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Kinetics and Mechanism of Reactions at a Chromium (IV) Centre in the Complex Diperoxoethylenediamineaquochromium(IV), $Cr(O_2)_2(en)(H_2O)$

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Although there are several instances in which chromium in its tetravalent state has been reported to be a substitution labile intermediate in Cr(VI) oxidations [1–3], there are relatively few stable complexes of Cr(IV) known. One of the few well characterized complexes of Cr(IV) is diperoxoethylenediamineaquochromium(IV), $Cr(O_2)_2(en)(H_2O)$, and the X-ray structure of this complex reveals a 7-coordinate pentagonal bipyramid structure [4–6]. It is known that $Cr(O_2)_2(en)(H_2O)$ undergoes reduction in highly acidic solutions with reductants such as I^- to give Cr(III) products [6]. Any reduction of this complex to give Cr(III) products involves a change in the coordination geometry and number. An investigation as to whether reorganisation takes place prior to or after the electron transfer is of interest. We have therefore investigated the aqueous chemistry of Cr(IV) in the complex, $Cr(O_2)_2(en)(H_2O)$ and its reaction with I^- in weakly acidic solutions.

Results and Discussion

The kinetics of the reaction of I^- with $Cr(O_2)_2(en)(H_2O)$ in ethylenediamine buffer (0.02–0.07 *M*) were investigated using pseudo-first-order excess concentrations of I^- over that of Cr(IV), where typically $[Cr(IV)] = (4.3–5.8) \times 10^{-4}$ *M*, $[I^-] = 0.0075–0.20$ *M*, $[H^+] = (2.95–40) \times 10^{-8}$ *M*, I = 0.50 *M* ($LiClO_4$). The kinetics were monitored using an Aminco Stopped-flow spectrophotometer at 410 nm. Two distinctly separated kinetic steps were observed and the faster step had a decreasing absorbance while the slower step with $t_{1/2} \geqslant 3$ min had an increasing absorbance at 410 nm. If the faster step with $t_{1/2}$ *ca.* 40 ms were to be an electron transfer reaction giving rise to I_3^-, an oxidation product of I^-, an increase in absorbance will be observed since I_3^- has a much higher molar absorptivity than the Cr(IV) complex at 410 nm. In fact the slower step with $t_{1/2} \geqslant 3$ min is indeed associated with large increases in absorbance at 410 nm, indicating the formation of I_3^-. Therefore while the overall reaction can be represented as in scheme 1,

$$2Cr(O_2)_2(en)(H_2O) + 10I^- + 16H^+ \longrightarrow 2Cr(H_2O)_4(en)^{3+} + 5I_2 + 2H_2O \quad (1)$$

$$I^- + I_2 \rightleftharpoons I_3^- \quad (2a)$$

$$I_2 + H_2O \rightleftharpoons HIO + H^+ + I^- \quad (2b)$$

the first kinetic step with decreasing absorbance is attributable to a fast substitution reaction at the Cr(IV) centre as in (3), rather than any electron transfer reaction:

$$Cr(O_2)_2(en)(H_2O) + I^- \rightleftharpoons Cr(O_2)_2(en)I^- + H_2O \quad (3)$$

At the low acid concentrations used, the second step (redox reaction) leading to the formation of I_3^- was considerably slower than the first kinetic step (substitution) observed and pseudo-first-order plots for reaction (3) were linear to about four half-lives. The observed rate constants, k_{obs}, are as in Table I and they were essentially independent of acid concentration in the region investigated. While it seems reasonable to conclude that the fast kinetic step corresponds to a substitution process in the Cr(IV) coordination sphere, ambiguities as to the ligand being displaced do exist.

Substitution of O_2^{2-} ligands by I^- can be considered unlikely because such a replacement would have resulted in free O_2^{2-} in solution, which would in turn lead to the formation of I_3^- at a rate faster than the observed second kinetic step wherein oxidation is invoked. Blank experiments in which typically 1×10^{-3} *M* H_2O_2 was reacted with 0.20 *M* I^- in ethylenediamine buffer (0.05 *M*) at pH 6.4 at 30 °C, I = 0.50 *M* ($LiClO_4$) indicated a reaction with $t_{1/2}$ 1 min as against the second kinetic step in the reaction of I^- with $Cr(O_2)_2(en)(H_2O)$ [7]. The observation that the final Cr(III) product had an ethylenediamine coordinated and the fact that I^- reaction was investigated in ethylenediamine buffer and the observed rate did not vary appreciably with $[en]_T$ at any pH suggest that the diamine is not the likely ligand to be replaced by I^-. However the formation of complexes of the type $Cr(O_2)_2(enH)(H_2O)I$ where ethylenediamine is unidentately bound has to be discounted on the basis that for such reactions $[H^+]$ dependence may be observed which is contrary to the experimental observation. Further related complexes of the type $Cr(O_2)_2(en)X$, where X = NH_3 and the displaced ligand is H_2O have been prepared by direct substitution [8].

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TABLE I. The Dependence of Observed Rate Constants, k_{obs}, on Iodide Concentrations at Various $[H^+]$ and $[(en)]_T$. I = 0.50 *M* ($LiClO_4$), Temperature = 30 °C, Wavelength 410 nm.

$10^8[H^+]$ (*M*)	$10^2[(en)]_T$ (*M*)	10^4[Cr(IV)] (*M*)	$10[I^-]$ (*M*)	k_{obs} (s^{-1})
2.95	5.0	4.42	0.075	13.4 ± 0.1
		4.42	0.10	13.9 ± 0.1
		5.84	0.20	14.5 ± 0.1
		4.32	0.25	14.7 ± 0.3
		4.32	0.50	15.1 ± 0.1
		5.84	1.00	16.7 ± 0.3
		4.42	1.50	18.7 ± 0.4
		5.84	2.00	20.0 ± 0.2
7.96	5.0	5.00	0.20	13.4 ± 0.1
8.91	5.0	5.33	0.075	13.2 ± 0.2
		5.33	0.10	13.7 ± 0.1
		5.34	0.25	13.9 ± 0.3
		5.34	0.50	14.8 ± 0.2
		5.34	1.50	18.4 ± 0.2
		5.00	2.00	19.7 ± 0.2
40.0	5.0	4.74	0.075	12.7 ± 0.2
		4.74	0.10	13.3 ± 0.2
		5.32	0.20	13.4 ± 0.2
		4.74	0.25	13.6 ± 0.3
		4.74	0.50	15.4 ± 0.3
		5.32	1.00	16.6 ± 0.2
		5.32	2.00	20.6 ± 0.2
2.95	2.0	5.00	0.10	13.6 ± 0.2[a]
		5.00	1.00	16.3 ± 0.4[a]
	7.0	5.00	1.00	16.1 ± 0.3[a]

[a] Not computed.

Assuming the displaced ligand to be H_2O, less than first-order dependence of k_{obs} on iodide concentrations, Table I, can be best explained in terms of both reaction schemes 2 and 3, corresponding to 'D' and I_d processes respectively:

Scheme 2 – 'D' process

$$Cr(O_2)_2(en)(H_2) \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} Cr(O_2)_2(en) + H_2O \quad (4)$$

$$Cr(O_2)_2(en) + I^- \underset{k_{-5}}{\overset{k_5}{\rightleftharpoons}} Cr(O_2)_2(en)I^- \quad (5)$$

Scheme 3 – I_d process

$$Cr(O_2)_2(en)(H_2O) + I^- \overset{K_{OS}}{\rightleftharpoons} Cr(O_2)_2(en)(H_2O), I^- \quad (6)$$

$$Cr(O_2)_2(en)(H_2O), I^- \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} Cr(O_2)_2(en)I^- + H_2O \quad (7)$$

The algebraic form of the rate law for both I_d and D mechanisms being the same as in equation 8, the rate law can be written as follows:

$$k_{obs} = \frac{A + BC[I^-]}{1 + C[I^-]} \quad (8)$$

where A, aquation rate, k_{-5} or k_{-7}; B, exchange rate, k_4 or k_7; and C = (k_5/k_{-4}) or K_{OS} for D and I_d processes respectively. The observed rate constants, k_{obs}, were fitted to equation 8 by a non-linear least squares program with $1/(y)^2$ weighting [9] and the values of 13.1 ± 0.07 s^{-1}, 52.2 ± 7.6 M^{-1} s^{-1} and 1.04 ± 0.38 M^{-1} were obtained for the terms A, B and C respectively.

The numerical value obtained for the term 'C' corresponds to K_{OS} for an outer-sphere mechanism I_d and the ratio of rates k_5/k_{-4} in a dissociative process, D. The value of 1.04 ± 0.38 M^{-1} can be considered rather high for an ion-pairing constant between a zero-charged and a uni-negative ion like I^-, if 'C' were to correspond to K_{OS} at I = 0.50 *M* ($LiClO_4$). Although a more direct distinction between schemes 2 and 3 may be possible by examining k_{obs} at very low $[I^-]$ (where [Cr(IV)] to $[I^-]$ may be close to 1:1), such an investigation could not be made in view of the low overall equilibrium constant, *ca.* 4 M^{-1}, and extremely small optical density changes at low $[I^-]$. The solubility of Cr(IV) being limited to 1.2×10^{-3} *M*, studies with excess Cr(IV) were not possible. Therefore on the basis that smaller ion-pairing constants (typically $\leqslant$ 0.1 M^{-1}) would be expected on electrostatic considerations, a dissociative D process is favoured. This would imply that a 6-coordinate Cr(IV) complex is formed at least in steady state concentrations, which might well be a redox active species and further work to assign firmly the nature of the redox active intermediates and redox mechanism is in progress. Detailed investigation of the electron-transfer process with a variety of reducing agents such as I^-, $Fe(CN)_6^{4-}$ and Fe^{2+} will be published elsewhere [10].

A substitution rate of 52.2 s^{-1} obtained for a Cr(IV) centre indicates the relative lability of tetravalent state. Although for a d^2 ion this first-order rate may not seem surprisingly high compared to isoelectronic $V(H_2O)_6^{3+}$ for example [11], meaningful comparisons are difficult at this stage in the absence of a true Mo(IV) analogue.

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