Solvent Effects on Discrimination in the Dissociative Substitution of Pentacyano(ligand)ferrate(II) Complexes in Alcohol–Water Mixtures

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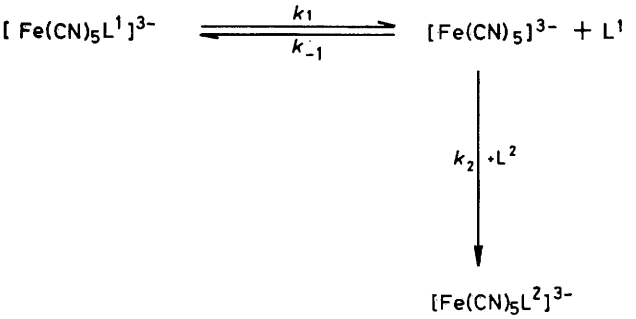
Solvent effects on the discriminatory properties of the transient $[Fe(CN)_5]^{3-}$ intermediate in the dissociative (*D*) substitution at the complex ions $[Fe(CN)_5L]^{3-}$ (L = 3- or 4-cyanopyridine) are described. The solvents employed are methanol–, ethanol–, and t-butyl alcohol–water mixtures; in each case the incoming group is cyanide ion.

SUBSTITUTION reactions of pentacyanoferrate(II) complexes [equation (1)] normally proceed by a limiting

$$[Fe(CN)_5L^1]^{3-} + L^2 \longrightarrow [Fe(CN)_5L^2]^{3-} + L^1 \quad (1)$$

dissociative [*D* or S_N1(lim)] mechanism (Scheme). Examples include aquation [1] of $[Fe(CN)_5(NO)]^{2-}$ and reactions of this anion with ammonia, hydroxylamine, or hydrazine; [2] reaction of $[Fe(CN)_5(3,5Me_2\text{-}py)]^{3-}$ with cyanide, pyrazine, or imidazole; [3] reaction of $[Fe(CN)_5(ONPh)]^{3-}$,[4] of $[Fe(CN)_5(SO_3)]^{5-}$,[5] of $[Fe(CN)_5(py)]^{3-}$,[6] and of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ (ref. 7) with cyanide; and reaction of a series of complexes $[Fe(CN)_5L]^{3-}$ with the *N*-methylpyrazinium cation.[8,†] The only reaction of this type whose mechanism may be different is the relatively rapid replacement of water in $[Fe(CN)_5(OH_2)]^{3-}$ by pyridine derivatives, where evidence has been presented to support the operation of a dissociative-interchange (I_d) mechanism.[9]



SCHEME

In the *D* mechanism of the Scheme there is competition between L^2 and the outgoing L^1 for the transient intermediate $[Fe(CN)_5]^{3-}$. This competition can be characterised by the ratio of the second-order rate constants $k_2 : k_{-1}$. It seems likely that this competition will be affected by solvation of the two ligands L^1 and L^2. Since the solvation of these ligands varies with the nature and the proportion of the cosolvent in binary aqueous mixtures, so the discrimination of the $[Fe(CN)_5]^{3-}$ intermediate between these nucleophiles will vary. Hence the kinetics of reactions of this type will reflect changing solvation of the species involved, and may be useful probes of solute–solvent interactions. Although the limiting rates for reactions of the type shown in equation (1) are relatively insensitive to solvent variation in many binary aqueous mixtures,[10] we hoped that discrimination ratios might be sensitive to solvent variation.

It is not practicable to monitor discrimination under the reaction conditions employed in our previous investigation.[10] In order to obtain satisfactory estimates of competition ratios ($k_2 : k_{-1}$) for reactions with cyanide it is necessary to work in the presence of an excess of the outgoing ligand. We now report the kinetics of reaction (1), with L^1 = 3- or 4-cyanopyridine and L^2 = cyanide, in various binary aqueous mixtures containing monohydroxylic alcohols, and show that ligand discrimination does vary significantly with solvent composition.

EXPERIMENTAL

Reagents.—The salts $Na_3[Fe(CN)_5(3CN\text{-}py)]$ and $Na_3[Fe(CN)_5(4CN\text{-}py)]$ were prepared by published methods.[8]

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† py = Pyridine; 3,5Me₂-py = 3,5-dimethylpyridine.

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

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

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Their analyses were satisfactory. 3-Cyanopyridine and 4-cyanopyridine (Koch–Light) were recrystallised from aqueous methanol or aqueous ethanol. Potassium cyanide was AnalaR material (B.D.H.). Methanol was dried over magnesium and iodine prior to distillation; ethanol and t-butyl alcohol were of the best commercially available quality.

Kinetics.—Kinetic runs were conducted in 10-mm silica cells in the thermostatted cell compartment of a Unicam SP 800A recording spectrophotometer. Rate constants were computed (PDP 11 or CDC Cyber 72) from the recorded variation of absorbance with time using a standard unweighted least-mean-squares program.

RESULTS

All the kinetic runs were conducted in the presence of an excess of the incoming ligand, cyanide ion. Under these conditions all the runs followed first-order kinetics up to at least three half-lives. Observed first-order rate constants for reaction of the $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ and $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ anions with cyanide ion, in the presence of added 3- or 4-cyanopyridine, are reported in Tables 1 and 2 respectively. In the case of the 3CN-py complex, kinetic runs in water–alcohol mixtures were conducted at various cyanide concentrations at the same concentration of added 3-cyanopyridine. In the case of the 4CN-py complex, kinetic runs in water and in water–alcohol mixtures were conducted at various concentrations of cyanide and in the presence of varying amounts of 4-cyanopyridine. The different ranges of experimental conditions are reflected in the different lay-outs of Tables 1 and 2.

TABLE 1

Mean first-order rate constants for the reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ (10^{-4} mol dm^{-3}) with cyanide ion in the presence of various concentrations of added 3-cyanopyridine at 298.6 K; $I = 0.12$ mol dm^{-3}, maintained with $K[NO_3]$

		[KCN]/mol dm^{-3}			
		0.03	0.06	0.09	0.12
Solvent *	[3CN-py]/mol dm^{-3}	$10^3k_{obs.}$/s^{-1}			
Water	0	2.72	2.80	2.84	2.81
	0.001	1.68	1.85	2.42	2.58
	0.003	0.88	1.39	1.73	1.93
	0.004	0.76	1.14	1.52	1.69
	0.009	0.40	0.66	0.93	1.11
MeOH (10)	0.009	0.32	0.40	0.51	0.62
(20)	0.009	0.57	0.70	0.82	0.98
(30)	0.009	0.75	0.91	1.09	1.16
(40)	0.009	0.92	1.08	1.21	1.51
EtOH (10)	0.009	0.33	0.36	0.52	0.61
(20)	0.009	0.56	0.63	0.82	0.96
(30)	0.009	0.78	0.79	1.06	1.25
(40)	0.009	0.90	0.99	1.21	1.42
Bu^{t}OH (10)	0.009	0.44	0.52	0.73	0.91
(20)	0.009	0.74	0.84	0.16	1.49
(30)	0.009	0.99	1.07	1.43	1.77
(40)	0.009	1.18	1.31	1.52	1.80

* Percentage compositions stated are by volume previous to mixing.

The variation of $k_{obs.}$ with cyanide concentration, at various concentrations of added cyanopyridine, is shown for the $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ anion in aqueous solution in Figure 1. The shapes of the curves are characteristic of substitution by the *D* mechanism outlined in the Scheme. As required for this mechanism, plots of $1/k_{obs.}$ against $1/[CN^-]$ are linear. This behaviour is illustrated for the $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ anion in water in Figure 2; similar linearity obtains for the other results in Tables 1 and 2.

TABLE 2

First-order rate constants for the reaction of $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ with cyanide ion in the presence of varying concentrations of added 4-cyanopyridine at 298.2 K; $I = 0.10$ mol dm^{-3}, maintained with $K[NO_3]$

		[4CN-py]/mol dm^{-3}			
		0	0.001	0.002	0.004
Solvent *	[KCN]/mol dm^{-3}	$10^4k_{obs.}$/s^{-1}			
Water	0.010	7.3	2.5	1.43	0.70
	0.020	9.0	4.2	2.5	1.41
	0.040	9.6	6.1	4.1	2.6
	0.060	9.8	6.8	5.0	3.2
	0.080	9.9	7.5	5.9	3.8
	0.100	9.9	8.2	6.7	4.8
MeOH (40)	0.020	9.4	5.4	3.6	2.0
	0.040	9.6	7.1	5.3	3.3
	0.060	9.6	7.8	6.3	4.4
	0.080	9.8	8.7	7.1	5.4
	0.100	10.0	8.8	8.3	5.8
EtOH (40)	0.012	11.1	4.5	2.5	1.30
	0.020	14.4	5.7	3.9	2.0
	0.040	13.3	8.3	6.3	3.3
	0.060	14.3	10.0	7.4	5.6
	0.100	12.5	11.1	9.1	6.3

* As in Table 1.

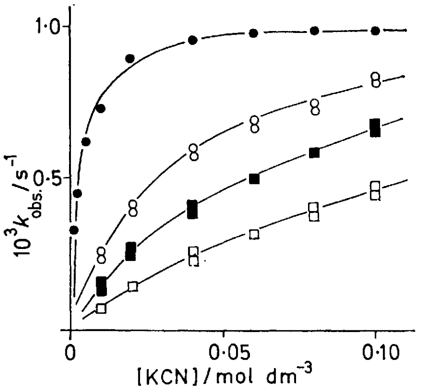

FIGURE 1 Dependence of observed first-order rate constants, $k_{obs.}$, on potassium cyanide concentration for reaction of $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ with cyanide ion in aqueous solution at 298.2 K: (●) runs with no added 4CN-py; (○), (■), and (□) correspond to 0.001, 0.002, and 0.004 mol dm^{-3} added 4CN-py respectively

Values of the first-order rate constant k_1 and of the ratio of second-order rate constants $k_2 : k_{-1}$ (Scheme) were calculated from intercepts and gradients respectively of plots of the type shown in Figure 2. These derived rate constants represent the limiting rate constants for dissociation of the pentacyano(cyanopyridine) complexes and the reactivity ratios for the transient pentacyanoferrate(II) intermediate discriminating between cyanide and cyanopyridine. The uncertainties in these derived parameters are 5—15%; this degree of precision is also suggested by the ranges of estimates in Tables 3 and 4.

The variation in the reactivity, or discrimination, ratio with solvent composition for the replacement of 3-cyanopyridine in the $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ anion by cyanide is illustrated in Figure 3.

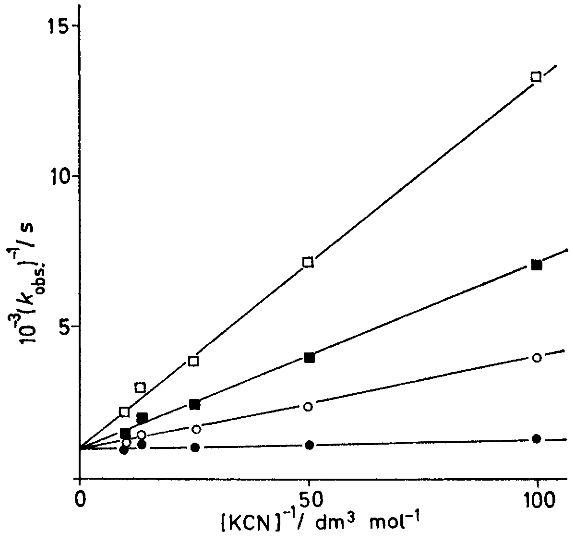

FIGURE 2 Dependence of the reciprocal of the first-order rate constant, $k_{obs.}$, on the reciprocal of the potassium cyanide concentration for the runs in Figure 1

TABLE 3

Limiting rate constants, k_1, and reactivity (discrimination) ratios, $k_2 : k_{-1}$, for the reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with cyanide in the presence of added 3-cyanopyridine at 298.6 K

Solvent *	[3CN-py] / mol dm^{-3}	10^3k_1 / s^{-1}	$k_2 : k_1$
Water	0	2.9	
	0.001	2.9	0.04_2
	0.003	3.3	0.03_7
	0.004	2.8	0.05_0
	0.009	2.7	0.05_3
MeOH (10)	0.009	2.4	0.05_5
(20)	0.009	2.5	0.12
(30)	0.009	2.3	0.17
(40)	0.009	2.5	0.21
EtOH (10)	0.009	2.3	0.04_6
(20)	0.009	2.3	0.08_5
(30)	0.009	2.2	0.14
(40)	0.009	2.5	0.17
Bu^{t}OH (10)	0.009	2.6	0.07_2
(20)	0.009	2.5	0.13
(30)	0.009	2.6	0.20
(40)	0.009	3.0	0.30

* As in Table 1.

TABLE 4

Limiting rate constants, k_1, and reactivity (discrimination) ratios, $k_2 : k_{-1}$, for the reaction of $[Fe(CN)_5(4CN\text{-}py)]^{3-}$ with cyanide in the presence of added 4-cyanopyridine at 298.2 K

Solvent *	[4CN-py] / mol dm^{-3}	10^3k_1 / s^{-1}	$k_2 : k_1$
Water	0	1.06	
	0.001	1.08	0.03
	0.002	1.06	0.03
	0.004	1.06	0.03
MeOH (40)	0	0.99	
	0.001	1.02	0.05
	0.002	1.11	0.05
	0.004	1.07	0.05
EtOH (40)	0	1.41	
	0.001	1.36	0.04
	0.002	1.51	0.04
	0.004	1.46	0.04

* As in Table 1.

DISCUSSION

There are two main points to consider. The first is to compare the reactivity ratio $k_2 : k_{-1}$ for our system with analogous ratios for similar reactions. This comparison is made, in all cases for reaction in aqueous solution, in Table 5. An idea of the relative affinities of a variety of ligands for the $[Fe(CN)_5]^{3-}$ intermediate can be obtained from the ratios listed in this Table. It is interesting to note that the $[Co(CN)_4(SO_3)]^{4-}$ intermediate shows, at least in the one system studied kinetically so far, similar discrimination to $[Fe(CN)_5]^{2-}$. The ratio $k_2 : k_{-1}$ for the system $[Co(CN)_4(SO_3)X]^{n-} + [CN]^-$ is 13 : 1,[11] which is comparable with the value of 9 : 1 quoted in Table 5 for the $[Fe(CN)_5(SO_3)]^{5-} + [CN]^-$ system.

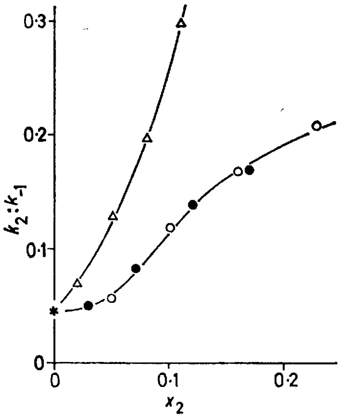

FIGURE 3 Variation of the reactivity ratio, $k_2 : k_{-1}$ (see text), with solvent composition for the reaction of $[Fe(CN)_5(3CN\text{-}py)]^{3-}$ with cyanide ion in binary aqueous mixtures containing MeOH (○), EtOH (●), and Bu^{t}OH (△) at 298.6 K

The second, and main, point for discussion is the effect of solvent composition on the ratio $k_2 : k_{-1}$ for a given system. The appropriate values for the $[Fe(CN)_5(3CN\text{-}py)]^{3-} + [CN]^-$ and $[Fe(CN)_5(4CN\text{-}py)]^{3-} + [CN]^-$ systems are given in Tables 3 and 4. The ratio $k_2 : k_{-1}$ appears to be considerably more affected by solvent composition for the 3-cyano- than for the 4-cyanopyridine complex, hence our concentration on the

TABLE 5

Reactivity ratios, $k_2 : k_{-1}$ (see text), for replacement of a ligand L^1 by an incoming ligand L^2 in complexes of the type $[Fe(CN)_5L]^{n-}$ (at 298 K in aqueous solution)

L^1	L^2	$k_2 : k_{-1}$	Ref.
4CN-py	$[CN]^-$	0.03	This work
3CN-py	$[CN]^-$	0.05 [a]	This work
p-$ONC_6H_4NMe_2$	$[CN]^-$	0.1 [b]	7
p-$ONC_6H_4NMe_2$	PhNO	0.8	7
$[SO_3]^{2-}$	$[CN]^-$	9	5
H_2O	$[CN]^-$	12 000	4

[a] A value of 0.1 has been estimated indirectly from the expression $k_f(CN^-)/k_f(3CN\text{-}py)$ where $k_f(X)$ is the second-order rate constant for reaction of X with $[Fe(CN)_5(OH_2)]^{3-}$ to form $[Fe(CN)_5X]^{n-}$.[7] [b] A value of 0.2 has been estimated in an analogous manner to that in footnote *a*.[7]

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former complex. Figure 3 shows the variation of $k_2 : k_{-1}$ as a function of solvent composition for the 3CN-py complex. The effects of added monohydric alcohols are in the order $\mathrm{Bu^tOH} > \mathrm{EtOH} \approx \mathrm{MeOH}$. The ratio $k_2 : k_{-1}$ is larger for reaction in all the mixed-solvent systems than in water. This trend is not unexpected when set against the predicted changes in chemical potentials with solvent composition for the entering and leaving groups. The solubilities of 3- and 4-cyanopyridine increase as the mol fraction of organic cosolvent increases, and so the changes in their chemical potentials relative to the respective values in water will be negative, *i.e.* $\delta_m\mu^\ominus < 0$. This stabilisation will lead to a decrease in the rate constant. Conversely, halide and related anions such as cyanide are destabilised when organic cosolvents are added to aqueous solutions containing these ions. Despite the problems involved in separating the thermodynamic properties of salts into the corresponding properties of the individual ions, it seems clear that the destabilisation [*i.e.* $\delta_m\mu^\ominus(\mathrm{CN^-}) > 0$] increases more rapidly with increasing mol fraction of organic cosolvent (x_2) in the order:[12] $\mathrm{Bu^tOH} > \mathrm{EtOH} > \mathrm{MeOH}$. It follows therefore that, with increasing x_2, the rate constant for attack by cyanide, k_2, will increase, while the rate constant for the recombination of cyanopyridine with $[\mathrm{Fe(CN)_5}]^{3-}$, k_{-1}, will decrease. Both effects combine to produce the pattern shown in Figure 3, and give a variation in kinetic behaviour which is larger than that observed in the individual variation of rate constant k_1 with solvent composition. Interestingly, the pattern in Figure 3 is, as expected, similar to that for the variation in relative stabilities of the $[\mathrm{Fe(CN)_5(py)}]^{3-}$ and $[\mathrm{Fe(CN)_5(3,5Me_2\text{-}py)}]^{3-}$ complex anions with solvent composition.[10,13] In this earlier example the variation in relative stabilities is less marked, just as the difference between the two ligands is smaller than in our kinetic competition between 3-cyanopyridine and cyanide ion.

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