Kinetics of Aquation of Bis(2,2′;6′,2″-terpyridyl)iron(II) in Acidic Media and its Reaction with Cyanide Ion

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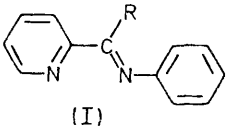
The kinetics of aquation of bis(2,2′;6′,2″-terpyridyl)iron(II), $[\mathrm{Fe(terpy)_2}]^{2+}$, have been examined in aqueous solution, and a mechanism consistent with the observed pH–rate profile proposed. Activation parameters for fission of the first iron–nitrogen bond have been determined and compared with those for related complexes. The rate law for reaction of $[\mathrm{Fe(terpy)_2}]^{2+}$ with cyanide ion is as in equation (*i*). Activation parameters for the

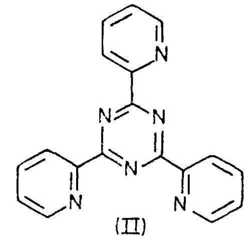
$$-\mathrm{d}[\mathrm{Fe(terpy)_2}^{2+}]/\mathrm{d}t = k_9 + k_{10}[\mathrm{CN}^-][\mathrm{Fe(terpy)_2}^{2+}] \qquad (i)$$

k_{10} path, which is the dominant reaction route, are compared with those for analogous second-order reactions of similar iron(II) complexes with cyanide ion. Solvatochromic behaviour is reported for the $[\mathrm{Fe(terpy)(CN)_3}]^-$ anion, the primary product of the reaction of $[\mathrm{Fe(terpy)_2}]^{2+}$ with cyanide.

The kinetics of a variety of reactions of low-spin iron(II) complexes of such bidentate ligands as 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), related Schiff bases (I), and their substituted derivatives, have been extensively studied.[1] Corresponding complexes of analogous terdentate ligands have been much less investigated. Limited kinetic information is available on ligand exchange,[2] aquation,[3,4] and base hydrolysis reactions of the $[\mathrm{Fe(terpy)_2}]^{2+}$ cation (terpy = 2,2′;6′,2″-terpyridyl). Unfortunately some of the results for aquation were obtained in acid–nitrate media, wherein there is likely to be oxidation as well as aquation of the complex.[5] The kinetics of aquation of the $[\mathrm{Fe(tptz)_2}]^{2+}$ cation [tptz = 2,4,6-tri(2-pyridyl)-1,3,5-triazine, (II)], in the presence of acid, hydroxide ion, or ethylenediaminetetra-acetate ion, have also been described.[6] However this system is complicated by the presence of unco-ordinated ligand nitrogen atoms which can be protonated.[7]



(I)



(II)

In this paper we present an account of an extensive study of the kinetics of aquation of $[\mathrm{Fe(terpy)_2}]^{2+}$, to produce $\mathrm{Fe^{2+}(aq)} + \mathrm{Hterpy^+}$, over a range of acid concentrations and temperatures. From these kinetic results we propose an aquation mechanism, and establish differences in behaviour between this terdentate ligand complex and its bidentate ligand analogue $[\mathrm{Fe(bipy)_3}]^{2+}$. We also report the rate law, rate constants, and activation parameters for the reaction of $[\mathrm{Fe(terpy)_2}]^{2+}$ with cyanide ion in aqueous solution. The product of this latter reaction is the $[\mathrm{Fe(terpy)(CN)_3}]^-$ anion, which reacts further only very slowly to give $[\mathrm{Fe(CN)_6}]^{4-}$. This mixed-ligand anion, like similar complexes of the type $[\mathrm{Fe(bipy)_2(CN)_2}]$, has an intense charge-transfer (c.t.) spectrum which exhibits marked solvatochromism.

EXPERIMENTAL

2,2′;6′,2″-Terpyridyl was obtained from Koch–Light Laboratories Ltd. or from J. T. Baker Chemical Co. Solutions of bis(2,2′;6′,2″-terpyridyl)iron(II) were prepared from AnalaR diammonium iron(II) bis(sulphate) solution and a slight excess of ligand. Solutions of other reagents were prepared from AnalaR grade materials. Kinetics of reactions were followed either by repetitive scanning over an extended wavelength range or at 552 nm, the wavelength of maximum absorption of the lowest-energy c.t. band of the $[\mathrm{Fe(terpy)_2}]^{2+}$ cation. Reactions were carried out in 1 cm silica cells in the thermostatted cell compartment of Perkin-Elmer 402, Unicam SP 800A, Beckmann DB, or Beckmann DB-G spectrophotometers.

RESULTS AND DISCUSSION

Aquation.—Rates of acid aquation of complexes containing bidentate nitrogen-donor ligands generally vary with acid concentration when the leaving group is flexible, for example bipy or ethylenediamine (en), as a result of reaction paths involving species containing unidentate protonated ligands. But when the bidentate leaving group is rigid, for instance, phen, acid-aquation rates are independent of acid concentration since it is not possible to protonate the ligand while it is bonded to a metal atom.

The rate of aquation of the ion $[\mathrm{Fe(terpy)_2}]^{2+}$ in sulphuric acid depended, as expected, on the acid concentration. Excellent first-order rate plots were obtained at any given, excess, acid concentration up to 95% of complete reaction. Clean isosbestic points were observed at 237, 278, 299, 330, and 346 nm. Observed first-order rate constants increased almost linearly with acid concentration in the region $[\mathrm{H_2SO_4}]$ = 0·3—2·0 mol $\mathrm{l^{-1}}$, but thereafter increased less rapidly with in-

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[1] See, for example, ' Inorganic Reaction Mechanisms,' ed. J. Burgess, Chem. Soc. Specialist Periodical Report, London, 1971, vol. 1, p. 177; 1972, vol. 2, pp. 168—169, 182; C. H. Langford and V. S. Sastri, ' Reaction Mechanisms in Inorganic Chemistry,' ed. M. L. Tobe, M. T. P. Internat. Rev. Sci., vol. 9, Butterworths, London, 1971, series 1, p. 252 and refs. therein.

[2] R. Hogg and R. G. Wilkins, *J. Chem. Soc.*, 1962, 341.

[3] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1965, 6061.

[4] R. Farina, R. Hogg, and R. G. Wilkins, *Inorg. Chem.*, 1968, **7**, 170.

[5] J. Burgess, *J. Chem. Soc.* (*A*), 1968, 1085.

[6] G. K. Pagenkopf and D. W. Margerum, *Inorg. Chem.*, 1968, **7**, 2514.

[7] F. H. Fraser, P. Epstein, and D. J. Macero, *Inorg. Chem.*, 1972, **11**, 2031.

creasing acid concentration until a limiting rate was reached (Figure 1). [^{3}H]terpy Exchange experiments showed that the rate of ligand exchange with the ion $[Fe(terpy)_2]^{2+}$ in neutral solution is considerably slower than that of $[Fe(bipy)_3]^{2+}$; presumably because in the former case three iron–nitrogen bonds have to be broken consecutively to remove a terpy molecule while only two have to be broken to remove a ligand from $[Fe(bipy)_3]^{2+}$. As a result of the slow rate of ligand exchange of $[Fe(terpy)_2]^{2+}$, the intercept of a plot of k_{obs} against [H$^+$] for acid aquation should be close to the origin, in contrast to that obtained for the ion $[Fe(bipy)_3]^{2+}$. However, extrapolated plots of k_{obs} against [H$^+$] ([H_2SO_4] = 0·3—1·5 mol l^{-1}) for the acid aquation of $[Fe(terpy)_2]^{2+}$ at three temperatures (Figure 2) did not pass through the origin but had negative intercepts on the rate axis suggesting that they are portions of sigmoid curves. A series of experiments at constant ionic strength (1M-Na_2SO_4) * (Table 1) demonstrated that ionic-strength effects are not very important in this reaction, and that they are not the cause of the negative intercepts.

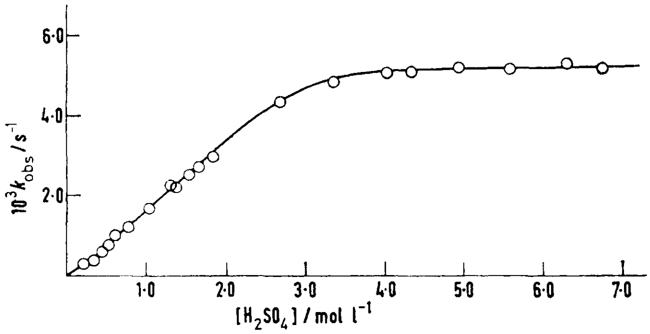


FIGURE 1 Dependence of k_{obs} on [H_2SO_4] at 25 °C for aquation of the ion $[Fe(terpy)_2]^{2+}$

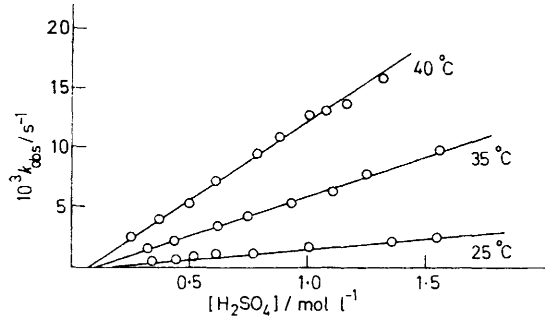
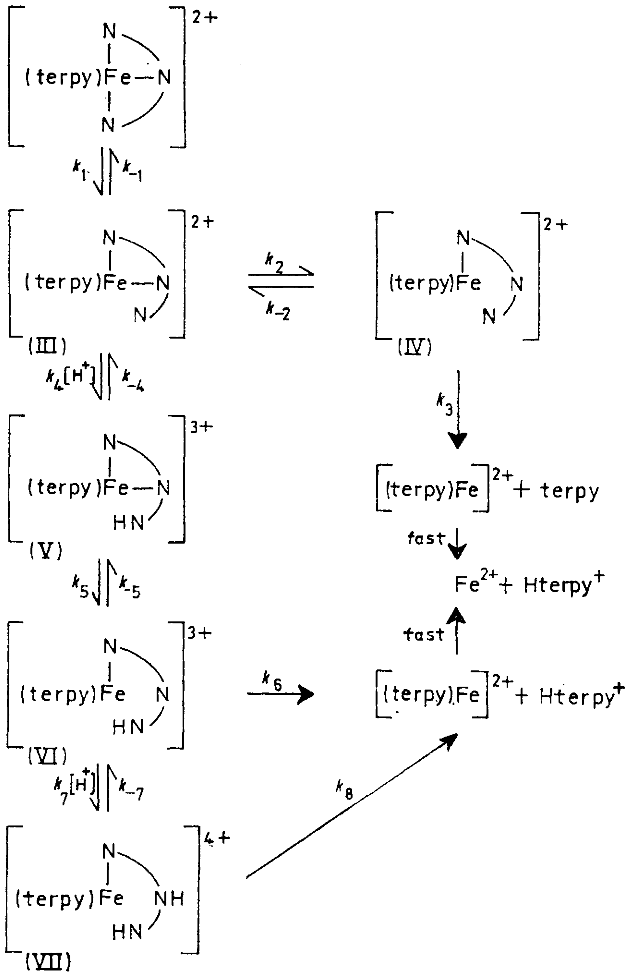


FIGURE 2 Variation of k_{obs} with temperature for aquation of the ion $[Fe(terpy)_2]^{2+}$ in H_2SO_4 (0·3—1·5 mol l^{-1})

The general reaction scheme we consider is shown in the Scheme and involves doubly protonated iron-containing species. It is likely that several of these rate constants are composite first-order ones involving terminal or middle iron–nitrogen bonds. Assuming that stationary-state kinetic conditions apply to species

$$k_{\text{obs}} = k_1 \left\{ \frac{\dfrac{k_2k_3}{k_{-2}+k_3} + \dfrac{k_4k_5k_6[\text{H}^+] + k_4k_5k_7k_8[\text{H}^+]^2/(k_{-7}+k_8)}{k_5k_6 + k_{-4}(k_{-5}+k_6) + k_7k_8(k_{-4}+k_5)[\text{H}^+]/(k_{-7}+k_8)}}{k_{-1} + \dfrac{k_2k_3}{k_{-2}+k_3} + \dfrac{k_4k_5k_6[\text{H}^+] + k_4k_5k_7k_8[\text{H}^+]^2/(k_{-7}+k_8)}{k_5k_6 + k_{-4}(k_{-5}+k_6) + k_7k_8(k_{-4}+k_5)[\text{H}^+]/(k_{-7}+k_8)}} \right\} \qquad (1)$$

(III)—(VII), the general expression (1) can be obtained for the observed pseudo-first-order rate constant. Although expression (1) is formidable, under certain



SCHEME

TABLE 1

Mean observed first-order rate constants (25 °C) for aquation of the $[Fe(terpy)_2]^{2+}$ cation in acid media at constant ionic strength, I = 1·00 mol l^{-1} (Na_2SO_4)

	$10^4k/s^{-1}$	
[H_2SO_4]/M	Obs.	Calc.*
0·57	3·6	3·4
0·72	5·0	4·8
0·86	6·5	6·2
1·00	7·7	7·6

* Interpolated from data obtained at variable ionic strength (Figure 1).

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* 1M = 1 mol dm^{-3}.

experimental conditions simplifying approximations can be made. (*a*) Putting $[H^+] \approx 0$ gives the rate of exchange in neutral solution [equation (2)]. (*b*) Expression (3) is obtained at low $[H^+]$ since terms in $[H^+]^2$ are small compared with $[H^+]$ terms, and $k_7k_8(k_{-4} + k_5)[H^+]/(k_{-7} + k_8) < [k_5k_6 + k_{-4}(k_{-5} + k_6)]$. The reaction path $[Fe(terpy)_2]^{2+} \longrightarrow$ (III) $\longrightarrow$ (V) $\longrightarrow$ (VI) $\longrightarrow$ products is now important. Expression (3)

$$k_{obs} = \frac{k_1k_2k_3}{k_{-1}(k_{-2} + k_3) + k_2k_3} \qquad (2)$$

$$k_{obs} = k_1\left\{\frac{\dfrac{k_2k_3}{k_{-2} + k_3} + \dfrac{k_4k_5k_6[H^+]}{(k_{-5} + k_6)k_{-4} + k_5k_6}}{k_{-1} + \dfrac{k_2k_3}{k_{-2} + k_3} + \dfrac{k_4k_5k_6[H^+]}{(k_{-4} + k_6)k_{-4} + k_5k_6}}\right\} \qquad (3)$$

predicts an increase of k_{obs} with increasing $[H^+]$, but as $[H^+]$ increases a point is reached where $[H^+]^2$ terms cannot be neglected. Then (3) is no longer valid. (*c*) At large $[H^+]$ terms in $[H^+]^2$ are larger than those in $[H^+]$, and $k_7k_8(k_{-4} + k_5)[H^+]/(k_{-7} + k_8) > [k_5k_6 + k_{-4}(k_{-5} + k_6)]$ giving (4). The rate constant k_{obs} continues to increase with $[H^+]$ until at very large $[H^+]$ a rate limit is approached with $k_{obs} = k_1$. As (III) is produced, rather than reforming any $[Fe(terpy)_2]^{2+}$, it undergoes reaction to form products *via* (IV) and (predominantly) the protonated species (V).

$$k_{obs} = k_1\left\{\frac{\dfrac{k_2 + k_3}{k_{-2} + k_3} + \dfrac{k_4k_5[H^+]}{k_{-4} + k_5}}{k_{-1} + \dfrac{k_2 + k_3}{k_{-2} + k_3} + \dfrac{k_4k_5[H^+]}{k_{-4} + k_5}}\right\} \qquad (4)$$

At 25 °C observed first-order rate constants increased as the concentration of sulphuric acid increased until a limiting rate was attained at *ca.* 4M-acid. In order to estimate activation parameters for fission of the first iron–nitrogen bond, rate constants (k_1) for aquation in 4·9M-H_2SO_4 were obtained at several temperatures in the range 19—35 °C (Table 2). Derived activation parameters are compared in Table 3 with those for fission of the first iron–nitrogen bond of some related low-spin iron(II) complexes. The order of reactivity, *i.e.* rate constants, is determined by the activation enthalpies; a plot of activation enthalpy against activation entropy was, within the limits of experimental uncertainty of the constituent points, linear. It is interesting that reactivities correlate with energies of the c.t. bands of the respective complexes, though this may be coincidental as such a correlation is not obtained [8] for aquation of a series of complexes $[Fe(substituted\ phen)_3]^{2+}$ for which kinetic data are available.[9]

Reaction with Cyanide Ion.—The $[Fe(terpy)_2]^{2+}$ cation, like other similar iron(II) complexes, reacted with cyanide ion. The product, isolated as the diamagnetic potassium salt, was $[Fe(terpy)CN)_3]^-$; subsequent reaction to give $[Fe(CN)_6]^{4-}$ was extremely slow. Repeated wavelength scans of kinetic runs of this reaction gave one clean isosbestic point in the region 360—700 nm at 404 nm.

The kinetics of this reaction were studied under a variety of conditions. In all cases cyanide ion was present in large excess and first-order kinetics were obeyed over at least three half-lives. Observed first-order rate constants (k_{obs}) are reported in Table 4. Plots of k_{obs} against cyanide-ion concentration * in water (against potassium cyanide concentration in aqueous ethanol) were linear with small or negligible intercepts on the rate-constant axis. The rate law for the reaction of $[Fe(terpy)_2]^{2+}$ with cyanide ion [equation (5)] is thus similar to those reported for other low-spin iron(II) complexes over the concentration range normally covered.[10-14] There is evidence for an additional term in $[CN^-]^2$ at cyanide concentrations approaching 1M.[15] In the $[Fe(terpy)_2]^{2+}$ case, $k_9 < k_{10}[CN^-]$, and indeed the sizes of many of the standard deviations of k_9 values given in Table 4 are such as to preclude any discussion of these k_9 values.

TABLE 2

Observed first-order rate constants for aquation of the ion $[Fe(terpy)_2]^{2+}$ in 4·9M-H_2SO_4

θ_c/°C	$10^3k_{obs}/s^{-1}$	θ_c/°C	$10^3k_{obs}/s^{-1}$
19·4	2·29	30·4	11·1
19·4	2·26	30·4	11·2
19·4	2·25	32·6	14·9
19·4	2·30	32·6	14·9
23·4	4·17	35·2	19·7
23·4	4·10	35·2	20·0
25·0	5·23	35·2	20·1
27·5	7·47		
27·5	7·48		

$$-d[Fe(terpy)_2{}^{2+}]/dt = (k_9 + k_{10}[CN^-])[Fe(terpy)_2{}^{2+}] \qquad (5)$$

The $k_{10}[CN^-]$ path of equation (5) is, from its cyanide-concentration dependence and by analogy with other reactions of low-spin iron(II) complexes with cyanide,

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* Cyanide-ion concentrations in aqueous solutions were calculated from known concentrations of potassium cyanide used and published pK_a values (R. M. Izatt, J. J. Christensen, R. T. Pack, and R. Bench, *Inorg. Chem.*, 1962, **1**, 828) for hydrogen cyanide over the temperature range of our kinetic study.

[8] J. Burgess, Ph.D. Thesis, Cambridge, 1963, p. 127.

[9] J. Burgess and R. H. Prince, *J. Chem. Soc.*, 1963, 5752.

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

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

[12] E. R. Gardner, F. M. Mekhail, J. Burgess, and J. M. Rankin, *J.C.S. Dalton*, 1973, 1340.

[13] J. Burgess, G. E. Ellis, D. J. Evans, A. Porter, R. Wane, and R. D. Wyvill, *J. Chem. Soc.* (*A*), 1971, 44.

[14] J. Burgess, *Inorg. Chim. Acta*, 1971, **5**, 133.

[15] R. D. Archer, L. J. Suydam, and D. D. Dollberg, *J. Amer. Chem. Soc.*, 1971, **93**, 6837.

ascribed to an associative process with incoming cyanide bonded to the iron atom in the transition state. A least-mean-squares procedure, in which each rate constant was assumed to have a constant percentage uncertainty, was used to calculate values of k_9 and k_{10}. The variation of k_{10} with ionic strength is consistent with such a bimolecular process.[16] Thus at 35·0 °C, $k_{10} = 0·019$ l mol^{-1} s^{-1} at $I = 0·1$ mol l^{-1}, while at $I = 0·5$ mol l^{-1}, $k_{10} = 0·13$ l mol^{-1} s^{-1}. As for the reactions of other iron(II) complexes with cyanide, k_{10} increases markedly in aqueous-ethanol mixed solvents (Table 4). This observation is consistent with a rate-determining step involving the approach of oppositely charged ions,[17] *i.e.* with the above bimolecular mechanism.

TABLE 3

Kinetic parameters (25 °C) for fission of the first iron–nitrogen bond in aquation of low-spin iron(II) complexes, and values of $\lambda_{max.}$, the wavelength of maximum absorption of the lowest-energy c.t. band for each complex

Complex	$\lambda_{max.}$/nm	k/s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}	Ref.
$[Fe(phen)_3]^{2+}$ [a]	510	$7·3 \times 10^{-5}$	29·4 ± 0·2	+21·1 ± 0·6	9
$[Fe(bipy)_3]^{2+}$	525	$7·8 \times 10^{-4}$	26·1 ± 0·1	+14·8 ± 0·3	*b*
$[Fe(terpy)_2]^{2+}$	552	$5·2 \times 10^{-3}$	24·2 ± 0·2	+12·3 ± 0·6	*c*
$[Fe(pma)_3]^{2+}$ [d]	574	$9·3 \times 10^{-2}$	22·1 ± 0·6	+10·7 ± 2·0	*e*

[a] Kinetic parameters are composite [$k_{obs} = k_1k_2/(k_{-1} + k_2)$] for this complex. [b] M. V. Twigg, unpublished work. [c] This work. [d] pma = *N*-(2-pyridylmethylene)aniline. [e] J. Burgess and R. H. Prince, *J. Chem. Soc.* (*A*), 1967, 434.

TABLE 4

Observed first-order (k_{obs}) and derived rate constants k_9 and k_{10} (*cf.* text) for reactions of the ion $[Fe(terpy)_2]^{2+}$ with cyanide; $I = 0·1$M (KCl)

(*a*) In water

θ_c/°C	10^4k_{obs}/s^{-1}				10^4k_9/s^{-1}	10^4k_{10}/l mol^{-1} s^{-1}
	[CN$^-$]/M					
	0·033	0·067	0·083	0·100		
27·6	2·7	5·1	6·7	8·1	0·1 ± 0·4	78 ± 8
30·0	3·6	6·9	8·1	10·4	0·4 ± 0·5	97 ± 10
35·0	7·0	13·1	16·6	19·5	0·8 ± 0·1	187 ± 9
40·0	12·4	23·6	28·4	34·5	1·6 ± 0·5	326 ± 9
43·0	18	35	41	48	3 ± 2	460 ± 37
45·8	25	47	57	67	4 ± 1	635 ± 15

(*b*) In 50% (v/v) EtOH

	[KCN]/M						
	0·033	0·050	0·067	0·083	0·100		
35·0	24	37	46	58	70	2 ± 2	677 ± 34

Quoted error limits are standard deviations corrected for the appropriate number of degrees of freedom such that doubling them produces 95% confidence limits.

TABLE 5

Kinetic parameters for second-order reactions of low-spin iron(II) complexes with cyanide ion

Ligand [a]	Solvent	k [b]/ l mol^{-1} s^{-1}	$\Delta H^‡$/kcal mol^{-1}	$\Delta S^‡$/cal K^{-1} mol^{-1}	Conditions	Ref.
$(terpy)_2$	H_2O	0·019	21·7 ± 0·6	+4 ± 2	$I = 0·1$M (KCl)	This work
$(phen)_3$ [c]	H_2O	0·025	20·6 ± 1·8 [d]	+1 ± 5 [d]	$I = 2·0$M (KCl)	10
$(5\text{-Mephen})_3$	H_2O	0·016	19·9 ± 1·8	0 ± 5	$I = 0·33$M (KCl)	*e*
$(bipy)_3$	H_2O	0·028	23·0 ± 0·8	+9 ± 2	$I = 0·1$M (KCl)	11
$(ppsa)_3$	H_2O	0·0034	25·2 ± 1·2	+12 ± 4	$I = 0·33$M (KCl)	12
(ppadd)	H_2O	0·000039	24·3 ± 1·1	0 ± 3	$I = 0·33$M (KCl)	*f*
(padd)	H_2O	0·0072	19·5 ± 1·0	0 ± 3	$I = 0·33$M (KCl)	*g*
$(pma)_3$	95% MeOH	5·6	17·5 ± 0·9	+2 ± 3	$I = 0·004$M (KNO_3)	13

[a] ppsa = 3-(2-Pyridyl)-5,6-bis(4-phenylsulphonato)-1,2,4-triazine, padd and ppadd = 1,12-di(2-pyridyl)- and 1,12-diphenyl-1,12-di(2-pyridyl)-2,5,8,11-tetra-azadodeca-1,11-diene, and pma = *N*-(2-pyridylmethylene)aniline. [b] Second-order rate constants at 35·0 °C. [c] Second-order rate constants for reactions of a range of substituted phen derivatives are given in ref. 14. [d] Recomputed from the experimental data of ref. 10. [e] J. Burgess and J. Chambers, preliminary observations. [f] E. R. Gardner, F. M. Mekhail, and J. Burgess, *Internat. J. Chem. Kinetics*, 1974, **6**, 133; [g] J.Burgess and G. M. Burton, unpublished work.

Activation parameters with their standard deviations were calculated using a weighted least-squares analysis. The results are reported in Table 5, which also includes activation parameters for cyanide attack at related iron(II) complexes for the purpose of comparison. We had hoped either to demonstrate a linear $\Delta H^‡$–$\Delta S^‡$ correlation for these reactions, or to be able to rationalise deviations from such a correlation in terms of ligand and solvent variations. Sadly, the total range of $\Delta H^‡$ and

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[16] See, for example, K. J. Laidler, ' Reaction Kinetics,' Pergamon Press, Oxford, 1963, vol. 2, pp. 18—22.

[17] See, for example, C. K. Ingold, ' Structure and Mechanism in Organic Chemistry,' Cornell University Press, Ithaca, New York, 1953, pp. 345—350.

of $\Delta S^\ddagger$ values is small, so that the confidence limits for individual values are an uncomfortably large percentage of the total range. We are thus only able to report that activation parameters for cyanide attack at $[Fe(terpy)_2]^{2+}$ are similar to those for other iron(II) complexes. Activation enthalpies are relatively high, as expected for low-spin d^6 complexes, but not as high as those for dissociative aquation, again as would be expected for associative nucleophilic attack. Activation entropies are of the magnitude expected [18] from simple electrostatic considerations for reactions between dipositive cationic complexes of this size and mononegative cyanide ion.

Solvatochromism of the $[Fe(terpy)(CN)_3]^-$ *Anion.*—Transition-metal complexes of bipy, phen, and related ligands generally exhibit strong metal–ligand c.t. bands. In mixed complexes containing one of this group of ligands and cyanide or carbonyl ligands it is found that the frequencies of the c.t. bands vary markedly with the nature of the solvent. Such behaviour has been reported, for example, for many complexes of the type $[FeL_2(CN)_2]$ (L = bipy or phen or one of their substituted derivatives),[19,20] for similar complexes $[M(CO)_4L]$ (M = Mo or W),[21] for $[Pt(bipy)X_2]$ (X = Cl, Br, or I),[22] and for $[Ni(mnt)(phen)]^{n+}$ [mnt = $^{-}S\cdot C(CN)\!:\!C(CN)\cdot S^{-}$] cations.[23] The positions of the c.t. absorption maxima can be fairly successfully correlated with empirical solvent parameters,[24] particularly Reichardt's E_T values. Some theoretical rationalisation of this solvatochromic behaviour has been offered.[25]

The $[Fe(terpy)(CN)_3]^-$ anion, which is the primary product of reaction between $[Fe(terpy)_2]^{2+}$ and cyanide, has a structure similar to the complexes mentioned in the previous paragraph. We therefore examined its c.t. spectrum in various solvents in order to define its solvatochromic behaviour. Unfortunately the salt $K[Fe(terpy)(CN)_3]$ proved, like the previously examined $K_2[Fe(CN)_4(bipy)]$, to be soluble in only a very few polar solvents. Wavenumbers of maximum absorption ($\bar{\nu}_{max.}$) for the lowest-energy c.t. band of the $[Fe(terpy)(CN)_3]^-$ anion in these solvents are reported in Table 6.

TABLE 6

Wavenumbers of maximum absorption ($\bar{\nu}_{max.}$) for the lowest-energy c.t. band of the ion $[Fe(CN)_3(terpy)]^-$ with respective solvent E_T values (from refs. 24 and 26)

Solvent [a]	E_T/kcal mol^{-1}	$\bar{\nu}_{max.}$/cm^{-1}
H_2O	63·1	20 240
MeOH	55·5	18 940
EtOH	51·6	18 690
Me_2SO	45·0	17 120
20% MeOH	61·0	20 000
40% MeOH	59·2	19 690
60% MeOH	57·8	19 190
80% MeOH	56·6	18 940

[a] Mixed solvents have the indicated composition by volume.

A plot of solvent E_T values [24,26] against the respective observed $\bar{\nu}_{max.}$ values for the polar protic solvents water, methanol, and ethanol had a gradient of 7·3 kcal mol^{-1}.* This slope lies, as expected, between the gradients of 8·6 and 3·8 kcal mol^{-1} for the complexes $[Fe(bipy)_2(CN)_2]$ and $[Fe(bipy)(CN)_4]^{2-}$ respectively.[20] It is unwise to include the dimethyl sulphoxide point on this E_T against $\bar{\nu}_{max.}$ plot in view of established differences of behaviour between protic and aprotic solvents.[20] The curved dependence of $\bar{\nu}_{max.}$ on E_T values in methanol–water was similar to that reported [27] for the complex $[Fe(phen)_2(CN)_2]$ in mixed aqueous solvents.

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* 1 cal = 4·184 J.

[18] See, for example, p. 13 of ref. 16.

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