Mechanism of the Bromate Ion Oxidation of the Cobalt(II) Complex of *trans*-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetic Acid

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Kinetics of the oxidation of $[Co(cdta)]^{2-}$ (H_4cdta = *trans*-cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetic acid) by bromate ion have been studied in the ranges of $[H^+] = 1 \times 10^{-2}$—1×10^{-3} mol dm^{-3} and $[BrO_3^-] = 5 \times 10^{-2}$—$37.5 \times 10^{-2}$ mol dm^{-3} at 60 °C with $I = 1.0$ mol dm^{-3} (KNO_3). The second-order rate constant k in the rate law $d[Co(cdta)^-]/dt = k[Co(cdta)^{2-}][BrO_3^-]$ is dependent on $[H^+]$: $k = a[H^+]^2/(b + [H^+])$. A reasonably good fit of the data to this equation is obtained with $a = (13.1 \pm 1.2) \times 10^{-2}$ dm^6 mol^{-2} s^{-1} and $b = (5.31 \pm 0.2) \times 10^{-3}$ mol dm^{-3}. A possible mechanism has been deduced. This involves an inner-sphere electron transfer path in which a binuclear species containing the cobalt(II) substrate and BrO_2^+ is formed in the slow step.

The bromate ion oxidation of various metal ions and complexes [1] has received considerable attention due to a remarkable variety of mechanistic behaviour exhibited by this oxidant and to the oscillating phenomenon observed with this oxidant in many cases.[2] The bromate ion often provides an efficient bridging mechanism involving replacement in the oxy-anion co-ordination sphere prior to electron transfer.[3] The present study was undertaken in order to determine whether this ion could oxidise a cobalt(II) complex by such a mechanism.

Experimental

trans-Cyclohexane-1,2-diamine-*NNN'N'*-tetra-acetic acid (H_4cdta) was purchased from BDH. The cobalt(II)–cdta complex was prepared following Margerum and co-workers.[4] Air oxidation of $[Co(cdta)]^{2-}$ to give $[Co(cdta)]^-$ is extremely slow and could not be detected even after a month. No precaution was therefore taken to maintain any inert atmosphere. Bromate ion solutions were prepared from recrystallised sodium bromate and were analyzed by titration (with sodium thiosulphate) of the iodine produced by reaction with excess sodium iodide. Perchloric acid was used to maintain the $[H^+]$ of the reaction mixtures and ionic strengths were adjusted with doubly recrystallised KNO_3 (AnalaR, BDH).

Kinetic Measurements.—A Pye-Unicam SP8-150 spectrophotometer was used for all kinetic measurements. The reactions were followed at 545 nm by measuring the change in absorbance of the reaction mixture at definite time intervals. For this a little of the aliquot had to be quickly withdrawn from the reaction vessel (kept in a thermostatted bath at 60 ± 0.2 °C) with the help of a jacketted pipette containing pieces of ice for quenching the reaction. The values of A_∞ were in accord with $\varepsilon_{max.}^{545} = 300 \pm 3$ dm^3 mol^{-1} cm^{-1} for $[Co(cdta)]^-$ as reported in the literature.[5,6] To avoid the possibility of the oxidation of water, especially at high acidities,[7] bromate ion was added to the solution within a few minutes of initiation of the reaction. Reactions were carried out under pseudo-first-order conditions with $[Co(cdta)^{2-}] = 1 \times 10^{-3}$ mol dm^{-3}, $[BrO_3^-] = 5 \times 10^{-2}$ — 37.5×10^{-2} mol dm^{-3} in the range of $[H^+] = 1 \times 10^{-2}$—1×10^{-3} mol dm^{-3} at 60 °C and with $I = 1.0$ mol dm^{-3} (KNO_3). Conventional first-order plots of log $(A_\infty - A_t)$ *vs.* time, *t*, were linear for at least 90% of the reaction.

Results and Discussion

The stoicheiometry of the reaction was determined by addition of excess $[Co(cdta)]^{2-}$ to an acidic BrO_3^- solution ($[H^+] = 10^{-2}$ mol dm^{-3}) giving a ratio of $\Delta[Co(cdta)^-]/\Delta[BrO_3^-] = 4.97 \pm 0.05$. Since the kinetics were carried out using excess BrO_3^-, it is reasonable to believe that the final product can not be Br^- [7] as Br^- and BrO_3^- would react to give Br_2. The formation of Br_2 was demonstrated by addition of solid $[Co(cdta)]^{2-}$ to an excess of BrO_3^- in an acidic medium (pH = 2). The resulting solution was immediately extracted with CCl_4 and tested for Br_2 by reaction with sodium iodide solution. By consideration of the kinetic results to be described, the stoicheiometry of the reaction in the presence of excess bromate appears to be represented by equation (1).

$$5\,[Co(cdta)]^{2-} + BrO_3^- + 6\,H^+ \longrightarrow 5\,[Co(cdta)]^- + 0.5\,Br_2 + 3\,H_2O \quad (1)$$

A kinetic study of the $[Co(cdta)]^{2-}$–Br_2 reaction by Margerum and co-workers [4] indicates that it would be much slower than the $[Co(cdta)]^{2-}$–BrO_3^- reaction under the conditions of our experiments with excess BrO_3^-. It is noteworthy that reactions in which reduction of Br_2 is a rapid and prevalent step generally follow autocatalytic [7] rather than first-order kinetics. The results in the Table show that at a constant $[H^+]$ of 5×10^{-3} mol dm^{-3} the present reaction follows a simple second-order equation, whereby k can be easily

$$d[Co(cdta)^-]/dt = k[Co(cdta)^{2-}][BrO_3^-] \quad (2)$$

obtained from the observed rate constant by $k = k_{obs.}/[BrO_3^-]$ under pseudo-first-order conditions keeping a large excess of $[BrO_3^-]$ over $[Co(cdta)^{2-}]$. The order of the reaction in $[H^+]$ at a constant $[BrO_3^-]$ of 0.3 mol dm^{-3} exceeded unity, and k was fitted to expressions (3) and (4). A reasonably

$$k = a[H^+] + b[H^+]^2 \quad (3)$$

$$k = a[H^+]^2/(b + [H^+]) \quad (4)$$

good fit of the data to equation (4) rather than (3) is obtained with values of $a = (13.1 \pm 1.2) \times 10^{-2}$ dm^6 mol^{-2} s^{-1} and $b = (5.31 \pm 0.2) \times 10^{-3}$ mol dm^{-3}. The agreement between the observed values of k and those calculated by equation (4)

Table. Rate constants for the reaction of $[\mathrm{Co(cdta)}]^{2-}$ with $\mathrm{BrO_3}^-$ at 60 °C and $I = 1.0$ mol dm^{-3} ($\mathrm{KNO_3}$) [a]

10^3 [H$^+$]/ mol dm^{-3}	10^2 [$\mathrm{BrO_3}^-$]/ mol dm^{-3}	10^5 $k_{\mathrm{obs.}}$/s^{-1}	10^5 k/mol dm^{-3}	
			Obs.[b]	Calc.[c]
5.0	5.0	1.59	31.8	
	7.0	2.23	31.85	
	8.0	2.53	31.62	
	9.0	2.85	31.67	
	10.0	3.19	31.9	
	15.0	4.78	31.86	
	20.0	6.46	32.3	
	25.0	7.99	31.96	
	30.0	9.59	31.96	30.75
	35.5	11.33	32.37	
	37.5	12.06	32.59	
			av. (32.0 ± 0.3)	
1.0	30.0	0.614	2.05	2.07
2.0		2.3	7.67	7.16
3.5		5.03	16.76	18.2
4.0		7.52	25.06	22.5
5.5		11.62	38.73	36.64
6.0		11.62	38.73	41.68
7.0		15.45	51.5	52.02
10.0		25.5	85.0	85.5
		25.7	85.7	

[a] In all runs $[\mathrm{Co(cdta)}^{2-}] = 1 \times 10^{-3}$ mol dm^{-3}. [b] $k = k_{\mathrm{obs.}}/[\mathrm{BrO_3}^-]$. [c] Calculated from equation (4) and values of the parameters given in the text.

with the help of these parameters is shown in the Table.

A mechanism which would lead to a kinetic equation having H$^+$ dependence of the form (4) is depicted by equations (5)—(8), applying a stationary-state approximation to the concentration of $[\mathrm{Co(cdta)}]^{2-}\cdot\mathrm{HBrO_3}$ with $k = k_1[\mathrm{H}^+]^2/(k_{-1}/k_2 + [\mathrm{H}^+])$ so that $a = k_1$ and $b = k_{-1}/k_2$ is obtained. In view of the earlier observations,[3,8] it is not unusual to visualise such a mechanism in which the rate-determining step (r.d.s.) involves a displacement process with the formation of a bridged intermediate of the substrate and $\mathrm{BrO_2}^+$. Significant steric compression [4] imposed by the cyclohexyl group in cdta^{4-} seems to favour a ring closure to the cobalt(III), $[\mathrm{Co(cdta)}]^-$ species.

$$[\mathrm{Co(cdta)}]^{2-} + \mathrm{H}^+ + \mathrm{BrO_3}^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [\mathrm{Co(cdta)}]^{2-}\cdot\mathrm{HBrO_3} \qquad (5)$$

$$[\mathrm{Co(cdta)}]^{2-}\cdot\mathrm{HBrO_3} + \mathrm{H}^+ \xrightarrow[\text{r.d.s.}]{k_2} [\mathrm{Co(cdta)}]^{2-}\text{—}\mathrm{BrO_2}^+ + \mathrm{H_2O} \qquad (6)$$

$$[\mathrm{Co(cdta)}]^{2-}\text{—}\mathrm{BrO_2}^+ \xrightarrow{\text{fast}} [\mathrm{Co(cdta)}]^- + \mathrm{Br^{IV}O_2} \qquad (7)$$

$$4\,[\mathrm{Co(cdta)}]^{2-} + \mathrm{Br^{IV}O_2} + 4\mathrm{H}^+ \xrightarrow{\text{fast}} 4\,[\mathrm{Co(cdta)}]^- + 0.5\,\mathrm{Br_2} + 2\mathrm{H_2O} \qquad (8)$$

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