Kinetics of Reaction of the Tris(2,2′-bipyridyl)iron(II) Cation with Cyanide Ion in Binary Aqueous Mixtures †

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Rate constants have been determined for the reaction of the tris(2,2′-bipyridyl)iron(II) cation with cyanide ion in mixed aqueous solvents containing up to 30% by volume methanol, ethanol, dioxan, and acetone, and up to 48% by volume t-butyl alcohol. Rate constants have also been determined for this reaction in aqueous solutions containing potassium, tetramethylammonium, and tetra-n-butylammonium halides. The observed reactivity trends are discussed in the light of established properties of the mixed solvents and salt solutions. In particular, the reactivity trends are compared with those forecast from consideration of the variation in estimated chemical potentials of the cyanide ion with solvent medium composition.

THERE have been numerous studies of the kinetics of reactions of inorganic complexes in mixed aqueous solvents.[1-3] These studies have generally fallen into one of two categories, either that of using the effect of solvent variation on reactivity to diagnose the mechanism of the reaction, or of deducing something about solvent–solute and solvent–solvent interactions from kinetic observations.[2] In investigations of the former type, the dependences of rate constants on such properties of the mixed solvents as their dielectric constants [3] or their Grunwald–Winstein Y values [4] are often used in the diagnosis of mechanism. Examples of the latter approach in the area of substitution reactions of transition-metal complexes include applications to aquation of cobalt(III)–halide,[5] chromium(III)–halide,[6] and iron(II)–phenanthroline [7] complexes. Of these reactions the first and last are dissociative in mechanism, the second arguably at least partially associative in character. We were interested in examining solvent effects on the kinetics of a bimolecular (associative) reaction of a transition-metal complex, both to see whether the Grunwald–Winstein analysis is capable of distinguishing between dissociative and associative mechanisms of substitution at inorganic complexes, and for the general interest of establishing the reactivity pattern for such a system. Two obvious choices of reaction present themselves, substitution at a square-planar d^8 complex [8] or cyanide attack at a low-spin iron(II) complex.[9,10] We now report our results on a reaction in the latter category, the attack of cyanide at the tris(2,2′-bipyridyl)iron(II) cation. Rate constants have been obtained for this reaction in methanol–, ethanol–, t-butyl alcohol–, acetone–, and dioxan–water, and in aqueous solutions of some tetra-alkylammonium salts. The dependence of these rate constants on solvent composition is discussed, and compared with the rate-constant patterns for aquation of this complex in the same range of mixed solvents.

We have also investigated how far the observed increases in rate on changing from water to the various aqueous mixtures can be attributed to changes in the chemical potential of the cyanide ion on going from water ($x_2 = 0$) to a mixture when the co-solvent mole fraction is x_2:

$$\delta_m\mu^\ominus(\mathrm{CN}^-) = \mu^\ominus(\mathrm{CN}^-;\ x_2) - \mu^\ominus(\mathrm{CN}^-;\ x_2 = 0)$$

Actually these single-ion values cannot be calculated in an absolute sense. Rather, some extrathermodynamic assumption is required, to calculate the thermodynamic transfer function for the ions from that for a salt. Consequently there is some disagreement between the values calculated for $\delta_m\mu^\ominus$ (ion). For example $\delta_m\mu^\ominus(\mathrm{Cl}^-)$ for the transfer from water to methyl alcohol is (on the molar scale) 12.6 kJ mol^{-1} according to Parker *et al.*[11] who assume $\delta_m\mu^\ominus(\mathrm{Ph_4B^-}) = \delta_m\mu^\ominus(\mathrm{Ph_4As^+})$ but 20.3 kJ mol^{-1} according to Abraham [12] who puts $\delta_m\mu^\ominus(\mathrm{Me_4N^+}) = 0$.

The extent of information on these transfer quantities is certainly limited for aqueous mixtures but their importance in the analysis of the kinetic data is clear cut. Thus for the reaction between CN$^-$ and the complex, the solvent dependence of $\Delta G^\ddagger$, $\delta_m\Delta G^\ddagger$, can be expressed in terms of the separate dependences of the chemical potentials for CN$^-$, complex, and transition state:

$$\delta_m\Delta G^\ddagger = \delta_m\mu^\ddagger - \delta_m\mu^\ominus(\text{complex}) - \delta_m\mu^\ominus(\mathrm{CN}^-)$$

For example, if CN$^-$ is destabilised on adding the co-solvent to water, *i.e.* $\delta_m\mu^\ominus(\mathrm{CN}^-) > 0$, $\delta_m\Delta G^\ddagger$ will decrease, the rate constant tending to increase. Hence if we can estimate $\delta_m\mu^\ominus(\mathrm{CN}^-)$ from the properties of salts in the mixtures, then it should be possible to compare the trends in $\delta_m\Delta G^\ddagger$ calculated from the kinetic data with those which stem directly from the change in the chemical potential of the ion. We have explored the usefulness of this method of analysis to the above reaction although the paucity of the data required that we make an additional extrathermodynamic assumption.

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† No reprints available.

[1] See *e.g.*, 'Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1971, vol. 1, pp. 163—166, 172—173, 201—204; 1972, vol. 2, pp. 150—151, 162—163, 168—169; 1974, vol. 3, pp. 182—184, 201—203, 318—324.

[2] M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, 1975, **4**, 55.

[3] *E.g.* J. Burgess, 'Inorganic Reaction Mechanisms,' ed. A. McAuley, Chem. Soc. Specialist Periodical Report, London, 1975, vol. 4, in the press.

[4] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846.

[5] *E.g.* C. H. Langford, *Inorg. Chem.*, 1964, **3**, 228; J. Burgess, *J. Chem. Soc. (A)*, 1970, 2703; G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688.

[6] J. Burgess, *J.C.S. Dalton*, 1973, 825.

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

[8] *E.g.* F. Basolo and R. G. Pearson, 'Mechanisms of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, ch. 5.

[9] D. W. Margerum and L. P. Morgenthaler, *J. Amer. Chem. Soc.*, 1962, **84**, 706.

[10] J. Burgess, *J.C.S. Dalton*, 1972, 1061.

[11] B. G. Cox, G. R. Hedwig, A. J. Parker, and D. W. Watts, *Austral. J. Chem.*, 1974, **27**, 477.

[12] M. H. Abraham, *J.C.S. Faraday I*, 1973, 1375.

EXPERIMENTAL

Solutions containing the tris(2,2′-bipyridyl)iron(II) cation were prepared from AnalaR iron(II) ammonium sulphate and a slight excess of ligand. Potassium cyanide and potassium chloride solution were made up by direct weighing from AnalaR materials. The organic co-solvents were of the best commercially available grade; tetramethylammonium chloride (B.D.H.) and tetra-n-butylammonium bromide (Eastman–Kodak) were used as supplied.

Kinetic runs were carried out in 1 cm cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Optical densities were monitored at 526 nm, the wavelength of maximum absorption of the starting material. The initial concentration of the complex was *ca.* 2×10^{-4} mol dm^{-3}; other initial reactant concentrations are detailed in the appropriate Table headings. Observed first-order rate constants were computed from recorded optical densities using a standard least-mean-squares program (PDP 11).

RESULTS

The product of the reaction was confirmed as $[Fe(bipy)_2(CN)_2]$ by spectrophotometry.[13] The reaction is thus as stated in equation (1) in mixed aqueous solution as in water.

First-order rate constants, k_{obs}, for the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide ion in binary aqueous mixtures are reported in Tables 1 and 2, in which each entry represents the mean of consistent duplicate determinations. In every solvent mixture named in Tables 1 and 2, and in every solution named in Table 3, the rate law for the reaction [equation (1)] is as shown in equations (2) and (3).

TABLE 1

First-order rate constants (k_{obs}) and derived second-order rate constants (k_2) for reaction of $[Fe(bipy)_3]^{2+}$ with cyanide ion in binary aqueous mixtures; at 308.2 K and ionic strength 0.1 mol dm^{-3}, maintained with potassium chloride. Solvent compositions are by volume before mixing

		$10^3k_{obs}/s^{-1}$				
[KCN]/mol dm^{-3}		0.025	0.050	0.075	0.100	k_2/ mol^{-1} dm^3 s^{-1}
Water						0.028 [a]
Methanol (%)	10	1.47	2.6	3.8	5.1	0.044
	20	1.75	3.2	4.6	6.2	0.058
	30	2.1	3.9	6.5	8.6	0.090
Ethanol (%)	10	1.54	2.8	3.9	4.2	0.040
	20	1.63	3.6	4.7	6.2	0.061
	30	3.0	6.4	8.1	8.6	0.080
Dioxan (%)	10	1.68	2.9	4.6	5.8	0.058
	20	2.3	4.5	6.8	9.1	0.090
	30	3.6	7.1	10.6	14.0	0.125
Acetone (%)	10	1.15	2.3	3.3	4.5	0.042
	20	1.55	3.0	4.6	6.1	0.059
	30	3.5	6.6	8.7	9.8	0.084

[a] From ref. 10.

Under the conditions of our experiments, the k_1 term of equations (2) and (3) is small.* Values of k_2 for each reaction medium were computed from the variation of k_{obs} with cyanide concentration, and are included in Tables 1 and 2.

TABLE 2

First-order rate constants (k_{obs}) and derived second-order rate constants (k_2) for reaction of $[Fe(bipy)_3]^{2+}$ with cyanide ion in aqueous t-butyl alcohol mixtures at 298.2 K and ionic strength 0.1 mol dm^{-3}, maintained with potassium chloride

	$10^3k_{obs}/s^{-1}$				
[KCN]/mol dm^{-3}	0.025	0.050	0.075	0.100	
mole fraction Bu^tOH					k_2/ mol^{-1} dm^3 s^{-1}
0.02	0.9	1.4	1.7	2.0	0.011
0.04	0.9	1.5	2.0	3.0	0.028
0.07	1.5	2.5	4.1	5.3	0.054
0.10	2.1	4.4	6.1	7.5	0.072
0.125	2.3	5.3	8.6	11.6	0.12
0.15	3.1	6.3	10.0	12.0	0.13

TABLE 3

First-order rate constants (k_{obs}) for reaction of $[Fe(bipy)_3]^{2+}$ with cyanide ion in the presence of various salts at 308.2 K and ionic strength 1.0 mol dm^{-3}

Salt		KCl	KBr	Me_4NCl	Bu^t_4NBr
[salt]/ mol dm^{-3}	[KCN]/ mol dm^{-3}	$10^3k_{obs}/s^{-1}$			
0.75	0.25	3.7	3.4	4.0	3.2
0.50	0.50	6.6	7.1	7.1	
0.25	0.75	10.9	10.3	10.4	

The effects of added salts on the rate constant for reaction (1) are shown in Table 3, which includes the experimentally determined k_{obs} values for cyanide attack.

$$[Fe(bipy)_3]^{2+} + 2CN^- \longrightarrow [Fe(bipy)_2(CN)_2] + bipy \quad (1)$$

$$-d[Fe(bipy)_3{}^{2+}]/dt = k_{obs}[Fe(bipy)_3{}^{2+}] \quad (2)$$

$$k_{obs} = k_1 + k_2\,[CN^-] \quad (3)$$

The dependence of first-order rate constants for aquation of the $[Fe(bipy)_3]^{2+}$ cation, k_{aq} [equation (4)], on acid concentration has been established for methanol–, ethanol–, and dioxan–water (Table 4). Satisfactorily reproducible results could not be obtained for acetone–water mixtures. The dependence of k_{aq} on acid concentration (Figure 1) is analogous to that established long ago for aqueous solution.[14] We have taken the maximum rate constant ($k_{max.}$) to correspond with iron–nitrogen bond-breaking in the complex.[14]

TABLE 4

First-order rate constants (k_{obs}) for aquation of $[Fe(bipy)_3]^{2+}$ in acidic binary aqueous mixtures, at 308.2 K. Values of maximum rate constant ($k_{max.}$) were estimated graphically from k_{obs} values cited here. Solvent compositions are by volume before mixing

		$10^3k_{obs}/s^{-1}$		
[H_2SO_4]/mol dm^{-3}		0.67	1.35	2.71
Methanol (%)	10	2.0	2.5	2.7
	20	1.7	2.2	2.3
	30	1.4	2.0	2.0
Ethanol (%)	10	1.8	2.3	2.3
	20	1.4	1.8	1.9
	30	1.3	1.5	1.5
Dioxan (%)	10	2.1	2.7	2.8
	20	1.8	2.4	2.4
	30	1.7	2.1	2.1

$$-d[Fe(bipy)_3{}^{2+}]/dt = k_{aq}[Fe(bipy)_3{}^{2+}] \quad (4)$$

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* The concentration of hydroxide ion present in aqueous solutions containing 0.025 mol dm^{-3} potassium cyanide, the lowest concentration used here, is such that direct attack of hydroxide at the complex contributes only *ca.* 1% to the total observed $-d[complex]/dt$. The importance of this contribution, relative to direct attack by cyanide ion, decreases as the concentration of potassium cyanide in the reaction mixture increases. It seems reasonable to assume that attack by hydroxide ion can also be neglected in the mixed aqueous media of the present investigation.

[13] J. Burgess and S. F. N. Morton, *J.C.S. Dalton*, 1972, 1712, and refs. therein.

[14] M. V. Twigg, *Inorg. Chim. Acta*, 1974, **10**, 17; and ref. 8, pp. 218—219.

DISCUSSION

Mechanism.—The rate law of equations (2) and (3) indicates parallel first- and second-order reactions. The former corresponds to rate-determining bond breaking in the $[Fe(bipy)_3]^{2+}$ cation.[10] This represents only a minor pathway under the conditions of the present investigation. We have obtained rate constants for this process independently from aquation in acid solution (see Table 4 and later), rather than use imprecise k_1 values from k_{obs} *vs*. cyanide concentration plots, for subsequent reactivity comparisons.

The $k_2[CN^-]$ term of equations (2) and (3) indicates bimolecular attack of cyanide ion at the complex. It used to be assumed that this attack takes place at the iron atom, being a simple nucleophilic substitution at this centre.[9,10,15] However in recent years an alternative mechanism, for hydroxide and for cyanide attack at this type of complex, has been suggested.[16] This involves attack at the 6- or 6′-position of the co-ordinated ligand, with subsequent rapid transfer of the nucleophile to the iron atom. The evidence in favour of such a mechanism for the apparently bimolecular attack of hydroxide at this type of low-spin iron(II) complex is persuasive. Indeed there is kinetic evidence for a two-step mechanism for the reaction of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation with cyanide ion.[17] There is much less evidence in favour of such a mechanism for cyanide attack.* Thus experiments with the $[Pt(bipy)_2]^{2+}$ cation in solutions containing hydroxide provide convincing evidence of equilibrium substitution of hydroxide at the bipyridyl ring,[18] but analogous experiments with $[Ru(bipy)_3]^{2+}$ in solutions containing cyanide provide no evidence for reversible addition of cyanide to the co-ordinated bipyridyl.[19] In the case of cyanide attack at low-spin iron(II) complexes there is no need to invoke indirect attack at the ligand rather than direct attack at the metal, as cyanide ion has a greater affinity for iron(II) than, say, $\frac{1}{2}$bipy. Fortunately our conclusions are affected very little by the position of attack of the cyanide at the complex, for this does not alter the bimolecular nature of the reaction.

Solvents.—We have conducted our kinetic experiments in several of the ranges of binary aqueous mixtures used originally by Grunwald and Winstein in their pioneering study of the kinetics of solvolysis of t-butyl chloride and their discussion of the use of solvent effects in mechanism diagnosis in organic chemistry.[4] We have also undertaken some runs in aqueous salt solutions, to see whether the modification of the structure of the water by added cations, *e.g*. $[R_4N]^+$, is reflected in the kinetics of cyanide attack (*cf*. the effects of such cations on the aquation of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation [20]).

Kinetics.—*General*. Nearly half a century ago Hughes, Ingold, and their associates systematised the effects of solvent variation on reactivities for organic reactions involving various combinations of charged and uncharged substrates.[21] For bimolecular reactions involving species of opposite charge {in their case $[Me_3S]^+ + OH^-$, in ours $[Fe(bipy)_3]^{2+} + CN^-$} one expects and finds a marked increase in rate in changing from water to aqueous mixtures containing, *e.g*., methanol or ethanol. Similar forecasts and conclusions follow from Laidler's general treatment of such reactions.[22]

Grunwald–Winstein analysis. For S_N1 solvolysis of an organic chloride, a plot of rate constants *vs*. solvent Y values, defined from the model S_N1 solvolysis of t-butyl chloride, should give a single straight line of slope (m) 1.0.[4] For S_N2 reactions, one expects a family of curves, one for each co-solvent, all with tangents considerably <1.0. As reactions studied get more distant from solvolysis of organic halides, so the value of the slope will depart further from 1.0. Thus dissociative aquations of cobalt(III)–amine–chloride complexes have plots with m values of *ca*. 0.3,[5,23] while aquation of $[Fe(bipy)_2(CN)_2]$ has a plot with $m = 0.2$.[24]

Logarithms of maximum rates of aquation of the $[Fe(bipy)_3]^{2+}$ cation (Table 4) correlate roughly with solvent Y values for the respective solvent mixtures. For this aquation the m value is 0.2 to 0.3. In other words the rate is very much less sensitive to solvent nature than in the case for t-butyl chloride solvolysis. This is as expected, for there is no charge separation in forming the transition state, and the groups which separate are both large. The similarity of m values for the aquation of $[Fe(bipy)_3]^{2+}$ and of $[Fe(bipy)_2(CN)_2]$ is consistent with these reactions involving a common leaving group.

The relationship between the second-order rate constants for cyanide attack at $[Fe(bipy)_3]^{2+}$ and solvent Y values is shown in the Figure, which suggests a family of curves rather than a single linear dependence, behaviour reminiscent of bimolecular solvolysis. The limiting m value estimated for water-rich mixtures is *ca*. -1.0 to -1.1. Negative m values have previously been reported for such bimolecular inorganic processes as mercury(II)-catalysed aquation of the $[Co(NH_3)_5Cl]^{2+}$ ($m = -0.35$) and the $[Rh(NH_3)_5Cl]^{2+}$ ($m = -0.25$) cations.[23] They arise from the solvation changes associated with the transfer of small inorganic ions from water to the less favourable mixed solvent environments (*vide infra*).

Cyanide attack and aquation. The much greater sensitivity of rates of cyanide attack than of rates of aquation to variation in solvent composition is obvious

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* On the other hand, there is no evidence disallowing this mechanism.

[15] *E.g*. J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[16] R. D. Gillard, *Inorg. Chim. Acta*, 1974, **11**, L21, and refs. therein.

[17] R. D. Gillard and C. T. Hughes, personal communication.

[18] R. D. Gillard and J. R. Lyons, *J.C.S. Chem. Comm*., 1973, 585.

[19] J. Burgess and J. G. Chambers, unpublished observations.

[20] M. J. Blandamer, J. Burgess, and S. H. Morris, *J.C.S. Dalton*, 1974, 1717.

[21] C. K. Ingold, 'Structure and Mechanism in Organic Chemistry,' 1st edn., Cornell University Press, Ithaca, New York, 1953, p.349.

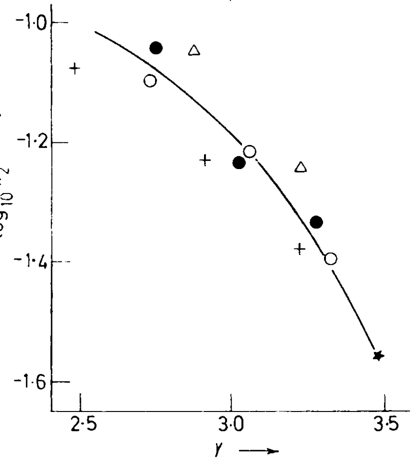
[22] K. J. Laidler, 'Chemical Kinetics,' 2nd edn., McGraw-Hill, London, 1965, pp. 210—217.

[23] J. Burgess and M. E. Price, *J. Chem. Soc.* (*A*), 1971, 3108.

[24] J. Burgess, *Chem. Comm*., 1969, 1422; *J.C.S. Dalton*, 1972, 203.

both from the tabulated rate constants and from the respective m values derived above. The small variation in rates of aquation suggests that insofar as iron–bipyridyl bond stretching is a contributor to the formation of the transition state for the reaction with cyanide it will not have a large effect on reactivity variation with solvent composition. The factor which seems to dominate this reactivity variation is the variation in chemical potential of the cyanide ion with solvent composition.

Cyanide chemical potential and reactivity. As already indicated, the significant change in the chemical potential of the cyanide ion from water to the various binary aqueous mixtures will be reflected in the rate constant for its reaction with the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation if this reaction proceeds by a bimolecular mechanism. We have therefore attempted to estimate the contribution of this factor from considerations of estimated Gibbs free-energies of transfer of cyanide ion $\delta_m\mu^{\ominus}(\mathrm{CN}^-)$, from water to the solvent mixtures examined in the present study. Unfortunately it is impossible to determine $\delta_m\mu^{\ominus}(\mathrm{CN}^-)$ from available data. We have therefore been forced to make the assumption that $\delta_m\mu^{\ominus}(\mathrm{CN}^-) = \delta_m\mu^{\ominus}(\mathrm{Cl}^-)$. This assumption is based on the observations that the thermochemical radii of these two anions are similar [$r(\mathrm{CN}^-)$ 1.84, $r(\mathrm{Cl}^-)$ 1.81 Å] as are their single-ion enthalpies of hydration (−347 for CN^-, −352 kJ mol^{-1} for Cl^-).[25] Fortunately sufficient data exist for us to estimate $\delta_m\mu^{\ominus}(\mathrm{Cl}^-)$ for transfer from water to most of the solvent mixtures in this investigation, as outlined in the following paragraphs.



The dependence of second-order rate constants (k_2/s^{-1}) for cyanide attack at the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation in mixed solvents on solvent Y values. Cosolvents: closed circle, MeOH; open circle, EtOH; open triangle, dioxan; cross, acetone; asterisk, water

(*a*) *Methanol + water.* Single-ion $\delta_m\mu^{\ominus}$ values have been estimated for a range of cations and anions from previously published solubility and e.m.f. data by Wells.[26] The split into single-ion values here was based ultimately on calculations for the transfer of a tetrahedrally solvated proton from water into aqueous methanol. Thence $\delta_m\mu^{\ominus}(\mathrm{Cl}^-)$ values were obtained from known $\delta_m\mu^{\ominus}(\mathrm{HCl})$ values. We obtained $\delta_m\mu^{\ominus}(\mathrm{CN}^-) = \delta_m\mu^{\ominus}(\mathrm{Cl}^-)$ by interpolation of Wells' values and conversion from the solution standard state, the hypothetical solution wherein the mole fraction of solute is unity, to the standard state where the concentration of solute is 1 mol dm^{-3} [*i.e.* $\delta_m\mu_x^{\ominus}(\mathrm{Cl}^-)$ to $\delta_m\mu_c^{\ominus}(\mathrm{Cl}^-)$].

(*b*) *Acetone + water.* Values of $\delta_m\mu^{\ominus}$(ion) for chloride in acetone + water mixtures were taken from the table given by Bax *et al.*[27] and converted into the molarity scale.

(*c*) *t-Butyl alcohol + water.* The quantities $\delta_m\mu^{\ominus}$ for alkali-metal chlorides were taken from the compilation given by Pointud *et al.*[28] for this mixture when $0 < w_2\% \leqslant 40$. The values for $\delta_m\mu^{\ominus}(\mathrm{Cl}^-)$ were obtained by fitting, using a least-squares technique, the numbers for each solvent mixture to the expression:

$$\delta_m\mu^{\ominus}(\mathrm{MCl}) = (B/r^+) + \delta_m\mu^{\ominus}(\mathrm{Cl}^-)$$

where r^+ is the Pauling radius of the cation, and thus $\delta_m\mu^{\ominus}(\mathrm{Cl}^-)$ is the value of $\delta_m\mu^{\ominus}(\mathrm{MCl})$ in the limit that $r \rightarrow \infty$. This method was used by Feakins[29] to analyse data for methanol–water although he has recently offered criticism of the method when used for the dioxan–water system.[30] The calculated values were converted from the molality to the molarity scale.

(*d*) *Dioxan + water.* The present situation with respect to single-ion values for Gibbs free-energies of transfer from water to aqueous dioxan is unclear.[30] We have therefore not estimated $\delta_m\mu^{\ominus}(\mathrm{CN}^-)$ for our range of solvent mixtures.

The variation of rate constant with solvent composition will depend on solvent effects on the initial state, *i.e.* both on the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation and on the CN^- anion, and on the transition state. The $[\mathrm{Fe(bipy)_3}]^{2+}$ cation and the transition state are both much larger than the CN^- anion, so it may be assumed that the solvation effects at the CN^- anion will be dominant. In fact there is evidence to suggest much smaller solvation changes at the $[\mathrm{Fe(bipy)_3}]^{2+}$ cation; rates of aquation for this presumably dissociative process vary only slightly with solvent composition (Table 4). We have therefore calculated expected ratios of rate constants ($k_2 : k_0$) in mixed solvents to that in water on the assumption that the difference is controlled solely by $\delta_m\mu_c^{\ominus}(\mathrm{CN}^-)$. Such ratios are compared with our experimentally determined ratios in Table 5. For methanol and t-butyl alcohol mixtures, agreement is, considering the approximations involved both in deriving the $\delta_m\mu_c^{\ominus}(\mathrm{CN}^-)$ values and in ignoring the solvation changes for the $[\mathrm{Fe(bipy)_3}]^{2+}$ and the transition state, remarkably good. For aqueous acetone the agreement is not good. We feel that this

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[25] N. N. Greenwood, 'Ionic Crystals, Lattice Defects and Nonstoicheiometry,' Butterworths, London, 1968, pp. 27, 35, 41.

[26] C. F. Wells, *J.C.S. Faraday I*, 1973, 984.

[27] D. Bax, C. L. de Ligny, and A. J. Remijnse, *Rec. Trav. chim.*, 1972, **91**, 1225.

[28] Y. Pointud, J. Juillard, J. P. Morel, and L. Avedikian, *Electrochim. Acta*, 1974, **19**, 229.

[29] D. Feakins, in 'Physico-chemical Processes in Mixed Aqueous Solvents,' ed. F. Franks, Heineman, London, 1967, p. 71.

[30] D. Feakins, B. E. Hickey, J. P. Lorimer, and P. J. Voice, *J.C.S. Faraday I*, 1975, 780.

may be attributed to the basic assumption that solvation at cyanide and chloride are the same. It does not seem unreasonable that chloride and cyanide solvation could be similar in solvent mixtures containing hydroxylic co-solvents such as the alcohols, but significantly different when the co-solvent is non-hydroxylic acetone. Parker *et al.* point out that $\delta_m\mu^\ominus$ for anions on going from water to pure solvents show a complex pattern, in part accounted for by the differences in intensity of hydrogen-bonding interactions between ion and solvent.

TABLE 5

Ratios ($k_2 : k_0$) of rate constants for cyanide attack at $[Fe(bipy)_3]^{2+}$ in mixed solvents to that in water, as calculated from estimated values for $\delta_m\mu^\ominus(CN^-)$ and as determined experimentally. Solvent compositions stated are by volume before mixing, or mole fraction organic component (x_2)

	Composition		$\delta_m\mu^\ominus(CN^-)$/ J mol^{-1}	$k_2 : k_0$	
Co-solvent	v/v (%)	x_2		Calc.	Found
Methanol	10.0	0.048	850	1.4	1.6
	20.0	0.102	2 100	2.3	2.1
	30.0	0.163	3 550	4.0	3.2
t-Butyl alcohol	9.7	0.02	1 790	2.0	1.4
	18.0	0.04	3 310	3.8	3.6
	28.4	0.07	5 260	8.3	7.0
	36.9	0.10	6 710	15	9.5
	43.0	0.125	7 780	23	16
	48.2	0.15	9 020	38	16
Acetone	10.0	0.033	1 880	2.1	1.5
	20.0	0.072	4 390	5.6	2.1
	30.0	0.117	7 110	16	3.0

It is interesting to compare the foregoing results and analysis with the situation recently described for the reaction of iron(III) with thiocyanate in water and in dimethyl sulphoxide. In this case a large value of $\delta_m\mu^\ominus(NCS^-)$ is not matched by a large difference in rate constant. This can readily be explained by the operation of a dissociative mechanism for this reaction.[31] Unfortunately the situation here cannot be quite as simple as this, as under some conditions the formation rate constant is greater than the rate constant for solvent exchange. This observation requires that there is at least some associative character to transition-state formation,[32] but the degree of associative character here may be much less than in the $[Fe(bipy)_3]^{2+}$ plus cyanide reaction.

Salt effects. Added alkali-metal halides and added tetra-alkylammonium halides have markedly different effects on rates of aquation of the $[Fe(5\text{-}NO_2phen)_3]^{2+}$ cation.[20] Such a marked difference is not apparent in the reaction of the $[Fe(bipy)_3]^{2+}$ cation with cyanide (Table 3). This contrast in behaviour between the two systems may be attributed to small values for $\delta_m\mu^\ominus(CN^-)$ for transfer from water to solutions of these salts.

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