Influence of Electrolytic Dissociation upon Rates of Reactions. Part VIII.[1] Acceleration of the Reaction between Chromium(II) and the Chloropenta-amminechromium(III) Complex by Sulphate Ion

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The rate of reaction between Cr^{2+} and $Cr(NH_3)_5Cl^{2+}$ has been studied over a range of ionic strength at 25 °C. The rate constant at zero ionic strength was found to be $2{\cdot}48 \times 10^{-3}$ l mol^{-1} s^{-1}. By using solutions of sodium sulphamate (which is redox-inert) buffered at pH 4·3, it was shown that addition of sulphate ions accelerates the reaction. This is attributed to the formation of kinetically active reactant–sulphate ion-pairs and the rate constant for the reaction of $CrSO_4$ with $Cr(NH_3)_5Cl^{2+}$ is calculated to be 0·068 l mol^{-1} s^{-1}.

Following our recent studies [2] of the acceleration by sulphate ions of the reaction between chromium(II) and protonated hydroxylamine we have examined the effect of sulphate ions on the rate of oxidation of chromium(II) by the chloropenta-amminechromium(III) complex. An earlier spectrophotometric study [3] of the latter reaction in acidic perchlorate media was carried out at high constant ionic strength to obtain activation parameters. Absorbance measurements have now been made over a range of ionic strength and acidity in order to extrapolate to a value of the rate constant at zero ionic strength. In addition we have used chloride-ion analysis to examine the increase in rate of reaction produced by addition of sulphate ions.

RESULTS AND DISCUSSION

In perchlorate media there are three reactions [(1)—(3)]

$$RCl^{2+} \xrightarrow{k_1} RH_2O^{3+} + Cl^- \tag{1}$$

$$5H^+ + Cr^{2+} + RCl^{2+} \xrightarrow{k_2} CrCl^{2+} + 5NH_4^+ + Cr^{2+} \tag{2}$$

$$Cr^{2+} + CrCl^{2+} \xrightarrow{k_3} Cr^{3+} + Cr^{2+} + Cl^- \tag{3}$$

to consider, where $R = Cr(NH_3)_5$. The contribution

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[1] Part VII, M. B. M. Campbell, M. R. Wendt, and C. B. Monk, preceding paper.

[2] Part VI, P. A. Jones and C. B. Monk, *J. Chem. Soc.*, (*A*), 1971, 971.

[3] A. E. Ogard and H. Taube, *J. Amer. Chem. Soc.*, 1958, **80**, 1084.

from reaction (3) is probably negligible under the conditions ($[H^+] \geqslant 0{\cdot}2$M) at which Ogard and Taube [3] made measurements, as shown by Sykes and Adin.[4] However, for the lower acidities used in the present experiments, a wavelength was chosen at an isosbestic point for $CrCl^{2+}$ and Cr^{3+} so that production of the latter in reaction (3) would not affect the absorbance readings. Ogard and Taube [3] assumed that only Cr^{2+} and $CrCl^{2+}$ were involved in the rate-determining step of reaction (2) and used the rate equation (4), where A_t is the absorbance of the reaction mixture at time t. It is easily shown by

$$\ln [RCl^{2+}]_0/[RCl^{2+}]_t = \ln \{(A_\infty - A_0)/(A_\infty - A_t)\} = (k_1 + k_2[Cr^{2+}])t \quad (4)$$

substitution and rearrangement that the Guggenheim treatment [5] can be applied and leads to equation (5),

$$2{\cdot}303 \log (A_t - A_{t'}) = \text{constant} - (k_1 + k_2[Cr^{2+}])t \quad (5)$$

where $(t' - t)$ is a fixed time interval Δt. This expression was used to analyse our absorbance data.

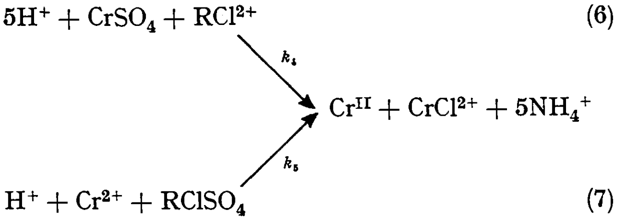
TABLE 1

Molar extinction coefficients ($l\ mol^{-1}\ cm^{-1}$) at 25 °C

Wavelength nm	$\varepsilon(RCl^{2+})$	$\varepsilon(RH_2O^{3+})$	$\varepsilon[Cr(H_2O)_6{}^{3+}]$	$\varepsilon[Cr(H_2O)_5Cl^{2+}]$
495	33·0	31·0	3·8	3·8
590	3·5	0·3	15·3	12·4

In studying the effect of sulphate ions we used solutions of pH $\geqslant 4{\cdot}3$ in order to avoid HSO_4^- formation. At this low acidity $Cr(H_2O)_6{}^{3+}$ is extensively hydrolysed [6] to $CrOH^{2+}$. Since the latter would contribute to the absorbance of the solutions and since a further complication is presented by the likely formation [6] of $Cr(H_2O)_5SO_4{}^+$, it was decided that direct spectrophotometry was not practicable. An additional problem is the large quantity of protons consumed by reaction (2) and in order to carry out the reaction at pH 4 it is necessary to buffer the solution. By using a kinetically indifferent buffer we have followed the release of chloride ions to the solution and observed the acceleration of reaction (2) produced by addition of sulphate ions.

The increase in rate is attributed to the formation of $CrSO_4$ and $RClSO_4$ ion-pairs which react according to equations (6), (7) [corresponding to reaction (2)], and (8)



$5H^+ + CrSO_4 + RCl^{2+}$ (6)

$\xrightarrow{k_4}$ $Cr^{II} + CrCl^{2+} + 5NH_4{}^+$ $\xleftarrow{k_5}$

$H^+ + Cr^{2+} + RClSO_4$ (7)

[which corresponds to reaction (1)]. There is documented evidence [7] for accelerated aquation of RCl^{2+} *via* equation (8) with $k_6 > k_1$. We assume that $k_4 \sim k_5 > k_2$.

$$RClSO_4 \xrightarrow{k_6} RH_2OSO_4{}^+ + Cl^- \quad (8)$$

The results, at 25 °C, were analysed to obtain values of k_4 and k_5.

Spectrophotometric Results.—The relevant molar extinction coefficients are given in Table 1. Absorbance changes at 495 nm were used to follow the rate of consumption of RCl^{2+} and the rate of formation of the chromium(III) products was monitored at 590 nm. The Guggenheim plots [equation (5)] were linear for the data obtained at 495 nm and for a given run the slope of the line did not vary when Δt was increased from 0·5 to 3 reaction half-lives. The values of k_2 are given in Table 2. In contrast, the absorbance data at 590 nm gave non-linear Guggenheim plots and for a given run the degree of curvature varied with the value of Δt. This is attributed to some decomposition of $CrCl^{2+}$ when its concentration becomes sufficiently high for reaction (3) to become significant. There would be little or no sign of this in the measurements at 495 nm since this is an isosbestic point for Cr^{3+} and $CrCl^{2+}$ (Table 1).

TABLE 2

Reaction rates in perchlorate media at 25 °C obtained by direct spectrophotometry. $[RCl(ClO_4)_2]_0$ *ca.* 2×10^{-3}M

$10^5[Cr(ClO_4)_2]$ M	$10^4[HClO_4]$ M	$10^3[NaClO_4]$ M	$10^3 I$ M	$10^4 k_2$ [a] $l\ mol^{-1}\ s^{-1}$	$10^5 k_2{}^0$ [b] $l\ mol^{-1}\ s^{-1}$
1660	1380	800	991	435	252
1660	917	834	987	435	252
1660	275	905	989	420	243
1250	275	923	994	434	251
833	275	936	994	426	246
1660	275	688	771	392	246
1660	275	476	559	341	245
1660	275	238	321	266	247
1660	275	0	83	128	242
833	275	0	60	112	250

[a] From equation (5) using $k_1 = 1 \times 10^{-5}\ s^{-1}$ (ref. 7). [b] Calculated from equation (9).

The variation of the rate constants with ionic strength (Table 2) can be accounted for by equation (9); the

$$\log k_2 = \log k_2{}^0 + 4[I^{\frac{1}{2}}/(1 + 2I^{\frac{1}{2}}) - 0{\cdot}024I] \quad (9)$$

calculated values for $k_2{}^0$ show no trend and lead to an

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[4] A. G. Sykes and A. Adin, *J. Chem. Soc.* (*A*), 1966, 1518.

[5] E. A. Guggenheim, *Phil. Mag.* (7), 1926, **2**, 538.

[6] J. E. Earley and R. D. Cannon, 'Transition Metal Chemistry,' ed. R. L. Carlin, Edward Arnold, London, 1965, vol. 1, ch. 2.

[7] J. B. Walker and C. B. Monk, *J. Chem. Soc.* (*A*), 1966, 1372.

average figure of $(2{\cdot}48 \pm 0{\cdot}05) \times 10^{-3}$ l mol^{-1} s^{-1}. For small values of I equation (9) closely approaches the limiting Debye–Huckel expression for the primary kinetic-salt effect and k_2^0 is the rate constant of reaction (2) at zero ionic strength. Ogard and Taube[3] reported a value of $5{\cdot}13 \times 10^{-2}$ l mol^{-1} s^{-1} for k_2 at $I = 1{\cdot}0$M and 25 °C. The discrepancy between this figure and that calculated from equation (9), namely $4{\cdot}28 \times 10^{-2}$ l mol^{-1} s^{-1}, may be due in part to the different ways in which the chromium(II) perchlorate solution was prepared. Ogard and Taube reduced $Cr(ClO_4)_3$ with amalgamated zinc so that their solutions contained a substantial amount of $Zn(ClO_4)_2$, whereas we dissolved chromium metal in perchloric acid.

Results from Potentiometric Titration of Chloride Ions.—Some preliminary runs were carried out with little success in unbuffered perchlorate media. If too little acid was present it was consumed quickly [equation (2)] and a green precipitate appeared; at this stage the remaining RCl^{2+} hydrolysed completely. Alternatively if acid was added to avoid precipitation, the pH was too low for reaction (3) to proceed and very little chloride was released to the solution. We examined the effect of the addition of small amounts of several weak acids in the hope of finding one which would supply protons for reaction (2) and hence buffer the solution at a pH sufficiently high for the release of chloride ions *via* reaction (3) to match the rate of loss of RCl^{2+} by reaction (2). (Thus there would be no significant concentration of $CrCl^{2+}$.) These requirements were met by protonated 4-chloroaniline ($pK_a = 4{\cdot}0$[8]).

The reaction was followed by analysis for chloride ion and the figures for $[Cl^-]$ were used in equation (10) to calculate $[RCl^{2+}]_t$. At the end of each run the solution was analysed for $[Cr^{2+}]$ and $[Cl^-]_\infty$; the latter was

$$[RCl^{2+}] = [RCl^{2+}]_0 - ([Cl^-]_t - [Cl^-]_0) \qquad (10)$$

$$[RCl^{2+}]_0 = [Cl^-]_\infty - [Cl^-]_0 \qquad (11)$$

compared with the value calculated from equation (11). With 4-chloroaniline as buffer the subsequent plots of $\log [RCl^{2+}]_t$ against time [equation (4)] were linear with slopes corresponding to k_2 values of $1{\cdot}58 \times 10^{-2}$ and $3{\cdot}5 \times 10^{-2}$ l mol^{-1} s^{-1} at ionic strengths 0·1 and 1·0M respectively. The slight discrepancy between these figures and those calculated from equation (9), namely $1{\cdot}45 \times 10^{-2}$ and $4{\cdot}28 \times 10^{-2}$ l mol^{-1} s^{-1}, is probably due to a medium effect produced by the different numbers of protons in these solutions. Other weak acids were less satisfactory; those with $pK_a \leqslant 3{\cdot}5$ gave plots of $\log [RCl^{2+}]_t$ against time which were curved, indicating that reaction (3) was too slow, while those with $pK_a > 4{\cdot}5$ led to precipitation of chromium(III) hydrolysis products. With carboxylic acids such as 4-hydroxybenzoic acid ($pK_a = 4{\cdot}6$[8]) the reaction apparently accelerated with time, presumably due to the formation of kinetically active chromium(II)–carboxylate ion-pairs. In contrast we found no evidence of complex formation between chromium(II) and ring-substituted anilines.

All these results were obtained in perchlorate media and the observed figure for $[Cl^-]_\infty$ was consistently greater than that calculated from equation (11). In addition the analyses for $[Cr^{2+}]$ showed that there was a small loss (up to 10%) during a run. These discrepancies would appear to be due to reduction of perchlorate by a chromium(II) species [perhaps the intermediate $Cr(NH_3)_5{}^{2+}$ is responsible] for when the runs were carried out in sodium sulphamate solutions equation (11) held exactly and there was no loss of chromium(II). At ionic strength 1·0M we obtained a value of 0·0373 l mol^{-1} s^{-1} which is very close to the figure 0·035 l mol^{-1} s^{-1} obtained in perchlorate solutions. (This agreement is probably fortuitous since the reaction rate will suffer different medium effects according to the nature of the swamping anion.) Similar results and rate constants were obtained with sodium benzenesulphonate and sodium toluene-4-sulphonate; the latter has been used previously[9] as a redox-inert electrolyte.

We chose sodium sulphamate as the reference medium and examined the acceleration produced by sulphate ions using 4-chloroaniline as buffer. The results (Tables 3 and 4) at ionic strengths 0·1 and 1·0M were treated as follows. The overall rate of consumption of RCl^{2+} follows a first-order rate equation (12) with pseudo-rate constant k_{obs} [*cf.* equation (4)]. Assuming the overall

$$2{\cdot}303 \log [RCl]_T/[RCl]_t = k_{obs}t \qquad (12)$$

reaction in the presence of sulphate ions is the sum of the contributions of concomitant reactions (1), (2), and (6)—(8) we can equate $k_{obs}\,[RCl]_T$ with the sum of the initial rates of these reactions [equation (13)]. The

$$k_{obs}\,[RCl]_T = k_1[RCl^{2+}]_0 + k_2[RCl^{2+}]_0[Cr^{2+}] + k_6[RClSO_4]_0 + k_4[RCl^{2+}]_0[CrSO_4]_0 + k_5[RClSO_4]_0[Cr^{2+}] \qquad (13)$$

subscripts refer to zero time and $[RCl]_T$ is the initial total concentration of this species. It is assumed that apart from k_2 all the rate constants are independent of the ionic strength since at least one of the reactants is uncharged. The influence of the ionic strength on k_2 was assumed to be described by equation (9), the value of k_2^0 being calculated from the rate constant obtained in sodium sulphamate at ionic strength 0·1M. The values 1×10^{-5} and $1{\cdot}6 \times 10^{-5}$ s^{-1} were taken[7] for k_1 and k_6. [A short study of the rate of release of chloride ions by reaction (1) in buffered sodium sulphamate solutions led to a value of $0{\cdot}9 \times 10^{-5}$ s^{-1} for k_1.] The dissociation constants of the reactant–sulphate ion-pairs are defined by equations (14) and (15) where the superscript refers to

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[8] R. A. Robinson and R. H. Stokes, 'Electrolyte Solutions,' 2nd edn., Butterworths, London, 1959, Appendix 12.1, Table 5.

[9] W. G. Movius and R. G. Linck, *J. Amer. Chem. Soc.*, 1969, **91**, 5394.

zero ionic strength. Substituting for $[CrSO_4]$ and

$$K_1^0/f_2^2 = K_1 = [Cr^{2+}][SO_4^{2-}]/[CrSO_4] \qquad (14)$$

$$K_2^0/f_2^2 = K_2 = [RCl^{2+}][SO_4^{2-}]/[RClSO_4] \qquad (15)$$

$[RClSO_4]$ in equation (13) we obtain expression (16)

$$k_{obs}\,[RCl]_T = k_1[RCl^{2+}]_0 + k_2[RCl^{2+}]_0[Cr^{2+}] + (k_6/K_2)[RCl^{2+}]_0[SO_4^{2-}] + \left(\frac{k_4}{K_1} + \frac{k_5}{K_2}\right)[RCl^{2+}]_0[Cr^{2+}][SO_4^{2-}] \qquad (16)$$

which applies at any ionic strength.

TABLE 3

Acceleration by sulphate ions in sodium sulphamate solutions at ionic strength 0·1M. $[Cr(ClO_4)_2]_0 = 0{\cdot}01$; $[H_2NC_6H_4Cl]_0$ [a] $= 0{\cdot}006$; and $[H_3{}^+NC_6H_4Cl,ClO_4{}^-]_0$ [a] $= 0{\cdot}02$M. Measurements of $[Cr^{2+}]_\infty$ and $[Cl^-]_\infty$ agreed within 2% of the calculated figures

Run	$10^4[Na_2SO_4]$ M	$10^5[RCl(ClO_4)_2]$ M	$10^4[NaNH_2SO_3]$ M	10^6k_{obs} [b] s^{-1}	$10^5[CrSO_4]$ M	$10^5[RClSO_4]$ M	10^4I [c] M	10^4k_2 [d] $l\ mol^{-1}\ s^{-1}$	$k_4\ (= k_5)$ [e] $l\ mol^{-1}\ s^{-1}$
1	0	442	350	165	0	0	990	157	—
2	25	452	275	226	54	32	949	153	$0{\cdot}069_5$
3	50	453	200	268	107	62	915	150	$0{\cdot}065_7$
4	75	431	125	317	158	86	877	147	$0{\cdot}070_5$

[a] This mixture of 4-chloroaniline species buffers the solution at *ca.* pH 4·3. [b] From equation (12). [c] From equation (23). [d] From equation (9) using $k_2^0 = 0{\cdot}0027$ l mol^{-1} s^{-1} to normalise k_2 on 0·0157 l mol^{-1} s^{-1} at $I = 0{\cdot}099$M (run 1). [e] From equation (16) assuming $k_4 = k_5$.

TABLE 4

Acceleration by sulphate ions in sodium sulphamate solutions at ionic strength 1·0M. $[Cr(ClO_4)_2]_0 = 0{\cdot}005$; $[H_2NC_6H_4Cl]_0 = 0{\cdot}006$; $[H_3{}^+NC_6H_4Cl,ClO_4{}^-]_0 = 0{\cdot}02$M; and pH *ca.* 4·3. Measurements of $[Cr^{2+}]_\infty$ and $[Cl^-]_\infty$ agreed within 2% of the calculated figures

Run	$10^2[Na_2SO_4]$ M	$10^5[RCl(ClO_4)_2]$ M	$10^2[NaNH_2SO_3]$ M	10^7k_{obs} [a] s^{-1}	Figures for $k_4\ (= k_5)$ [b] ($l\ mol^{-1}\ s^{-1}$) corresponding to the following values for $K_1\ (= K_2)$ ($mol\ l^{-1}$)			
					0·05	0·1	0·2	0·4
5		454	95	197 ($k_2 = 0{\cdot}0373$)				
6	5	417	80	265	0·080	0·077	0·085	0·110
7	10	424	65	345	0·137	0·113	0·113	0·150

[a] From equation (12). [b] From equation (16) assuming $k_4 = k_5$ and $K_1 = K_2 = 0{\cdot}0373$ l mol^{-1} s^{-1} (run 5).

The composition of the solutions at ionic strength 0·1M was calculated with the help of previously reported figures [2,7] for K_1^0 and K_2^0, namely 0·004 and 0·003 mol l^{-1} respectively, and the dissociation constant [10] for $NaSO_4^-$, namely $K_3^0 = 0{\cdot}2$ mol l^{-1} [equation (17)]. Activity

$$K_3^0/f_2 = K_3 = [Na^+][SO_4^{2-}]/[NaSO_4^-] \qquad (17)$$

coefficients were calculated from the Davies [11] expression (18) and the various concentrations were related by

$$-\log f_i = 0{\cdot}5Z_i^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}3I] \qquad (18)$$

means of the mass-balance expressions (19)—(22). The

$$[SO_4]_T = [SO_4^{2-}] + [NaSO_4^-] + [CrSO_4] + [RClSO_4] \qquad (19)$$

$$[Na^I]_T = [Na^+] + [NaSO_4^-] \qquad (20)$$

$$[Cr^{II}]_T = [Cr^{2+}] + [CrSO_4] \qquad (21)$$

$$[RCl]_T = [RCl^{2+}] + [RClSO_4] \qquad (22)$$

effective ionic strength was calculated from equation (23) where I_{formal} is the total ionic strength calculated from the stoicheiometric amount of each electrolyte present at the start of the reaction, ignoring ion-association.

$$I = I_{formal} - 4[CrSO_4] - 4[RClSO_4] - 2[NaSO_4^-] \qquad (23)$$

Our procedure was to calculate the true composition of the reaction solutions by an iterative method of solving equations (14), (15), and (17)—(23), and to substitute the derived concentrations into equation (16) together with the values [7] of k_1 and k_6 and those of K_1, K_2, and k_2 calculated from equations (14), (15), and (9) respectively. This leaves k_4 and k_5 as the only unknowns in equation (16). Since it is not possible to solve this equation for individual values of these rate constants we have to make an assumption about the relative rates of reactions (6) and (7). Since the reactants are similar charge types we assume $k_4 = k_5$. The values of k_4 (and k_5) thus obtained (Table 3) show no trend with $[SO_4^{2-}]$ and have an average value of 0·068 l mol^{-1} s^{-1}.

The data obtained at ionic strength 1·0M were analysed in a similar manner save that sodium sulphate ion-pairs were ignored. In the absence of any definite information on the values of K_1 and K_2 we tried figures in the range 0·05—0·4 mol l^{-1} and for convenience we assumed that, in view of the similar charge types involved, K_1 and K_2 are equal. The results of these calculations are given in Table 4 and a plot of k_4 against K_1 is a gentle curve with a minimum at a K_1 value of 0·1—0·2 mol l^{-1}. The figures suggest that the average value of k_4 (and k_5) is 0·1 ± 0·03 l mol^{-1} s^{-1} which agrees reasonably well with 0·068 at $I = 0{\cdot}1$M.

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[10] C. W. Davies, 'Ion Association,' Butterworths, London, 1962, p. 169.

[11] Ref. 10, p. 41.

CONCLUSIONS

In the above treatment we have not distinguished between inner- and outer-sphere complexes of chromium(II) and sulphate ions since the rate data do not differentiate between the subsequent reaction paths. However, if such a distinction were possible, the present analysis would still hold provided equation (6) was regarded as representing the overall reaction of $CrSO_4$ species with RCl^{2+}.

Equations (6) and (7) imply that electron transfer occurs *via* a bridging chloride ion, as was demonstrated by Ogard and Taube[3] for reaction (2) in the absence of sulphate ions. It is possible that the sulphate ion is directly involved in the electron-transfer step leading to break-up of the transition state, but since the rate data alone do not indicate whether bridging is by sulphate or chloride ion we have assumed the latter. Thus, although the detailed mechanistic consequences of involvement of sulphate ions is a matter for speculation, the rate constants k_4 and k_5 can be considered as representing the overall kinetic reactivity of $CrSO_4$ and $RClSO_4$ ion-pairs.

The agreement in the values of k_4 obtained at low and high ionic strength is evidence that the chromium(II)–sulphate ion-pair is a discrete kinetic entity. A similar concordance in the values of the rate constant for the reaction between the chromium(II)–sulphate ion-pair and protonated hydroxylamine was obtained[2] from studies of the kinetic effect of sulphate ions on the reduction of hydroxylamine by chromium(II). In this analysis[2] of previously reported data obtained at ionic strength 1·5M, a value of 10 mol l^{-1} was taken for the formation constant β_1 $(= K_1^{-1})$ of $CrSO_4$, and use was made of the general equation (24) given by Rossotti and Rossotti.[12]

$$k_{obs} = \sum_0^n k_n\beta_n[L]^n / \sum_0^n \beta_n[L]^n \qquad (24)$$

At first sight it may seem odd that the values for k_4 do not decrease monotonically with decreasing values for K_1 (Table 4). However we can readily show, with the help of equation (24), that this is a necessary consequence when a large fraction of the chromium(II) is present as $CrSO_4$. Let us consider the general case of a reaction where both reactants A and B ion-pair with the ligand L to give species AL and BL. Then equation (24) may be written as (25). For simplicity we shall assume

$$k_{obs} = \frac{k_0 + k_1\beta_1[L] + k_2\beta_2[L]}{(1 + \beta_1[L])(1 + \beta_2[L])} \qquad (25)$$

that $k_1 = k_2 = k'$ and that $\beta_1 = \beta_2 = K^{-1}$ (*i.e.* K is a dissociation constant); on substitution into (25) we obtain equation (26). If [L] is large compared with the concentration of the reactants then [L] will not vary

$$k_{obs} = \frac{k_0 + 2k'[L]/K}{(1 + [L]/K)^2} \qquad (26)$$

when K is altered, in which case we can differentiate (26) to give equation (27). This expression shows how,

$$dk'/dK = 1/K\{k' - k_{obs}(1 + [L]/K)\} \qquad (27)$$

for given values of k_{obs} and [L], the calculated figures for k' vary with the assumed values for K. If the reaction is accelerated by addition of ligand L then $k' > k_{obs}$. Thus dk'/dK will be positive provided F is positive [equation (28)], which will be true for sufficiently small

$$k' - k_{obs}(1 + [L]/K) = F \qquad (28)$$

values of [L]. However for large values of [L] the term $[L]/K$ $(= [AL]/[A])$ may be sufficiently great to make F negative, so that dk'/dK is negative.*

We conclude that the variation of k_4 with K_1 presented in Table 4 is a fortuitous consequence of choosing conditions where the value of $[CrSO_4]/[Cr^{2+}]$ $(\triangleq [L]/K)$ is sufficiently great to make the figure for dk_4/dK_1 small and change sign in the range of values taken for K_1. Nonetheless many complexes have dissociation constants which are in this range at ionic strength 1·0M and it is common practice to add up to 0·2M of complexing ligand to reaction mixtures, so our findings for the system Cr^{2+}–SO_4^{2-}–RCl^{2+} are not untypical. The investigation of complex formation by analysis of kinetic data obtained at high ionic strength may not be profitable in the absence of independent measurements of the formation constants. (This criticism does not apply to systems where only one reactant is complexed.*)

Finally, if the rate-constant ratio $k_4 : k_2^0$ (*ca.* 35 : 1) is compared with the corresponding ratio for the rate of reaction between $CrSO_4$ and NH_3^+OH and Cr^{2+} and NH_3^+OH, namely[2] 17 : 1, we see that the increase in reactivity of Cr^{2+} due to association with sulphate ions is greater with $Cr(NH_3)_5Cl^{2+}$ as substrate than with hydroxylamine. This difference may be a consequence of greater stabilisation of a 4+ transition state (compared with one of charge 3+) by a 2− ion.

EXPERIMENTAL

Chromium(II) perchlorate was made as previously described[2] by dissolving chromium in perchloric acid. In this process some chloride ions are produced and this was minimised by using ice-cooled, dilute acid. The complex $[Cr(NH_3)_5Cl](ClO_4)_2$ was made by recrystallisation of the chloride salt[13] from perchloric acid solutions. Solutions of sodium perchlorate and sodium sulphamate were prepared by careful neutralisation of the acid [AnalaR perchloric acid and recrystallised sulphamic acid (G.P.R.)] with sodium carbonate (AnalaR). Other reagents were recrystallised from G.P.R. grade material.

The direct spectrophotometric kinetic runs were carried

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* If only one of the reactants forms ion-pairs with the ligand we obtain the following equations in place of (26) and (27). $k_{obs} = \frac{k_0 + k'[L]/K}{1 + [L]/K}$, $dk'/dK = (k' - k_{obs})/K$. Clearly, if $k' > k_{obs}$, dk'/dK is positive and independent of [L]. Thus dk'/dK can never be zero.

[12] F. J. C. Rossotti and H. Rossotti, 'The Determination of Stability Constants in Solution,' McGraw-Hill Inc., London, 1961, pp. 229—306.

[13] T. Moeller, *Inorg. Synth.*, 1957, **5**, 131.

out in a way similar to that previously described [2] save that absorbances were measured at 495 and 590 nm. For the kinetic studies based on analysis for chloride ion the reaction mixture was kept under hydrogen and at timed intervals samples were displaced into sulphuric acid (0·01M) through which air was bubbled rapidly to oxidise the chromium(II). At the end of the run the chromium(II) content was measured by displacing a sample into an oxygen-free solution containing iron(III); the iron(II) so produced was estimated by the absorbance at 510 nm after addition of o-phenanthroline and malonate buffer.[2] Chloride ions were determined by potentiometric titration ($AgNO_3$) in sulphuric acid (0·5M) using a Radiometer pH meter with silver and mercury(II) sulphate electrodes.

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