Reaction of Tetra-aquoethylenediaminechromium(III) with Oxalate

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Spectrophotometric changes observed during the reaction of oxalate with tetra-aquoethylenediaminechromium(III) are consistent with the reaction sequence $Cr(en)(H_2O)_4^{3+} \longrightarrow Cr(en)(C_2O_4)(H_2O)_2^{+} \longrightarrow Cr(enH)(C_2O_4)(H_2O)_3^{2+} \longrightarrow Cr(C_2O_4)(H_2O)_4^{+} \longrightarrow Cr(C_2O_4)_2(H_2O)_2^{-}$, and the same sequence without intermediate formation of $Cr(en)(C_2O_4)(H_2O)_2^{+}$ (*ca.* 40% contribution, 45—60 °C), total oxalate in the range $[C_2O_4^{2-}]_T = 1 \times 10^{-3}$ to 22×10^{-1}M, $[H^+] = 0{\cdot}03$—$0{\cdot}50$M. Growth and decay curves have been plotted for the various species following ion-exchange separation of the products, and determination of the chromium(III) content by atomic absorption spectrometry. The kinetics of the complexing of the first oxalate have been investigated at 45—60 °C, $I = 1{\cdot}0$M ($NaClO_4$), where formation of a unidentate oxalato-complex with the displacement of a water ligand is believed to be rate determining and common to both reaction sequences. Second-order rate constants, k_{obs}, give a dependence on hydrogen-ion concentration

$$1/k_{obs} = 1/k_1 + [H^+]/k_1K_1$$

where k_1 is for the reaction of $Cr(en)(H_2O)_4^{3+}$ with $HC_2O_4^-$, and K_1 is the first acid dissociation constant of oxalic acid. At 50 °C the rate constant k_1 (= kK_{IP}, where K_{IP} is for ion-pair formation) is $(4{\cdot}02 \pm 0{\cdot}02) \times 10^{-2}$ l mol^{-1} s^{-1} and activation parameters for k_1 are $\Delta H^‡ = 23{\cdot}4 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^‡ = 7{\cdot}4 \pm 3{\cdot}1$ cal mol^{-1} K^{-1}. Chelation of the oxalate to give $Cr(en)(C_2O_4)(H_2O)_2^{+}$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ is rapid.

PREVIOUSLY the reaction of oxalate with hexa-aquochromium(III),[1] tetra-aquo-oxalatochromium(III),[2] and *cis*-diaquobis(oxalato)chromium(III) [3] have been studied. The anation reaction of hexa-aquochromium(III) with malonic acid has also been investigated.[4] A feature of the studies with oxalate is the rapid chelation once the unidentate complex has formed. The dissociation of ethylenediamine from the tetra-aquoethylenediaminechromium(III) complex, $Cr(en)(H_2O)_4^{3+}$, is notable for the build-up of the penta-aquo-complex containing unidentate ethylenediamine, which dissociates only slowly to hexa-aquochromium(III).[5] The first stage in the aquation of *trans*-$Cr(en)_2F_2^{+}$, likewise gives a product in which the ethylenediamine is unidentate.[6] In the light of these studies it seemed of interest to investigate the complexing of oxalate to $Cr(en)(H_2O)_4^{3+}$, and to identify the stage at which the ethylenediamine ligand is displaced.

Reaction Sequence.—Relevant spectra are shown in Figure 1. Details of peak positions and minima are given in Table 1. For the conditions total oxalate $[C_2O_4^{2-}]_T = 1 \times 10^{-3} - 22 \times 10^{-3}$M and $[H^+] = 0{\cdot}03$—$0{\cdot}50$M spectrophotometric changes with time are consistent with contributions from the reaction sequence: $Cr(en)(H_2O)_4^{3+} \longrightarrow Cr(en)(C_2O_4)(H_2O)_2^{+} \longrightarrow Cr(enH)(C_2O_4)(H_2O)_3^{2+} \longrightarrow Cr(C_2O_4)(H_2O)_4^{+}$. Of particular help in assigning this sequence were the isosbestic points for $Cr(en)(C_2O_4)(H_2O)_2^{+}$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ at 410 and 563 nm ($\varepsilon = 49{\cdot}5$ and $37{\cdot}5$ l mol^{-1} cm^{-1} respectively).† We believe this sequence to be more effective than one involving $Cr(en)(H_2O)_4^{3+} \longrightarrow Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ without intermediate formation of $Cr(en)(C_2O_4)(H_2O)_2^{+}$ because the absorbance at 510—530 nm increases initially. If the reaction $Cr(en)(H_2O)_4^{3+} \longrightarrow Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ were dominant there would be a decrease in absorption at 515 nm. However the rate constants evaluated at 410 and *ca.* 560 nm were not in agreement with those evaluated at other wavelengths 380—430 nm assuming $Cr(en)(C_2O_4)(H_2O)_2^{+}$ to be the sole product, see next section and Table 4. Good agreement is obtained if the absorbance OD_∞ is calculated assuming the products to be 60 ± 3% $Cr(en)(C_2O_4)(H_2O)_2^{+}$ and 40 ± 3% $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$, although (as is to be expected) the linearity of plots at these other wavelengths is not as extensive. Further points to note are that at 410 and 563 nm the complex $Cr(C_2O_4)(H_2O)_4^{+}$ has $\varepsilon = 40{\cdot}0$ and $34{\cdot}5$ l mol^{-1} cm^{-1} (*i.e.* the absorption begins

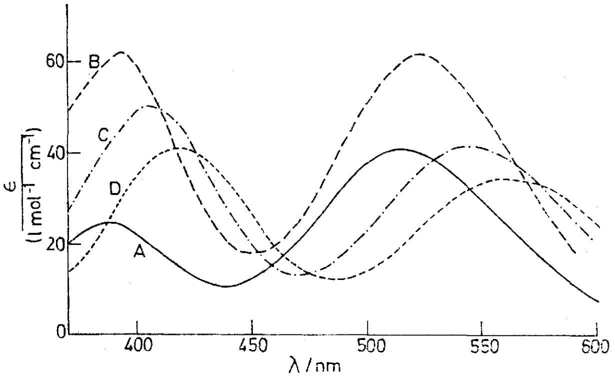

FIGURE 1 Aqueous solution spectra of A, $Cr(en)(H_2O)_4^{3+}$; B, $Cr(en)(C_2O_4)(H_2O)_2^{+}$; C, $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$; and D, $Cr(C_2O_4)(H_2O)_4^{+}$

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† Kinetic plots (see below) are linear over a slightly longer period at 560 rather than 563 nm. It is possible that free oxalate has an effect on the position of this isosbestic. Rate constants determined at 560 and 563 nm are within ±0·5% of each other.

[1] D. Banerjea and S. D. Chaudhuri, *J. Inorg. Nuclear Chem.*, 1970, **32**, 1617.

[2] D. Banerjea and M. S. Mohan, *Z. anorg. Chem.*, 1966, **347**, 107.

[3] H. Kelm and G. M. Harris, *Inorg. Chem.*, 1967, **6**, 706.

[4] D. Banerjea and C. Chatterjee, *J. Inorg. Nuclear Chem.* 1969, **31**, 3845; see also D. H. Huchital and H. Taube, *Inorg. Chem.*, 1965, **4**, 1660.

[5] R. F. Childers, K. G. Vander Zyl, D. A. House, R. G. Hughes, and C. S. Garner, *Inorg. Chem.*, 1968, **7**, 749.

[6] S. C. Pyke and R. G. Linck, *Inorg. Chem.*, 1971, **10**, 2445.

to decrease). Over longer periods the bisoxalato-complex $Cr(C_2O_4)_2(H_2O)_2^-$, ε = 67·5 l mol^{-1} cm^{-1} at 410 nm, ε = 52·6 l mol^{-1} cm^{-1} at 563 nm,[8] is formed and the absorbance increases. Both these trends have been observed (curvature of second-order plots), depending on reactant concentrations. At higher oxalate concentrations, $[C_2O_4^{2-}]_T/[Cr^{III}]_T > 10$ formation of $Cr(en)(C_2O_4)_2^-$ (ε = 82·5 l mol^{-1} cm^{-1} at 410 nm, ε = 65·0 l mol^{-1} cm^{-1} at 563 nm) precedes dissociation of the ethylenediamine ligand. The latter step would seem to require a *cis* rather than a *trans* geometry for the complex $Cr(en)(C_2O_4)(H_2O)_2^+$. We have no other information regarding the geometry of this complex.

TABLE 1

Maxima (and minima) observed in ultraviolet–visible spectra of relevant complexes

Complex	λ/nm	ε / l mol^{-1} cm^{-1}
$Cr(en)(H_2O)_4^{3+}$ [a]	387	24·5
	438	10·6 [b]
	516	42·0
$Cr(en)(C_2O_4)(H_2O)_2^+$	393	62·0
	450	18·2 [b]
	524	62·0
$Cr(enH)(C_2O_4)(H_2O)_3^{2+}$	405	50·4
	468	13·0 [b]
	544	41·7
$Cr(C_2O_4)(H_2O)_4^+$ [c]	418	41·3
	485	12·2 [b]
	560	34·7
$Cr(en)(C_2O_4)_2^-$ [d]	397	95
	455	20·5 [b]
	533	83
cis-$Cr(C_2O_4)_2(H_2O)_2^-$ [d]	417	70
	485	13 [b]
	566	53

[a] Details as obtained in this work are in agreement with values reported in refs. 5 and 7. [b] Minima. [c] From D. Banerjea and M. S. Mohan, *J. Inorg. Nuclear Chem.*, 1964, **26**, 613. [d] From information in ref. 8.

The above observations have been confirmed by ion-exchange separation of products at different reaction times as described in the Experimental section, and determination of the chromium(III) content in each fraction using atomic absorption spectrometry.[9] The latter is an accurate method for determining low concentrations (p.p.m.) of metal ions. The conditions investigated were [complex] = 0·0043M, $[C_2O_4^{2-}]_T$ = 0·0085M, $[H^+]$ = 0·33M, I = 1·0M ($NaClO_4$) at 50°. The decrease in concentration of $Cr(en)(H_2O)_4^{3+}$, and growth and decay curves for the initial products are shown in Figure 2. In particular we note the evidence obtained for the 2+ product $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ in the early stage of our experiments, thus confirming that both reaction sequences are effective. The complex $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ containing half-bonded ethylenediamine, has been identified previously. Also, for the conditions chosen, no $1-$ ions were detected in the early stages, and $Cr(en)(C_2O_4)_2^-$ is not a primary product. After *ca.* 2·5 h the total chromium recovered is <100%, and a grey-blue band is observed at the top of the ion-exchange column which is not eluted by 3·0M-$HClO_4$ (curve E of Figure 2). From elution characteristics previously reported,[5] it is most likely that the band corresponds to the formation of $Cr(enH)(H_2O)_5^{4+}$. At no time does this fraction correspond to more than a few percent of the total chromium(III).

Finally the possibility that free oxalate might coordinate with the initial displacement of ethylenediamine was examined by mixing 0·003M-$Cr(en)_3^{3+}$ with *ca.* 0·001M-oxalate at 50° ($[H^+]$ = 0·10M). If $Cr(en)_3^{3+}$ ($\lambda_{max.}$ 351 nm, ε = 61 l mol^{-1} cm^{-1}; $\lambda_{max.}$ 457 nm, ε = 75 l mol^{-1} cm^{-1}) reacts directly with oxalate to give $Cr(en)_2(C_2O_4)^+$ ($\lambda_{max.}$ 372 nm, ε = 85 l mol^{-1} cm^{-1}; $\lambda_{max.}$ 496 nm, ε = 91 l mol^{-1} cm^{-1}) then the absorbance should increase appreciably in the regions 360 and 470 nm. The slow absorbance changes observed were consistent with the aquation of $Cr(en)_3^{3+}$.[10] Since H_2O (and OH^-) ligands are not expected to have any marked labilizing effect on the ethylenediamine in $Cr(en)(H_2O)_4^{3+}$ at the hydrogen-ion concentrations under investigation, it is concluded that direct displacement of the ethylenediamine in $Cr(en)(H_2O)_4^{3+}$ by free oxalate is unlikely to make a significant contribution.

The first step in the reaction of $Cr(en)(H_2O)_4^{3+}$ with oxalate is therefore the formation of the unidentate oxalate complex with the displacement of an H_2O ligand [see equation (1)]. The inclusion of $C_2O_4H^-$ on the left-hand side of this equation is not at this stage meant to exclude $C_2O_4^{2-}$ and $C_2O_4H_2$ as possible reactants. No evidence consistent with the build-up of appreciable concentrations of the unidentate oxalato-complex have been obtained in this or any other chromium(III) study, and chelation of the oxalate with displacement of a second H_2O or one end of the ethylenediamine [see equation (2)]

$$Cr(en)(H_2O)_4^{3+} + C_2O_4H^- \longrightarrow Cr(en)(C_2O_4H)(H_2O)_3^{2+} + H_2O \quad (1)$$

$$\begin{tikzcd} & Cr(en)(C_2O_4)(H_2O)_2^+ + H^+ + H_2O \\ Cr(en)(C_2O_4H)(H_2O)_3^{2+} \arrow[ur] \arrow[dr] & & (2) \\ & Cr(enH)(C_2O_4)(H_2O)_3^{2+} \end{tikzcd}$$

is therefore presumed to be rapid. The fairly well defined cross-over point at 468 nm observed in the early stages of the reaction (concentrations as for Figure 2) is attributed to $Cr(en)(H_2O)_4^{3+}$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ which have an isosbestic at 458 nm (Figure 1).

Kinetics of the First Stage.—The kinetics of equation (1) were investigated with concentrations $[C_2O_4^{2-}]_T$ = 1×10^{-3}—22×10^{-3}M, and $[H^+]$ = 0·03—0·50M. Absorbance changes were monitored at 410 and 560 nm, the ionic strength of reactant solutions being adjusted to I = 1·0M ($NaClO_4$). Initial (total) reactant concentrations $[Cr^{III}]_T/[C_2O_4^{2-}]_T$ were varied from 3 : 1 to 1 : 3, and second-order rate constants k_{obs}, as defined in the

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[7] D. A. House and C. S. Garner, *Inorg. Chem.*, 1966, **5**, 840.

[8] A. D. Kirk, K. C. Moss, and J. G. Valentin, *Canad. J. Chem.*, 1971, **49**, 375.

[9] M. B. Davies, J. W. Lethbridge, and Othman Nor, *J. Chromatog.*, 1972, **68**, 231.

[10] H. L. Schlafer and O. Kling, *J. Inorg. Nuclear Chem.*, 1958, **8**, 320.

rate law (3) were evaluated by plotting $\log_{10} \{1 + (b - a)F/a\}$ against time, where $F = (OD_\infty - OD_0)/(OD_\infty - OD_t)$

$$\text{Rate} = k_{obs}\,[Cr^{III}]_T[C_2O_4^{2-}]_T \qquad (3)$$

and a and b are initial total concentrations of the reactants, $b > a$. Such plots were linear to 35—75% completion, and the gradient gives $k_{obs}(b - a)/2{\cdot}303$. Curvature corresponding to formation of $Cr(C_2O_4)(H_2O)_4^+$ (lower ε's) at low oxalate concentrations, and $Cr(en)(C_2O_4)_2^-$ and/or $Cr(C_2O_4)_2(H_2O)_2^-$ (higher ε's) at high oxalate concentrations, was observed. For the runs in which $[Cr^{III}]_T = [C_2O_4^{2-}]_T$ the integration requires a plot of $1/(OD_\infty - OD_t)$ against time to be linear, and rate constants k_{obs} were evaluated from the gradient which is $k_{obs}\,[Cr^{III}]_T/(OD_\infty - OD_0)$. The dependence on hydrogen-ion concentration was investigated in order to specify the extent of protonation of the reactants, Table 2. From this data a plot of $1/k_{obs}$ against $[H^+]$ is linear (Figure 3). At 25°, $I = 1{\cdot}0$M ($NaClO_4$), first and second acid dissociation constants for oxalic acid which have been reported are $K_1 = 8{\cdot}4 \times 10^{-2}$ mol l^{-1} and $K_2 = 2{\cdot}79 \times 10^{-4}$ mol l^{-1}.[11] For the reaction sequence (4)—(5), the expression (6) can be derived. Alternative reaction sequences to (4) and (5)

$$H_2C_2O_4 \underset{\text{fast}}{\overset{K_1}{\rightleftharpoons}} HC_2O_4^- + H^+ \qquad (4)$$

$$Cr(en)(H_2O)_4^{3+} + HC_2O_4^- \xrightarrow{k_1} Cr(en)(C_2O_4H)(H_2O)_3^{2+} + H_2O \qquad (5)$$

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{[H^+]}{k_1K_1} \qquad (6)$$

will be considered in the Discussion section. Values of k_1 and K_1 evaluated assuming (6) to apply are listed in Table 3. Activation parameters for k_1 from a plot of $\log(k_1/T)$ against $1/T$ are $\Delta H^\ddagger = 23{\cdot}4 \pm 1{\cdot}0$ kcal mol^{-1} and $\Delta S^\ddagger = 7{\cdot}4 \pm 3{\cdot}1$ cal mol^{-1} K^{-1}.* The thermo-

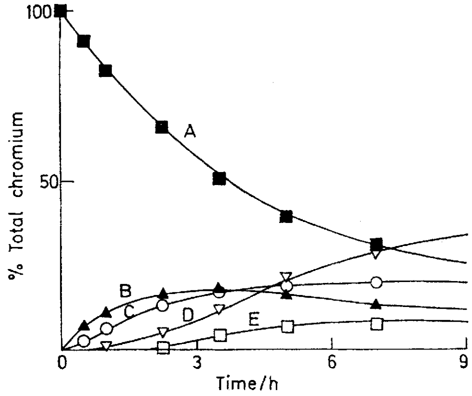

FIGURE 2 Growth and decay curves for reaction of $Cr(en)(H_2O)_4^{3+}$ with oxalate at 50 °C, $[Cr(en)(H_2O)_4^{3+}] = 0{\cdot}0043$M, $[C_2O_4^{2-}]_T = 0{\cdot}0085$M, $[H^+] = 0{\cdot}33$M, $I = 1{\cdot}0$M ($NaClO_4$). Curve A is for $Cr(en)(H_2O)_4^{3+}$, B for $Cr(en)(C_2O_4)(H_2O)_2^+$, C for $Cr(enH)(C_2O_4)(H_2O)_2^{2+}$, D for $Cr(C_2O_4)(H_2O)_4^+$, and E is believed to correspond to $Cr(enH)(H_2O)_5^{4+}$

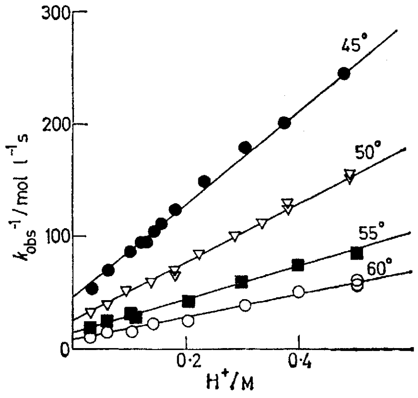

FIGURE 3 The dependence of $1/k_{obs}$ on $[H^+]$ for the first stage of the reaction of $Cr(en)(H_2O)_4^{3+}$ with oxalate, $I = 1{\cdot}0$M ($NaClO_4$)

TABLE 2

Rate constants, k_{obs}, for the reaction of oxalate with tetraaquoethylenediaminechromium(III), $I = 1{\cdot}0$M ($NaClO_4$). Reaction monitored at 410 nm, and (rate constants in brackets) 563 nm

Temp./°C	$[H^+]$/M	$10^3[Cr(en)(H_2O)_4^{3+}]$/M	$10^3[C_2O_4^{2-}]$/M	10^2k_{obs}/l mol^{-1}s^{-1}
45·0	0·032	3·06	6·13	1·84
	0·061	3·06	6·13	1·42
	0·101	3·06	6·13	1·15
	0·121	5·52	5·52	1·06
	0·127	0·61	1·84	1·05
	0·144	3·06	9·19	0·945
	0·155	4·26	8·52	0·889
	0·181	4·90	4·90	0·803
	0·232	4·90	9·80	0·674
	0·303	3·06	9·19	0·560
	0·373	4·90	14·7	0·499
	0·478	3·98	11·9	0·407
50·0	0·032	3·09 [a]	6·18	3·07 (3·08)
	0·060	3·09 [a]	6·18	2·47
	0·095	1·53	3·06	1·92
	0·138	5·26 [a]	10·5	1·66
	0·180	4·64 [a]	9·28	1·45 (1·49)
	0·222	2·32 [a]	4·64	1·17
	0·285	4·64 [a]	9·28	0·99 (1·00)
	0·335	4·29	8·58	0·88
	0·380	4·64 [a]	9·28	0·80 (0·77)
	0·490	3·09 [a]	6·18	0·66 (0·64)
55·0	0·031	1·33	3·99	5·38
	0·060	1·99	3·99	4·04
	0·103	3·99	3·99	3·17
	0·110	8·55	2·85	3·54
	0·203	9·58	9·58	2·38
	0·298	8·51	17·0	1·68
	0·398	7·45	22·3	1·33
	0·501	6·38	19·1	1·15
60·0	0·031	3·19	1·06	9·22
	0·061	3·19	1·60	6·77
	0·105	9·58	3·19	6·23
	0·139	1·06	3·19	4·49
	0·203	7·98	3·99	3·91
	0·304	1·60	3·19	2·51
	0·398	3·19	6·38	1·95
	0·398	3·19	6·38	1·95
	0·502	3·19	9·58	1·63
	0·502	3·19	9·58	1·68

[a] $Cr(en)(H_2O)_4^{3+}$ prepared from $Cr(en)(H_2O)_2Cl_2^+$.

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[11] E. G. Moorhead and N. Sutin, *Inorg. Chem.*, 1966, **5**, 1866.

* Data were fitted to the equation $k_{obs} = k_1K_1/(K_1 + [H^+])$, where k_{obs} and $[H^+]$ are the experimental quantities, using the Los Alamos Report LA 2367 (1959) non-linear least-squares programme and Addenda by R. H. Moore and R. K. Zeigler. Each data point was given a $1/k^2_{obs}$ weighting.

dynamic quantities for K_1 of $\Delta H_0 = -3{\cdot}7 \pm 1{\cdot}5$ kcal mol^{-1} and $\Delta S_0 = -16{\cdot}1 \pm 4{\cdot}7$ cal mol^{-1} K^{-1} are in satisfactory agreement with those of Davies and Watkins.[12] Individual values of K_1 are not as consistent with those of Moorhead and Sutin [11] as we would have wished (factor of *ca.* 2 discrepancy).

Table 4 contains a summary of kinetic evidence for the product analysis 60% $Cr(en)(C_2O_4)(H_2O)_2^+$ and 40% $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ for reaction (2). If formation of 100% $Cr(en)(C_2O_4)(H_2O)_2^+$ is assumed then rate constants k_{obs} at different wavelengths do not agree with those evaluated at 410 and 563 nm [isosbestics for $Cr(en)(C_2O_4)(H_2O)_2^+$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$], part (i) of Table 4. On varying the proportions of $Cr(en)(C_2O_4)(H_2O)_2^+$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$, for purposes of calculating OD$_\infty$ for reactions (1) and (2), 60% formation of $Cr(en)(C_2O_4)(H_2O)_2^+$ is seen to give a rate constant k_{obs} at 387 nm in agreement with those evaluated at 410 and 563 nm [see part (ii) of Table 4]. With this product ratio rate constants k_{obs} at five wavelengths are now in satisfactory agreement, although the linearity of plots is reduced. The procedure used here is we believe sensitive to ±3% in the two products. A similar detailed analysis of three other runs was carried out. These indicated that the same product analysis applies at 50°, $[H^+] = 0{\cdot}40$M, and at 60° $[H^+] = 0{\cdot}40$ and 0·06M; other concentrations were as specified in Table 4.

TABLE 3

A summary of k_1 $(=kK_{IP})$ and K_1 values evaluated from kinetic data, $I = 1{\cdot}0$M (NaClO$_4$)

Temp. / °C	$10^2\, k_1$ / l mol^{-1}s^{-1}	$10^2\, K_1$ / mol l^{-1}
45·0	2·27 ± 0·05	10·5 ± 0·5
50·0	4·02 ± 0·02	9·59 ± 0·27
55·0	7·11 ± 0·20	8·8 ± 0·5
60·0	12·5 ± 0·7	8·1 ± 0·8

TABLE 4

The determination of the product ratio for reaction (2) from a kinetic run at 50 °C, [complex] = 0·0046M, $[C_2O_4^{2-}]_T$ = 0·0093M, $[H^+]$ = 0·086M, I = 1·0M (NaClO$_4$)

(i) OD$_\infty$ calculated assuming 100% $Cr(en)(C_2O_4)(H_2O)_2^+$

λ / (nm)	$10^2\, k_{obs}$ / l mol^{-1}s^{-1}	Linearity (%)
410	1·79	72
563	1·76	59
387	1·23	27
400	1·42	30
426	2·0	*ca.* 10

(ii) λ = 387 nm, varying amounts $Cr(en)(C_2O_4)(H_2O)_2^+$ [a]

$Cr(en)(C_2O_4)(H_2O)_2^+$ (%)	$10^2\, k_{obs}$ / l mol^{-1}s^{-1}	Linearity (%)
100	1·23	27
70	1·66	27
60	1·78	40
50	1·97	38

(iii) OD$_\infty$ calculated assuming 60% $Cr(en)(C_2O_4)(H_2O)_2^+$ [a]

λ / nm	$10^2\, k_{obs}$ / l mol^{-1}s^{-1}	Linearity (%)
410	1·79	72
563	1·76	59
387	1·78	40
400	1·76	33
426	1·81	37

[a] The other product is $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$.

DISCUSSION

No evidence has been obtained in this study which supports displacement of the ethylenediamine ligand in the first step, equation (1). Nor is there evidence for significant build-up of the unidentate oxalato-complex formed in reaction (1), and we presume, as in other chromium(III) studies that chelate ring formation of the unidentate complex is rapid. It is likely that such a step has a high degree of S_N2 character.[13] A significant observation is that the oxalate exercises little discrimination between displacement of a second water ligand and ethylenediamine in reaction (2). The product ratio observed is near to that expected on a statistical basis assuming no steric effects or *cis/trans* labilizations to be effective in reaction (2). Re-chelation of the unidentate ethylenediamine ligand cannot occur readily because the free nitrogen is protonated for the range of hydrogen-ion concentrations investigated. Graphs of $1/k_{obs}$ against $[H^+]$ for equation (1) give satisfactory linearity, and at hydrogen-ion concentrations as low as 0·03M there was no evidence (*i.e.* curvature towards the origin in Figure 3) for the participation of $C_2O_4^{2-}$ ions. At smaller hydrogen-ion concentrations contribution from this path are to be expected. Such a range of conditions is difficult to investigate however, because of lack of conformity to the reaction sequence which we have indicated, *i.e.* $Cr(en)(C_2O_4)_2^-$ is formed. Since rate constants for the aquation of $Cr(en)(H_2O)_4^{3+}$ to $Cr(enH)(H_2O)_5^{4+}$ ($k = 3 \times 10^{-6}$ s^{-1} at 60°) [5] are small compared with those for reaction (1) for the range of $[H^+]$ and $[C_2O_4^{2-}]_T$ investigated (Table 2), they would not be expected to contribute more than a few percent to the reaction observed (see Figure 2).

The simplest interpretation of the dependence of k_{obs} on hydrogen-ion concentration, equation (6), is as indicated in equations (4) and (5). A possible elaboration is to consider ion-pair formation. Thus the reaction sequence is (4) followed by reactions (7) and (8). Equations (4), (7), and (8) give rise to the expression (9) for

$$Cr(en)(H_2O)_4^{3+} + HC_2O_4^- \overset{K_{IP}}{\rightleftharpoons} Cr(en)(H_2O)_4^{3+},HC_2O_4^- \qquad (7)$$

$$Cr(en)(H_2O)_4^{3+},HC_2O_4^- \xrightarrow{k} \text{products} \qquad (8)$$

$$\frac{1}{k_{obs}} = \frac{1}{kK_{IP}} + \frac{[H^+]}{kK_{IP}K_1} + \frac{[C_2O_4^{2-}]_T}{k} \qquad (9)$$

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[12] G. Davies and K. O. Watkins, *Inorg. Chem.*, 1970, **9**, 2735.

[13] See also discussion in R. Davies, M. Green, and A. G. Sykes, *J.C.S. Dalton*, 1972, 1171. For other examples see R. Dyke and W. C. E. Higginson, *J. Chem. Soc.*, 1960, 1998; R. N. F. Thorneley, A. G. Sykes, and P. Gans, *J. Chem. Soc.* (*A*), 1971, 1494; H. M. Comley and W. C. E. Higginson, *J.C.S. Dalton*, 1972, 2522.

k_{obs}. No evidence was obtained for contributions from the third term on the right-hand side of (9), which means that for the range of oxalate concentrations investigated a negligible amount of $Cr(en)(H_2O)_4^{3+}$ is ion-paired to oxalate at any one time. The first two terms on the right-hand side of (9) are of the same form as (6) with $k_1 = kK_{IP}$. Equation (5) represents a simplified form of (7) and (8).

The same hydrogen-ion dependence is obtained if (10), involving the conjugate-base form $Cr(en)(H_2O)_3(OH)^{2+}$ is the sole reaction path, or if it makes a contribution alongside (5). However, there is no evidence for the reaction of $Cr(en)(H_2O)_3(OH)^{2+}$ with $HC_2O_4^-$, which would give rise to a term in $[H^+]^{-2}$. Since, moreover, $HC_2O_4^-$ is in excess of $H_2C_2O_4$ for the conditions investigated, and the 1 — species is expected to co-ordinate much more readily ($HC_2O_4^-$ is more basic and has more sites available for co-ordination) it is unlikely that $H_2C_2O_4$ is involved to any large extent. At the most we expect reaction (10) to make only a minor contribution, and we feel justified in neglecting this path in our treatment.

$$Cr(en)(H_2O)_3(OH)^{2+} + H_2C_2O_4 \longrightarrow \text{products} \qquad (10)$$

Finally, in Table 5, a comparison is made of activation parameters for reactions of oxalate (and malonate) with chromium(III) aquo-complexes. The reaction of $Cr(H_2O)_6^{3+}$ with oxalate was studied over a range of $[H^+] = 0·3 - 1·9$M, and there is evidence for $H_2C_2O_4$ as the reactant. The activation parameters are noticeably more positive for this reaction.

TABLE 5

Summary of activation parameters for reactions of oxalate (and malonate) with chromium(III) aquo-complexes

	$\Delta H^\ddagger$ kcal mol^{-1}	$\Delta S^\ddagger$ cal mol^{-1} K^{-1}	Ref.
$Cr(H_2O)_6^{3+} + C_2O_4H_2$	29·0	14·1	1
$Cr(C_2O_4)(H_2O)_4^+ + C_2O_4H^-$	23·9	8·6	2
$Cr(C_2O_4)_2(H_2O)_2^- + C_2O_4H^-$	21·7	−2·4	3
$Cr(en)(H_2O)_4^{3+} + C_2O_4H^-$	23·4	7·4	This work
$Cr(H_2O)_6^{3+} + CH_2C_2O_4H^-$	24·4	−0·13	4

EXPERIMENTAL

Tetra-aquoethylenediaminechromium(III) *Perchlorate.*—Solutions of this cation were prepared either by dissolving 0·5 g of the diperoxo-complex $[Cr(en)(O_2)_2(H_2O)]H_2O$ in 50 ml of 0·5M-$HClO_4$, and heating to 50° for 1·5—2·0 h, or by aquation of 1·7 g of the dichloro-complex $[Cr(en)(H_2O)_2(Cl)_2]Cl$ in 50 ml of 0·1M-$HClO_4$ for *ca.* 20 h at 50°.[14] The preparations of both the diperoxo- and dichloro-complexes [7] have been described previously. The crude solution of $Cr(en)(H_2O)_4^{3+}$ was purified using Dowex-50W-X8, 100—200 mesh size, ion-exchange resin. A 20 ml volume of solution was charged onto a 1 × 11 cm column at room temperature and with a flow rate of 3 ml/min. About 250 ml of 1·5M-$HClO_4$ were required to elute the blue $Cr(H_2O)_6^{3+}$ cation (which is present in the preparation from the diperoxo-complex) or the $Cr(H_2O)_6^{3+}$ and $Cr(en)(H_2O)_3Cl^{2+}$ complexes (species present in the preparation from the dichloro-complex). Elution with this amount of acid brings the red band of $Cr(en)(H_2O)_4^{3+}$ to the bottom of the column. Finally $Cr(en)(H_2O)_4^{3+}$ was eluted with *ca.* 75 ml of 3M-$HClO_4$. The column was covered with aluminium foil throughout to avoid possible photochemical reactions. The solution was analysed for chromium content by oxidizing 1 ml of solution with hydrogen peroxide in basic solution (final solution *ca.* 1M in NaOH), and measuring the chromium(VI) absorption at 372 nm. The hydrogen-ion concentration of the solution was determined by first exchanging the complex ions for H^+ on a cation exchange column, and then titrating in the normal way. Typical solutions were 0·027M in $Cr(en)(H_2O)_4^{3+}$ and 2·87M in $HClO_4$. The solution was further diluted with an equal volume of 2·0M-NaOH at 0 °C to give a solution 0·013M in complex, 1·0M in $NaClO_4$, and 0·43M in $HClO_4$. This stock solution was stored at 0 °C, and its spectrum checked periodically for any signs of decomposition.

Diaquoethylenediamineoxalatochromium(III) *Perchlorate.*—A solution of the complex was prepared by reaction of $[Cr(en)(H_2O)_2Cl_2]Cl$ with sodium oxalate in a 1 : 1 mol ratio in 0·01M-$HClO_4$ at 50 °C for 1·5 h in the dark. From this solution the cation was separated by elution from a 1 × 10 cm column of Dowex 50W-X8, 100—200 mesh, with 0·5M-$HClO_4$, after any unchanged $Cr(en)(H_2O)_2Cl_2^+$ and $Cr(C_2O_4)(H_2O)_4^+$ had been washed off with 0·03M-$HClO_4$. The chromium(III) content was determined as described above. The spectrum is identical with that of a sample of $Cr(en)(C_2O_4)(H_2O)_2^+$ separated by ion-exchange technique from the reaction of $Cr(en)(H_2O)_4^{3+}$ with oxalate.

2-*Aminoethylammoniumtriaquo-oxalatochromium*(III) *Perchlorate.*—Aquation of $Cr(en)(C_2O_4)(H_2O)_2^+$ in 0·5M-$HClO_4$ for 1·5 h at 50 °C in the dark yielded $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$. The cation was separated using a 1 × 10 cm column of Dowex 50W-X8, 100—200 mesh ion-exchange resin, and eluting with 2·0M-$HClO_4$ after unchanged $Cr(en)(C_2O_4)(H_2O)_2^+$ and $Cr(C_2O_4)(H_2O)_4^+$ had been washed off with 0·5M-$HClO_4$. The chromium content was determined as previously.

Tris(*ethylenediamine*)*chromium*(III) *Chloride.*—A sample of $[Cr(en)_3]Cl_3,3H_2O$ was prepared as described in ref. 15. This was converted into the perchlorate salt.

Formation and Decay of Products.—The products of the reaction of $Cr(en)(H_2O)_4^{3+}$ and oxalate were separated and the chromium content determined as follows. At appropriate time intervals 0·5 ml of the reaction mixture was pipetted into 20 ml of ice-cold water to quench the reaction and at the same time to achieve sufficient dilution to make separation of the various fractions possible. Each diluted sample of the reaction mixture was forced down a 7 × 40 mm column of Dowex 50W-X8 100—200 mesh cation-exchange resin (hydrogen form), by compressed air (rate *ca.* 10 ml/min). The column was then washed with solutions of $HClO_4$ of increasing concentration, and the eluate collected in 12·5 ml quantities, until the chromium content had decreased to zero. A solution of higher perchloric acid concentration was then used. Complexes in order of elution were, $Cr(C_2O_4)(H_2O)_4^+$, 50 ml of 0·02M; $Cr(en)(C_2O_4)(H_2O)_2^+$, 25 ml of 0·10M; $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ 25 ml of 1·0M; $Cr(en)(H_2O)_4^{3+}$ 50 ml of 3·0M, where volumes

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[14] D. M. Tully-Smith, R. K. Kurimoto, D. A. House, and C. S. Garner, *Inorg. Chem.*, 1967, **6**, 1524.

[15] R. D. Gillard and P. R. Mitchell, *Inorg. Synth.*, 1972, **13**, 184.

and concentrations refer to the perchloric acid. Each eluate fraction was analysed for its chromium content using a Perkin-Elmer model 303 atomic absorption spectrometer with a chromium lamp under standard conditions. A calibration curve at each perchloric acid concentration was obtained from sets of chromium standard in the range 0—6 p.p.m. prepared from B.D.H. 0·1N-potassium dichromate primary standard. For the range of chromium concentrations 0—6 p.p.m. the accuracy of each determination was ±0·03 p.p.m., and this is equivalent to ±0·6% of the total chromium (Figure 2) for eluates in 0·02, 0·10, and 1·0M-$HClO_4$, and ±1% for the eluates in 3·0M-$HClO_4$. The experiment was repeated twice and reproducibility was satisfactory. The procedure was tested on a mixture of $Cr(en)(C_2O_4)(H_2O)_2^+$ and $Cr(enH)(C_2O_4)(H_2O)_3^{2+}$ of known composition. An independent experiment with $Cr(en)(H_2O)_4^{3+}$ indicated that this complex is eluted quantitatively from the ion-exchange column with 3·0M-perchloric acid.

Kinetics Runs.—Solutions of $Cr(en)(H_2O)_4^{3+}$, 1·0M-$HClO_4$ or 1·0M-NaOH, and 5·02M-$NaClO_4$ were pipetted into a 25-ml volumetric flask, and after thermostatting to the required temperature, a volume of 0·20M AnalaR sodium oxalate at the same temperature was added. The reaction was monitored on a Unicam SP 500 spectrophotometer, complete with thermostatted cell housing. Final absorbance readings (OD_∞) were calculated from known molar absorption coefficients for $Cr(en)(C_2O_4)(H_2O)_2^+$. Reactions were generally followed to 60—70% completion of the first stage. AnalaR sodium perchlorate and perchloric acid were used to prepare stock solutions.

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