Kinetic and Equilibrium Properties of Pentacyano(3,5-dimethylpyridine)-iron(II) and Related Anions in Mixed Aqueous Solvents †

By **Michael J. Blandamer, John Burgess,*** and **Robert I. Haines,** Chemistry Department, University of Leicester, Leicester LE1 7RH

The kinetic pattern for reaction of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ and $[Fe(CN)_5(3\text{-}CNpy)]^{3-}$ with a range of incoming groups, in water and in 40% glycol and 40% t-butyl alcohol, is consistent with the operation of a *D* mechanism under all the conditions studied. Rate constants for the reaction of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with cyanide ion have been determined in binary aqueous mixtures containing up to 40% by volume of methanol, ethanol, t-butyl alcohol, glycerol, or tetrahydrofuran. Correlation of these rate constants with Grunwald–Winstein *Y* values gives a value of *m* of −0.1; this small value reflects the low sensitivity of the rate to solvent composition. Free energies of activation determined from the observed rate constants have been plotted against excess Gibbs free energies of mixing (G^E) for the respective solvent mixtures. The resulting pattern indicates how far the thermodynamic characteristics of mixing of the solvent are reflected in the kinetics of this substitution reaction. The relation between the relative stabilities of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ and its pyridine analogue, and solvent mixture G^E values, has also been examined. The solvatochromic behaviour of the charge-transfer band of $[Fe(CN)_5(N\text{-methylpyrazinium})]^{2-}$ has been investigated, and contrasted with that of organic analogues.

THE majority of the numerous investigations of kinetics of substitution at inorganic complexes in mixed aqueous solvents have been of reactions with a dissociative interchange (I_d) mechanism. In the present paper we report the results of a study of the kinetics of substitution at complexes of the type $[Fe(CN)_5L]^{3-}$, which proceeds by a limiting $S_N1(D)$ mechanism, in some mixed aqueous solvents. We compare the reactivity trends for these reactions with those for I_d aquation of typical cobalt(III) amine halide complexes, and investigate whether there is any connection between the variation of kinetic parameters with solvent composition and the excess molar Gibbs free energies of mixing of the respective solvent mixtures.

The relative stabilities of pairs of complexes $[Fe(CN)_5L]^{3-}$ (L = an alkylpyridine and pyridine itself) are known to depend on solvent composition. We report how these relative stabilities depend on solvent composition for several series of binary aqueous mixtures, and compare these trends with reactivity trends for these complexes. These studies indicate how a comparison of both kinetic and equilibrium quantities describing the behaviour of solvents in solution on the one hand, and thermodynamic parameters characterising the respective binary aqueous mixtures on the other, can prove fruitful and informative.

EXPERIMENTAL

Reagents.—The salts $Na_3[Fe(CN)_5(3,5\text{-}Me_2py)]$,‡ $Na_3[Fe(CN)_5(3\text{-}Clpy)]$,‡ and $Na_3[Fe(CN)_5(3\text{-}CNpy)]$ ‡ were prepared by published methods; [1] they analysed satisfactorily. Potassium cyanide, potassium thiocyanate, potassium nitrate, pyrazine, and thiourea were AnalaR grade materials. The salt $Na_3[Fe(CN)_5(NH_3)]$ (Hopkin and Williams) and *NN*-dimethyl-*p*-nitrosoaniline (Ralph N. Emanuel) were used as supplied. *N*-Methylpyrazinium iodide was prepared from pyrazine and methyl iodide.[2] Methanol was dried over magnesium and iodine and then distilled; tetrahydrofuran and dioxan were freed from peroxides by passing down a column of activated alumina; other organic solvents were of the best commercially available grade and were used as received.

Kinetics.—Kinetic runs were conducted in 1 cm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Rate constants were computed (PDP 11) from the observed variation of optical density using a standard least-mean-squares program.

Equilibrium Studies.—Values for the equilibrium constant *K* § for reaction (1) were obtained by a method fully described elsewhere.[3] We allowed a period of 3 h for equilibration; results were calculated from optical densities

$$[Fe(CN)_5(py)]^{3-} + 3,5\text{-}Me_2py \rightleftharpoons [Fe(CN)_5(3,5\text{-}Me_2py)]^{3-} + py \quad (1)$$

measured at 650 nm. For a selection of reaction mixtures, optical densities were monitored at intervals to check that the 3-h period was long enough for attainment of equilibrium, but not so long that significant decomposition was detectable.

RESULTS

All the kinetic runs were in the presence of an excess of the incoming ligand. Under these conditions all the runs were first order in iron(II) complex concentration up to at least three half-lives. For the reactions of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with thiocyanate, thiourea, pyrazine, and *N*-methylpyrazinium, isosbestic points were observed at 431, 515, 393, and 456 nm respectively. In these cases the rate of formation of the product was confirmed to be the same as the rate of disappearance of the starting complex (*cf.* Table 2).

First-order rate constants for reactions of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$, $[Fe(CN)_5(3\text{-}CNpy)]^{3-}$, and $[Fe(CN)_5(3\text{-}Clpy)]^{3-}$ with cyanide ion, in water and in 40% ethylene glycol or 40% t-butyl alcohol, are reported in Table 1. First-order rate constants for reactions of the 3,5-Me_2py and 3-CNpy complexes with a range of incoming ligands are in Table 2. These rate constants were, except where stated otherwise, determined by monitoring the disappearance of the starting complex.

---

† No reprints available.

‡ py = Pyridine, 3,5-Me_2py = 3,5-dimethylpyridine, *etc.*

§ $K = K_{2B}/K_{2P}$ from ref. 3.

[1] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.

[2] C. T. Bahner and L. L. Norton, *J. Amer. Chem. Soc.*, 1950, **72**, 2881.

[3] D. P. Biddiscombe and E. F. G. Herington, *Analyst*, 1956, **81**, 711.

TABLE 1

First-order rate constants, $k_{obs.}$, for reaction of $[Fe(CN)_5(X\text{-}py)]^{3-}$ anions with cyanide ion, at 298.6 K and an ionic strength of 0.024 mol dm^{-3} (maintained with potassium nitrate) [a]

X	Solvent	10^3[KCN]/mol dm^{-3} → 0.6	1.2	1.8	2.4	3.0	3.6	4.2	4.8	6.0	7.2	8.4	9.0	9.6	12.0	15.0	18.0	21.0	24.0
		10^3k/s^{-1}																	
3,5-Me$_2$	Water	0.97	1.15	1.23	1.26	1.29	1.24	1.35	1.33	1.30			1.33		1.24		1.35		1.32
	40% Bu^{t}OH [b]		1.55		1.71		1.76		1.83	1.58					1.67		1.63		1.94
3-CN	Water	1.74	1.94	1.93	2.12	2.09	2.00	2.15	2.20						2.25		2.24		2.54
	40% Bu^{t}OH [b]	2.40	2.44	2.47	2.41	2.44	2.42		2.49	2.46			2.58		2.61		2.60		2.76
	40% glycol [b]	0.22	0.80		1.11		1.32		1.40	1.23		1.35			1.43	1.35	1.38	1.42	1.39
3-Cl	Water	1.64	1.64	1.75	1.76		1.93		1.88	2.05	2.00			2.15			2.28	2.43	
	40% Bu^{t}OH [b]	2.31	2.38		2.40		2.55		2.61	2.45	2.46	2.57		2.56	2.49		2.73		2.75

[a] Runs were monitored at 369 nm for the 3,5-Me$_2$py complex, at 403 nm for the 3-CNpy complex, and at 382 nm for the 3-Clpy complex. [b] Solvent compositions are expressed in volume percentages.

TABLE 2

First-order rate constants, $10^3k_{obs.}$/s^{-1}, for reactions of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ and $[Fe(CN)_5(3\text{-}CNpy)]^{3-}$ anions with a range of incoming ligands (L) in aqueous solution at 298.6 K; initial [complex] $\leqslant 10^{-3}$ mol dm^{-1} and $I = 0.20$ mol dm^{-3} (KNO_3) except where otherwise indicated

	[L]/mol dm^{-3}	CN$^-$ [a]	SCN$^-$	tu	4,4′-bipy	im	pz	mpz$^+$
$[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$	0.024 [b]	1.3_2	0.30	1.2_2 (1.3_0) [c]			1.3_9 (1.4_2) [c]	1.8_2 (1.7_2) [c]
$[Fe(CN)_5(3\text{-}CNpy)]^{3-}$	0.024	2.5 [b]			2.5 [d]			
	0.04					2.1		
	0.05						2.4	
	0.06						2.0	
	0.10			2.4_1				
	0.14			2.3_8		2.1	2.6	
	0.15						2.4	
	0.16			2.4_2				
	0.20			2.3_9		2.0	2.5	

[a] tu = Thiourea, im = imidazole, pz = pyrazine, and mpz$^+$ = *N*-methylpyrazinium. [b] $I = 0.024$ mol dm^{-3} (K[NO$_3$]). [c] From +d[product]/d*t*. [d] $I = 10^{-3}$ mol dm^{-3}.

TABLE 3

First-order rate constants, $k_{lim.}$, for the reaction of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with cyanide ion ([KCN] = 0.024 mol dm^{-3}) at 298.6 K in ranges of binary aqueous mixtures (mole fraction x_2 of organic component), and respective excess molar Gibbs free energies of mixing, G^E

	Volume per cent of organic co-solvent: 10			20			30			40		
Co-solvent	x_2	$10^3k_{lim.}$/s^{-1}	G^E/J mol^{-1}	x_2	$10^3k_{lim.}$/s^{-1}	G^E/J mol^{-1}	x_2	$10^3k_{lim.}$/s^{-1}	G^E/J mol^{-1}	x_2	$10^3k_{lim.}$/s^{-1}	G^E/J mol^{-1}
Methanol	0.047	1.36	116	0.100	1.45	211	0.160	1.49	284	0.229	1.61	335
Ethanol	0.033	1.45	107	0.072	1.65	224	0.117	1.84	349	0.171	2.10	479
t-Butyl alcohol	0.021	1.41	129	0.046	1.60	269	0.076	1.85	419	0.113	2.21	576
Glycol	0.044	1.28	−101	0.094	1.28	−197	0.151	1.19	−288	0.217	1.10	−371
Glycerol	0.031	1.19	−84	0.067	1.11	−123	0.110	1.14	−274	0.161	1.05	−367
Tetrahydrofuran				0.053	1.85	343	0.087	2.28	532	0.129	2.55	728

The dependence of the limiting rates for cyanide substitution, at relatively high cyanide concentrations, on the nature of the mixed solvent is shown in Table 3. For solvent mixtures for which the dependence of the observed first-order rate constants, $k_{obs.}$, on cyanide concentration was established over a range of cyanide concentrations (*i.e.* values in Tables 1 and 2), $k_{lim.}$ values were estimated from plots of $1/k_{obs.}$ against $1/[CN^-]$ (see below). For other solvent mixtures, $k_{lim.}$ values in Table 3 are mean rate constants determined at the maximum cyanide concentration, 0.024 mol dm^{-3}. Values for the equilibrium constant for reaction (1) above in series of binary aqueous mixtures are reported in Table 4.

DISCUSSION

Kinetics of Substitution at $[Fe(CN)_5L]^{3-}$ *Anions.*—There have been many kinetic studies of substitution at complexes of the pentacyanoferrate(II) type, $[Fe(CN)_5L]^{n-}$, in aqueous solution. These include: aquation of $[Fe(CN)_5(NO)]^{2-}$ (ref. 4) and reactions of this anion with ammonia, hydroxylamine, and hydrazine;[5] reaction of $[Fe(CN)_5(ONPh)]^{3-}$,[6] of $[Fe(CN)_5$-

---

[4] R. P. Mitra, B. K. Sharma, and S. P. Mittal, *J. Inorg. Nuclear Chem.*, 1972, **34**, 3919.

[5] L. Dozsa, I. Szilassy, and M. T. Beck, *Magyar Kém. Folyóirat*, 1973, **79**, 45.

[6] D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1973, 602.

$(SO_3)]^{5-}$,[7] of $[Fe(CN)_5(py)]^{3-}$,[8] and of $[Fe(CN)_5(3\text{-CNpy})]^{3-}$ (ref. 9) with cyanide; and of a series of complexes $[Fe(CN)_5L]^{3-}$ with the *N*-methylpyrazinium cation.[1] In all these reactions, the kinetic evidence indicates the operation of a limiting S_N1, or *D*, mechanism [equations (2) and (3)].

$$[Fe(CN)_5L^1]^{3-} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + L^1 \quad (2)$$

$$[Fe(CN)_5]^{3-} + L^2 \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [Fe(CN)_5L^2]^{3-} \quad (3)$$

TABLE 4

Dependence of the relative stabilities, *K*, of $[Fe(CN)_5\text{-}(3,5\text{-}Me_2py)]^{3-}$ and $[Fe(CN)_5(py)]^{3-}$ for equation (1) on solvent composition at 298.6 K

Solvent	x_2	K	G^E/J mol^{-1}
Methanol	0.047	0.98	116
	0.100	0.92	211
	0.160	0.81	284
	0.229	0.80	335
Ethanol	0.033	0.89	107
	0.072	0.84	224
	0.117	0.77	349
	0.171	0.70	479
t-Butyl alcohol	0.021	0.8	129
	0.046	0.6	269
	0.076	0.5	419
	0.113	0.4	576
Glycerol	0.03	0.94	−84
	0.05	0.94	−140
	0.08	0.92	
Tetrahydrofuran	0.05	0.67	340

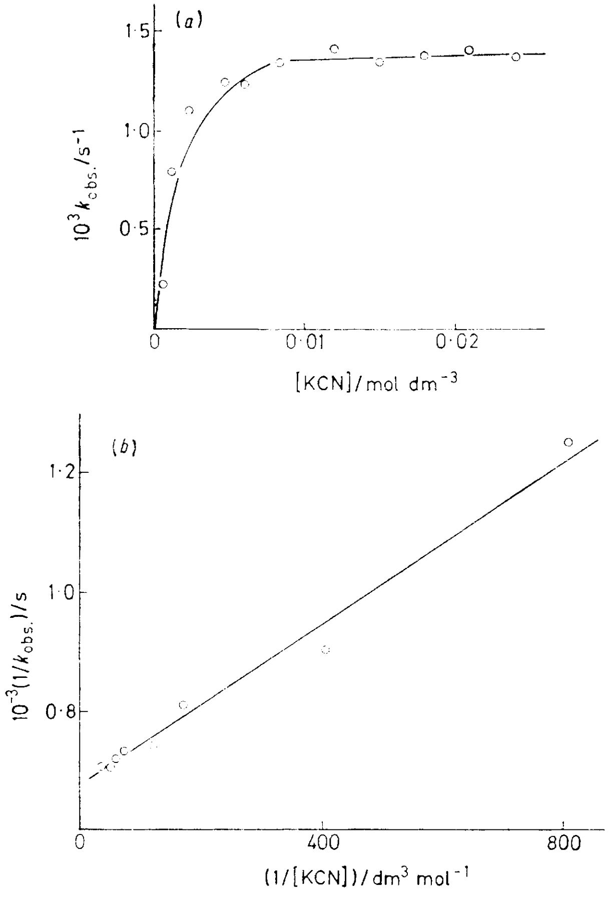


FIGURE 1 Dependence of the first-order rate constant ($k_{obs.}$) on cyanide concentration (*a*) and of the reciprocal of the first-order rate constant on the reciprocal of the cyanide concentration (*b*) for the reaction of $[Fe(CN)_5(3\text{-CNpy})]^{3-}$ with cyanide ion in aqueous glycol (40% glycol by volume) at 298.6 K

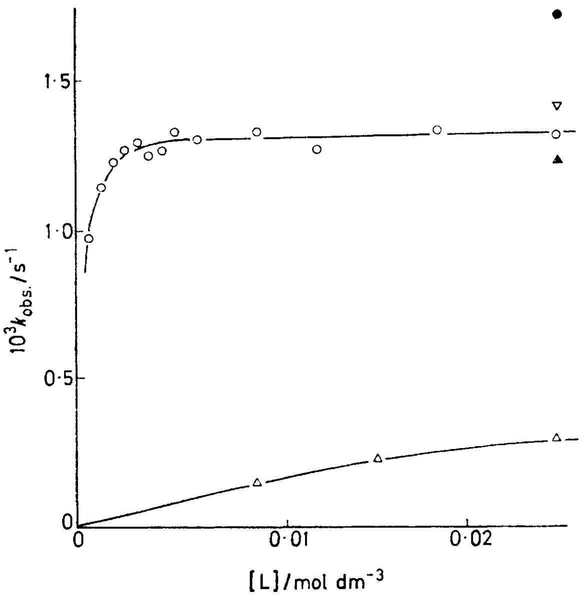


FIGURE 2 Dependence of the first-order rate constant ($k_{obs.}$) on the nature and concentration of the incoming ligand (L) for substitution at $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ in aqueous solution at 298.6 K. L = SCN^- (△), thiourea (▲), CN^- (○), pz (▽), and mpz^+ (●)

The operation of the *D* mechanism for several substituted pyridines as leaving groups has been demonstrated, for aqueous solutions.[1] We have examined in detail the kinetics of the reaction of $[Fe(CN)_5(3\text{-CNpy})]^{3-}$ with cyanide in 40% glycol solution, and of the reactions of this anion and of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ with a range of nucleophiles in aqueous solution in order to test the operation of the *D* mechanism here for these specific pyridine derivatives in mixed aqueous solution as well as in aqueous media. This mechanism is confirmed by the characteristic curve for the dependence of $k_{obs.}$ on cyanide concentration [Figure 1(*a*)] and the linear dependence of $1/k_{obs.}$ on reciprocal cyanide concentration [Figure 1(*b*)] [7] for the reaction of the 3-CNpy complex in 40% glycol. Similarly the kinetic pattern in Figure 2, with the characteristic dependence of $k_{obs.}$ on incoming ligand concentration but independence of $k_{lim.}$ on the nature of the incoming ligand, confirms the operation of a *D* mechanism for substitution at $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$. The slightly higher

---

[7] Z. Bradić, D. Pavlović, I. Murati, and S. Ašperger, *J.C.S. Dalton*, 1974, 344.

[8] B. Jezowska-Trzebiatowska, A. Keller, and J. Ziolkowski, *Bull. Acad. polon. Sci., Sér. Sci. chim.*, 1972, **20**, 649; A. D. James and R. S. Murray, *J.C.S. Dalton*, 1975, 1530.

[9] Z. Bradić, M. Pribanić, and S. Ašperger, *J.C.S. Dalton*, 1975, 353.

$k_{lim.}$ value for the reaction of this complex with the *N*-methylpyrazinium cation is consistent with a similar observation for reactions of the 3-CNpy complex.[9] In this case the irregularity may be ascribed to the consequences of electrostatic interaction between the negatively charged complex or intermediate and the positively charged incoming group. The very different behaviour of thiocyanate as entering group (Figure 2) indicates that it competes only feebly with the leaving 3,5-Me$_2$py; indeed these reactions go to equilibrium rather than to completion.

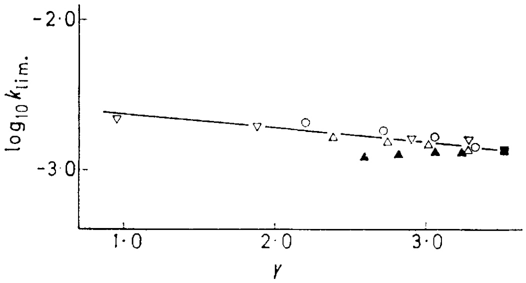


FIGURE 3 Grunwald–Winstein plot for the reaction of [Fe(CN)$_5$-(3,5-Me$_2$py)]$^{3-}$ with cyanide ion. Co-solvents: (△), MeOH; (○), EtOH; (▽), Bu^{t}OH; (▲), glycol; (■), water

Rates of substitution at these [Fe(CN)$_5$L]$^{3-}$ anions are remarkably insensitive to the composition of the mixed aqueous solvent. In this they resemble the complex [Fe(CN)$_2$(bipy)$_2$] [10] (bipy = 2,2′-bipyridyl). The dependence of reactivity on solvent composition is illustrated, for the 3,5-Me$_2$py complex, by the form of a Grunwald–Winstein *mY* plot [11] in Figure 3. The correlation lines corresponding to the three organic co-solvents do not quite coincide; such behaviour for dissociative inorganic reactions has been established for cobalt(III) complexes.[12] The Grunwald–Winstein *m* value for aquation of cobalt(III) chloride complexes is *ca.* 0.3,[12] but for substitution at [Fe(CN)$_5$(3,5-Me$_2$py)]$^{3-}$ is *ca.* −0.1.† Negative *m* values have previously been reported for inorganic substitution reactions, for example aquation of the hexabromorhenate(IV) anion, where $m = -0.55$.[13] Both these negative *m* values are associated with reactions in which one of the separating moieties is a negatively charged species containing several hydrophilic groups, *viz.* cyanide or bromide ligands.‡ If indeed it is the solvation of the [Fe(CN)$_5$]$^{3-}$ moiety rather than that of the 3,5-Me$_2$py leaving group which determines the solvent variation of reactivity in our system, then it is easy to understand how the ratio of substitution rates in say water and in 40% aqueous t-butyl alcohol is very similar for the leaving groups 3,5-Me$_2$py, 3-CNpy, and 3-Clpy (Table 1) despite the expected differences in solvation of these three species, as evidenced by their very different solubilities in water.

We are currently interested in examining whether reactivities in substitution reactions in binary aqueous mixtures can be correlated with excess Gibbs free energies of mixing of the respective mixtures. We have had some success in such an analysis of aquation of the tris(5-nitro-1,10-phenanthroline)iron(II) cation, [Fe(5-NO$_2$phen)$_3$]$^{2+}$, and of the solvolysis of t-butyl chloride.[15] Binary aqueous mixtures can be classified in three groups according to their excess molar thermodynamic functions of mixing.[16] These are the 'typically aqueous' (t.a.) mixtures where G^E is positive and is dominated by its entropy component over the enthalpy component ($|TS^E| > |H^E|$), 'typically non-aqueous positive' (t.n.a.p.) with positive G^E and $|H^E| > |TS^E|$, and 'typically non-aqueous negative' (t.n.a.n.) with negative G^E but again $|H^E| > |TS^E|$.[17,18] Satisfactory results for substitution at the [Fe(CN)$_5$L]$^{3-}$ complexes have been obtained for a range of t.a. mixtures and for t.n.a.n. mixtures containing glycol or glycerol. In Figure 4 our kinetic results, in terms of the change in the Gibbs free energy of activation ($\delta_m\Delta G^\ddagger$) derived from transition-state theory treatment of the experimental rate constants, are plotted against the respective G^E values. The latter were calculated from published thermodynamic data (for detailed references see ref. 15) and

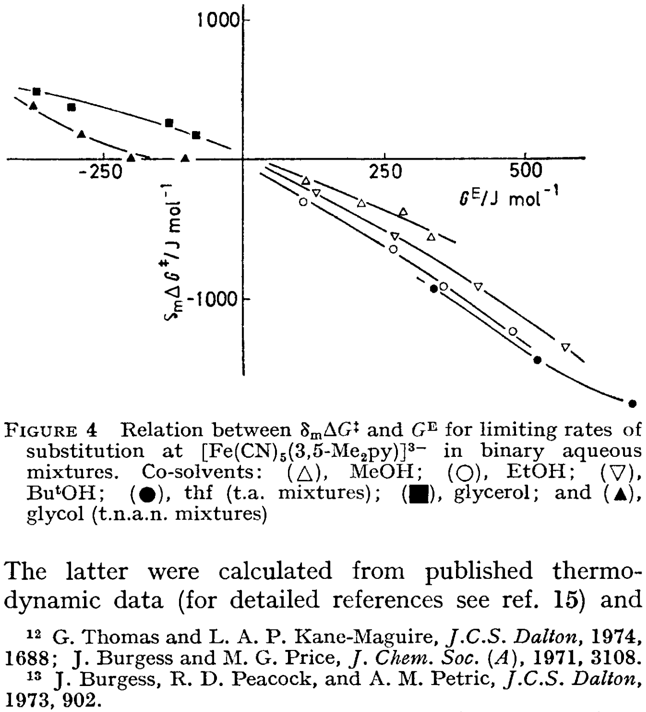


FIGURE 4 Relation between $\delta_m\Delta G^\ddagger$ and G^E for limiting rates of substitution at [Fe(CN)$_5$(3,5-Me$_2$py)]$^{3-}$ in binary aqueous mixtures. Co-solvents: (△), MeOH; (○), EtOH; (▽), Bu^{t}OH; (●), thf (t.a. mixtures); (■), glycerol; and (▲), glycol (t.n.a.n. mixtures)

---

† This value was estimated from the results in the 'typically aqueous' (t.a.) solvent mixtures, ignoring results in aqueous glycol ('typically non-aqueous negative', t.n.a.n.).

‡ Interestingly, rates of substitution at [Co(CN)$_5$(OH$_2$)]$^{2-}$, *e.g.* by [N$_3$]$^-$, also increase on going from aqueous solution to aqueous ethanol or to aqueous t-butyl alcohol.[14]

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

[11] E. Grunwald and S. Winstein, *J. Amer. Chem. Soc.*, 1948, **70**, 846; E. M. Kosower, 'Introduction to Physical Organic Chemistry,' Wiley, New York, 1968, chs. 2.6 and 2.7.

[12] G. Thomas and L. A. P. Kane-Maguire, *J.C.S. Dalton*, 1974, 1688; J. Burgess and M. G. Price, *J. Chem. Soc.* (*A*), 1971, 3108.

[13] J. Burgess, R. D. Peacock, and A. M. Petric, *J.C.S. Dalton*, 1973, 902.

[14] M. J. Blandamer, J. Burgess, S. P. Edwards, and G. P. Gisby, unpublished work.

[15] M. J. Blandamer, J. Burgess, and R. I. Haines, *J.C.S. Dalton*, 1976, 385.

[16] F. Franks, in 'Hydrogen-bonded Solvent Systems,' eds. A. Covington and P. Jones, Taylor and Francis, London, 1968, p. 31.

[17] F. Franks in 'Water—A Comprehensive Treatise,' ed. F. Franks, Plenum Press, New York, 1973, ch. 1.

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

interpolated[15] using the Guggenheim–Scatchard[19,20] equation for expressing the dependence of G^E on mole fraction of the aqueous mixtures. Thus $\delta_m\Delta G^\ddagger$ represents the change in $\Delta G^\ddagger$ on going from a solution in water to a mixture where the mole fraction of co-solvent is x_2, *i.e.* $\delta_m\Delta G^\ddagger = \Delta G^\ddagger(x_2) - \Delta G^\ddagger\,(x_2 = 0)$. The function G^E expresses the extent to which the molar Gibbs function of the mixture differs from that of the corresponding ideal mixture.

There is a satisfactory correlation between the kinetic and thermodynamic parameters. In the present case, unlike that of aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$, but like that of t-butyl chloride solvolysis, results in aqueous glycol can be accommodated within the general $\delta_m\Delta G^\ddagger$–$G^E$ correlation. The close similarity of the $\delta_m\Delta G^\ddagger$–$G^E$ patterns for these three dissociative substitutions is gratifying.

Relative Stabilities of $[Fe(CN)_5L]^{3-}$ *Complexes.*—The values of K in Table 4 represent the relative stabilities of $[Fe(CN)_5(3,5\text{-}Me_2py)]^{3-}$ and $[Fe(CN)_5(py)]^{3-}$ anions in the respective solvent mixtures. Values for the corresponding differences in standard-state Gibbs free energies ($\Delta G^\ominus = -RT\ln K$) are plotted against the respective G^E values for the solvent mixtures in Figure 5.

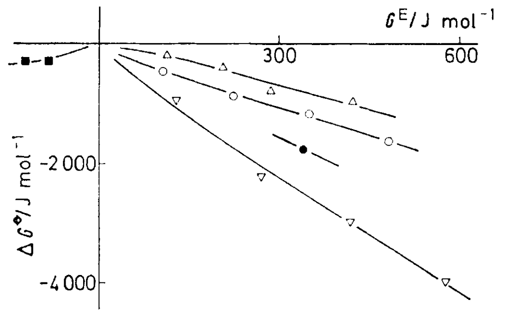
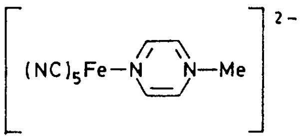


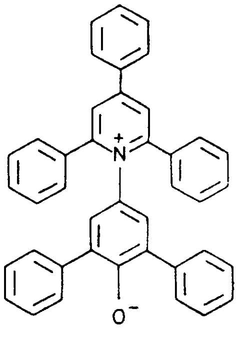
FIGURE 5 Relation between $\Delta G^\ominus$, the Gibbs free energy for the equilibrium between the pyridine and $3,5\text{-}Me_2py$ complexes $[Fe(CN)_5L]^{3-}$ [equation (1) in text], and G^E in binary aqueous mixtures. Symbols as in Figure 4

As for the analogous kinetic plot (Figure 4), there is a good correlation of $\Delta G^\ominus$ with G^E for t.a. mixtures. But the $\Delta G^\ominus$ values for the t.n.a.n. solvent glycerol do not fall on the correlation line for the t.a. mixtures. As with similar plots for aquation of $[Fe(5\text{-}NO_2phen)_3]^{2+}$ and for solvolysis of t-butyl chloride, a consistent pattern is obtained for t.a. mixtures, but a complex pattern emerges for t.n.a.n. mixtures.

The above kinetic and thermodynamic aspects of reactions of $[Fe(CN)_5L]^{3-}$ anions are related, *cf.* equations (1)—(3). Trends in stability constants should be reflected in the discriminatory tendencies of the transient $[Fe(CN)_5]^{3-}$ intermediate, in other words in the curvature of plots of $k_{obs.}$ against the concentration of the incoming nucleophile of the type illustrated in Figures 1(*a*) and 2. In practice, the curvature of such plots for reactions of $[Fe(CN)_5L]^{3-}$ anions with cyanide, pyrazine, or N-methylpyrazinium is too sharp for accurate intercomparisons between different solvent mixtures. At the other extreme, reaction with thiocyanate is unsuitable as this ligand does not compete sufficiently strongly with substituted pyridines for reaction to proceed far enough towards completion.



(I)



(II)

Solvatochromism of the $[Fe(CN)_5(mpz)]^{2-}$ *Anion.*—The charge-transfer (c.t.) spectrum of the product of the reaction of $[Fe(CN)_5(X\text{-}py)]^{3-}$ anions with the N-methylpyrazinium cation, anion (I), varies markedly with solvent composition. The anion (I) bears a resemblance to the betaine (II), whose solvent-sensitive intramolecular c.t. band is the basis for Reichardt's scale of solvent E_T values,[21] in that intramolecular charge transfer is possible across an aromatic ring to a quaternary nitrogen. The c.t. spectrum of (I) might therefore be

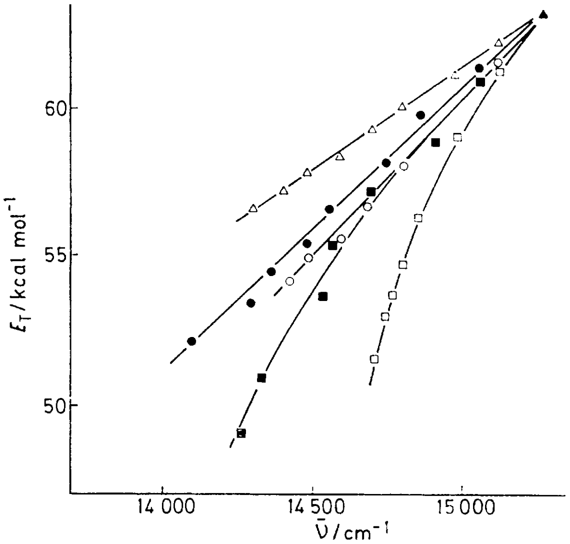


FIGURE 6 Dependence of the frequency of maximum absorption (ν) for the charge-transfer band of the $[Fe(CN)_5(mpz)]^{2-}$ anion on solvent E_T values in binary aqueous mixtures. Co-solvents: (△), MeOH; (○), EtOH; (□), Pr^{i}OH; (●), acetone; (■), dioxan; (▲), water

---

[19] G. Scatchard, *Chem. Rev.*, 1949, **44**, 7.

[20] E. A. Guggenheim, *Trans. Faraday Soc.*, 1937, **33**, 151.

[21] C. Reichardt, 'Lösungsmitteleffekte in der Organischen Chemie,' Verlag Chemie, Weinheim, 1968.

useful for providing a comparable scale of empirical solvent-polarity values of direct relevance to inorganic solutes.

The sodium salt of anion (I) is soluble in many binary aqueous mixtures, but insoluble in all the organic solvents tried. The frequencies of maximum absorption for the c.t. band of the anion are plotted against the respective solvent E_T values in Figure 6. The slight curvature of the isopropanol and dioxan plots is consistent with preferential solvation by water in aqueous mixtures containing these co-solvents {*cf.* $[Fe(CN)_2(phen)_2]$, ref. 22}. The tetraphenylarsonium salt of (I) is soluble in many organic solvents. The wavelength of maximum absorption varies between 676 nm in acetonitrile and 721 nm in tetrahydrofuran (655 nm in water). There is no correlation with solvent E_T values, which is consistent with the very different solvation characteristics for (I) and (II), but contrasts with the good correlation reported for such complexes as $[Fe(CN)_2(bipy)_2]$ [23] and $[W(CO)_4(bipy)]$.[24]

We are grateful to Mrs. Christine Stokes for carrying out preliminary equilibrium studies, to Dr. E. F. G. Herington for helpful discussions, and to the Royal Society for a grant-in-aid for the purchase of the spectrophotometer.

[5/1215 *Received*, 23*rd June*, 1975]

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

[23] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, 1956, **10**, 329; J. Burgess, *Spectrochim. Acta*, 1970, **A26**, 1369, 1957.

[24] J. Burgess, *J. Organometallic Chem.*, 1969, **19**, 218.