

Kinetics of Aquation of Chloro- and Thiocyanato-chromium(III) Complexes in Mixed Aqueous Solvents

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Rate constants are reported for spontaneous thermal aquation of the complexes $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ (en = ethylenediamine), $\text{trans-}[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$, and $[\text{Cr}(\text{NCS})_6]^{3-}$ in a range of solvents, including methanol-, ethanol-, acetone-, dioxan-, and t-butyl alcohol-water binary mixtures. These results, and previously published results on similar chromium(III) complexes, are discussed in terms of the Grunwald-Winstein treatment of solvolyses in mixed aqueous solvents. Although this empirical approach can usefully be employed in discussing the aquation of chlorochromium(III) complexes, its extension to thiocyanatochromium(III) complexes does not seem profitable.

SOLVATION is an important factor in determining reactivity; the variation of reaction rates with solvent composition often provides insight into reaction mechanisms. This approach has frequently proved fruitful in organic chemistry, where the Grunwald-Winstein treatment of the dependence of solvolysis rates on the nature of the solvent provides useful criteria for the assignment of mechanisms.¹ Rates of solvolyses of complexes of cobalt(III) and of chromium(III) are said to be relatively insensitive to solvent composition,² but there is sufficient variation in rates with different solvents for reactivity trends to be established. In view of recent discussions on the mechanism of substitution of the chromium(III) ion,³ it is of interest to compare the effects of solvation on reactivity for analogous complexes of chromium(III) and cobalt(III), for the mechanism of substitution of aminohalogenocobalt(III) complexes is firmly established as dissociative in character.

Grunwald and Winstein¹ proposed a scale of solvent Y values based on the kinetics of S_N1 solvolysis of organic halides. The Y values were defined by application of equation (1), where k is the rate constant in a given

$$\log k/k_0 = mY \quad (1)$$

solvent and k_0 that in the reference solvent ethanol (80%), to the model S_N1 solvolysis of t-butyl chloride for which an m value of 1.00 was chosen. For S_N2 solvolyses plots of $\log k$ against Y are either curved, with a mean m value of ca. 0.2–0.4, or show no correlation. It has recently been found that for aquation of many chloroammino- and chloroamino-complexes of cobalt(III) there is a correlation of logarithms of the rate constants with solvent Y values for a variety of water-rich organic solvent mixtures.⁴ Values of m lie between 0.23 and 0.36, which suggests considerably lower solvation requirements for moieties of the type $\text{Co}^{\text{III}}\text{L}_5^{n+}$ than for R_3C^+ . The rates of aquation of three chlorochromium(III) complexes, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ (en = ethylenediamine), and $\text{trans-}[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$, have now been investigated in a similar range of mixed aqueous solvents. Approximately linear correlations

of logarithms of the aquation rate constants with solvent Y values are again found; values of m for aquation of the chlorochromium(III) complexes are significantly less than those for analogous cobalt(III) complexes. An attempt was also made to extend this method of investigation to chromium(III) complexes in which thiocyanate ion is the leaving group, but with much less success.

RESULTS AND DISCUSSION

Aquation of the three chlorochromium(III) complexes, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$, and $\text{trans-}[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$, in water-rich methanol, ethanol, acetone, and dioxan mixed solvents results, as in aqueous solution, in the replacement of chloride ion by water. Kinetic experiments were not undertaken in aqueous formic or acetic acids, as the reaction products in these mixed solvents are not the aquo-complexes but, presumably, formato- or acetato-complexes. Aquation of the monochloro-complex, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, resulted in complete replacement of chloride ion by water in all the solvent mixtures for which we report kinetic results. For the dichloro-complexes, $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ and $\text{trans-}[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$, loss of the first chloride ion was monitored; again these reactions went to completion. The dependence of aquation rate constants on acid concentration is described below for the tetra-aquodichloro-complex; for the other complexes checks were carried out in a few randomly selected solvent mixtures to ensure that, as in water, there was no significant variation of the rate constants with acid concentration (at constant ionic strength).

Chlorochromium(III) Complexes.—Rate constants for aquation of the complexes $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ (for loss of the first chloride ion) in mixed aqueous solvents are reported in Tables 1 and 2. Plots of logarithms of these rate constants against the respective solvent Y values showed a reasonable correlation {that for the complex $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ is shown in Figure 1}. The gradients, m , of these plots were both +0.12 for the complexes $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$ and $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]^+$. The

¹ See, for example, E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; P. R. Wells, 'Linear Free Energy Relationships,' Academic Press, London, 1968, ch. 4.

² C. H. Langford, *Canad. J. Chem.*, 1971, **49**, 1497.

³ 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1972, vol. 2, pp. 157–159 and references therein.

⁴ J. Burgess, *J. Chem. Soc. (A)*, 1970, 2703; J. Burgess and M. G. Price, *ibid.*, 1971, 3108.

mY plots represent linear free-energy comparisons between the chromium(III) complexes and *t*-butyl chloride; similar comparisons between more closely

TABLE 1

First-order rate constants (k) for aquation of the pentaamminechlorochromium(III) complex in mixed aqueous solvents at 35 °C and $[\text{HClO}_4] = 0.013\text{M}$

Non-aqueous component % (v/v)	Methanol		Ethanol	
	Y	10^5k s ⁻¹	Y	10^5k s ⁻¹
10	3.28	2.9	3.31	3.0
20	3.03	2.7	3.05	2.6
30	2.75	2.5	2.72	2.5

Non-aqueous component % (v/v)	t-Butyl alcohol		Acetone	
	Y	10^5k s ⁻¹	Y	10^5k s ⁻¹
10	3.0	3.0	3.23	2.8
20	3.0	3.0	2.91	2.6
30			2.48	2.4

TABLE 2

First-order rate constants (k) for aquation of the *cis*-dichlorobis(ethylenediamine)chromium(III) complex in mixed aqueous solvents at 35 °C and $[\text{HClO}_4] = 0.010\text{M}$

Non-aqueous component % (v/v)	Methanol		Ethanol	
	Y	10^4k s ⁻¹	Y	10^4k s ⁻¹
10	3.28	7.8		
20	3.03	7.2		
30	2.75	6.4	2.72	6.4

Non-aqueous component % (v/v)	Acetone		Dioxan	
	Y	10^4k s ⁻¹	Y	10^4k s ⁻¹
10	3.23	7.7		
20	2.91	7.0		
30	2.48	6.8	2.46	6.0

related substrates are provided by plots of logarithms of the rate constants for aquation of pairs of structurally similar transition-metal complexes. Such a plot is

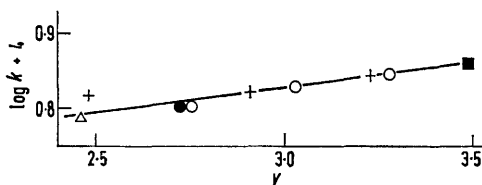


FIGURE 1 Correlation of logarithms of the first-order rate constants (k) with solvent Y values for aquation of the complex *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ in mixed aqueous solvents: (■), water; non-aqueous component (○), methanol, (●), ethanol, (+), acetone, (Δ), dioxan

illustrated in Figure 2 for the pair of complexes *cis*- $[\text{M}(\text{en})_2\text{Cl}_2]^+$ ($\text{M} = \text{Co}^{\text{III}}$ or Cr^{III}). This plot and that corresponding to the complexes $[\text{M}(\text{NH}_3)_5\text{Cl}]^{2+}$ ($\text{M} = \text{Co}^{\text{III}}$ or Cr^{III}) are indeed linear, with gradients of $2.9 \pm$

0.4 and 2.0 ± 0.4 respectively. Figure 2 provides a direct comparison of solvent effects on the reactivities of complexes differing only in the nature of the central transition-metal cation.

Whether one compares solvent effects on the reactivities of the chlorochromium(III) complexes with their cobalt(III) analogues directly (Figure 2) or indirectly using m values [0.12 for the chromium(III) complexes, 0.23 – 0.36 for the cobalt(III) complexes⁴], it is clear that there is a significantly smaller solvent effect on

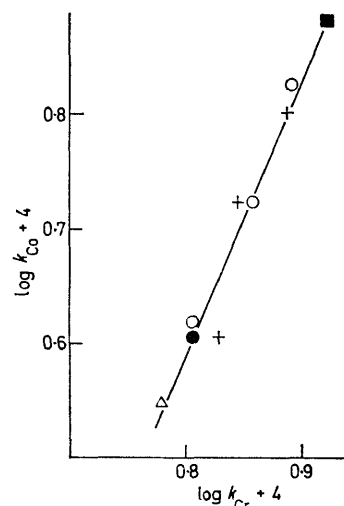


FIGURE 2 Correlation of logarithms of the first-order rate constants (k_{Cr} and k_{Co}) for aquation of the complexes *cis*- $[\text{Cr}(\text{en})_2\text{Cl}_2]^+$ and *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ in mixed aqueous solvents; for key see Figure 1

aquation of the chlorochromium(III) complexes. The much lower m values for aquation of the transition-metal chloro-complexes compared with the value of $m = 1.00$, by definition, for *t*-butyl chloride can readily be explained in terms of differences in the solvation requirements of the inorganic or organic moieties from which the chloride ion is leaving. It is slightly more difficult to explain the lower solvent effects for chromium(III) as compared with cobalt(III) complexes in this manner, for the peripheries of a given pair of these complexes are of identical composition and very similar geometry (the radii of the central metal ions Cr^{3+} and Co^{3+} are 0.69 and 0.63 Å respectively⁵). It is possible that the difference in solvent effects may arise from a small difference in aquation mechanism for it is often suggested that, whereas substitution at the cobalt(III) centre in aminohalogeno-complexes is purely dissociative in character, substitution at chromium(III) might have a certain degree of associative character; in organic solvolyses, variations of rate constants with solvent composition are very much less for associative than for dissociative reactions.¹

It is hoped to extend this investigation to aquohalogenochromium(III) complexes to determine whether

⁵ N. N. Greenwood, 'Ionic Crystals, Lattice Defects, and Non-stoichiometry,' Butterworths, London, 1968, pp. 40–41.

their behaviour is similar to the above aminohalogeno-complexes. The situation is complicated both by the acid dependence of aquation rates for aquohalogeno-complexes⁶ and by difficulties in preparing isomerically pure samples of convenient substrates such as $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$.⁷ However, preliminary results on a predominantly *trans*-sample of the complex $[\text{Cr}(\text{OH}_2)_4\text{Cl}_2]^+$ show that the limiting rate constant k of the rate law (2) is within the range 1.0×10^{-4} — $1.5 \times 10^{-4} \text{ s}^{-1}$ for ethanol

$$-\text{d}[\text{Cr}(\text{OH}_2)_4\text{Cl}_2^+]/\text{d}t = (k + k'[\text{H}^+]^{-1})[\text{Cr}(\text{OH}_2)_4\text{Cl}_2^+] \quad (2)$$

(0–30%) at 35.0 °C. Thus solvent effects here are of comparable, very small, magnitude with those for the analogous amino-complexes.

The addition of small quantities of some organic solvents to water has an effect on solvent structure; this effect is particularly marked for *t*-butyl alcohol.⁸ Solvent structural changes are often reflected in reactivity trends, for such changes affect both solvation of the initial and transition states and, for an associative hydrolysis, the ease of entry of water into the transition state. On adding successive small amounts of *t*-butyl alcohol to water, the structure of the solvent is at first enhanced but, beyond about 0.04 mole fraction *t*-butyl alcohol, becomes progressively disrupted. The kinetic consequences of these trends have been much studied for organic substrates, and described for aquation of a few transition-metal complexes, *e.g.* *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ ⁹ and some tris(1,10-phenanthroline)iron(II) derivatives.¹⁰ Rates of aquation of the complex $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$ seemed to vary smoothly with solvent composition in mixed solvents for which $0 < x_2 < 0.1$, where x_2 is the mole fraction of *t*-butyl alcohol.⁴ For the complex $[\text{Cr}(\text{NH}_3)_5\text{Cl}]^{2+}$, on the other hand, rates of aquation (Table 3) decrease slightly as the mole fraction of *t*-butyl

TABLE 3

Average first-order rate constants for aquation of the penta-amminechlorochromium(III) complex in aqueous *t*-butyl alcohol, at 35 °C and $[\text{HClO}_4] = 0.013\text{M}$

<i>t</i> -Butyl alcohol % (v/v)	10^5k s^{-1}	<i>t</i> -Butyl alcohol % (v/v)	10^5k s^{-1}
0	3.2 ₀	16.7	3.0 ₀
3.3	3.0 ₅	20.0	3.0 ₅
6.7	2.9 ₅	23.3	3.4 ₀
10.0	3.0 ₀	26.7	3.6 ₀
13.3	2.8 ₅	30.0	3.6 ₅

alcohol increases, up to x_2 *ca.* 0.03–0.04, then increase steadily with further increases in the proportion of

* Thus, for example, information on aquation of the complex $[\text{CrCl}_4]^{3-}$ is restricted to qualitative observations on the hydrolysis of $[\text{Co}(\text{NH}_3)_5][\text{CrCl}_4]$ (H. H. Eysel, *Z. anorg. Chem.*, 1972, **390**, 210).

⁶ C. W. Meredith, W. D. Mathews, and E. F. Orlemann, *Inorg. Chem.*, 1964, **3**, 320.

⁷ See, for example, E. L. King, *J. Amer. Chem. Soc.*, 1958, **80**, 5015; J. P. Birk, *Inorg. Chem.*, 1970, **9**, 735.

t-butyl alcohol. These variations are very small, only just outside the limits of experimental uncertainty, but this slight difference in behaviour between chromium(III) and cobalt(III) complexes of analogous composition may again betoken a small difference in aquation mechanism.

Thiocyanatochromium(III) Complexes.—Extension of the Grunwald–Winstein treatment of solvent effects on solvolysis rates from organic to inorganic chemistry has met with a fair degree of success in its application to compounds of, *e.g.* phosphorus,¹¹ sulphur,¹² cobalt(III),⁴ and, as described above, chromium(III). In most cases the leaving group is chloride ion, as in the reference substrate *t*-butyl chloride. A few studies have shown that the solvolysis of bromide compounds, as for example those of boron¹³ and of cobalt(III),^{2,4} can be treated similarly. It was therefore of interest to see whether this approach could be further extended to different leaving groups, *e.g.* the pseudo-halide group, thiocyanate. In earlier work on cobalt(III) complexes, and in the above work on chromium(III) complexes, *mY* plots have been constructed only for complexes of overall charge +2 or +1. One would expect *m* to depend somewhat on the charge, and would therefore like to investigate a range of complexes with a range of positive and negative overall charges. This is difficult to undertake for chloro- or bromo-complexes of cobalt(III) or chromium(III),* but straightforward for thiocyanate complexes, a range of complexes $[\text{CrL}_5(\text{NCS})]^{2+}$ to $[\text{Cr}(\text{NCS})_6]^{3-}$ being available.

Indeed, a considerable number of rate constants for aquation of thiocyanatochromium(III) complexes in mixed aqueous solvents are available in the literature. Here, *mY* plots have been constructed from these available results, and aquation rates for the complex

TABLE 4

Average first-order rate constants for aquation of the hexathiocyanatochromate(III) complex in mixed aqueous solvents at 35 °C and $[\text{HClO}_4] = 0.01\text{M}$

Non-aqueous component % (v/v)	Methanol		Acetone	
	<i>Y</i>	10^6k s^{-1}	<i>Y</i>	10^6k s^{-1}
10	3.28	3.5	3.23	3.4
20	3.03	3.2	2.91	3.2
30	2.75	3.1	2.48	2.9

$[\text{Cr}(\text{NCS})_6]^{3-}$ determined in aqueous methanol and in aqueous acetone (Table 4) in order to construct an *mY* plot for aquation of this complex. Estimated *m*

⁸ M. J. Blandamer, D. E. Clarke, T. A. Claxton, M. F. Fox, N. J. Hidden, J. Oakes, M. C. R. Symons, G. S. P. Verma, and M. J. Wootten, *Chem. Comm.*, 1967, 273.

⁹ J. Burgess, *Chem. Comm.*, 1967, 1134.

¹⁰ J. Burgess, *J. Chem. Soc. (A)*, 1968, 1085.

¹¹ E. W. Crunden and R. F. Hudson, *J. Chem. Soc.*, 1962, 3591.

¹² O. Rogne, *J. Chem. Soc. (B)*, 1969, 663.

¹³ References to further illustrations may be found in 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1971, vol. 1, pp. 202–203.

values are collected in Table 5, where complexes are grouped according to their overall charge. No obvious

TABLE 5

Estimated m values for aquation of thiocyanatochromium(III) complexes in mixed aqueous solvents

Complex	Co-solvent(s)	Temp. °C	m	Ref.
$[\text{Cr}(\text{NH}_3)_5(\text{NCS})]^{2+}$	a, b	50	+0.20	c
$\text{trans-}[\text{Cr}(\text{NH}_3)_2(\text{NCS})_4]^-$	b	60	+0.4	d
$\text{cis-}[\text{Cr}(\text{en})(\text{NCS})_4]^-$	a	35	+0.6	e
$[\text{Cr}(p\text{-toluidine})_2(\text{NCS})_4]^-$	f	40	-0.01	g
$[\text{Cr}(p\text{-phenetidine})_2(\text{NCS})_4]^-$	f	40	0	g
$[\text{Cr}(p\text{-anisidine})_2(\text{NCS})_4]^-$	f	40	0	h
$[\text{Cr}(p\text{-ethyl-aniline})_2(\text{NCS})_4]^-$	f	40	0	i
$[\text{Cr}(\text{NCS})_6]^{3-}$	a, b	35	+0.08 ^j	k

^a Methanol. ^b Acetone. ^c V. Holba and P. Sevcik, *Chem. Zvesti*, 1966, **20**, 161. ^d C. H. Langford and J. F. White, *Canad. J. Chem.*, 1967, **45**, 3049. ^e G. Thomas and V. Holba, *J. Inorg. Nuclear Chem.*, 1969, **31**, 1749. ^f Ethanol. ^g I. Zsako, *Studia Univ. Babes-Bolyai, Ser. Chem.*, 1970, **15**, 93. ^h I. Zsako, I. Ganesco, C. Varhelyi, and A. Popescu, *Z. anorg. Chem.*, 1971, **380**, 216. ⁱ I. Zsako, I. Ganesco, C. Varhelyi, and A. Popescu, *Rev. Chim. minerale*, 1970, **7**, 927. ^j An m value of *ca.* +0.1 can be estimated for solvolysis of this complex in water, methanol, and pyridine from kinetic results reported in S. Behrendt, C. H. Langford, and L. S. Frankel, *J. Amer. Chem. Soc.*, 1969, **91**, 2236. ^k This work.

pattern can be detected; indeed there is a large range of m values, rather than a characteristic value, for the complexes $[\text{CrL}_2(\text{NCS})_4]^-$. There is perhaps some uncertainty in the values quoted for the complexes with

$L = p\text{-toluidine}$, $p\text{-phenetidine}$, $p\text{-anisidine}$, or $p\text{-ethyl-aniline}$, for the overall rate of disappearance of complex corresponds to parallel aquation and ethanolysis reactions. Nonetheless, the m values of Table 5 are sufficiently scattered to suggest that extension of the empirical Grunwald-Winstein approach from the solvolysis of carbon-chlorine or -bromine compounds and transition metal chloro- or bromo-complexes to transition metal thiocyanato-complexes is unlikely to prove fruitful.

EXPERIMENTAL

The complexes $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$,¹⁴ $\text{cis-}[\text{Cr}(\text{en})_2\text{Cl}_2]\text{Cl}$,¹⁵ and $\text{K}_3[\text{Cr}(\text{NCS})_6]$,¹⁶ and solutions containing $\text{trans-}[\text{Cr}(\text{OH})_2\text{Cl}_2]^+$ ¹⁷ were prepared by standard procedures. Aquation of the chloro-complexes was followed spectrophotometrically, in 1 cm cells, in the thermostatted cell compartment of a Unicam SP 800 A recording spectrophotometer. Aquation of the complex $[\text{Cr}(\text{NCS})_6]^{3-}$ was monitored by estimation of the thiocyanate ion produced, the latter being determined spectrophotometrically *via* its complexation with iron(III) ions. Rate constants were determined graphically. Values reported in Tables 1-4 represent means of two or three independent determinations; probable errors are thought to be *ca.* 5%.

I thank the Royal Society for a grant-in-aid for the purchase of the spectrophotometer and C. J. Bolter, A. J. Clark, M. E. Delf, and C. R. Hall for preliminary determinations of many of the rate constants reported in this paper.

[2/1919 Received, 14th August, 1972]

¹⁴ W. G. Palmer, 'Experimental Inorganic Chemistry,' Cambridge University Press, 1959, p. 391.

¹⁷ H. B. Johnson and W. L. Reynolds, *Inorg. Chem.*, 1963, **2**, 469.

¹⁴ G. Schlessinger, *Inorg. Synth.*, 1960, **6**, 138.

¹⁵ C. L. Rollinson and J. C. Bailar, *Inorg. Synth.*, 1946, **2**, 200.