Kinetics of Aquation of *trans*-Dichlorobis(1,3-diaminopropane)cobalt(III) Chloride in Mixed Aqueous Solvents

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Kinetic data are reported for aquation of the salt *trans*-[Co(dap)$_2$Cl$_2$]Cl [dap = 1,3-diaminopropane (trimethylenediamine)] in a variety of mixed water–organic solvents. Plots of log k_{H_2O} against Grunwald–Winstein Y values are linear with gradients of 0·36, 0·34, and 0·17 in methanol–, ethanol–, and acetone–water mixtures, respectively. The results are consistent with a dissociative mechanism.

MIXED-SOLVENT studies have been successfully employed in organic chemistry for diagnosis of solvolysis mechanisms.[1] This application followed the proposal by Grunwald and Winstein [1a] of a linear free-energy relation (1), where k is the rate constant for solvolysis of a

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

compound in any solvent, k_0 the rate constant in the standard solvent (80% ethanol, 20% water), Y a measure of the ionising power of the solvent, and m gives the sensitivity of the substrate to changes in the medium. By arbitrarily assigning $m = 1·0$ for the well established S_N1(lim) solvolysis of t-butyl chloride Grunwald and Winstein derived Y values for a wide range of binary mixed solvents. It was observed that while compounds reacting *via* an S_N1 process yielded m values close to unity, much lower values (0·25—0·35) were obtained for compounds known to react by an S_N2 mechanism.

More recently this type of analysis has been applied to the interesting problem of the mechanism of aquation of octahedral metal complexes.[2-8] Most of these studies have been concerned with cobalt(III) aminechloro-complexes, for which plots of log k_{H_2O} against Y generally yielded gradients of $m \sim 0·3$.[6] Since most other experimental evidence [9] indicates an essentially dissociative (S_N1) mechanism for cobalt(III) aquation, the low m value compared to t-butyl chloride was ascribed [6] to lower solvation requirements of the five-co-ordinate cobalt(III) amine intermediate than of the carbonium ion Me_3C^+. In addition, the 'ionic' nature of the ground-state Co^{III}–Cl bond might result in less ionisation

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[1] (*a*) E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; (*b*) A. H. Fainberg and S. Winstein, *ibid.*, 1956, **78**, 2770; (*c*) P. R. Wells, *Chem. Rev.*, 1963, **63**, 171, and refs. therein.

[2] C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228.

[3] V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1968, **13**, 1279 and refs. therein.

[4] J. Burgess, *J. Chem. Soc.* (*A*), 1969, 1899.

[5] J. Burgess, *J. Chem. Soc.* (*A*), 1970, 2351.

[6] (*a*) J. Burgess and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 3108; (*b*) J. Burgess, *ibid.*, 1970, 2703.

[7] J. Burgess, *J.C.S. Dalton*, 1973, 825 and refs. therein.

[8] L. A. P. Kane-Maguire and G. Thomas, unpublished work.

[9] F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., John Wiley, New York, 1967, ch. 3.

being required to achieve the transition state for aquation.[10]

However, definite mechanistic conclusions remain difficult for octahedral metal complexes, due to the absence of model compounds which are known to aquate by established S_N1(lim) and S_N2 mechanisms. For this reason we decided to study aquation of the complex *trans*-[Co(dap)$_2$Cl$_2$]Cl [dap = 1,3-diaminopropane (trimethylenediamine)] in a variety of mixed solvents. The strain imposed on this molecule by the presence of the six-membered cobalt–amine rings is considered [11] to promote a dissociative process, and this complex might thus provide a more suitable model for S_N1(lim) aquation than other cobalt(III) complexes studied to date. The scope of such Grunwald–Winstein correlations has also been extended by examining mixtures containing up to 50% organic component.

EXPERIMENTAL

The complex *trans*-[Co(dap)$_2$Cl$_2$]Cl (dap = 1,3-diaminopropane) was prepared by the published method.[12] All organic solvents were of analytic grade. Mixed-solvent compositions quoted are v/v percentages calculated before mixing.

Kinetic Procedure.—All runs were carried out in 0·02M-toluene-*p*-sulphonic acid to eliminate any base catalysis. Solutions (2·5 cm^3) of the desired composition were thermostatted at 10 °C (±0·1 °C) in a 1 cm silica cell placed in a Beckman DK2A thermostat compartment. After 15 min, sufficient solid sample was added to give $[\mathrm{Co^{III}}] = 7{\cdot}5 \times 10^{-3}$M, and rapidly dissolved by shaking. The reaction was then followed by observing the increase in absorbance at 540 nm. Pseudo-first-order rate constants were obtained from plots of $\log (A_\infty - A_t)$ against time, where A_∞ = absorbance at infinite time and A_t = absorbance at time t. Theoretical A_∞ values were employed for all solvent mixtures, being calculated from the known complex concentration and the absorption coefficient observed for the reaction products at 540 nm in pure water (51 l mol^{-1} cm^{-1}).

As a check, the aquation of *trans*-[Co(dap)$_2$Cl$_2$]Cl was also followed conductimetrically in some solvents using a Pye Unicam type E7566/2 conductivity bridge. In these runs, dilute nitric acid was employed (0·001M) and $[\mathrm{Co^{III}}] = 4 \times 10^{-3}$M. Rate constants were calculated from gradients of plots of $\log (\mathscr{K}_0 - \mathscr{K}_\infty)/(\mathscr{K}_t - \mathscr{K}_\infty)$ against time, where $\mathscr{K}_t$ = conductance in Ω^{-1} at time *t*, *etc.*

RESULTS AND DISCUSSION

Good first-order kinetics were generally observed for up to 90% completion of reaction in water-rich solvents. However, as the organic-solvent fraction was increased to ⩾30%, curvature occurred in first-order plots at progressively earlier reaction times (*e.g.* 45% reaction in 1 : 1 water–organic solvent). This behaviour was expected since numerous studies [11,13,14] have indicated that aquation equilibria of related cobalt(III) aminechloro-species are displaced back towards the chloro-complexes in organic-rich solvents. The rate constants in Table 1 refer only to the forward aquation reaction, since the use of theoretical A_∞ values (see Experimental section) eliminates interference from the reverse chloride-anation process. Confirmation that the spectroscopically observed rate constants do, in fact, refer to loss of the first chloride ion was obtained from the agreement with conductimetric kinetic data (Table 1). The change in conductance during the reaction in 50% aqueous methanol (or ethanol) was consistent with the release of a chloride ion and formation of a 2+ complex. Since the final spectrum revealed a mixture containing largely the ion *cis*-[Co(dap)$_2$Cl(H$_2$O)]$^{2+}$, rapid isomerisation of the initial aquochloro-products is suggested, as was observed [15] with the analogous ethylenediamine (en) complex.

TABLE 1

Rate constants for aquation of the salt *trans*-[Co(dap)$_2$Cl$_2$]Cl in mixed aqueous solvents at 10·0 °C

Organic component (% v/v)	Methanol		Ethanol		Acetone	
	Y	10^3k/ s^{-1}	Y	10^3k/ s^{-1}	Y	10^3k/ s^{-1}
0	3·49	10·8 [a]	3·49	10·8 [a]	3·49	10·8 [a]
10	3·28	8·78	3·31	9·06	3·23	9·36
20	3·03	7·27	3·05	7·68	2·91	8·62
30	2·75	5·60	2·72	5·56	2·48	7·20
40	2·39	4·20	2·20	3·83	1·98	5·76
50	1·97	3·10 (3·06) [b]	1·655	2·71 (3·28) [b]	1·40	4·51

[a] This value agrees well with that of $10{\cdot}0 \times 10^{-3}$ s^{-1} at 10 °C (ref. 11). [b] The value in parentheses was obtained conductimetrically.

The reported k_{obs} values are averages of duplicate determinations, which showed a reproducibility of ±2%. No spectral evidence was observed for solvolysis by the organic component in any of the solvent mixtures employed. For example, the same isosbestic points (588, 475, 402, and 355 nm) were observed in both water and 50% aqueous ethanol. Such solvolysis would have been surprising since, even at 50% organic component, water was never present in less than a two-fold excess, and it is known [16] to be about an order of magnitude more effective than alcohols in solvolysis of cobalt(III).

Plots of $\log k_{\mathrm{H_2O}}$ against Y showed excellent linearity for each pair of solvents (Figure). However, different gradients were obtained for different solvent pairs. Thus while both methanol- and ethanol–water mixtures yielded m values of $0{\cdot}34 \pm 0{\cdot}01$, the gradient for acetone–water was significantly lower (0·18). These observations show a striking resemblance to data previously obtained for *cis*- and *trans*-[Co(en)$_2$Cl$_2$]$^+$ and [Co(NH$_3$)$_5$Cl]$^{2+}$, since, although these complexes were reported [6] to show a gradient of *ca.* 0·30 in a wide variety of solvents, individual analysis of each solvent pair shows a similar variation depending on the nature

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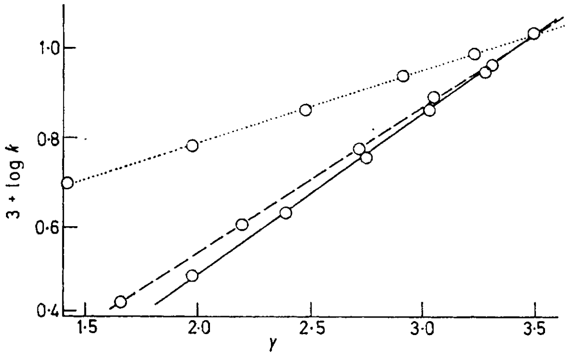
of the non-aqueous component (Table 2). Such behaviour has been well documented in organic reactions,[17,18] and was attributed to the fact that some other property of the solvent, apart from its ionizing power, must be important in determining the solvolysis rate of some substrates. An obvious candidate is the nucleophilicity (N) of the solvent, and Winstein *et al.*[19] have proposed the more comprehensive relation (2) to

$$\log (k/k_0) = lN + mY \qquad (2)$$

account for both factors. Here l is a measure of the sensitivity of the substrate to changes in nucleophilicity of the solvent. A recent study[20] has provided N values for a variety of solvents using methyl *p*-toluenesulphonate as substituent. The similar 'apparent *m*' values observed for cobalt(III) complexes in aqueous methanol and ethanol mixtures are thus explained by comparable nucleophilicities of the alcohols. On the other hand, the low 'apparent *m*' in acetone–water solvents is associated with the lower N value of acetone.



Variation of log k with Y for aquation of the ion *trans*-$[Co(dap)_2Cl_2]^+$ in mixed aqueous solvents: (——), methanol; (— — —), ethanol; and (· · · ·), acetone

TABLE 2

Dependence of m values on the nature of the mixed-solvent pair for aquation of various cobalt(III) complexes

Complex	MeOH–H_2O	EtOH–H_2O	Me_2CO–H_2O	Ref.
$[Co(NH_3)_5Cl]^{2+}$	0·33	0·20	0·16	6*a* *
cis-$[Co(en)_2Cl_2]^+$	0·37	0·37	0·27	6*b* *
trans-$[Co(en)_2Cl_2]^+$	0·38	0·32	0·20	6*a* *
trans-$[Co(dap)_2Cl_2]^+$	0·35	0·33	0·18	This work †

* t = 35 °C. † t = 10 °C.

The close agreement in the magnitude of m for *trans*-$[Co(dap)_2Cl_2]^+$ with values reported for other less-strained cobalt(III) complexes [6] indicates that the degree of dissociation in the transition state is similar for aquation of all these systems. This is consistent with an essentially dissociative mechanism in each case, and suggests that the ion *trans*-$[Co(dap)_2Cl_2]^+$ holds no special merit as a model for an S_N1(lim) process.

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