Kinetics of Solvolysis of the *trans*-Dichlorotetra(4-methylpyridine)-cobalt(III) Ion in Water and in Water–Propan-2-ol Mixtures

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The solvolysis of *trans*-$[Co(4\text{-}Mepy)_4Cl_2]^+$ followed spectrophotometrically in water and in water–propan-2-ol is always first order in the complex, showing no isosbestic points. The logarithm of the rate constant shows no linear correlation with the reciprocal of the dielectric constant or with the Grunwald–Winstein *Y* factor. However, extrema in the variation of the enthalpy and entropy of activation correlate well with the extrema in the physical properties of the mixture which are related to changes in solvent structure. Correlation of the free energies of activation in the mixture with that in water using Gibbs free energies of transfer of individual ionic species suggests that the effect of changes in solvent structure on the complex ion in the transition state dominates over that on the complex ion in the initial state. These findings are compared with similar results for the solvolysis of other Co^{III} complexes in water–propan-2-ol and in mixtures of water with other co-solvents.

In the investigation of the effect of changes in solvent structure on the kinetics of solvolysis of *trans*-$[Co(py)_4Cl_2]^+$ (py = pyridine) in water–methanol [1] and water–propan-2-ol,[2] it was found that the effect of addition of the co-solvent to water on the enthalpy and entropy of activation could be correlated with the effect of changes in solvent structure on the physical properties of the mixture.[3] As the addition of the branched-chain alcohol propan-2-ol to water has a greater effect on solvent structure than the addition of methanol,[3] we have also investigated the kinetics of the solvolysis in water–propan-2-ol for *trans*-$[Co(en)_2Cl_2]^+$ (en = ethylenediamine),[4] and for *cis*- and *trans*-$[Co(en)_2(N_3)Cl]^+$.[5,6] For the last two complexes linear plots of log (rate constant) against the reciprocal of the dielectric constant in water–co-solvent mixtures, with the slope independent of the nature of the co-solvent,[7] suggested that the kinetics of the solvolysis conform to interpretations based on point charges immersed in a dielectric continuum,[8-10] but the correlation of the extrema in ΔH^* and ΔS^* found [5,6] for water–propan-2-ol with the regions of composition where considerable changes in solvent structure occur shows the importance of the latter property. We now report the results of a kinetic investigation of the solvolysis in water–propan-2-ol of a complex related to *trans*-$[Co(py)_4Cl_2]^+$, namely the *trans*-dichlorotetra(4-methylpyridine)cobalt(III) ion, *trans*-$[Co(4\text{-}Mepy)_4Cl_2]^+$.

Experimental

Materials.—*trans*-$[Co(4\text{-}Mepy)_4Cl_2]Cl$ was prepared by a procedure analogous to that used for *trans*-$[Co(py)_4Cl_2]Cl$.[1,11] The pale green perchlorate was then prepared by adding to the cold solution dilute perchloric acid, in a procedure analogous to that used for the preparation of the nitrates of this type of complex cation.[11] Water was distilled once in an all-glass still; AnalaR propan-2-ol was used.

Procedure.—Spectra were measured using a Unicam SP 800 spectrophotometer. Rates of change of optical density due to solvolysis were measured in the thermostatted cell compartment of a Unicam SP 500 series 6 spectrophotometer with digital display. Temperatures were controlled to ±0.05 °C by circulating water from a Pye Unicam cell temperature controller. The initial concentration of the complex used in the kinetic work was 1.7×10^{-5} mol dm^{-3}.

Results and Discussion

Preliminary Experiments.—The spectrum of the complex ion in water was found to have a maximum at 233 nm with $\varepsilon = 4.57 \times 10^5$ dm^3 mol^{-1} cm^{-1}, and a flat or small broad peak at *ca.* 300 nm with $\varepsilon = 5.6 \times 10^3$ dm^3 mol^{-1} cm^{-1}. The wavelengths of these peaks did not move on addition of propan-2-ol to the aqueous solutions. The spectrum of the product of the aquation has a maximum at 253 nm with $\varepsilon = 4.08 \times 10^3$ dm^3 mol^{-1} cm^{-1}, and a minimum in the region of 233 nm. A more accurate determination of the wavelength for the secondary maximum for *trans*-$[Co(4\text{-}Mepy)_4Cl_2]ClO_4$ could not be made owing to the low solubility of this salt in water and in water–propan-2-ol mixtures.

During the aquation, no isosbestic points were detected. The decay of the optical density (o.d.) with time was measured at 233 nm, and linear plots were always obtained for log ($\text{o.d.}_t - \text{o.d.}_\infty$) against time. To determine o.d._∞, the reaction mixture was left overnight and the optical density measured; it was then compared with the value determined after a further 24 h at the temperature being investigated. As the first-order rate constant for the solvolysis has been shown to be independent of pH in the range 1—8.5,[12] no additions of acid or neutral salt were made to reaction mixtures.

Variation of Rate Constant with Solvent Composition and with Temperature.—First-order rate constants were determined for the solvolysis in pure water and in a range of water–propan-2-ol mixtures ranging from 10 to 90% v/v in propan-2-ol at 40, 45, 50, and 55 °C. Two to four determinations were made for each mixture at each temperature; the mean values for the rate constants are collected in Table 1. Linear plots were obtained for the variation of log *k* with the reciprocal of the absolute temperature for each mixture. The values for the enthalpy, ΔH^*, and entropy, ΔS^*, of activation were determined for each mixture by applying the least-squares procedure to these plots with the aid of a computer, using all the individual values of the rate constants. These values of ΔH^* and ΔS^*, together with their standard errors, are given in Table 2, which also contains values for the free energy of activation with the standard error.

Consideration of a dissociative reaction of this type on the basis of point charges in a dielectric continuum suggests [8-10] that plots of log (rate constant) against the reciprocal of the dielectric constant, D_s, should be linear. Values for log *k* at

Table 1. Variation of the rate constant, $10^4k/s^{-1}$, with composition of solvent and with temperature

[Propan-2-ol] Wt. %	[Propan-2-ol] Mole fraction	T/°C 40.0	45.0	50.0	55.0
0	0	0.87	1.66	3.25	4.99
8.04	0.0255	0.68	1.47	2.73	5.3
16.44	0.0557	0.452	1.03	1.96	4.59
25.22	0.0918	0.53	1.06	2.10	4.68
34.41	0.136	0.498	1.10	2.49	4.95
44.04	0.191	0.54	1.25	2.49	5.5
54.15	0.261	0.60	1.17	2.63	5.4
64.76	0.355	0.61	1.38	2.49	5.5
75.90	0.486	0.67	1.19	2.57	5.3
87.63	0.680	0.57	1.19	2.45	5.2

Table 2. Variation of transition state parameters with solvent composition

[Propan-2-ol] Wt. %	[Propan-2-ol] Mole fraction	ΔH^* kJ mol^{-1}	ΔS^* (25 °C) J K^{-1} mol^{-1}	ΔG^* (25 °C) kJ mol^{-1}
0	0	102 ± 12	3.7 ± 38	101 ± 23
8.04	0.0255	114 ± 5	39 ± 15	102 ± 10
16.44	0.0557	127 ± 7	76 ± 21	104 ± 13
25.22	0.0918	120 ± 3	55 ± 11	103 ± 7
34.41	0.136	130 ± 4	86 ± 13	104 ± 8
44.04	0.191	130 ± 5	88 ± 17	104 ± 10
54.15	0.261	125 ± 4	73 ± 12	103 ± 7
64.76	0.355	120 ± 5	57 ± 14	103 ± 9
75.90	0.486	118 ± 9	52 ± 29	103 ± 18
87.63	0.680	124 ± 2	69 ± 7	103 ± 4

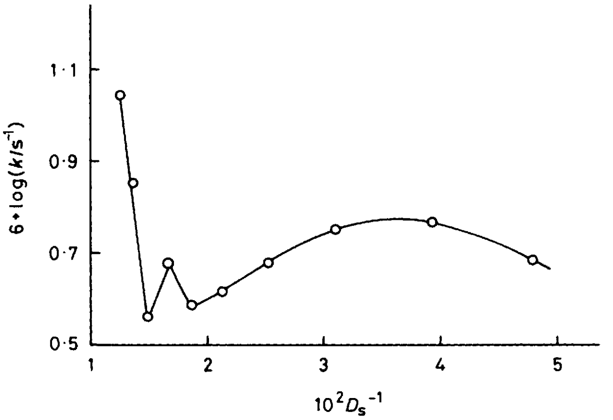

Figure 1. Plot of log k against the reciprocal of the dielectric constant (25 °C)

25 °C have been calculated using the values of ΔH^* and ΔS^* in Table 2, but Figure 1 shows that a plot of log k against D_s^{-1} over the whole range of solvent composition has no region

$$2.303\,RT\log\frac{k_w}{k_s} = \frac{Ne^2}{2}\left(\frac{1}{D_s}-\frac{1}{D_w}\right)\left[\frac{Z_M{}^2}{r_M}+\frac{Z_x{}^2}{r_x}-\frac{Z_C{}^2}{r_C}+\frac{3}{2}\left(\frac{G_M}{r_M{}^3}+\frac{G_x}{r_x{}^3}-\frac{G_C}{r_C{}^3}\right)\right]+\Delta G^\circ{}_t(M)_n+\Delta G^\circ{}_t(X)_n-\Delta G^\circ{}_t(C)_n \quad (1)$$

of linearity: values of D_s were interpolated from those of Åkerlöf.[13] A similar plot is obtained using the experimental values of k at 50 °C and D_s at 50 °C. When the equation of Laidler and Landskroener [8] is extended to allow for changes in solvent structure with varying solvent composition,

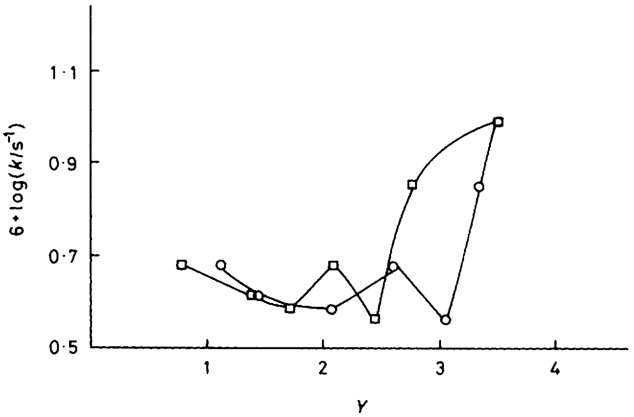

Figure 2. Plot of log k against the Grunwald–Winstein Y factor: values of Y calculated [4] from the rate data of R. E. Robertson and S. E. Sugamori (○, *J. Am. Chem. Soc.*, 1969, **91**, 7254) and of E. Aktar and R. A. Begum (□, *J. Bangladesh Acad. Sci.*, 1978, **2**, 9)

equation (1) results,[14] as applied to a dissociation of C^{Z_C} in the initial state into M^{Z_M} and X^{Z_X} in the transition state, where Z_C, Z_M, and Z_x are the appropriate ionic charges, N is Avogadro's number, e is the charge on the electron, subscript w and s indicate pure water and the mixture, respectively, r is radius, G is related to the dipole moment and $\Delta G^\circ{}_t(i)_n$ is the free energy of transfer of the species from water into the mixture excluding the contribution from Born and Kirkwood effects represented by the first term on the right hand side. Deviations from linearity of log k against D_s^{-1} have been found with other complexes in water–propan-2-ol [2,4–6] and with *trans*-$[Co(py)_4Cl_2]^+$ in water–methanol,[1] but the complete absence of any suggestion of linearity in Figure 1 indicates how considerable is the deviation of $\Delta G^\circ{}_t(C)_n$ from $\Delta G^\circ{}_t(M)_n + \Delta G^\circ{}_t(X)_n$ in this case.

Values for the Grunwald–Winstein Y function [15] have been calculated for mixtures of water and propan-2-ol.[4] Figure 2 shows that log k does not vary linearly with either of the two sets of Y values.[4] This is perhaps surprising in view of the linear plots for log k against Y found for *trans*-$[Co(py)_4Cl_2]^+$ in water–methanol [1] and in water–propan-2-ol,[2] and for *trans*-$[Co(en)_2Cl_2]^+$[4] and *cis*- and *trans*-$[Co(en)_2(N_3)Cl]^+$ [5,6] in water–propan-2-ol. As there is no reason for supposing that this particular complex, closely related to the others in structure, differs from the dissociative D-type mechanism established generally [16] from measurements of the volume of activation for complexes of Co^{III}, it seems likely that this non-linearity with Y and the complete non-linearity with D_s^{-1} derive from the same source, a large differential effect of solvent structure between the initial and transition states, *i.e.* $\Delta G^\circ{}_t(C)_n \gg \Delta G^\circ{}_t(M)_n + \Delta G^\circ{}_t(X)_n$ or $\Delta G^\circ{}_t(C)_n \ll \Delta G^\circ{}_t(M)_n + \Delta G^\circ{}_t(X)_n$.

Variation of Transition State Parameters with Solvent Composition.—A plot of ΔH^* against ΔS^* is linear despite the irregular variation of ΔH^* and ΔS^* with composition as shown in Figures 3 and 4. The errors found in ΔH^* and ΔS^* are not abnormal and Figures 3 and 4 show within these errors two extrema, one at mole fraction of propan-2-ol x_2 *ca.* 0.05, and the other at x_2 *ca.* 0.15. This corresponds roughly to the extrema for ΔH^* and ΔS^* in water–propan-2-ol

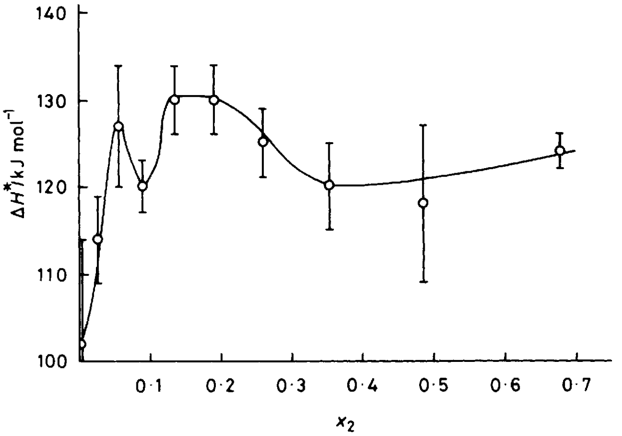

Figure 3. Plot of the enthalpy of activation against mole fraction of propan-2-ol

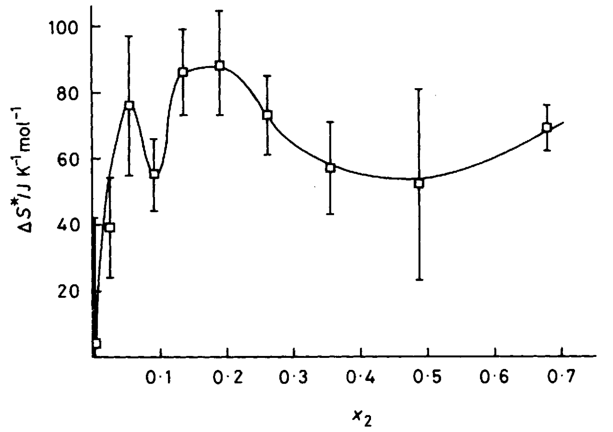

Figure 4. Plot of the entropy of activation at 25 °C against mole fraction of propan-2-ol

found for the solvolysis of *trans*-[Co(en)$_2$Cl$_2$]$^+$,[4] and *cis*- and *trans*-[Co(en)$_2$(N$_3$)Cl]$^+$.[5,6] Values of ΔH^* and ΔS^* for the solvolysis of *trans*-[Co(py)$_4$Cl$_2$]$^+$ show only a single broad maximum at x_2 *ca.* 0.1 in water–propan-2-ol,[2] and in water–methanol[1] at x_2 *ca.* 0.2—0.3. The structural contribution to the temperature of maximum density shows[17] that solvent structure in water-rich water–propan-2-ol mixtures is enhanced over that of pure water. The extremum at the lower x_2 for those complexes exhibiting two corresponds with the minimum found[18] in the decrease in the partial molar volume, $\bar{V}_2 - V_2^0$, for water–propan-2-ol: it is suggested[19] that this situation corresponds to the maximum stress imposed in the 'flickering clusters' of water structure surrounding the branched chain alkyl group of the alcohol.[20] The extremum at the higher x_2 correlates with the maximum found in the ultrasonic absorption[21] and the minimum shown by the excess enthalpy of mixing,[22] ΔH^E, for water–propan-2-ol: it seems likely[19] that this corresponds to the onset of the breakdown of the water structure by the strain of the alkyl groups in the cavities, resulting at higher x_2 in the formation of a dominant alcohol structure in the solvent.

The free energies of activation in water and in the mixture can be related *via* a free energy cycle[14] using also the free energies of transfer of the individual ionic species between water and the mixture, assuming an I_d reaction with extension of the Co–Cl bond sufficiently long to correspond to a D reaction, as suggested by the data for ΔV^*[16] for such Co complexes (Scheme); $\Delta G^{\ominus}_t(i)$ is the total standard free energy of transfer of species i from water into the mixture. Equation (2) can be derived from the Scheme.

$$2.303\,RT\log\frac{k_w}{k_t} - \Delta G^{\ominus}_t(\mathrm{Cl}^-) = \Delta G^{\ominus}_t[\mathrm{Co(4\text{-}Mepy)_4Cl}^{2+}] - \Delta G^{\ominus}_t[\mathrm{Co(4\text{-}Mepy)_4Cl_2}^{+}] \quad (2)$$

Using the values for $\Delta G^{\ominus}_t(\mathrm{Cl}^-)$ in water–propan-2-ol derived[23] from the investigation of solvent sorting around H$^+$ and k_w/k_s calculated for 25 °C from the values of ΔH^* and ΔS^* in Table 2, values for the left hand side of equation (2) can be calculated. These are plotted against mole fraction of propan-2-ol in Figure 5. Minor numerical corrections have been applied[24] to the published values for $\Delta G^{\ominus}_t(\mathrm{Cl}^-)$ arising from the inclusion of additional electrochemical values for $\Delta G^{\ominus}_t(\mathrm{HCl})$ in the calculation from Bose *et al.*,[25] from Smits *et al.*,[26] from Elsemongy and Fonda,[27] and from Schwabe and Nhuan,[28] the inclusion in the small Born contribution to $\Delta G^{\ominus}_t(\mathrm{H}^+)$ of a scale correction from the molar to the mole fraction scale, and the re-calculation of [H$_2$O] used in deriving $\Delta G^{\ominus}_t(\mathrm{H}^+)$ based on the densities of the mixture and the pure liquids. These new values for $\Delta G^{\ominus}_t(\mathrm{Cl}^-)$ show[24] only small differences from the previous ones[23] and are given in Table 3. In general,[23,24] $\Delta G^{\ominus}_t(i)$ for i = a cation M are negative in water-rich conditions, which shows that the effect of solvent structure on the transfer from water to mixture predominates over the Born contributions, which would require positive values for $\Delta G^{\ominus}_t(i)$ irrespective of the charge on i. Moreover, the value of $-\Delta G^{\ominus}_t(\mathrm{M})$ increases with the magnitude of the positive charge on a metallic M:[23,24] in particular, for cations of approximately the same size $-\Delta G^{\ominus}_t(\mathrm{M}^{2+}) > -\Delta G^{\ominus}_t(\mathrm{M}^+)$.[29] The negative values for the left hand side of equation (2) found in Figure 5 show that [Co(4-Mepy)$_4$Cl]$^{2+}$ and [Co(4-Mepy)$_4$Cl$_2$]$^+$ conform to this with $-\Delta G^{\ominus}_t[\mathrm{Co(4\text{-}Mepy)_4Cl}^{2+}] > -\Delta G^{\ominus}_t[\mathrm{Co(4\text{-}Mepy)_4Cl_2}^{+}]$. Therefore, in the composition range used in our experiments, the influence of solvent structure on the complex ion in the transition state must dominate over that on the complex ion in the initial state. This is similar to the findings in water-rich conditions for *trans*-[Co(en)$_2$Cl$_2$]$^+$,[4] and *cis*- and *trans*-[Co(en)$_2$(N$_3$)Cl]$^+$,[5,6] in

$$\begin{tikzcd}
{[\mathrm{Co(4\text{-}Mepy)_4Cl_2}]^+_w} \arrow[r, "\Delta G^{*}_{w}"] & {[\mathrm{Co(4\text{-}Mepy)_4Cl}]^{2+}_w} \arrow[d, "\Delta G^{\ominus}_t{[\mathrm{Co(4\text{-}Mepy)_4Cl}^{2+}]}"'] & + & \mathrm{Cl}^-_w \arrow[d, "\Delta G^{\ominus}_t(\mathrm{Cl}^-)"'] \\
{[\mathrm{Co(4\text{-}Mepy)_4Cl_2}]^+_s} \arrow[u, "-\Delta G^{\ominus}_t{[\mathrm{Co(4\text{-}Mepy)_4Cl_2}^{+}]}"] \arrow[r, "\Delta G^{*}_{s}"] & {[\mathrm{Co(4\text{-}Mepy)_4Cl}]^{2+}_s} & + & \mathrm{Cl}^-_s
\end{tikzcd}$$

Scheme.

Table 3. Values for the free energy of transfer of the Cl$^-$ ion from water into water–propan-2-ol at 25 °C

Wt. % propan-2-ol	$\Delta G^{\ominus}_t(\mathrm{Cl}^-)$ kJ mol^{-1}
5	1.32
10	3.07
15	5.5
20	8.8
25	9.3
30	10.3
35	10.9
40	11.1
45	11.2
50	11.3

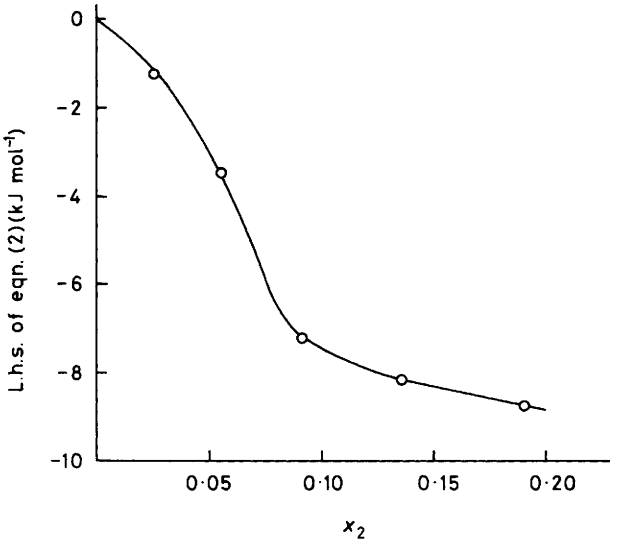

Figure 5. Plot of the left hand side of equation (2) (25 °C) against mole fraction of propan-2-ol

water–propan-2-ol, for *trans*-$[Co(py)_4Cl_2]^+$ in water–methanol [1,29] and in water–propan-2-ol,[2] and for a range of Co^{III} complexes with a variety of co-solvents mixed with water.[14]

References

1 C. N. Elgy and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1980, 2405.
2 C. N. Elgy and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1982, 1617.
3 F. Franks and D. J. G. Ives, *Quart. Rev.*, 1966, **20**, 1.
4 G. S. Groves and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1982, **78**, 619.
5 A. E. Eid and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1981, **77**, 1621.
6 A. E. Eid and C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1983, **79**, 253.
7 V. D. Panasyuk and A. V. Arkharov, *Russ. J. Inorg. Chem.*, 1970, **15**, 356.
8 K. J. Laidler and H. Eyring, *Ann. N. Y. Acad. Sci.*, 1940, **39**, 303; S. Glasstone, K. J. Laidler, and H. Eyring, ' The Theory of Rate Processes,' McGraw-Hill, New York, 1941, ch. 8; K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, 1956, **52**, 200; K. J. Laidler, *Suomen Kem.*, 1960, **A33**, 44; K. J. Laidler, ' Chemical Kinetics,' 2nd edn., McGraw-Hill, New York, 1965, ch. 5.
9 E. A. Moelwyn-Hughes, *Proc. R. Soc. London, A*, 1936, **155**, 308; 1936, **157**, 667; ' The Kinetics of Reactions in Solution,' 2nd edn., Oxford University Press, London, 1947, chs. 4, 5, and 7; ' Physical Chemistry,' 2nd edn., Pergamon, Oxford, 1961, chs. 7—9 and 24.
10 E. S. Amis, ' Kinetics of Chemical Change in Solution,' Macmillan, New York, 1949, chs. 5 and 9; ' Solvent Effects on Reaction Rates and Mechanisms,' Academic Press, New York, 1966, chs. 1—3; ' Solvent Effects on Chemical Phenomena,' Academic Press, New York, 1973, vol. 1, ch. 5.
11 A. Werner and R. Feenstra, *Ber.*, 1906, **39**, 1538.
12 R. G. Pearson, R. E. Meaker, and F. Basolo, *J. Inorg. Nucl. Chem.*, 1955, **1**, 341.
13 G. Åkerlöf, *J. Am. Chem. Soc.*, 1932, **54**, 4125.
14 C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1977, **73**, 1851.
15 E. Grunwald and S. Winstein, *J. Am. Chem. Soc.*, 1948, **70**, 846.
16 W. E. Jones, L. R. Carey, and J. W. Swaddle, *Can. J. Chem.*, 1972, **50**, 2739; D. A. Palmer and H. Kelm, *Coord. Chem. Rev.*, 1981, **36**, 89.
17 G. Wade and S. Umeda, *Bull. Chem. Soc. Jpn.*, 1962, **35**, 646.
18 K. Nakanishi, *Bull. Chem. Soc. Jpn.*, 1960, **33**, 793.
19 C. F. Wells, *Trans. Faraday Soc.*, 1970, **66**, 204; *J. Chem. Soc., Faraday Trans. 1*, 1974, **70**, 694.
20 H. S. Frank and M. W. Evans, *J. Chem. Phys.*, 1945, **13**, 507; H. S. Frank and W.-Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133; G. Némethy and H. A. Sheraga, *J. Chem. Phys.*, 1962, **36**, 3382, 3401; N. Laiden and G. Némethy, *J. Phys. Chem.*, 1970, **74**, 3501.
21 M. J. Blandamer, ' Introduction to Chemical Ultrasonics,' Academic Press, London, 1973, ch. 11.
22 R. F. Lama and B. C.-Y. Lu, *J. Chem. Eng. Data*, 1965, **10**, 215.
23 C. F. Wells, *J. Chem. Soc., Faraday Trans. 1*, 1973, **69**, 984; 1974, **70**, 694; 1975, **71**, 1868; 1976, **72**, 601; 1978, **74**, 636, 1569; 1981, **77**, 1515; *Adv. Chem. Ser.* No. 178, 1979, p. 53; G. S. Groves and C. F. Wells, unpublished work.
24 C. F. Wells, unpublished work.
25 K. Bose, K. Das, A. K. Das, and K. K. Kundu, *J. Chem. Soc., Faraday Trans. 1*, 1978, **74**, 1051.
26 R. Smits, D. L. Massart, J. Juillard, and J.-P. Morel, *Electrochim. Acta*, 1976, **21**, 431.
27 M. M. Elsemongy and A. S. Fonda, *J. Electroanal. Chem.*, 1980, **114**, 25.
28 K. Schwabe and N. F. Nhuan, *Z. Elektrochem.*, 1961, **65**, 891.
29 I. M. Sidahmed and C. F. Wells, *J. Chem. Soc., Dalton Trans.*, 1981, 2034.

Received 22nd July 1982; *Paper* 2/1251