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The Kinetics of the General Base Hydrolysis of the Dichromate Anion[1]

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The kinetics of the base hydrolysis of dichromate by ammonia, hydroxide, water, and 2,6-lutidine were studied spectrally by the stopped-flow technique. Conflicting results obtained by previous workers for hydrolysis by hydroxide ion were resolved. The reactions were first-order in base and dichromate. The rate constant (M^{-1} sec.$^{-1}$), enthalpies of activation (kcal. mole^{-1}), and entropies of activation (e.u.) at 25° are 3.9×10^2, 4.9, and -30.2 for OH^- hydrolysis; 8.6×10^2, 1.9, and -38.5 for NH_3 reaction; ~ 0.5, ~ 0.1, and ~ -57 for lutidine reaction; and 4.6×10^{-4}, 8.8, and -44.2 for the water reaction. These unusual activation parameters are discussed in terms of an SN2 mechanism.

Introduction

Thermodynamic studies[3] have established that several oxy species and equilibria can exist in aqueous solutions of chromium(VI), dependent upon the pH, *viz.*

$$Cr_2O_7^{2-} + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2HCrO_4^- \quad K_{25°\mu=3} = 10^{-2.2};\ K_{25°\mu=0} = 10^{-1.6} \tag{1}$$

$$Cr_2O_7^{2-} + OH^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HCrO_4^- + CrO_4^{2-} \tag{2}$$

$$HCrO_4^- + OH^- \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} CrO_4^{2-} + H_2O \tag{3}$$

$$HCrO_4^- \rightleftharpoons CrO_4^{2-} + H^+ \quad K_{25°\mu=3} = 10^{-5.9};\ K_{25°\mu=0} = 10^{-6.5} \tag{4}$$

$$H_2CrO_4 \rightleftharpoons HCrO_4^- + H^+ \quad K_{25°\mu=1} = 4.2;\ 5.0 \tag{5}$$

Above pH 8 only CrO_4^{2-} ions exist, whereas in the pH 2–6 range, $HCrO_4^-$ and $Cr_2O_7^{2-}$ ions are in coequilibrium. At pH $\leqslant 1$, other species such as H_2CrO_4 are reported.

The rate constants associated with equilibria 1–3 have been obtained by a variety of methods (Table I).[4-12] The hydrolysis of dichromate by hydroxide ion was one of the earliest reactions examined by continuous flow. Two studies using this method with thermal observation have given conflicting results. La Mer and Read[9] reported that the rate of the reaction was independent of hydroxide ion concentration and proposed that the rate-determining step was the attack of a water molecule (reaction 1) and that the function of hydroxide was simply to react with $HCrO_4^-$ produced (reaction 3). It is now known that the latter reaction is rapid.[12] More recently, however, Lifshitz and Perlmutter-Hayman[11] found that the reaction between dichromate and several bases (including hydroxide ion) was first order in concentration of base (second-order over-all), and this is more consistent with some earlier work of Saal[4] and Chance.[10] The very recent measurements of the dichromate–water reaction by a relaxation method[6] show that hydrolysis by water is much slower than base hydrolysis and this is further evidence that the observations of La Mer and Read are incorrect.

The present study of reactions 1 and 2 using a stopped-flow technique with spectral observation was undertaken to attempt to finally resolve the conflicting views. In addition, however, activation parameters were determined for the first time for the base hydrolysis with hydroxide ion, ammonia, and water. After this work was completed, Perlmutter-Hayman reported further observations on reaction 1 in acetate buffers.[7]

Experimental Section

Materials.—Potassium hydroxide and ammonia solutions were prepared from B.D.H. standard volumetric reagent phials using boiled-out distilled water, cooled in a stream of nitrogen. These solutions were stored in carefully sealed bottles and the reagents siphoned off as required. They were standardized with hydrochloric acid immediately before use. Commercial 2,6-lutidine was distilled from KOH pellets and the middle fraction (b.p. 143°) used. It was converted to the nitrate salt, m.p. 149–150°.

Anal. Calcd. for $C_7H_{10}N_2O_3$: C, 49.4; H, 5.9; N, 16.5; equiv. wt., 170. Found: C, 49.7; H, 5.9; N, 16.4; equiv. wt., 171.

Potassium chromate, dichromate, and nitrate were Analar quality.

Kinetic Experiments.—The stainless-steel stopped-flow apparatus which we have used since 1961[13] has recently been described in detail.[14] The concentration of chromium(VI) necessary to give reasonably small optical densities in the 200–400 mμ range in our stopped-flow apparatus was so low[15] that little dichromate ion was present with such conditions; see (1). A suitable monitoring wave length was 475 mμ, however, where solutions containing 2 mM chromium(VI) could be used. An ionic strength of 0.1 M was maintained by adding potassium nitrate.

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(1) Reported at the Eighth International Coordination Chemistry Conference, Vienna, Sept. 1964.

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(3) "Stability Constants," Special Publication No. 17, The Chemical Society, London, 1964, pp. 89, 90; Y. Sasaki, *Acta Chem. Scand.*, **16**, 719 (1962); G. P. Haight, Jr., D. C. Richardson, and N. H. Coburn, *Inorg. Chem.*, **3**, 1777 (1964); J. Y. Tong, *ibid.*, **3**, 1804 (1964).

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(10) B. Chance, *J. Franklin Inst.*, **229**, 758 (1940).

(11) A. Lifshitz and B. Perlmutter-Hayman, *J. Phys. Chem.*, **65**, 2098 (1961).

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TABLE I

KINETIC DATA FOR EQUILIBRIA 1–3

k_1,[a] M^{-1} sec.$^{-1}$	Temp., °C.	Method[b]	Ref.
2.2×10^{-4}	Room	C.f. conductivity	4
$\sim 3.6 \times 10^{-4}$	20	C.f. pH	5
4.9×10^{-4}	23	Concn. jump	6
5.5×10^{-4}	25	Spectral	7
9×10^{-5} [c]	25	O^{18} exchange	8
k_2, M^{-1} sec.$^{-1}$			
1.1×10^2	Room	C.f. conductivity	4
8.8 (sec.$^{-1}$)	25	C.f. thermal	9
1.6×10^2 [d]	18	S.f. spectral	10
4.6×10^2	25	C.f. thermal	11
2.3×10^3 [c]	25	O^{18} exchange	8
k_3, M^{-1} sec.$^{-1}$			
$\sim 6 \times 10^9$	20	Sound absorption	12

[a] On basis of second-order reaction with water; *i.e.*, $k_{obsd}/55$. [b] C.f. = continuous flow; S.f. = stopped-flow. [c] From Cr(VI) oxy anion–H_2O exchange with high concentrations (~ 2 M) of chromium(VI). [d] Mean of two runs.

TABLE II

KINETIC DATA FOR HYDROLYSIS OF DICHROMATE[a]

[base]$_{max}$,[b] mM	[base]$_{mean}$,[c] mM	Temp., °C.	k_1, sec.$^{-1}$	$10^{-2}k_2$,[d] M^{-1} sec.$^{-1}$		
		Hydroxide Ion				
10.0	8.3	0.8	1.4	1.7		
20.0	18.3	0.8	3.0	1.6		
30.0	28.3	0.8	4.5	1.6		
50.0	48.3	0.8	8.0	1.7		
70.0	68.3	0.8	11.2	1.6		
10.0	8.3	8.8	2.0	2.4		
20.0	18.3	8.8	4.3	2.3		
30.0	28.3	8.8	6.2	2.2		
10.0	8.3	16.8	2.7	3.3		
20.0	18.3	16.8	5.4	3.0		
30.0	28.3	16.8	8.1	2.9		
4.0	2.3	25.0	0.77	3.4		
7.0	5.3	25.0	1.8	3.3		
10.0	8.3	25.0	4.1	4.9		
20.0	18.3	25.0	7.2	3.9		
30.0	28.3	25.0	10.8	3.8		
		Ammonia				
10.0	8.3	0.8	5.2	6.3		
10.0	8.3	8.8	6.6	8.0		
10.0	8.3	12.0	5.6	6.7		
10.0	8.3	16.8	7.0	8.4		
10.0	8.3	25.0	7.6	9.2		
20.0	18.3[e]	25.0	12.9	7.1		
20.0	16.8[e]	25.0	15.1	9.0		
30.0	26.8	25.0	24.0	9.0		
10.0	8.3	35.1	9.5	11.0		
					k_2[f]	k_{H_2O}[f]
		2,6-Lutidine				
5.0	3.3	0.9	0.0070			
15.0	13.3	0.9	0.0107			
35.0	33.3	0.9	0.0166		0.32	0.006
5.0	3.3	11.9	0.014			
15.0	13.3	11.9	0.018			
20.0	18.3	11.9	0.017			
35.0	33.3	11.9	0.025		0.36	0.012
15.0	13.3	25.0	0.034			
20.0	18.3	25.0	0.033			
35.0	33.3	25.0	0.049			
50.0	48.3	25.0	0.048		0.51	0.025
5.0	3.3	35.0	0.044			
15.0	13.3	35.0	0.047			
20.0	18.3	35.0	0.050		0.39	0.043

[a] $[Cr(VI)]_{total} = 2.0$ mM; $[Cr_2O_7^{2-}] = 0.26$ mM; $[HCrO_4^-] = 1.5$ mM. [b] Maximum value before any reaction occurred (half of concentration in driving syringe). [c] Average base concentration during dichromate reaction $= {}^1/_2\{[OH^-] - [HCrO_4^-] + [OH^-] - [HCrO_4^-] - 2[Cr_2O_7^{2-}]\}$. [d] $k_2 = k_1/[\text{base}]_{av.}$ [e] $[Cr(VI)]_{total} = 4.0$ mM. [f] From Figure 2, $k_1 = k_{H_2O} + k_2[\text{lutidine}]$.

TABLE III

ACTIVATION PARAMETERS FOR THE BASE HYDROLYSIS OF THE DICHROMATE ANION (25°)

Base	k_2, M^{-1} sec.$^{-1}$	ΔS^*, cal. deg.$^{-1}$ mole^{-1}	ΔH^*, kcal. mole^{-1}
OH^-	3.9×10^2	-30.2 ± 1.5[a]	4.9 ± 0.4[a]
NH_3	8.6×10^2	-38.5 ± 1.0	1.9 ± 0.3
H_2O	4.6×10^{-4}	-44.2 ± 0.2	8.8 ± 0.1
C_7H_9N	~ 0.5	$\sim(-57)$	~ 0.8

[a] Standard deviations, linear regression.

The initial optical density after mixing chromium(VI) and base was far less than that calculated from simple 1:1 mixing. This was attributed to the fast reaction between $HCrO_4^-$ and base (reaction 3). The subsequent reaction between $Cr_2O_7^{2-}$ and base had optical density changes from about 0.16 to 0.06 (1.5-cm. path length) and gave excellent pseudo-first-order kinetic plots (rate constant k_1) over several half-lives.

Allowance was made for the base consumed by the rapid reaction with $HCrO_4^-$, the concentration of which was taken as one-half the concentration in the driving syringe. These values were calculated using a dimerization constant estimated[11] at $\mu = 0.10$ as 1.64×10^{-2}. The correction for base consumed by $HCrO_4^-$ was usually small and therefore variation of the dimerization constant with temperature was neglected. The results are collected in Table II.

Results

Reaction with Hydroxide Ion.—The constancy of k_2 values given in Table II shows that the reaction is over-all second-order. The Arrhenius plot is shown in Figure 1 and the rate constants and activation parameters given in Table III.

Reaction with Ammonia.—This study was carried out at pH 8–10 so that the hydroxide reaction was negligibly slow. The ammonium ions produced by the initial rapid reaction between $HCrO_4^-$ and NH_3 caused pH changes. In some runs, therefore, ammonium nitrate was added to the ammonia solutions before mixing; this had no effect on the rate. The second-order rate constant and the activation parameters are given in Table III, from Arrhenius plots shown in Figure 1.

Reaction with 2,6-Lutidine and Water.—In principle k_{H_2O} can be obtained from the reaction of dichromate with a basic nucleophile by extrapolation of the rate constant to zero base concentration. This is impractical for bases with $k_B \gg k_{H_2O}$. Pritchard and Long[16] have suggested the use of a number of bases which have low nucleophilic power and can thus be used as a buffer without significantly enhancing the rate of a reaction involving another nucleophile. We have studied the reaction of dichromate with 2,6-lutidine (pK = 7.4)

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(16) J. G. Pritchard and F. A. Long, *J. Am. Chem. Soc.*, **79**, 2365 (1957).

$$Cr_2O_7^{2-} + H_2O \longrightarrow 2HCrO_4^- \quad k_{H_2O}$$
$$HCrO_4^- + C_7H_9N \longrightarrow CrO_4^{2-} + C_7H_9NH^+ \quad \text{fast}$$
$$Cr_2O_7^{2-} + C_7H_9N \longrightarrow [C_7H_9N\cdot CrO_3] + CrO_4^{2-} \quad k_L$$
$$[C_7H_9N\cdot CrO_3] + H_2O \longrightarrow \text{products} \quad \text{fast}$$

The observed (pseudo-first-order) rate constant $k_{obsd} = k_{H_2O}[H_2O] + k_L[C_7H_9N]$ and Figure 2 supplies values for the second-order rate constants for the water (k_{H_2O}) and lutidine (k_L) reaction. These are given in Table III with activation parameters (Figure 1). The values obtained with lutidine are only approximate since a limited range of base concentrations was used. The experiments did, however, provide accurate values for k_{H_2O}, because of the shallow slopes of Figure 2.

Discussion

The rate constants reported in Table III are in close agreement with values reported previously (Table I),[17] and the second-order nature of the reactions is confirmed.[11] This is gratifying in view of the different techniques used in each study.

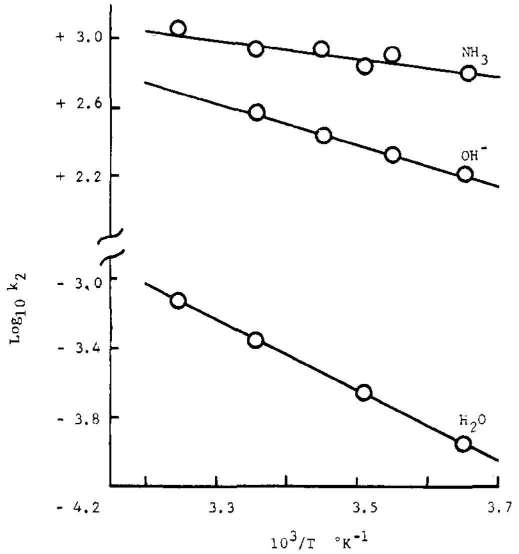

Figure 1.—Arrhenius plots of the base hydrolysis of the dichromate anion.

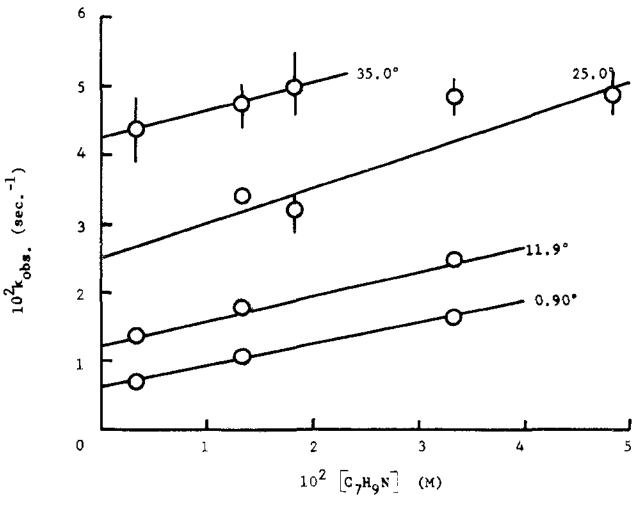

Figure 2.—Hydrolysis of the dichromate ion in excess of 2,6-lutidine.

The order of reactivity of the bases, $NH_3 > OH^- > CH_3COO^- > C_7H_9N > H_2O$, is consistent with their decreasing basicity if some allowance is made for electrostatic repulsion in the reaction with hydroxide and for steric hindrance in the attack of 2,6-lutidine. The polarizability of the nucleophile may be a better parameter.[18] The position of water is reflected in the larger enthalpy of activation, but except for this reaction (and possibly with acetate[7] for which no data are available) the activation parameters are unusual and difficult to interpret. The reactions have very low enthalpies of activation, in fact values expected for diffusion-controlled processes, and are only slow compared with many base-catalyzed ionic reactions because they have large negative entropies of activation. For this reason we focus our attention on the values of ΔS^*, considerations of which can often lead to some understanding of reaction mechanism.[19] An SN2 mechanism has been proposed previously for the general base (B) hydrolysis of dichromate[11]

$$Cr_2O_7^{2-} + B \longrightarrow BCrO_3 + CrO_4^{2-} \quad k_2^B$$
$$BCrO_3 + H_2O \longrightarrow BH^+ + HCrO_4^- \quad \text{rapid}$$
$$HCrO_4^- + B \longrightarrow BH^+ + CrO_4^{2-} \quad \text{rapid}$$

For the reaction with hydroxide ($B = OH^-$, second step omitted), the standard entropies of the reactants, intermediates ($HCrO_4^-$, CrO_4^{2-}), and products are all known.[20,21] If an allowance is made for the activated complex $[HOCrO_3\cdots CrO_4^{3-}]^*$ having one less translational degree of freedom (~14 e.u.)[22] than the intermediates ($HCrO_4^-$, CrO_4^{2-}), then the entropy of activation, ΔS^*, and the entropy difference between reactants and intermediates, $\Delta S_1°$, are very similar and afford good evidence for similarity of transition state and intermediate (Table IV).

TABLE IV

ENTROPY CHANGES DURING THE BASE HYDROLYSIS OF THE DICHROMATE ANION[a]

$$Cr_2O_7^{2-} + 2B + H_2O \longrightarrow 2CrO_4^{2-} + 2BH^+ \quad \Delta S°$$
$$Cr_2O_7^{2-} + B \longrightarrow BCrO_3 + CrO_4^{2-} \quad \Delta S_1°$$

B	ΔS^*	$\Delta S_1°$	$\Delta S°$
OH^-	−30.2	−11.0	−30.4
NH_3	−38.5	−60.5	−67.4
H_2O	−44.2	−60.5	+ 8.4

[a] Units cal. deg.$^{-1}$ mole^{-1} (25°). Standard entropies of $Cr_2O_7^{2-}$ and $HCrO_4^-$ from ref. 20. Other standard entropies from ref. 21. Standard state 1 *M*. Temperature 25°.

The large negative ΔS^* in the water reaction is understandable for the same reasons in view of the large negative value for $\Delta S_1°$. There is a considerable loss of

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[17] $k_2^{NH_3}$ has been determined[11] as $7.4 \times 10^2\ M^{-1}$ sec.$^{-1}$, and $k_2^{OAc^-}$ is[7] $1.92\ M^{-1}$ sec.$^{-1}$.

(18) B. N. Figgis, R. G. Kidd, and R. S. Nyholm, *Can. J. Chem.*, **43**, 145 (1965).

(19) L. L. Schaleger and F. A. Long, *Advan. Phys. Org. Chem.*, **1**, 1 (1963).

(20) U. S. National Bureau of Standards, "Selected Values of Chemical Thermodynamic Properties," U. S. Government Printing Office, Washington, D. C., 1952.

(21) C. H. Muldrow and L. G. Hepler, *J. Am. Chem. Soc.*, **79**, 4045 (1957), report substantially revised values of $S°$ for $Cr_2O_7^{2-}$ and $HCrO_4^-$ from those quoted in ref. 20.

(22) R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).

entropy in forming the compact chromate ions ($S° = +9.2$ e.u.) from dichromate ions ($S° = +70.5$ e.u.). Therefore the flow of charge toward one end of the transition-state complex (the "chromate end") must be hindered by a considerable degree of electrostriction. The larger (negative) value for $\Delta S_1°$ than ΔS^* must mean that the gain of a translational degree of freedom from the dissociation of the transition-state complex is offset by a considerable amount of electrostriction when the chromate ion is finally released. Similar considerations apply to the ammonia reaction. However, in this case an estimation of the standard entropy of the postulated intermediate ($NH_3 \cdot CrO_3$) must be made. We have used the equations

$$S°_{NH_3 \cdot CrO_3} = S°_{NH_3} + S°_{CrO_3} - (\Delta S_t°)_1$$

$$S°_{H_2O \cdot CrO_3} = S°_{H_2O} + S°_{CrO_3} - (\Delta S_t°)_2$$

where $\Delta S_t°$ is approximately the entropy of one translational degree of freedom.[22] We have made the reasonable assumption that $(\Delta S_t°)_1 \approx (\Delta S_t°)_2$ for these similar molecules and that $S°_{H_2O \cdot CrO_3} \approx S°_{H_2CrO_4}$, and this enables us to estimate $S°_{NH_3 \cdot CrO_3} \approx 27$ e.u. It is obvious with all reactions examined that the large negative entropy of activation arises from an associated large entropy of formation of the intermediates which are postulated in the S_N2 mechanism. Correlation with the over-all entropy of reaction is not possible.

Finally, we can compare the behavior of $Cr_2O_7^{2-}$ with the formally analogous $S_2O_7^{2-}$. Only recently[23,24] has the hydrolysis of pyrosulfate been measured ($S_2O_7^{2-} + H_2O \rightarrow 2H^+ + 2SO_4^{2-}$). The first-order rate constant at 20° (3.8×10^{-3} or 9.8×10^{-3} sec.$^{-1}$)[25] and the energy of activation (11.3[23] or 11.1[24]) are remarkably similar to those for dichromate hydrolysis. The reaction does not appear to have been studied at pH values higher than 10 so that the question of an OH^- catalyzed reaction analogous to $Cr_2O_7^{2-}$ remains unanswered at present.

P. M. proposes to study other bases and salt effects to elucidate further the mechanism of the dichromate base hydrolysis.

Acknowledgment.—We thank the Department of Scientific and Industrial Research for a grant (to P. M.).

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[23] H. K. Hofmeister and J. R. Van Wazer, *Inorg. Chem.*, **1**, 811 (1962).

[24] E. Thilo and F. V. Lampe, *Z. anorg. allgem. Chem.*, **319**, 387 (1963); *Ber.*, **97**, 1775 (1964).

[25] There appears to be disagreement over the rate constant; however, there is known to be strong cationic catalysis and this may explain the differences.

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Mechanism of the Acid Hydrolysis of the Iodopentaaquochromium(III) Ion. Evidence for a *trans* Effect of Iodide in a Chromium(III) Complex

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Tracer studies with $H_2{}^{18}O$ in perchloric acid solutions have shown that the hexaaquochromium(III) ion produced from aquation of the iodopentaaquochromium(III) ion, $[CrI]^{2+}$, contains *two* labeled water molecules.

$$[Cr(H_2O)_5I]^{2+} + 2H_2{}^*O \rightarrow [Cr(H_2O)_4(H_2{}^*O)_2]^{3+} + H_2O + I^-$$

It has been shown that considerable exchange of *one* water molecule in $[CrI]^{2+}$ occurs prior to hydrolysis. These facts, plus our observation that the chloropentaaquochromium(III) ion, $[CrCl]^{2+}$, only undergoes very slow water exchange, lead us to suggest that iodide ion in $[CrI]^{2+}$ has a labilizing influence on the water molecule *trans* to it: *trans*-$[H_2OCr(H_2O)_4I] + H_2{}^*O \rightleftharpoons$ *trans*-$[H_2{}^*OCr(H_2O)_4I] + H_2O$. This mechanism can also account for a previous observation that more than 10% $[CrCl]^{2+}$ is formed when $[CrI]^{2+}$ is hydrolyzed in 1 *M* hydrochloric acid. Exchange of $H_2{}^{18}O$ with the complex $[Cr(H_2O)_5NO]^{2+}$ is also reported.

Introduction

It is known that iodide ion exhibits a *trans* effect in Pt(II) and Rh(III) complexes.[1] The possibility that a similar effect might occur in a chromium(III) complex such as $[CrI]^{2+}$[2] has not been investigated. However, recent observations by Ardon[3] that the acid hydrolysis of $[CrI]^{2+}$ in the presence of 1 *M* chloride or bromide ions produces more than 10% of the respective complex $[CrX]^{2+}$ ($X = Cl^-, Br^-$) in addition to $[Cr(H_2O)_6]^{3+}$ led us to suspect that iodide might have a strong *trans* effect in $[CrI]^{2+}$ also. If this were the case, we might expect reaction 1 to proceed at a rate comparable to or greater than the rate of hydrolysis (reaction 2). It would then be possible to explain

$$trans\text{-}[H_2OCr(H_2O)_4I]^{2+} + H_2{}^*O \xrightleftharpoons{k_{H_2O}} trans\text{-}[H_2{}^*OCr(H_2O)_4I]^{2+} + H_2O \quad (1)$$

$$[Cr(H_2O)_4(H_2{}^*O)I]^{2+} + H_2{}^*O \xrightarrow{k} [Cr(H_2O)_4(H_2{}^*O)_2]^{3+} + I^- \quad (2)$$

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[1] For a review of the *trans* effect in metal complexes see F. Basolo and R. G. Pearson, *Progr. Inorg. Chem.*, **4**, 381 (1962); F. Basolo, E. J. Bounsall, and A. J. Poë [*Proc. Chem. Soc.*, 366 (1963)] discuss the *trans* effect of iodide in Rh(III).

[2] We shall abbreviate all [ligandpentaaquochromium(III)] complexes as $[CrX]^{2+}$ (X = ligand).

[3] M. Ardon, *Inorg. Chem.*, **4**, 372 (1965).