shows that the initial product is neither hexa-

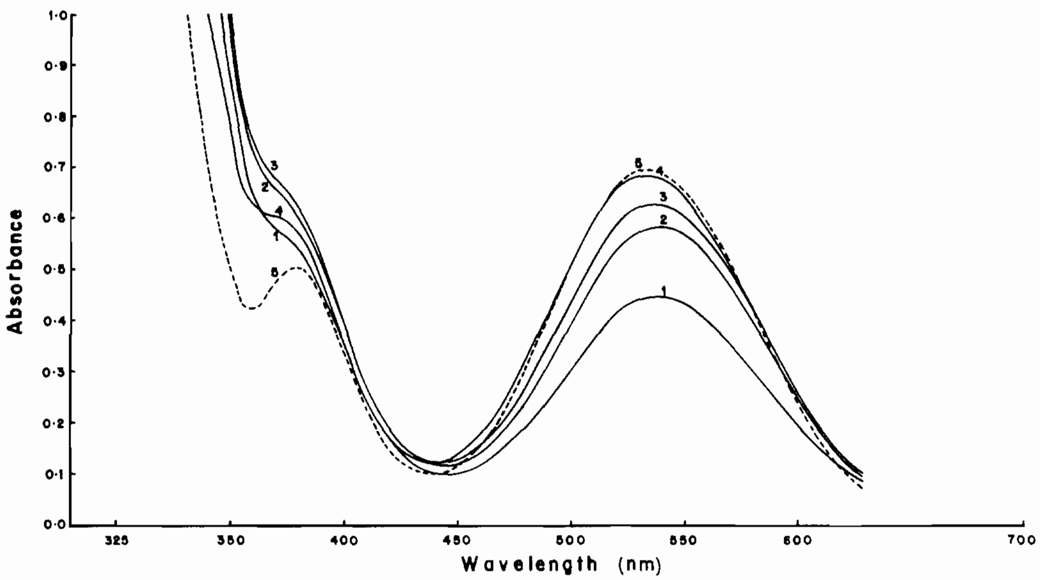

Figure 1. Change in absorbance as a function of time (curves 1–4). Curve 5 shows the final absorbance for the Co(III) product.

TABLE I. Stoichiometric Results

10^3 [CoEDTA^{2-}]$_0$ M	10^4 [Periodate]$_0$ M	10^3 [CoEDTA$^-$] M	[CoEDTA$^-$]/[Periodate]
2.50	7.60	1.50	1.97
2.50	9.20	1.83	1.99
3.50	10.00	2.02	2.02
3.50	12.00	2.41	2.01

dentate CoEDTA$^-$ nor CoEDTA(OH$_2$). The spectrum of these complexes is well characterised [11]. The absorption of the initial Co(III) product increases with time to reach its maximum value, which almost remains constant in the wavelength range 530–540 nm, but slowly decreases at wavelengths below 400 nm with formation of a peak at 380 nm. The final spectrum, recorded after 24 hours, is identical to that of hexadentate CoEDTA$^-$ with peaks at 534 and 379 nm [11]. The ratio of the molar absorptivities at the two maxima is in agreement with literature values, thus indicating quantitative formation of CoEDTA$^-$ [11, 12].

The stoichiometry of the reaction was investigated by measuring the absorbance of the reaction product at 377 and 534 nm after at least 24 hours from the onset of the reaction. The Co(II) complex concentration was always greater than twice the concentration of periodate used. Table I summarises the stoichiometric results. The last column shows that the reaction could be represented by eq. 1:

$$2\text{CoEDTA}^{2-} + \text{L}^- \rightarrow 2\text{CoEDTA}^- + \text{IO}_3^- \qquad (1)$$

where L$^-$ stands for $H_4IO_6^-$ and/or IO_4^-, the two periodate species that predominate in the pH range where the kinetics were studied [13]. L$^-$ is taken to represent the total periodate concentration. Preliminary experiments showed that CoEDTA^{2-}–IO_3^- reaction is extremely slow at pH 5.0.

Kinetics of CoEDTA^{2-}–Periodate Reaction

The kinetics of this reaction were studied over the pH range 4.0–5.56, ionic strength 0.10–0.50 M and temperatures 25.0, 20.0 and 15.0 °C over a range of L$^-$ and complex concentrations.

Plots of $\log(A_\infty - A_t)$ *vs.* t were linear up to >80% of the oxidation reaction at the two wavelengths where the change in absorbance as a function of time was followed. Pseudo-first order rate constants obtained from the slopes of these plots are collected in Table II. Under similar conditions the magnitude of k_{obs} is independent of the wavelength used to follow the reaction. The constancy of k_{obs} at fixed L$^-$, pH and temperature over a range of complex concentration is in agreement with a first-order dependence on its concentration.

The variation of k_{obs} with L$^-$ is shown in Table II at pH 5.02, I 0.50 M and temperatures 25.0, 20.0 and 15.0 °C. Plots of k_{obs}^{-1} against $[L^-]^{-1}$ were found to be linear but with definite intercepts on the k_{obs}^{-1} axis as shown in Figure 2. The dependence of k_{obs} on [L$^-$] is thus described by eq. 2

$$k_{obs} = \frac{k_3K_1[L^-]}{1 + K_1[L^-]} \qquad (2)$$

TABLE II. Kinetic Data[a].

Temp. °C	I *M*	pH	$10^4 \times$ [CoEDTA^{2-}] *M*	$10^2 \times$ [Periodate] *M*	$10^3 \times k_{obs}$ sec^{-1}
25.0	0.50	5.02	5.0	5.0	10.7
				5.0	10.9[b]
				4.5	9.8
				4.0	8.4
				4.0	8.2[b]
				3.5	7.7
				3.0	6.7
				2.5	5.5
				2.0	4.53
				1.5	3.4
				0.5	1.26
20.0				5.0	6.42
				4.0	5.26
				3.0	3.90
				2.0	2.94
15.0				5.0	4.44
				4.0	3.70
				3.0	2.77
				2.0	2.04
25.0			3.0	3.0	6.67
			10.0	3.0	6.40
			15.0	3.0	6.75
		5.56	5.0	1.5	3.50
		4.63		1.5	3.63
		4.45		1.5	3.67
		4.26		1.5	3.70
		4.01		1.5	3.40
	0.10	5.02		1.5	2.14
	0.25			1.5	2.70
	0.35			1.5	3.0

[a]λ = 534 nm. [b]λ = 360 nm.

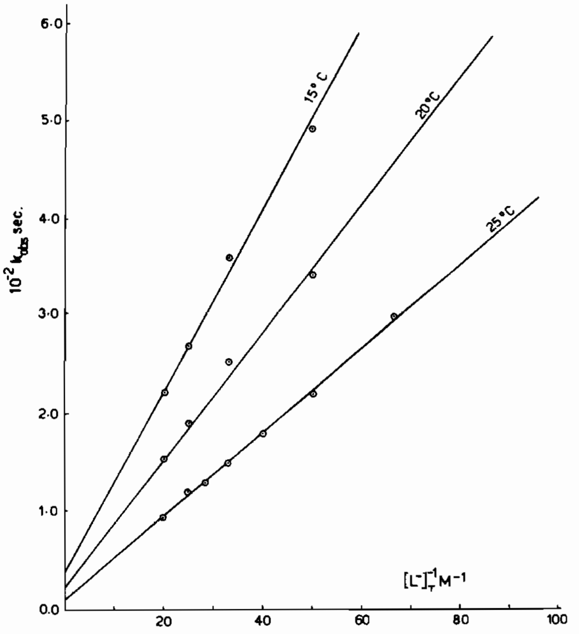

Figure 2. Plots of k_{obs}^{-1} against $[L^-]_T^{-1}$ (total periodate concentration).

Values of k_3 and K_1, calculated from the intercepts and slopes of plots in Figure 2 are listed in Table III. The activation parameters obtained from a least-squares fit to the Eyring equation are $\Delta H_3^* = 22 \pm 1$ kcal/mol and $\Delta S_3^* = +10.8 \pm 3.5$ cal K^{-1} mol^{-1}. The enthalpy of the pre-equilibrium reaction $\Delta H_1^\circ = -9.6 \pm 0.4$ kcal/mol, is obtained from the temperature variation of K_1. It is interesting to note that ΔH_1° is negative as found in the $Fe(CN)_6^{3-}$–Co-EDTA^{2-} reaction [14].

TABLE III. Parameters Derived from Figure 2.

Temp. °C	10^2 k_3 sec^{-1}	K_1 *M*$^{-1}$
25.0	10.0	2.40
20.0	5.0	3.07
15.0	2.66	4.2

The results in Table II show that the magnitude of k_{obs} is not affected by variation of pH over the range 4.0–5.56. However k_{obs} decreases with decreasing ionic strength.

TABLE IV. Rate of Ring Closure.[a]

10^2 [Periodate] *M*	10^4 k_4
5.0	4.80
4.0	5.42
3.0	4.80
2.0	5.10

[a] = 360 nm, [CoEDTA^{2-}] = 5.0 × 10^{-4}, T = 25.0 C, pH 5.02 and I = 0.50 *M*.

Ring Closure

It has been established from Figure 1 that the spectrum of the initial product differs from that of CoEDTA$^-$, but gradually reverts to that of hexadentate Co(III)–EDTA complex. The decrease in absorbance that accompanied the ring closure was followed as a function of time at 360 nm (see Figure 1). From the linear plots of log (A_t − A_∞) *vs.* t the rate constant of ring closure (k_{rc}) was determined as (5.0 ± 0.20) × 10^{-4} sec^{-1} at 25.0 °C, I = 0.50 *M* and pH = 5.02 (Table IV). The relatively low rate of ring closure indicates that this intermediate is more stable than that identified in the oxidation with $Fe(CN)_6^{3-}$. (k_{rc} = 5.40 × 10^{-3} sec^{-1} at 25 °C, I = 0.66 and pH 5.0) [14].

Discussion

The oxidation of CoEDTA^{2-} by periodate seems to proceed by an inner-sphere mechanism. The direct evidence is the formation of an initial Co(III) product, other than hexadentate CoEDTA$^-$, which undergoes a slow ring closure. This type of mechanism has been proposed for the oxidation of this Co(II) complex by various oxidants [14–16]. A reaction scheme compatible with experimental observations as well as the rate law is described by eq. 3–6:

$$\mathrm{Co(II)EDTA^{2-} + L^-} \rightleftharpoons \mathrm{[EDTACo(II)–L(VII)]^{3-}} \quad K_1 \qquad (3)$$

$$\mathrm{[EDTA\ Co(II)–L(VII)]^{3-}} \xrightarrow[\text{rds}]{k_3} \mathrm{[EDTA\ Co(III)–L(VI)]^{3-}} \qquad (4)$$

$$\mathrm{[EDTA\ Co(III)–L(VI)]^{3-}} \xrightarrow{k_{rc}} \mathrm{CoEDTA^- + L^{2-}(VI)} \qquad (5)$$

$$\mathrm{2L^{2-}(VI)} \xrightarrow{\text{rapid}} \mathrm{L^-(VII) + IO_3^-} \qquad (6)$$

Reaction (4) is the rate-determining electron-transfer step, and reaction (5) is the slower ring closure.

The recombination and disproportionation of L^{2-} (VI) seems to be reasonable as its release from the Co(III) intermediate is very slow and by then all the Co(II) complex would have been oxidised. However when Co(II) complex concentration is in excess then oxidation by L^{2-}(VI) takes place (see Table I).

Inner-sphere oxidation of the Co(II)–EDTA complex requires the rupture of one of the acetate groups as this complex is now believed to be predominantly hexadentate in solution at pH 5 [17, 18]. The absence of any [H$^+$] dependence is expected at the range of pH investigated as this is higher than the pK_a(3) of the complex. The increase of reaction rate with increasing ionic strength is also expected as the two reactants are similarly charged.

The nature of the periodate reactive species is not unambiguous, but IO_4^- might be favoured over $H_4IO_6^-$ for steric hindrance consideration.

The enthalpy and entropy of activation determined for the electron-transfer step are comparable to those obtained for such a step in the oxidation of this reductant by I_2 and I_3^- where the mechanism is believed to be inner-sphere.

In conclusion, the results of this study serve as an additional support to the hypothesis that an inner-sphere mechanism is the preferable route for periodate oxidations.

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