Kinetics of Complexing of Oxalate to Penta-ammineaquochromium(III)

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The complex penta-ammineaquochromium(III) reacts with oxalate ions to form tetra-ammineoxalatochromium(III) and there is no evidence for any significant build-up of the monodentate oxalato-intermediate $[Cr(NH_3)_5(C_2O_4)]^+$. It is concluded that the step in which the oxalate ion chelates is rapid. The kinetics of the first stage of the reaction, involving co-ordination of oxalate ion to $[Cr(NH_3)_5H_2O]^{3+}$, have been investigated at pH 3—4 and at temperatures in the range 40—60 °C, I = 1·0M ($NaClO_4$). The interpretation given is consistent with the formation of ion-pairs between the oxalate ions $C_2O_4^{2-}$(K') and $C_2O_4H^-$(K'') and $[Cr(NH_3)_5H_2O]^{3+}$, where, at 50 °C, $K' = 4·5 \pm 0·2$ l mol^{-1} and $K'' = 1·16 \pm 0·06$ l mol^{-1}. The rate constants k_1 and k_2 for the reactions of the ion-pairs $[Cr(NH_3)_5H_2O]^{3+}, C_2O_4^{2-}$ and $[Cr(NH_3)_5H_2O]^{3+}, C_2O_4H^-$ are equal ($6·2 \times 10^{-4}$ s^{-1} at 50 °C), with $\Delta H^\ddagger = 26·4 \pm 0·8$ kcal mol^{-1} and $\Delta S^\ddagger = 8·6 \pm 0·4$ cal K^{-1} mol^{-1}. Rate constants do not differ significantly from values obtained for the water exchange of the ion $[Cr(NH_3)_5H_2O]^{3+}$, which suggests that the reactions proceed by a dissociative-interchange mechanism.

WHEN oxalate ion reacts with the ions $[Cr(H_2O)_6]^{3+}$,[1,2] $[Cr(C_2O_4)(H_2O)_4]^+$,[2,3] *cis*-$[Cr(C_2O_4)_2(H_2O)_2]^-$,[4] and $[Cr(en)(H_2O)_4]^{3+}$ (en = ethylenediamine),[5] no evidence is obtained for the formation of species containing a monodentate oxalato-group, and the step involving chelation with the displacement of a second water molecule is presumed to be rapid. The cobalt(III) complexes $[Co(NH_3)_5(C_2O_4)]^+$ and $[Co(NH_3)_4(C_2O_4)]^+$ have both been isolated and are well characterised;[6] conversion of the first of these complexes into the second, with the displacement of NH_3, does not occur readily (if at all). The chromium(III) complex $[Cr(NH_3)_4(C_2O_4)]^+$ is also well known,[7,8] but as yet the complex $[Cr(NH_3)_5(C_2O_4)]^+$ containing a monodentate oxalato-group has not been identified. As part of our studies on the chelation of oxalate ion to chromium(III), it was decided to study the kinetics and mechanism of the reaction of oxalate ion with the complex $[Cr(NH_3)_5H_2O]^{3+}$. At the outset, the identity of the product and possible formation of the complexes $[Cr(NH_3)_5(C_2O_4)]^+$ *and* $[Cr(NH_3)_4(C_2O_4)]^+$ was of interest.

RESULTS

Preliminary Studies.—U.v.-visible spectra of the complexes $[Cr(NH_3)_5H_2O]^{3+}$ and $[Cr(NH_3)_4(C_2O_4)]^+$ are shown in Figure 1. Isosbestic points at 339, 424, and 465 nm were observed for the first 26% of the reaction of 0·18M-sodium oxalate with $3·6 \times 10^{-3}$M-$[Cr(NH_3)_5H_2O]^{3+}$ at 25 °C and pH 3·0, in agreement with Figure 1. It is concluded that there is no significant build-up of the complex $[Cr(NH_3)_5(C_2O_4)]^+$ during the conversion of $[Cr(NH_3)_5H_2O]^{3+}$ into $[Cr(NH_3)_4(C_2O_4)]^+$. The isosbestic points are not retained over longer periods of time because aquation of ammonia ligands occurs. The rate constant for the loss of the first ammonia ligand from the $[Cr(NH_3)_4(C_2O_4)]^+$ complex is $0·74 \times 10^{-4}$ s^{-1} at 50 °C and I = 0·01M ($NaClO_4$).[9] Commencing with a sample of the perchlorate salt of the complex $[Cr(NH_3)_4(C_2O_4)]^+$ in 0·1M-$HClO_4$, we observed isosbestic points at 389 and 528 nm. However, before completion of this reaction, further loss of ammonia occurs,[9] and, when free oxalate ion is present, additional complexing with oxalate may take place. No evidence was obtained for a first step in which unco-ordinated oxalate ion displaces an ammonia ligand. The reaction sequence is accordingly as in (1)—(3). The inclusion of $C_2O_4^{2-}$ on the left-hand side of (1) does not necessarily exclude $C_2O_4H^-$ (or $C_2O_4H_2$) as a reactant.

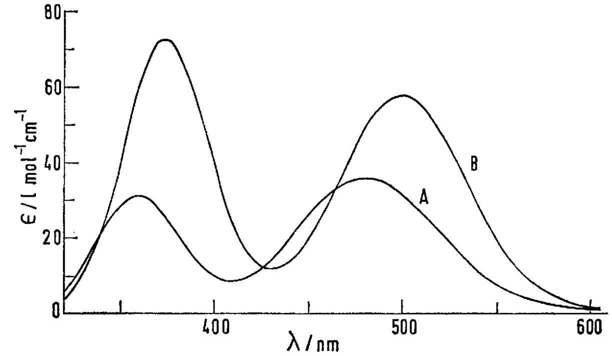

FIGURE 1 U.v.-visible range spectra for perchlorate salts of the complexes $[Cr(NH_3)_5H_2O]^{3+}$ (A) and $[Cr(NH_3)_4(C_2O_4)]^+$ (B) in 0·1M-perchloric acid and I = 1·0M ($NaClO_4$)

$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4^{2-} \longrightarrow [Cr(NH_3)_5(C_2O_4)]^+ + H_2O \quad (1)$$

$$[Cr(NH_3)_5(C_2O_4)]^+ \xrightarrow{\text{fast}} [Cr(NH_3)_4(C_2O_4)]^+ + NH_3 \quad (2)$$

$$[Cr(NH_3)_4(C_2O_4)]^+ \longrightarrow [Cr(NH_3)_3(H_2O)(C_2O_4)]^+ + NH_3 \quad (3)$$

Kinetic Studies.—The kinetics of reaction (1) were studied by following absorbance (OD) changes at the isosbestic points at 389 and 528 nm for (3). At these wavelengths, absorption coefficients for the complex $[Cr(NH_3)_5H_2O]^{3+}$ are 14·5 and 17·0 l mol^{-1} cm^{-1}, and for $[Cr(NH_3)_4(C_2O_4)]^+$ 58·0 and 42·0 l mol^{-1} cm^{-1} respectively. The total con-

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

[2] C. Schenk, H. Stieger, and H. Kelm, *Z. anorg. chem.*, 1972, **391**, 1.

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

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

[5] Othman Nor, J. W. Lethbridge, and A. G. Sykes, *J.C.S. Dalton*, 1973, in the press.

[6] See for example, C. Hwang and A. Haim, *Inorg. Chem.*, 1970, **9**, 500 and references therein.

[7] G. G. Schlessinger, 'Inorganic Laboratory Preparations,' Chemical Publishing Co. Inc., New York, 1962, p. 226.

[8] R. Davies and R. B. Jordan, *Inorg. Chem.*, 1971, **10**, 2432.

[9] M. B. Davies, J. W. Lethbridge, and M. S. Mirrlees, unpublished work; see also the data of D. A. House, *Acta Chem. Scand.*, 1972, **26**, 2847.

centration of oxalate ion, $[C_2O_4^{2-}]_T$, was always in at least a ten-fold excess over the complex and effective hydrogen-ion concentrations were in the range 10^{-3}—10^{-4}M. At higher $[H^+]$ values, reaction (1) is much slower and (3) is more significant. The concentration of $H_2C_2O_4$ species is small for the conditions investigated and, in view of the slowing down of (1) on increasing $[H^+]$, contributions from the reaction of $H_2C_2O_4$ have been neglected in our treatment. The total hydrogen-ion concentration (*i.e.* the perchloric acid required in making-up solutions) was calculated from (4), where K_1 and K_2 are as defined in (5)

$$[H^+]_T = \frac{[H^+]\{[C_2O_4^{2-}]_T(1 + 2[H^+]/K_1) + K_2 + [H^+]\}}{K_2 + [H^+]} \qquad (4)$$

and (6) respectively. Throughout the paper terms in

$$H_2C_2O_4 \xrightleftharpoons{K_1} HC_2O_4^- + H^+ \qquad (5)$$

$$HC_2O_4^- \xrightleftharpoons{K_2} C_2O_4^{2-} + H^+ \qquad (6)$$

$[H^+]^2/K_1$ have been neglected. For initial runs the hydrogen-ion concentration was monitored throughout using a duplicate run solution and was found to be consistent with (4) over the required reaction time. Contributions from $2[H^+]/K_1$ in (4) are $\ll 1$ over the pH range 3·4—4·0 at all three temperatures employed, and for these conditions could be neglected. Concentrations of the ions $C_2O_4^{2-}$ and $C_2O_4H^-$ were calculated from (7) and (8).

$$[C_2O_4^{2-}] = K_2[C_2O_4^{2-}]_T/([H^+] + K_2) \qquad (7)$$

$$[C_2O_4H^-] = [H^+][C_2O_4^{2-}]_T/([H^+] + K_2) \qquad (8)$$

The acid dissociation constants K_1 and K_2 were obtained by extrapolation of existing data;[10] values used were $K_1 = 6{\cdot}52 \times 10^{-2}$ (40), $5{\cdot}62 \times 10^{-2}$ (50), and $4{\cdot}79 \times 10^{-2}$ mol l^{-1} (60 °C) and $K_2 = 2{\cdot}61 \times 10^{-4}$ (40), $2{\cdot}50 \times 10^{-4}$ (50), and $2{\cdot}40 \times 10^{-4}$ mol l^{-1} (60 °C). The ionic strength was adjusted to $I = 1{\cdot}0$M using $NaClO_4$. First-order plots of log $(OD_\infty - OD_t)$ against time showed good linearity to 20—35%, and in some cases up to 45% completion. Curvature was in the direction of slower reaction, and further aquation of the ammonia ligands of the complex $[Cr(NH_3)_3(H_2O)(C_2O_4)]^+$ may occur since the product formed had smaller ε values than those of the complexes $[Cr(NH_3)_4(C_2O_4)]^+$ and $[Cr(NH_3)_3(H_2O)(C_2O_4)]^+$ at 389 and 528 nm. The direction of curvature is not consistent with formation of one of the isomers of $[Cr(NH_3)_2(C_2O_4)_2]^-$, which is reported[11] to have stronger absorption at both the wavelengths investigated. Pseudo-first-order rate constants, k_{obs} evaluated at 389 and 528 nm, agreed to within 1% (5 runs). Subsequently runs were monitored at 389 nm (Table 1).

TABLE 1

Rate constants for the complexing of oxalate ion with the complex $[Cr(NH_3)_5H_2O]^{3+}$: λ = 389 nm; $I = 1{\cdot}0$M ($NaClO_4$)

Temp. °C	$10^4[H^+]$ M	$10^3[Cr(NH_3)_5H_2O^{3+}]$ M	$[C_2O_4^{2-}]_T$ M	10^4k_{obs} s^{-1}
40	1·0	2·90	0·18	0·665
		2·39	0·18	0·645
		2·90	0·12	0·478
		2·90	0·078	0·411
		2·90	0·06	0·304
		2·71	0·04	0·209
	4·0	2·20	0·10	0·368
		2·71	0·067	0·257
		1·87	0·05	0·204
		2·46	0·04	0·166
		3·17	0·03	0·127
	7·1	2·32	0·12	0·348
		3·83	0·067	0·218
		2·47	0·05	0·168
		3·27	0·04	0·136
	10·0	2·90	0·12	0·310
		2·70	0·12	0·317
		2·54	0·083	0·242
		2·28	0·067	0·199
		2·32	0·05	0·151
50	1·0	1·00	0·18	2·63
		1·85	0·067	1·20
		1·89	0·04	0·775
		2·67	0·03	0·614
	4·0	1·80	0·18	2·03
		2·00	0·067	0·914
		2·14	0·05	0·699
		2·28	0·04	0·560
	7·1	3·27	0·18	1·57
		5·88	0·10	1·05
		1·92	0·067	0·752
		2·24	0·05	0·576
	10·0	4·02	0·18	1·49
		7·75	0·10	0·983
		1·80	0·067	0·676
		1·95	0·05	0·514
60	1·0	0·904	0·18	8·00
		1·49	0·067	3·68
		1·23	0·04	2·48
		1·23	0·03	1·90
	4·0	1·35	0·18	6·45
		1·42	0·067	2·94
		1·55	0·05	2·30
		1·65	0·04	1·80
	7·1	4·62	0·18	5·30
		5·89	0·10	3·30
		1·47	0·067	2·34
		1·24	0·05	1·78
	10·0	2·87	0·18	4·57
		7·11	0·10	2·97
		1·65	0·067	2·05
		2·01	0·05	1·57

For the reaction sequence (9)—(12), where (9) and (11)

$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4^{2-} \xrightleftharpoons{K'} [Cr(NH_3)_5H_2O]^{3+},C_2O_4^{2-} \qquad (9)$$

$$[Cr(NH_3)_5H_2O]^{3+},C_2O_4^{2-} \xrightarrow{k_1} \text{Products} \qquad (10)$$

$$[Cr(NH_3)_5H_2O]^{3+} + C_2O_4H^- \xrightleftharpoons{K''} [Cr(NH_3)_5H_2O]^{3+},C_2O_4H^- \qquad (11)$$

$$[Cr(NH_3)_5H_2O]^{3+},C_2O_4H^- \xrightarrow{k_2} \text{Products} \qquad (12)$$

involving ion-pair formation are assumed to be rapid, the dependence of k_{obs} on $[C_2O_4^{2-}]_T$ and $[H^+]$ is as in (13).

$$\frac{k_{obs}}{[C_2O_4^{2-}]_T} = \frac{k_1K'K_2 + k_2K''[H^+]}{[H^+] + K_2 + (K'K_2 + K''[H^+])[C_2O_4^{2-}]_T} \qquad (13)$$

This equation can be rearranged to give (14), where $A = k_1K'K_2 + k_2K''[H^+]$.

$$\frac{1}{k_{obs}} = \frac{[H^+] + K_2}{A} \cdot \frac{1}{[C_2O_4^{2-}]_T} + \frac{K'K_2 + K''[H^+]}{A} \qquad (14)$$

At constant $[H^+]$, plots of $1/k_{obs}$ against $1/[C_2O_4^{2-}]_T$ were linear (see for example, a plot of

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[10] G. Davies and K. O. Watkins, *Inorg. Chem.*, 1970, **9**, 2735; 'Stability Constants of Metal-ion Complexes,' *Chem. Soc. Special Publ.*, No. 25, 1971, p. 245.

[11] E. Kyuno, M. Kamada, and N. Tanaka, *Bull. Chem. Soc. Japan*, 1967, **40**, 1848.

the data at 50 °C in Figure 2). Since data at different $[H^+]$ values had a common intercept, this suggests that $k_1 = k_2$. From (14) the intercepts and gradients of these plots (see for example the plot in Figure 2) should exhibit an $[H^+]$ dependence as in (15). Linear plots of the left-hand side of this equation against $[H^+]$ were observed at all three temperatures (Figure 3). Values of $K'K_2$ and K'' were evaluated from the intercept and gradient respectively. Finally (13) can be rearranged to (16)

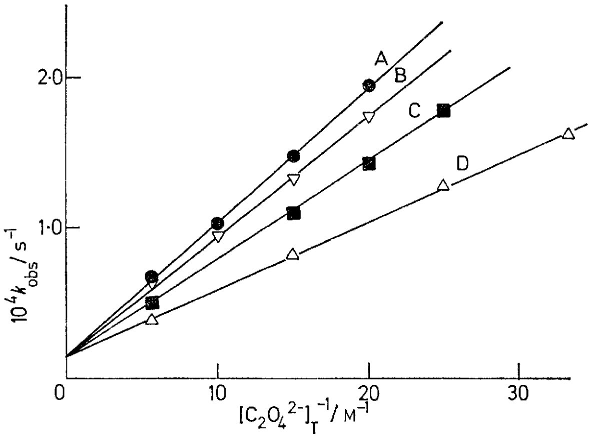

FIGURE 2 Dependence of k_{obs} on $[C_2O_4^{2-}]_T$ at 50 °C and $I = 1{\cdot}0$M ($NaClO_4$); $10^4[H^+] = 10{\cdot}0$, 7·1, 4·0, and 1·0M for A—D respectively

$$(\text{Intercept/Gradient})([H^+] + K_2) = K'K_2 + K''[H^+] \quad (15)$$

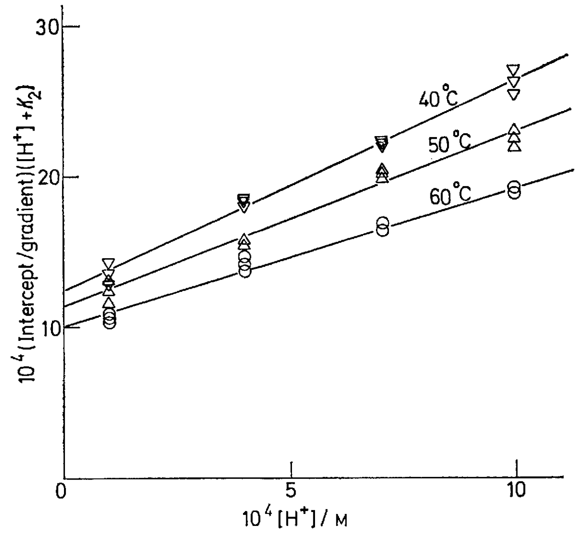

FIGURE 3 Dependence of intercepts and gradients on $[H^+]$ for plots illustrated in Figure 3. Lines drawn are as obtained by least-squares fitting of the data

$$k_{obs}\left(\frac{[H^+] + K_2}{[C_2O_4^{2-}]_T} + K'K_2 + K''[H^+]\right) = k_1K'K_2 + k_2K''[H^+] \quad (16)$$

and Figure 4 is a plot of the left-hand side of equation (16) (designated B) against $[H^+]$. The intercept and gradient give $k_1K'K_2$ and k_2K'' respectively. Values of k_1, k_2, K', and K'' are given in Table 2. Enthalpies ($\Delta H^‡$) and entropies of activation ($\Delta S^‡$) were obtained from plots of log (k/T) against $1/T$. Thermodynamic parameters were evaluated for K' and K'' from plots of log K against $1/T$ (Table 3). Errors were determined in all cases by a least-squares treatment of data. Experimental points lying outside two standard deviations were given half the weighting of points lying inside this range. It is concluded that, within experimental error, $k_1 = k_2$. From the combined data: $k_1 = 6{\cdot}2 \times 10^{-4}\ s^{-1}$ at 50 °C; $\Delta H^‡ = 26{\cdot}4 \pm 0{\cdot}8$ kcal mol^{-1}; and $\Delta S^‡ = 8{\cdot}6 \pm 0{\cdot}4$ cal K^{-1} mol^{-1}.

TABLE 2

Values for rate constants k_1 and k_2 and ion-pair constants K' and K'', $I = 1{\cdot}0$M ($NaClO_4$)

Temp./°C	40	50	60
$10^4k_1/s^{-1}$	1·68 ± 0·07	6·46 ± 0·35	22·4 ± 0·9
$10^4k_2/s^{-1}$	1·55 ± 0·09	5·86 ± 0·50	22·2 ± 3·3
K'/l mol^{-1}	4·7 ± 0·1	4·5 ± 0·2	4·17 ± 0·08
K''/l mol^{-1}	1·4 ± 0·05	1·16 ± 0·06	0·92 ± 0·03

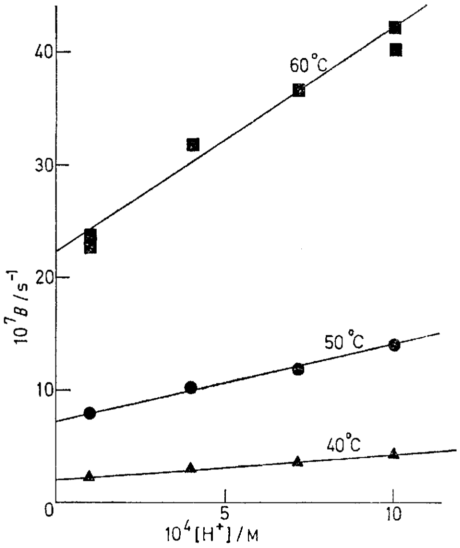

FIGURE 4 Dependence of B, as defined in equation (16), on $[H^+]$. Lines drawn are as obtained by least-squares fitting of the data

TABLE 3

Activation parameters for rate constants k_1 and k_2 and thermodynamic parameters for ion-pair constants K' and K'', $I = 1{\cdot}0$M ($NaClO_4$)

Constant	Enthalpy term kcal mol^{-1}	Entropy term cal K^{-1} mol^{-1}
k_1	$\Delta H^‡ = 26{\cdot}2 \pm 0{\cdot}3$	$\Delta S^‡ = 7{\cdot}8 \pm 0{\cdot}1$
k_2	$\Delta H^‡ = 26{\cdot}7 \pm 1{\cdot}3$	$\Delta S^‡ = 9{\cdot}4 \pm 0{\cdot}6$
K'	$\Delta H_0 = -1{\cdot}3 \pm 1{\cdot}0$	$\Delta S_0 = -0{\cdot}9 \pm 5{\cdot}0$
K''	$\Delta H_0 = -4{\cdot}3 \pm 0{\cdot}4$	$\Delta S_0 = -13{\cdot}0 \pm 1{\cdot}0$

DISCUSSION

At 50 °C, first-order rate constants k_{obs} for reaction (1) are in the range $0{\cdot}5 \times 10^{-4}$—$2{\cdot}6 \times 10^{-4}\ s^{-1}$, (2) is rapid, and the rate constant for (3) is *ca.* $0{\cdot}74 \times 10^{-4}\ s^{-1}$. The rate constant for further loss of an ammonia ligand to give the complex $[Cr(NH_3)_2(H_2O)_2(C_2O_4)]^+$ is *ca.* $0{\cdot}6 \times 10^{-4}$ s^{-1} at 50 °C and $I = 0{\cdot}01$M.[9] The kinetics of reaction (1) are satisfactorily accounted for by the sequence (9)—(12). Rate constants k_1 and k_2, equations (10) and (12), are identical and are believed to correspond to the replacement of the water ligand in the complex $[Cr(NH_3)_5H_2O]^{3+}$. Reaction paths in which an ammonia instead of a water ligand is replaced by an oxalato-group in the first step are not included in our treatment, since, at the temperatures investigated, the exchange of water in the $[Cr(NH_3)_5H_2O]^{3+}$ complex is an order of magnitude faster than aquation of an ammonia ligand.[12] The conjugate base $[Cr(NH_3)_5OH]^{2+}$ does not appear to be sufficiently reactive for the path involving this species and loss of an ammonia ligand to be relevant.[12]

The finding that reaction (2), involving chelation of a monodentate oxalato-group and displacement of an ammonia ligand, is rapid is of interest in the context of other studies,[1-5] in which chelation of the oxalato-group with displacement of a water ligand has been shown to be rapid. Clearly these reactions have considerable S_N2 character. No information is available as to the relative rates of displacement of ammonia and water ligands in such a situation. The observation that the ammonia ligand is displaced, *cf.* the complex $[Co(NH_3)_5(C_2O_4)]^+$, is consistent with the decrease in stability of Cr–NH$_3$ as opposed to Co–NH$_3$ bonds.[13]

Ion-pair formation constants K' and K'' were calculated for 3+,2– and 3+,1– interactions using the Fuoss equation.[14] Variation of the dielectric constant with temperature was taken into account. For 5 and 10 Å separations of the ions and at an ionic strength $I = 0{\cdot}5$M, values of K' and K'' were calculated at 40, 50, and 60 °C.[15] Hence it is possible to estimate ΔH_0 and ΔS_0 (Table 4). While individual K' and K'' values at 40 °C may be considered to be in satisfactory agreement with experimentally determined values, the temperature variation, although small, is in the opposite direction to that observed experimentally. Hydrogen bonding between the oxalato-group and the protons of NH$_3$ and H$_2$O ligands may be effective. The Fuoss treatment does not take account of this factor.

TABLE 4

Comparison of K' and K'' values, equations (9) and (11), and corresponding thermodynamic parameters as obtained from the Fuoss equation, for 5 and 10 Å separation of the reactants, with those obtained experimentally at 40 °C

	Ion-pair constant / l mol.$^{-1}$	ΔH_0 / kcal mol^{-1}cal	ΔS_0 / cal K^{-1} mol^{-1}
Fuoss (5 Å) [a]	$K' = 22{\cdot}4$	3·48	17·5
(10 Å) [a]	$K' = 10{\cdot}2$	1·74	10·2
Experimental [b]	$K' = 4{\cdot}7$	–1·3	–0·9
Fuoss (5 Å) [a]	$K'' = 1{\cdot}9$	1·74	12·2
(10 Å) [a]	$K'' = 0{\cdot}7$	0·87	6·0
Experimental [b]	$K'' = 1{\cdot}4$	–4·3	–13

[a] $I = 0{\cdot}5$M; the Fuoss equation does not give satisfactory values at higher ionic strengths. [b] $I = 1{\cdot}0$M (NaClO$_4$).

The rate constant k_1 ($= k_2$) has been extrapolated to 30 °C, at which temperature data are available for the water-exchange reaction of the complex $[Cr(NH_3)_5H_2O]^{3+}$.[16] A comparison with other data for the anation of $[Cr(NH_3)_5H_2O]^{3+}$ by Cl$^-$ and NCS$^-$ is made in Table 5. Rate constants for the different charge types $C_2O_4^{2-}$, $C_2O_4H^-$, and H$_2$O do not show any significant dependence on the nature of the incoming ligand, which strongly suggests a dissociative (S_N1) interchange mechanism. The assignment of mechanism to reactions of the $[Cr(NH_3)_5H_2O]^{3+}$ complex is less straightforward than for hexa-aquometal ions, however, since $[Cr(NH_3)_5H_2O]^{3+}$ has non-identical sites for ion-pairing. Thus with Cl$^-$ and NCS$^-$ it is possible that the remote side of the complex away from the H$_2$O ligand is the preferred site for ion-pairing,[16] and that this factor is largely responsible for the slower rate constants observed for Cl$^-$ and NCS$^-$ in Table 5. Activation parameters reported for the water-exchange reaction[17] (see footnote *b* in Table 5) differ significantly from those obtained for $C_2O_4^{2-}$ and $C_2O_4H^-$ in this study.

TABLE 5

Summary of data (30 °C) for the water exchange and anation of the complex $[Cr(NH_3)_5H_2O]^{3+}$ {product $[Cr(NH_3)_5X]^{n+}$}. An allowance has been made for ion-pair formation

X	k / s^{-1}	Reference
Cl$^-$	$3{\cdot}3 \times 10^{-6}$ [a]	16
NCS$^-$	$4{\cdot}9 \times 10^{-6}$ [a]	16
H$_2$O	$1{\cdot}1 \times 10^{-4}$ [b]	16
$C_2O_4^{2-}$	$0{\cdot}45 \times 10^{-4}$ [c]	This work
$C_2O_4H^-$	$0{\cdot}35 \times 10^{-4}$ [c]	This work

[a] $I = 0{\cdot}11$M; also studied at $I = 1{\cdot}71$M. [b] No significant variation with ionic strength $I = 0{\cdot}11$ and $1{\cdot}71$M. Activation parameters are $\Delta H^‡ = 23{\cdot}2 \pm 0{\cdot}5$ kcal mol^{-1} and $\Delta S^‡ = 0{\cdot}0 \pm 1{\cdot}6$ cal K^{-1} mol^{-1} (ref. 17). [c] $I = 1{\cdot}0$M (NaClO$_4$); the rate constant was obtained by extrapolation of data at 40—60 °C. Within experimental error, k values for $C_2O_4^{2-}$ and $C_2O_4H^-$ are equal.

EXPERIMENTAL

Solutions of perchloric acid, sodium perchlorate, and sodium oxalate were prepared from AnalaR grade reagents.

Preparations.—Penta-ammineaquochromium(III) *perchlorate.* The perchlorate salt of this complex was prepared from ammonium penta-ammineaquochromium(III) nitrate[18] by dissolving the latter (5 g) in the minimum amount of water at 50 °C.[19] Sufficient solid sodium perchlorate was

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[12] J. Bjerrum and E. Jorgensen, *J. Inorg. Nuclear Chem.*, 1958, **8**, 313; E. Jorgensen and J. Bjerrum, *Acta Chem. Scand.*, 1958, **12**, 1047.

[13] See for example, C. S. Garner and D. A. House, *Transition Metal Chem.*, ed. R. L. Carlin, vol. 6, 1970, p. 263.

[14] R. M. Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[15] See for example, M. R. Hyde and A. G. Sykes, *J.C.S. Chem. Comm.*, 1972, 1340. The approach used is not satisfactory for $I > 0{\cdot}5$M.

[16] N. V. Duffy and J. E. Early, *J. Amer. Chem. Soc.*, 1967, **89**, 272.

[17] T. W. Swaddle and D. R. Stranks, *J. Amer. Chem. Soc.*, 1972, **94**, 8357.

[18] T. Moeller, *Inorg. Synth.*, 1957, **5**, 132.

[19] R. K. Wharton, Ph.D. Thesis, University of Leeds, 1973.

then added to give a cloudy precipitate at 50 °C. The mixture was cooled in ice and the product filtered off and rinsed with cold 1M-$HClO_4$. The crude product was dissolved in the minimum amount of water at 40 °C and solid $NaClO_4$ (*ca.* 0·5 g) added to the clear solution. The solution became cloudy and a little water was added until the turbidity just disappeared. The mixture was allowed to cool to room temperature and then in ice. The product was filtered, washed with ethanol, and stored in a desiccator {Found: H, 3·75; N, 15·5. $[Cr(NH_3)_5H_2O](ClO_4)_3$ requires H, 3·75; N, 15·4%}. Spectrum: $\lambda_{max.}$ at 360 (ε 31·3) and 480 nm (ε 36·3 l mol^{-1} cm^{-1}); $\lambda_{min.}$ at 406 nm (ε 8·7 l mol^{-1} cm^{-1}).

Tetra-ammineoxalatochromium(III) *perchlorate*. The perchlorate salt of this complex was prepared from the bromide salt, the preparation of which has been described by Schlessinger.[7] To a saturated solution of $[Cr(NH_3)_4(C_2O_4)]Br$ at 50 °C (2 g in *ca.* 30 cm^3 of water), saturated sodium perchlorate (30 cm^3) was added. Red-orange crystals of the perchlorate salt appeared on cooling the mixture in ice. After 3 h the crystals were filtered off and washed with cold 1M-$HClO_4$ until the washing was colourless. The sample was dried over silica gel [Found: C, 7·30; H, 4·3; N, 17·15. $[Cr(NH_3)_4(C_2O_4)]ClO_4,H_2O$ requires C, 7·35; H, 4·30; N, 17·20%}. The visible spectrum was in good agreement with that reported by Davies and Jordan;[8] $\lambda_{max.}$ at 373 (ε 73·0) and 501 nm (ε 58·0 l mol^{-1} cm^{-1}); $\lambda_{min.}$ at 429 nm (ε 11·8 l mol^{-1} cm^{-1}).

Kinetic Runs.—Solutions of 1·0M-(sometimes 0·10M-) $HClO_4$, 5·02M-$NaClO_4$, and 0·3M-sodium oxalate were pipetted into a volumetric flask (25 cm^3) and the volume made up to the mark with water. After thermostatting this solution to the required temperature, a weighed amount (0·010—0·090 g) of the complex $[Cr(NH_3)_5H_2O](ClO_4)_3$ was added, which quickly dissolved, and the resulting solution was transferred to an optical cell in the thermostatted cell housing of a Unicam SP 500 spectrophotometer. Reactions were generally followed to 40—60% completion of reactions (1) and (2). Final absorbance (OD_∞) values were calculated from the known molar absorption coefficients for the $[Cr(NH_3)_4(C_2O_4)]^+$ complex.

pH *Measurements.*—For a representative number of solutions in the kinetic runs, the pH was monitored with a Radiometer pH meter 4 using Radiometer glass (type G202C) and calomel (type K401) electrodes throughout the run. The pH meter was standardised against Radiometer type S1001 buffer solution (pH 6·50) and B.D.H. universal buffer solution (pH 3·1). The pH was found to be constant over the period for which kinetic plots were linear.

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