Kinetic and Equilibrium Studies on Iron(II) and Iron(III) Pentacyanoferrates

By **Alan D. James** and **Robin S. Murray,*** Department of Chemistry, The University of Hull, Hull HU6 7RX

The results of a kinetic investigation of the reaction of $[Fe^{II}(CN)_5(py)]^{3-}$ (py = pyridine) with CN^- and HCN are reported, together with a linear free-energy treatment of data obtained for aquation reactions of species of the type $[Fe^{II}(CN)_5X]$ (X = an uncharged or univalent anion). Equilibrium studies of $[Fe^{II}(CN)_5OH_2]^{3-}$ and $[Fe^{III}(CN)_5OH_2]^{2-}$ with a number of substituents have confirmed the class (b) or 'soft' character of the iron centre in these complexes.

THE reactions and properties of species $[Fe^{II}(CN)_5X]$ [1-3] and $[Fe^{III}(CN)_5X]$ [4-6] have been reported recently. In general the rates of substitution of iron(II) species are much greater than those of corresponding iron(III) complexes.[4] The rates of substitution of the former are slower [1,7] when $X = [SO_3]^{2-}$, $[AsO_2]^-$, and CN^- than when $X = H_2O$, where very rapid rates of substitution by, for example, pyridine (py) are observed.[3] In this paper we report the results of a kinetic investigation of

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the substitution reactions of $[Fe^{II}(CN)_5(py)]^{3-}$ with CN^- and HCN.

The values of the association constants K_1 and K_2 for equilibria (1) and (2) with a number of ligands X show the class (b) character of the iron centre. Stability

$$[Fe^{II}(CN)_5OH_2]^{3-} + X \underset{k_{-1}X}{\overset{k_1X}{\rightleftharpoons}} [Fe^{II}(CN)_5X] + H_2O; \quad K_{1X} = k_1/k_{-1} \qquad (1)$$

$$[Fe^{III}(CN)_5OH_2]^{2-} + X \overset{K_2}{\rightleftharpoons} [Fe^{III}(CN)_5X] + H_2O \qquad (2)$$

constants of the previously unreported species $[Fe^{III}(CN)_5I]^{3-}$, $[Fe^{III}(CN)_5Br]^{3-}$, and $[Fe^{III}(CN)_5Cl]^{3-}$ are included in this treatment.

EXPERIMENTAL

All chemicals were AnalaR grade unless otherwise stated. Samples of $Na_3[Fe^{II}(CN)_5NH_3]$ were prepared and characterised according to previously reported methods.[4,8] Solutions of $[Fe^{II}(CN)_5(py)]^{3-}$ were prepared by allowing solutions of $[Fe^{II}(CN)_5NH_3]^{3-}$ (*ca.* 5×10^{-4}M) * to hydrolyse ($t_{\frac{1}{2}} = 40$ s at 25 °C) in the presence of pyridine.[2] Pyridine, NaI (Hopkins and Williams, G.P.R.), NaBr (Hopkins and Williams, G.P.R.), and NaCl solutions were prepared by weight. Sodium cyanide (B.D.H.) solutions were standardised against $Ag[NO_3]$ in the presence of NH_3 and KI.[9] The ionic strength of the reaction mixtures was maintained with $Na[ClO_4]$, which was standardised against 1.00M-NaOH (B.D.H. ampoule) after passing the solution down an ion-exchange column (Amberlite I.R. 120) in the acid form. Buffers were mixtures of $Na[H_2PO_4]$, $Na_2[HPO_4]$, and $Na_3[PO_4]$ (pH 6.8, 10.2, and 10.9) or $Na_2[CO_3]$ and $Na[HCO_3]$ (pH 8.6).

The kinetics of substitution of $[Fe^{II}(CN)_5(py)]^{3-}$ by CN^- and HCN were followed at 390 nm in a thermostatted cell compartment of a Unicam SP 600 spectrophotometer. Spectra were obtained using a Unicam SP 800 spectrophotometer. Gradients and intercepts of plots of k against $[py]([HCN] + [CN^-])^{-1}$ and of Arrhenius plots were obtained from least-squares calculations and the errors quoted are standard deviations. The reduction potentials were obtained by the method previously reported.[4]

Solutions of $[Fe^{III}(CN)_5I]^{3-}$, $[Fe^{III}(CN)_5Br]^{3-}$, and $[Fe^{III}(CN)_5Cl]^{3-}$ were prepared by allowing solutions of $[Fe^{III}(CN)_5OH_2]^{2-}$ and the appropriate halide ion to equilibrate in the presence of trace amounts of the catalytic species $[Fe^{II}(CN)_5OH_2]^{3-}$.[4] When solutions containing $[Fe^{III}(CN)_5OH_2]^{2-}$ (3.5×10^{-4}), $[Fe^{II}(CN)_5OH_2]^{3-}$ (*ca.* 5×10^{-6}), and NaI (1.3×10^{-2}—9.1×10^{-1}M) were allowed to equilibrate at 25 °C a new band ($\lambda_{max.}$ 730 nm) was observed in the visible region of the spectrum. Plots of $(D - D_0)^{-1}$ against $[I^-]^{-1}$ were linear (where D and D_0 are optical densities at 730 nm in the presence and absence of NaI respectively), consistent with the establishment of equlilbrium (2) where $X = I^-$. From the gradients of these plots, K_{2I^-} was found to be 38.4 ± 0.1 [at 25 °C and $I = 4.55$M ($NaClO_4$)] and 5.3 ± 0.4 l mol^{-1} [at 25 °C and $I = 1.00$M ($NaClO_4$)]. From the intercepts of the plots, ε was calculated as 830 ± 70 l mol^{-1} cm^{-1} at 730 nm.

Similar experiments with NaBr (0.18—4.55M) gave a species with $\lambda_{max.} = 490$ nm (ε 920 ± 70 l mol^{-1} cm^{-1}; Figure 1) and $K_{2Br^-} = 1.73 \pm 0.09$ l mol^{-1} [at 25 °C and $I = 4.55$M ($NaClO_4$)]; K_{2Br^-} was estimated as 0.3 l mol^{-1} at $I = 1.00$M using the absorption coefficient obtained at the higher ionic strength. Addition of NaCl did not lead to significant changes in the visible spectrum of $[Fe^{III}(CN)_5OH_2]^{2-}$. However an estimate of K_{2Cl^-} of 0.53 ± 0.13 l mol^{-1} [$I = 4.6$M ($NaClO_4$) at 25 °C] was obtained from (3), by measuring $[Fe(CN)_5Br^{3-}]$ spectrophotometrically in solutions containing both NaBr (0.20—1.34M) and NaCl (0.77 and 1.34M); $[Fe^{III}]_T$ is the total concentration of

$$[Fe^{III}(CN)_5Br^{3-}]^{-1} = \frac{K_{2Cl^-}[Cl^-] + 1}{[Br^-][Fe^{III}]_T K_{2Br^-}} + \frac{1}{[Fe^{III}]_T} \qquad (3)$$

iron(III) species. No spectral changes were observed when NaI and NaBr were added to solutions of $[Fe^{II}(CN)_5OH_2]^{3-}$ which may imply that the stabilities of $[Fe^{II}(CN)_5I]^{4-}$ and $[Fe^{II}(CN)_5Br]^{4-}$ are less than the corresponding iron(III) complexes.

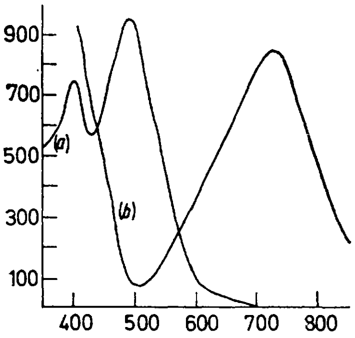

FIGURE 1 Visible spectra of $[Fe(CN)_5Br]^{3-}$ (*a*) and $[Fe(CN)_5I]^{3-}$ (*b*)

RESULTS AND DISCUSSION

(a) *Substitution of* $[Fe^{II}(CN)_5(py)]^{3-}$ *by* CN^- *and* HCN.—Studies of substitution reactions of $[Fe^{III}(CN)_5OH_2]^{3-}$ are complicated by the dimerisation of this species to give $[Fe^{II}_2(CN)_{10}]^{6-}$. An indirect method was therefore used to obtain the second-order rate constants k_8 and k_9 for substitution of $[Fe^{II}(CN)_5OH_2]^{3-}$ by CN^- and HCN. The kinetics of reactions (4) and (5) were studied at different ratios of [HCN], $[CN^-]$, and [py].

$$[Fe^{II}(CN)_5(py)]^{3-} + HCN \longrightarrow [Fe(CN)_6]^{4-} + H^+ + py \qquad (4)$$

$$[Fe^{II}(CN)_5(py)]^{3-} + CN^- \longrightarrow [Fe(CN)_6]^{4-} + py \qquad (5)$$

In all kinetic runs the reaction proceeded to completion, as expected from the relative values of K_{1py} (3.3×10^5 l mol^{-1}) and K_{1CN^-} (1.2×10^{10} l mol^{-1}) (Table 2). The formation of $[HFe(CN)_6]^{3-}$ was unimportant in the pH range employed in this work (pK_a 2.33 [10], $I = 1.0$M). The reaction obeyed rate law (6) for at least 80% completion of reaction and values

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* 1M = 1 mol dm^{-3}, 1 cal = 4.184 J.

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TABLE 1

Kinetic data for substitution of $[Fe(CN)_5(py)]^{3-}$ by CN^- and HCN at $I = 1.0$M ($NaClO_4$)

θ_c/°C	pH	$\frac{[HCN] + [CN^-]}{mol\ l^{-1}}$	$\frac{[py]}{mol\ l^{-1}}$	$\frac{10^4 k_{obs.}}{s^{-1}}$	$\frac{10^{-2}\ Gradient}{mol\ l^{-1}\ s}$	$\frac{10^{-2}\ Intercept}{s}$	$\frac{k_{-7}}{k_8} = \frac{Gradient}{Intercept}$
25	10.9	0.0312	0.0240	1.29	88.4 ± 1.3	9.3 ± 0.6	
		0.0333	0.0128	2.25			
		0.0345	0.0066	3.83			
25	10.2	0.0277	0.0426	0.83	71.8 ± 0.9	9.6 ± 0.8	
		0.0312	0.0240	1.50			
		0.0333	0.0128	2.73			
		0.0345	0.0066	4.22			
25	8.6	0.0135	0.0259	2.50	16.5 ± 0.8	8.7 ± 0.8	
		0.0312	0.0240	4.48			
		0.0333	0.0128	7.25			
25	6.8	0.0090	0.0462	1.73	9.5 ± 0.3	8.3 ± 0.8	1.15 ± 0.15
		0.0161	0.0448	2.83			
		0.0277	0.0426	4.72			
		0.0485	0.0372	6.13			
15	6.8	0.0152	0.0450	0.49	54.2 ± 1.6	43.2 ± 2.6	1.25 ± 0.04
		0.0277	0.0426	0.80			
		0.0236	0.0289	0.88			
		0.0689	0.0066	1.92			
35	6.8	0.0147	0.0451	9.58	2.51 ± 0.07	2.54 ± 0.12	0.99 ± 0.07
		0.0277	0.0426	16.1			
		0.0485	0.0372	23.0			
		0.0349	0.0040	33.3			
44	6.8	0.0342	0.0079	11.3	0.81 ± 0.06	0.72 ± 0.12	1.12 ± 0.09
		0.0147	0.0451	31.2			
		0.0214	0.0438	39.0			
		0.0277	0.0426	57.5			

TABLE 2

Equilibrium data at $I = 1.0$M

X	E_x (0 °C)/V	K_1 (25 °C)/l mol^{-1}	K_2 (25 °C)/l mol^{-1}
CN^-	0.509 [a]	1.2×10^{10} (k) [b,c]	$(5 \pm 3) \times 10^8$ (e)
$[SCN]^-$	0.385 [a]	90 ± 30 (e)	$(2.57 \pm 0.15) \times 10^2$ (s) [d]
N_3^-	0.265,[a] 0.24 (*I* 0.05M) [e]	4 ±3 (e)	$(1.93 \pm 0.16) \times 10^3$ (s) [d]
OH^-	0.159 [a]	8 ± 5 (e)	$(3.9 \pm 0.5) \times 10^5$ (s) [d]
$[NO_2]^-$		3×10^3 (s) [f]	
I^-		<1	5.3 ± 0.4 (s),[c] 38.4 ± 0.1 (*I* 4.55M) (s) [c]
Br^-		<1	*ca.* 0.3 (s),[c] 1.73 ± 0.09 (*I* 4.55M) (s) [c]
Cl^-		<1	0.53 ± 0.13 (*I* 4.6M) (s) [c]
py	0.508 [a]	$3.3 \times 10_5$ (k) [g]	$(6.5 \pm 0.8) \times 10^3$ (s) [d]
H_2O	0.409 [a]		
NH_3	0.399,[a] 0.33 (*I* 0.05M) [e]	1.25×10^4 (k),[b] $(7 \pm 3) \times 10^3$ (e)	$(7.5 \pm 0.7) \times 10^3$ (s) [d]
HCN		1.0×10^9 (k) [b,c]	*ca.* 50 (e) [h]
$[SO_3]^{2-}$	0.44,[c] 0.57 (pH 4) [c]	*ca.* 1×10^4 (0 °C) (k) [b]	*ca.* 1×10^3 (e)
$[Co(CN)_6]^{3-}$	0.457 [a]	2.0×10^3 (9.4 °C) (k), $(2 \pm 1.5) \times 10^3$ (e)	$(2.17 \pm 0.20) \times 10^2$ (9.4 °C) (s) [a]
$[Co(CN)_6]$	0.510 [c]		

k = Kinetic method, s = spectrophotometric method, and e = calculated from either K_1 or K_2 and E_X.

[a] Ref. 4. [b] Ref. 1. [c] This work. [d] Refs. 5 and 6. [e] Ref. 12. [f] J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 1966, **5**, 573. [g] Ref. 3. [h] Using pK_a 0.5 for $[Fe(CN)_5CNH]^{2-}$; J. Duplessis-Legros, *Compt. rend.*, 1970, **270**, 1768.

of $k_{obs.}$ are given in Table 1. Plots of $k_{obs.}^{-1}$ against $[py]([HCN] + [CN^-])^{-1}$ were linear at constant $[H^+]$, consistent with the reaction scheme (7)—(9).

$$-d[Fe^{II}(CN)_5(py)^{3-}]/dt = k_{obs.}[Fe^{II}(CN)_5(py)^{3-}] \tag{6}$$

$$[Fe^{II}(CN)_5(py)]^{3-} + H_2O \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [Fe^{II}(CN)_5OH_2]^{3-} + py \tag{7}$$

$$[Fe^{II}(CN)_5OH_2]^{3-} + HCN \xrightarrow{k_8} [Fe(CN)_6]^{4-} + [H_3O]^+ \tag{8}$$

$$[Fe^{II}(CN)_5OH_2]^{3-} + CN^- \xrightarrow{k_9} [Fe(CN)_6]^{4-} + H_2O \tag{9}$$

The species $[Fe^{II}(CN)_5OH_2]^{3-}$ substitutes very rapidly[3] [k_{-7} 365 l mol^{-1} s^{-1} (25 °C)] and did not form in detectable quantities [ε (440 nm) 700 l mol^{-1} cm^{-1}]. Applying steady-state treatment to $[Fe^{II}(CN)_5OH_2]^{3-}$, equation (10) was obtained from which (11) could be derived where K_{HCN} is the acidity constant of HCN.

$$\frac{-d[Fe^{II}(CN)_5(py)^{3-}]}{dt} = \frac{k_7[Fe^{II}(CN)_5(py)^{3-}](k_8[HCN] + k_9[CN^-])}{k_{-7}[py] + k_8[HCN] + k_9[CN^-]} \tag{10}$$

$$k_{obs.}^{-1} = k_7^{-1} + \frac{k_{-7}(1 + K_{HCN}[H^+]^{-1})[py]}{k_7(k_8 + K_{HCN}[H^+]^{-1}k_9)([HCN] + [CN^-])} \tag{11}$$

From the intercepts of plots of $k_{obs.}^{-1}$ against $[py]([HCN] + [CN^-])^{-1}$ for data obtained at 25 °C, a value of k_7 of $(1.1 \pm 0.05) \times 10^{-3}$ s^{-1} was obtained compared with the previously reported[3] value of 1.1×10^{-3} s^{-1}.

An expression for the gradient of these plots is given by (12). The data from experiments at 25 °C in the pH

$$(\text{Gradient})^{-1} = \frac{[\text{H}^+]K_{1\text{py}}^{-1}(k_8 - k_9)}{([\text{H}^+] + K_{\text{HCN}})} + k_9\, K_{1\text{py}}^{-1} \quad (12)$$

range 6.8—10.9 gave a best fit to (12) if a value of pK_{HCN} of 8.75 was assumed and gave k_8 and k_9 as 344 ± 25 and 29.2 ± 3.4 l mol^{-1} s^{-1} respectively using $K_{1\text{py}} = 3.3 \times 10^5$ l mol^{-1}.[3] A value of pK_{HCN} of 8.90 ± 0.05 was obtained from direct measurements under the same conditions as the kinetic experiments. The above values of k_8 and k_9 differ from those obtained by Legros[7] (3.3 and 0.68 l mol^{-1} s^{-1} respectively), where the experiments were made using reaction mixtures containing excess of $[\text{Fe(CN)}_6]^{4-}$. Under these conditions spuriously low rates of substitution by CN^- and HCN are to be expected due to complications arising from reaction of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{OH}_2]^{3-}$ and $[\text{Fe(CN)}_6]^{4-}$ to give $[\text{Fe}^{\text{II}}{}_2(\text{CN})_{11}]^{7-}$.[11]

Activation parameters $\Delta H_8^{\ddagger}$ and $\Delta S_8^{\ddagger}$ for substitution of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{OH}_2]^{3-}$ by HCN were obtained from a temperature-dependence study at pH 6.8. The previously reported[3] values of $\Delta H_{-7}^{\ddagger}$, $\Delta S_{-7}^{\ddagger}$, and k_7 were used in these calculations. Values of $\Delta H_8^{\ddagger}$ and $\Delta S_8^{\ddagger}$ of 17.0 ± 1.3 kcal mol^{-1} and 11 ± 5 cal K^{-1} mol^{-1} respectively were obtained.

(b) *The Relative Stabilities of Iron*(II) *and Iron*(III) *Pentacyanoferrates*.—Reduction potentials (E_{X}) for $[\text{Fe}^{\text{III}}(\text{CN})_5\text{X}]$–$[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]$ couples for a variety of complexes including $\text{X} = \text{H}_2\text{O}$ ($E_{\text{H}_2\text{O}}$) are given in Table 1. These are related to the stability constants K_1 and K_2 by (13). From the data in Table 1 it can be

$$E_{\text{X}} - E_{\text{H}_2\text{O}} = +(RT/F)\ln(K_1/K_2) \quad (13)$$

seen that $K_2 > K_1$ when $\text{X} = \text{OH}^-, \text{N}_3^-, [\text{SCN}]^-$, and NH_3, and $K_2 < K_1$ when $\text{X} = [\text{SO}_3]^{2-}, [\text{HSO}_3]^-, [\text{Co(CN)}_5(\text{NC})]^{3-}, [\text{Co(CN)}_5(\text{CN})]^{3-}$, py, and CN^-.

For the iron(II) complexes the order of stability constants (K_1) is $\text{CO} > \text{CN}^- >$ acyclic $\text{N} > [\text{SO}_3]^{2-} \approx \text{NH}_3 > [\text{NO}_2]^- > [\text{SCN}]^-$ [12] $> \text{N}_3^- \gg \text{OH}^- >$ halides. This behaviour is typical of a class (b) or 'soft' metal centre,[13] and is similar to the order of decreasing bond character of the Fe-X bond obtained in a Mössbauer study of a series of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]$ species[14,15] where $\text{CO} > \text{CN}^- > [\text{SO}_3]^{2-} > \text{NH}_3 \approx [\text{NO}_2]^-$. The order of decreasing stability constants (K_2) for the iron(III) complexes is $\text{CN}^- > [\text{SCN}]^- \sim \text{OH}^- > \text{N}_3^- \approx \text{py} \approx \text{HN}_3 > \text{I}^- > \text{Br}^- > \text{Cl}^-$, and class (b) character is evident particularly where X = halide.

(c) *Linear Free-energy Treatment of Data*.—Figure 2 is a linear free-energy plot of data for the reverse reactions of equation (1), where X is (*a*) an uncharged ligand or (*b*) a univalent anion. The gradient of the plot for ligands of type (*a*) is 1.0 ± 0.05 and for type (*b*) is 0.77 ± 0.05. A gradient of 1.0 suggests that the aquation reaction is dissociative in nature[16] and further substantiates the mechanisms proposed here and elsewhere[1,3] for substitution reactions of pentacyanoferrate(II) complexes. The agreement between the results where X = HNC and pyrazine, pyridine, 4-methylpyridine, dimethyl sulphoxide, and ammonia may imply a high degree of covalency in the bonding between the cyano-ligand and the proton,* rather than the alternative ion-pair association between $[\text{H}_3\text{O}]^+$ and $[\text{Fe(CN)}_6]^{4-}$. The gradient of 0.8 obtained when X is a univalent anion is consistent with some degree of solvent-assisted aquation.

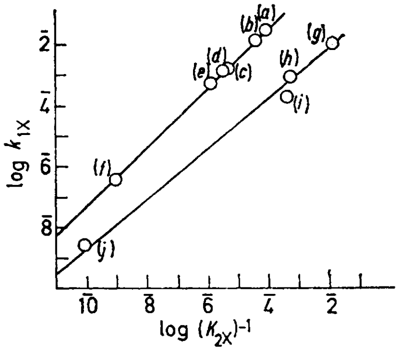

FIGURE 2 Linear free-energy relation for aquation of $[\text{Fe}^{\text{II}}(\text{CN})_5\text{X}]$ complexes: X = (*a*) NH_3, ref. 1; (*b*) dimethyl sulphoxide, ref. 2; (*c*) methylpyridine, ref. 3; (*d*) pyridine, ref. 3; (*e*) pyrazine, ref. 3; (*f*) HNC, ref. 1 and this work; (*g*) $[\text{SCN}]^-$, refs. 5, 6, this work, and A. D. James and R. S. Murray, unpublished work; (*h*) $[\text{HSO}_3]^-$, ref. 1; (*i*) $[\text{NO}_2]^-$, J. H. Swinehart and P. A. Rock, *Inorg. Chem.*, 1966, **5**, 573; and (*j*) CN^-, ref. 1 and this work

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