Iron(II) Catalysis in Substitution Reactions of Amminepentacyano- and Aquopentacyano-ferrate(III) Ions

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

Substitution reactions of the ions $[Fe^{III}(CN)_5X]^{2-}$ ($X = NH_3$ and H_2O) by Y {$Y = N_3^-$, SCN^-, OH^-, and $[Co(CN)_6]^{3-}$} are catalysed by $[Fe^{II}(CN)_5X]^{3-}$. At iron(II) concentrations greater than *ca.* 1% of the total iron species present, the rate-determining step of these reactions is substitution of the ions $[Fe^{II}(CN)_5X]^{3-}$ by Y.

IRON(II) and iron(III) complexes of general formula $[Fe(CN)_5X]$ undergo substitution reactions as in equation (*i*) and the kinetics and equilibria of several reactions of

$$[Fe(CN)_5X] + Y \longrightarrow [Fe(CN)_5Y] + X \qquad (i)$$

this type have been studied.[1] It appears that rates of substitution of the iron(II) species are usually more rapid than those of the iron(III) analogues.

We have observed [2] that rates of formation and hydrolysis of the binuclear species $[Fe^{III}_2(CN)_{10}]^{4-}$ are markedly affected by the presence of iron(II) complexes, and the hydrolysis reaction of the ion $[Fe^{III}(CN)_6]^{3-}$ has been shown [3] to be catalysed by the presence of $[Fe^{II}(CN)_6]^{4-}$, although the mechanism of the latter reaction has not been established. We have subsequently investigated the importance of iron(II) catalysis in substitution reactions of the ions $[Fe^{III}(CN)_5X]^{2-}$ ($X = NH_3$ and H_2O) with a variety of substituents, Y. Here we report the results of investigations where (*a*) $X = NH_3$ and $Y = N_3^-$, OH^-, and SCN^-, and (*b*) $X = H_2O$ and $Y = [Co(CN)_6]^{3-}$.

EXPERIMENTAL

The salt $Na_3[Fe(CN)_5NH_3]$ was prepared according to the method of Hoffman,[4] and characterised from its visible and i.r. spectra.[5-7] The usual method of preparing the salt $Na_2[Fe(CN)_5NH_3]$ involves oxidation of $Na_3[Fe(CN)_5NH_3]$ with HNO_2 at 0 °C,[8] but to avoid any possibility of substitution by nitrite ion, we used the minimum amount of bromine water as oxidising agent, followed by precipitation of $Na_3[Fe(CN)_5NH_3]$ with diethyl ether–ethanol (1 : 1). The product was recrystallised from water–ethanol {Found: C, 21·3; H, 2·60; Fe, 19·1; N, 28·45. $Na_2[Fe(CN)_5NH_3]$,-$2{\cdot}5H_2O$ requires C, 20·5; H, 2·70; Fe, 19·0; N, 28·6%}. I.r. and visible spectra agreed well with previous studies.[1c,6,7] Solutions of the ion $[Fe(CN)_5H_2O]^{2-}$ were prepared by a method adapted from Espenson.[1b] Instead of using the

---

[1] (*a*) J. Legros, *J. Chim. phys.*, 1964, **61**, 923; (*b*) J. H. Espenson and S. G. Wolenuck, *Inorg. Chem.*, 1972, **11**, 2034; (*c*) B. Jaselskis, *J. Amer. Chem. Soc.*, 1961, **83**, 1082.

[2] A. D. James, R. S. Murray, and W. C. E. Higginson, unpublished work.

[3] J. Duplessis-Legros, *Compt. rend.*, 1970, **270**, 1768.

[4] K. A. Hoffmann, *Annalen*, 1900, 312, 1.

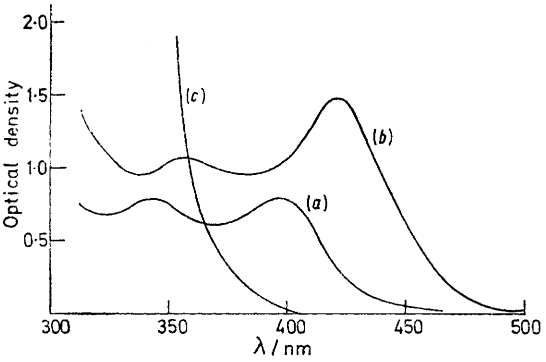
[5] E. Baran and A. Muller, *Z. anorg. Chem.*, 1969, **368**, 144.

[6] W. Haberditzl, K. D. Schleintz, and H. G. Bartel, *Z. Naturforsch.*, 1968, **236**, 891.

[7] L. Tosi and J. Danon, *Inorg. Chem.*, 1964, **3**, 150.

[8] G. Brauer, 'Handbuch der Praparativen Anorganischen Chemie,' Ferdinand Enke, Stuttgart, 1954, 1364.

purple dimeric ion $[Fe^{III}_2(CN)_{10}]^{4-}$ as starting material, a solution of $[Fe^{III}(CN)_5NH_3]^{2-}$ (*ca.* 0·05M) in KOH (0·1M) was allowed to hydrolyse to $[Fe^{III}(CN)_5OH]^{3-}$. The resulting bright yellow solution was then brought to pH 4 with acetic acid containing Br_2, passed down a Sephadex G25 column, and a yellow fraction consisting of the aquo-complex was collected. {Bromine was added to prevent the iron(II)-catalysed dimerisation of the ion $[Fe^{III}(CN)_5H_2O]^{2-}$.[2]} Thus solutions of up to 0·02M in the ion $[Fe^{III}(CN)_5H_2O]^{2-}$ were obtained which were stable at 5 °C for several hours. The visible spectrum was very similar to that of the complex prepared by Espenson [1b] (Figure).



Visible spectra of the ions: (a), $[Fe(CN)_5H_2O]^{2-}$ (1·00 × 10^{-3}); (b) $[(CN)_5Fe(NC)Co(CN)_5]^{5-}$ (1·00 × 10^{-3}); and (c) $[Co(CN)_6]^{3-}$ (1·0 × 10^{-1}M)

Reduction potentials were obtained from potentiometric titrations of the pentacyano-complexes with $Na_2[IrCl_6],2H_2O$ or ascorbic acid at I = 1·0M and are quoted in Table 1. Values for the $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$ couple are included for comparison. The potentials were originally measured relative to a calomel electrode; values in Table 1 were obtained by adding 0·244 V. The constants K_3 and K_7 were calculated from the equation $F(E_X - E_Y) = 2{\cdot}303RT \log_{10}K$, where E_X and E_Y are reduction potentials of the $[Fe^{III}(CN)_5X]^{2-}$–$[Fe^{II}(CN)_5X]^{3-}$ and $[Fe^{III}(CN)_5Y]$–$[Fe^{II}(CN)_5Y]$ couples respectively.

The equilibrium constant K_{12} for the reaction between the ions $[Fe^{III}(CN)_5H_2O]^{2-}$ and $[Co(CN)_6]^{3-}$ was estimated spectrophotometrically at the absorption maximum of the dimer at 422 nm (Figure). Solutions containing the salt $K_3[Co(CN)_6]$ (0·005—0·10M) and $[Fe(CN)_5H_2O]^{2-}$ (*ca.* 10^{-4}M) were allowed to reach equilibrium at pH 4 and I = 1·0M. A plot of $1/(A - A_0)$ against $1/[Co(CN)_6^{3-}]$, where A_0 is the absorbance at 422 nm when $[Co(CN)_6^{3-}] = 0$, gave a straight line, from the gradient and intercept of which K_{12} and the absorption coefficient of the dimer were calculated.

TABLE 1

Equilibrium data

X	Y	E_X/V [a]	E_Y/V [a]	K_2/l mol^{-1}	K_3	K_7	K_{12}/l mol^{-1} [b]
NH_3	OH^-	0·399	0·159 [c]	8 ± 5	(2·8 ± 1·0) × 10^4	(5 ± 2) × 10^4	(3·9 ± 0·5) × 10^5 [b]
NH_3	N_3^-	0·399	0·265 [e]	4 ± 3	(3·0 ± 1·0) × 10^2	(5 ± 2) × 10^2	(1·97 ± 0·16) × 10^3 [d]
NH_3	SCN^-	0·399	0·385 [f]	(9 ± 3) × 10	1·8 ± 1	3 ± 1	(2·57 ± 0·15) × 10^2 [d]
H_2O	$[Co(CN)_6]^{3-}$	0·409	0·457 [g]	(2 ± 1·5) × 10^3		(1 ± 0·5) × 10^{-1}	(2·17 ± 0·20) × 10^2
H_2O	py	0·409	0·508 [h]	(6 ± 3) × 10^5		(1 ± 0·5) × 10^{-2}	(6·5 ± 0·8) × 10^3 [d]
CN^-		0·509					

[a] At 0 °C, I = 1·0M, ±0·005 V. [b] At 25·0 °C. [c] At pH 13·5. [d] From refs. 1(*a*) and 1(*b*). [e] $[N_3^-]$ = 1·0M. [f] $[SCN^-]$ = 1·0M. [g] $[Co(CN)_6^{3-}]$ = 0·1M. [h] [py] = 0·1M.

All kinetic measurements were carried out under N_2 on freshly prepared O_2-free solutions at I = 1·0M on a Unicam SP 600 spectrophotometer.

Rates of hydrolysis of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$ with and without pyridine (py) present to give $[Fe^{II}(CN)_5(py)]^{3-}$ and $[Fe^{II}(CN)_5H_2O]^{3-}$ respectively were measured at pH 4; the initial concentration of $[Fe^{II}(CN)_5NH_3]^{3-}$ was 3 × 10^{-4}M. Both the aquo- and pyridine complexes have a single absorption maximum above 350 nm, at 440 (ε 700) and 365 nm (ε 4 200 l mol^{-1} cm^{-1}) respectively, whereas $[Fe^{II}(CN)_5NH_3]^{3-}$ has a maximum at 405 nm (ε 450 l mol^{-1} cm^{-1}). The uncertainty of ±10% in values of k_1 obtained from these data is in part due to complications caused by a slower dimerisation reaction of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ to give $[Fe^{II}_2(CN)_{10}]^{6-}$.[2]

For the reaction of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ with $[Co(CN)_6]^{3-}$, solutions of the former were prepared by hydrolysis of $[Fe^{II}(CN)_5NH_3]^{3-}$ or by reduction of $[Fe^{III}(CN)_5H_2O]^{2-}$ with ascorbic acid at pH 4. The rate of disappearance of the 440 nm peak of the aquo-ion when various concentrations of $[Co(CN)_6]^{3-}$ (10^{-3}—10^{-2}M) were added at 9·4 °C was measured, and the second-order rate constant k_2 was calculated from the observed first-order rate constant (= $k_2[Co(CN)_6^{3-}] + k_{-2}$). The product $[(CN)_5Fe^{II}(NC)Co^{III}(CN)_5]^{6-}$ has an absorption maximum at *ca.* 380 nm (ε 300 l mol^{-1} cm^{-1}).

Reactions between the ions $[Fe^{III}(CN)_5NH_3]^{2-}$ and N_3^-, SCN^-, and OH^-, at 25 °C with different amounts of $[Fe^{II}(CN)_5NH_3]^{3-}$ added ($0 < c < 0{\cdot}6$), were followed using solutions of *ca.* 10^{-4}M-$[Fe^{III}(CN)_5NH_3]^{2-}$ at 590, 560, and 390 nm, respectively, where the complexes $[Fe^{III}(CN)_5SCN]^{3-}$, $[Fe^{III}(CN)_5N_3]^{3-}$, and $[Fe^{III}(CN)_5OH]^{3-}$ exhibit maxima (ε 2 680, 3 700, and 1 600 l mol^{-1} cm^{-1}, respectively). The concentrations of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$ in solutions used were obtained by addition of N_3^- or SCN^-, followed by oxidation to the iron(III) complex with H_2O_2, and spectroscopic determinations at 590 and 560 nm respectively.[9] We estimate the error in c to be ±5%.

The reaction between the ions $[Fe^{III}(CN)_5H_2O]^{2-}$ (1 × 10^{-4}M) and $[Co(CN)_6]^{3-}$ at pH 4 was followed at 422 nm, the absorption maximum of $[(CN)_5Fe^{III}(NC)Co^{III}(CN)_5]^{5-}$ (ε 1 400 l mol^{-1} cm^{-1}), with different amounts of $[Fe^{II}(CN)_5H_2O]^{3-}$ ($0 < c < 1{\cdot}0$). The source of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ was again $[Fe^{II}(CN)_5NH_3]^{3-}$. The dependence of k_{obs} on the concentration of the ion $[Co(CN)_6]^{3-}$ was investigated at c = 0·13. Attempts were made to isolate solid $Na_5[(CN)_5Fe^{III}(NC)Co^{III}(CN)_5]$. Aqueous bromine was added to a solution of the dimer [to prevent iron(II)-catalysed hydrolysis] and the solution was then passed down a Sephadex G-25 column, followed by evaporation

---

[9] B. Jaselskis and J. C. Edwards, *Analyt. Chem.*, 1960, **32**, 381.

under vacuum at room temperature. A solution in water of the resulting solid gave a u.v. and visible spectrum with maxima at 422, 360, and 292 nm, but analysis revealed an excess of the ion $[\mathrm{Co(CN)_6}]^{3-}$. The i.r. spectrum of this solid showed two peaks in the region of the cyanide stretch at 2 135 and 2 185 cm^{-1} in the ratio 8 : 1. Haim *et al.*[10] have shown that bridging cyanide ligands absorb at higher energy and we therefore assign the upper band to bridging cyanide.

RESULTS

Since the presentation of our results is simplified by referring to our suggested reaction mechanisms, we introduce the latter at this stage. When X = $\mathrm{NH_3}$ the proposed catalytic path is as follows, where (1) is a slow substitution and (3) a rapid equilibrium. In the case where equilibrium (2) is established rapidly this leads to equation (4). An integrated form of (4) is (5). When $K_3'c \gg 1$ and $0{\cdot}05 \leqslant c \leqslant 1{\cdot}0$, expression (5) can be expressed as (6).

$$[\mathrm{Fe^{II}(CN)_5NH_3}]^{3-} + \mathrm{H_3O^+} \xrightarrow{k_1} [\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} + \mathrm{NH_4^+} \quad (1)$$

$$[\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} + \mathrm{Y} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [\mathrm{Fe^{II}(CN)_5Y}] + \mathrm{H_2O};\; K_2 = k_2/k_{-2} \quad (2)$$

$$[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-} + [\mathrm{Fe^{II}(CN)_5Y}] \overset{K_3}{\rightleftharpoons} [\mathrm{Fe^{II}(CN)_5NH_3}]^{3-} + [\mathrm{Fe^{III}(CN)_5Y}] \quad (3)$$

$$\frac{-\mathrm{d}[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]}{\mathrm{d}t} = k_1K_3'c[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]\Big/\left\{1 + p[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}] + \frac{cK_3'}{1 + p[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]}\right\} \quad (4)$$

where $c = \dfrac{[\mathrm{Fe^{II}}]_\mathrm{T}}{[\mathrm{Fe^{III}}]_\mathrm{T}}$, $K_3' = K_3\left(1 + \dfrac{1}{K_2[\mathrm{Y}]}\right)^{-1}$,

and $p = \dfrac{K_3' - 1}{[\mathrm{Fe^{III}}]_\mathrm{T}}$

$$\begin{aligned}-k_1K_3'ct &= -k_{\mathrm{obs}}K_3't \\ &= (K_3'c + 1)\ln[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}] - K_3'c\ln\{(1/p) + [\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]\} + p[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}] + \text{constant} \quad (5)\end{aligned}$$

$$-k_1ct = -k_{\mathrm{obs}}t = [\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]/[\mathrm{Fe^{III}}]_\mathrm{T} \quad (6)$$

When X = $\mathrm{H_2O}$ the proposed catalytic path is (2) followed by equilibrium (7). Under conditions where $k_2 > k_{-2}$ and the rate of substitution is dependent on [Y], this leads to expression (8). On integration (8) becomes (9).

$$[\mathrm{Fe^{II}(CN)_5Y}] + [\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} \overset{K_7}{\rightleftharpoons} [\mathrm{Fe^{III}(CN)_5Y}] + [\mathrm{Fe^{II}(CN)_5H_2O}]^{3-} \quad (7)$$

$$\frac{-\mathrm{d}[\mathrm{Fe^{III}(CN)_5H_2O^{2-}}]}{\mathrm{d}t} = k_2K_7c[\mathrm{Y}][\mathrm{Fe^{III}(CN)_5H_2O^{2-}}]\Big/\left\{1 + q[\mathrm{Fe^{III}(CN)_5H_2O^{2-}}] + \frac{cK_7}{1 + q[\mathrm{Fe^{III}(CN)_5H_2O^{2-}}]}\right\} \quad (8)$$

where $q = \dfrac{(K_7 - 1)}{[\mathrm{Fe^{III}}]_\mathrm{T}}$

$$\begin{aligned}-k_2K_7c[\mathrm{Y}]t &= -k_{\mathrm{obs}}K_7t = \\ &= (K_7c + 1)\ln[\mathrm{Fe^{III}(CN)_5H_2O^{2-}}] - K_7c\ln\{(1/q) + [\mathrm{Fe^{III}(CN)_5H_2O^{2-}}]\} + q[\mathrm{Fe^{III}(CN)_5H_2O^{2-}}] + \text{constant} \quad (9)\end{aligned}$$

Unless otherwise specified, all experiments were carried out at 25 °C, pH 4 (acetate or phthalate buffers), and $I = 1{\cdot}0$M (maintained by the use of KCl). Under the conditions chosen reactions (10) and (11) are essentially complete (K_{10} and K_{11} are 4×10^5 and 50 ± 7 respectively).[1b,c] Equilibrium constants, K_{12}, for reactions (12) are quoted in Table 1.

$$[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-} + \mathrm{H_3O^+} \overset{K_{10}}{\rightleftharpoons} [\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + \mathrm{NH_4^+} \quad (10)$$

$$[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-} + \mathrm{OH^-} \overset{K_{11}}{\rightleftharpoons} [\mathrm{Fe^{III}(CN)_5OH}]^{3-} + \mathrm{NH_3} \quad (11)$$

$$[\mathrm{Fe^{III}(CN)_5H_2O}]^{2-} + \mathrm{Y} \overset{K_{12}}{\rightleftharpoons} [\mathrm{Fe^{III}(CN)_5Y}] + \mathrm{H_2O} \quad (12)$$

(a) *Reactions of the* $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$ *Ion with* $\mathrm{N_3^-}$ *and* $\mathrm{SCN^-}$.—Preliminary experiments indicated that the presence of trace quantities of iron(II) species catalysed substitution reactions of the ion $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$. Consequently $\mathrm{Br_2}$ or $\mathrm{IrCl_6}^{2-}$ (*ca.* 1×10^{-4}M) were added to reaction mixtures of the ions $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$ (1×10^{-4}M) and Y (Y = $\mathrm{N_3^-}$ and $\mathrm{SCN^-}$; 0·10M) to oxidise rapidly traces of iron(II) species present in the samples of $\mathrm{Na_2[Fe^{III}(CN)_5NH_3]}$. The excess of oxidant was observed spectrophotometrically to disappear over a period of 5—10 min, presumably with oxidation of $\mathrm{N_3^-}$ or $\mathrm{SCN^-}$ ion. However there was no spectral evidence for formation of any new iron(III) complexes during these rapid reactions and we have no evidence that the products of these reactions had an effect on the subsequent slow substitution reactions of the ion $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$. The latter reactions [equation (13)] were investigated spectrophotometrically and values of the initial rates $-\{\mathrm{d}[\mathrm{Fe^{III}(CN)_5NH_3{}^{2-}}]/\mathrm{d}t\}$, where Y = $\mathrm{N_3^-}$ (0·10M) and $\mathrm{SCN^-}$ (0·10M), of $\leqslant 1 \times 10^{-7}$ and $\leqslant 3 \times 10^{-8}$ mol l^{-1} s^{-1} were obtained respectively. Rates of substitution were found to increase with time, and we ascribe this to slow formation of the ion $[\mathrm{Fe^{II}(CN)_5NH_3}]^{3-}$, possibly due to reduction of $[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-}$ by $\mathrm{N_3^-}$ and $\mathrm{SCN^-}$.

$$[\mathrm{Fe^{III}(CN)_5NH_3}]^{2-} + \mathrm{Y} + \mathrm{H^+} \longrightarrow [\mathrm{Fe^{III}(CN)_5Y}] + \mathrm{NH_4^+} \quad (13)$$

Plots of k_{obs} [equation (5)] against the concentration of added iron(II) (at constant $[\mathrm{Fe^{III}}]_\mathrm{T}$) for data discussed in section (*d*) gave straight lines with positive intercepts. Values of c_0 (0·025, 0·020, and 0·040 for Y = $\mathrm{N_3^-}$, $\mathrm{SCN^-}$,

---

[10] P. A. Doors, A. Haim, and W. K. Wilmarth, *J. Inorg. Nuclear Chem.*, 1961, **21**, 33.

TABLE 2

Kinetic data for iron(II)-catalysed substitution reactions of the ions $[Fe^{III}(CN)_5NH_3]^{2-}$ and $[Fe^{III}(CN)_5H_2O]^{2-}$

$10^3[Y]/M$	$10^4[Fe^{III}]_T/M$	c	$10^3k_{obs}/s^{-1}$	$10^2k_1/s^{-1}$	$k_2/l\ mol^{-1}\ s^{-1}$
$X = NH_3$, $Y = N_3^-$, at 25 °C					
100	2·0	0·076	1·5	1·9	
100	2·0	0·13	3·0	2·3	
100	2·0	0·25	5·2	2·0	
100	2·0	0·36	6·8	1·9	
100	2·0	0·47	9·0	1·9	
1 000	1·5	0·56	11	2·0	
660	1·5	0·56	12	2·1	
330	1·5	0·56	11	2·0	
100	1·5	0·56	11	2·0	
50	1·5	0·56	10	1·9	
17	1·5	0·56	10	1·9	
5·0	1·5	0·56	8·2	1·5	
1·3	1·5	0·56	11	2·0	
100	0·31	0·15	3·0	2·0	
100	0·62	0·15	2·7	1·8	
100	2·8	0·15	2·7	1·8	
100	1·9	0·15	3·0	2·0	
$X = NH_3$, $Y = OH^-$, at 25 °C					
50	3·0	0·13	2·7	2·1	
50	3·0	0·19	3·7	2·0	
50	3·0	0·27	5·0	1·9	
50	3·0	0·34	6·5	1·9	
50	0·5	0·31	6·7	2·1	
50	1·6	0·31	6·1	2·0	
50	2·3	0·31	6·0	2·0	
50	3·1	0·31	6·1	2·0	
$X = NH_3$, $Y = SCN^-$, at 25 °C					
100	2·0	0·14	2·8	2·0	
100	2·0	0·19	3·6	1·9	
100	2·0	0·20	4·0	2·0	
100	2·0	0·32	5·8	1·8	
100	2·0	0·44	9·7	2·2	
100	1·0	0·46	9·0	2·0	
660	1·0	0·46	8·3	1·8	
330	1·0	0·46	8·7	1·9	
100	1·0	0·46	8·5	1·8	
100	0·5	0·58	12	2·1	
100	1·0	0·58	12	2·1	
100	1·6	0·58	10	1·7	
100	3·2	0·58	10	1·7	
100	4·8	0·58	10	1·7	
$X = H_2O$, $Y = [Co(CN)_6]^{3-}$, at 9·4 °C					
33	3·0	0·11	2·3		5·1
33	3·0	0·32	4·8		3·9
33	3·0	0·42	5·2		3·2
33	3·0	0·63	9·0		3·8
33	3·0	0·84	11·5		3·6
100	2·5	0·13	5·0		3·7
75	2·5	0·13	4·2		4·1
50	2·5	0·13	2·5		3·5
33	3·0	0·13	1·6		3·3
33	0·85	0·13	1·6		3·3
33	1·5	0·13	1·6		3·3
33	4·0	0·13	1·6		3·3
33	5·0	0·13	1·5		3·0

TABLE 3

Kinetic data for the substitution reaction of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ by $[Co(CN)_6]^{3-}$, at 9·4 °C

$10^5[Fe^{II}(CN)_5H_2O^{3-}]/M$	$10^3[Co(CN)_6^{3-}]/M$	$10^2\{k_{-2} + k_2[Co(CN)_6^{3-}]\}/s^{-1}$	$k_2/l\ mol^{-1}\ s^{-1}$
4·0	1·0	0·44	3·36
4·0	3·0	1·18	3·60
4·0	5·0	1·72	3·24
4·0	7·0	2·52	3·43
4·0	10·0	3·60	3·50

and OH^- respectively) corresponding to the contribution to c of traces of iron(II) impurities in samples of the salt $Na_2[Fe^{III}(CN)_5NH_3]$ were calculated from the values of these intercepts. The values of c in Table 2 are the sum of c_0 and c_1, the contribution from deliberate addition of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$.

(b) *Reaction of the* $[Fe^{III}(CN)_5H_2O]^{2-}$ *Ion with* $[Co(CN)_6]^{3-}$.—The rate of the substitution reaction of the ions $[Fe^{III}(CN)_5H_2O]^{2-}$ and $[Co(CN)_6]^{3-}$ to form the binuclear species $[(CN)_5Fe(NC)Co(CN)_5]^{5-}$ was also found to be increased by traces of iron(II) impurities in samples of $Na_2[Fe^{III}(CN)_5H_2O]$. The rate of the uncatalysed reaction $\{-d[Fe^{III}(CN)_5H_2O^{2-}]/dt\}$, in experiments where $[Fe^{III}(CN)_5H_2O^{2-}] = 1 \times 10^{-4}$, $[IrCl_6^{2-}] = 1 \times 10^{-4}$, and $[Co(CN)_6^{3-}] = 3{\cdot}3 \times 10^{-2}$M, was found by spectrophotometric investigations to be $\leqslant 3 \times 10^{-7}$ mol l^{-1} s^{-1}. The rate of this reaction did not increase with time. From the value of the intercept of the straight-line plot of k_{obs} [equation (9)] against the concentration of added iron(II) [section (*d*) below] a value of c_0 of 0·003 was obtained.

(c) *Reactions of the* $[Fe^{II}(CN)_5NH_3]^{3-}$ *Ion with* H_2O *and Pyridine, and of* $[Fe^{II}(CN)_5H_2O]^{3-}$ *with* N_3^-, SCN^-, *and* $[Co(CN)_6]^{3-}$.—Substitution reactions of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$ by H_2O and pyridine (py) [11] to give $[Fe^{II}(CN)_5H_2O]^{3-}$ and $[Fe^{II}(CN)_5(py)]^{3-}$, respectively, both follow first-order rate laws and give rate constants of $(1{\cdot}8 \pm 0{\cdot}2) \times 10^{-2}$ and $(1{\cdot}77 \pm 0{\cdot}12) \times 10^{-2}$ s^{-1} respectively. The value of k_{obs} is independent of the concentration of py over the range $4{\cdot}5 \times 10^{-3}$—$6{\cdot}6 \times 10^{-2}$M (Table 4). The reaction with H_2O was complicated by dimerisation of the product to give $[Fe^{II}{}_2(CN)_{10}]^{6-}$,[2] whereas no dimerisation was observed in the reaction with py where $K_2 > 3 \times 10^5$ l mol^{-1}. Reactions of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ with N_3^- and SCN^- were found to be extremely rapid, confirming the observations of Wilkins.[12] The reaction of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ with $[Co(CN)_6]^{3-}$ was much slower, and we found that the rate of substitution was dependent on the concentration of $[Co(CN)_6]^{3-}$ (Table 3).

(d) *Catalysis of Substitution Reactions of the Ions* $[Fe^{III}(CN)_5NH_3]^{2-}$ *and* $[Fe^{III}(CN)_5H_2O]^{2-}$ *by* $[Fe^{II}(CN)_5NH_3]^{3-}$ *and* $[Fe^{II}(CN)_5H_2O]^{3-}$.—For the systems where $X = NH_3$ and $Y = N_3^-$, SCN^-, or OH^-, and $X = H_2O$ and $Y = [Co(CN)_6]^{3-}$, relevant values of K_3 and K_7 deduced from reduction potentials are included in Table 1. Values of K_{12} and $K_2 = K_{12}/K_7$ are also included.

TABLE 4

Kinetic data for substitution reaction of the ion $[Fe^{II}(CN)_5NH_3]^{3-}$ by pyridine at 25 °C

$10^4[Fe^{II}(CN)_5NH_3{}^{3-}]$/M	10^2[py]/M	$10^2k_1/s^{-1}$
3·0	6·6	1·75
3·0	3·3	1·75
3·0	1·4	1·62
3·0	0·45	1·62
1·0	3·3	1·83
7·0	3·3	2·00

(*i*) When $X = NH_3$ and $Y = N_3^-$, SCN^-, and OH^-, values of k_{obs} were found to be directly proportional to c, and independent of the concentration of Y, as predicted by equation (5). When $Y = N_3^-$ and OH^-, $K_3 = (3 \pm 1) \times 10^2$ and $(2{\cdot}8 \pm 1{\cdot}0) \times 10^4$, respectively and, except where [Y] is low, $K_3' \simeq K_3 > 50$ leading to a linear decrease in $[Fe^{III}(CN)_5NH_3{}^{2-}]$ with time. When $[N_3^-] < 5 \times 10^{-3}$M the term $1/K_2[N_3^-]$ becomes important and $K_3' \leqslant 6$. In these cases this simple kinetic behaviour was not observed, although a plot of the complete expression gave straight lines and values of k_1 so obtained were similar to those at higher concentrations of N_3^- ion. When $Y = SCN^-$, $K_3 = 1{\cdot}8 \pm 0{\cdot}8$ (Table 1). Values of K_3k_{obs} were obtained by plotting the right-hand side of equation (5) against the appropriate value of t. The values of k_{obs} so obtained (Table 2) were relatively insensitive to the value of K_3 chosen. For example the calculated value of k_{obs} was increased by only 10% on increasing the value of K_3 from 1·0 to 1·8. The values of k_1 obtained from the data in Table 2 where $Y = N_3^-$, SCN^-, and OH^- are $(1{\cdot}94 \pm 0{\cdot}15) \times 10^{-2}$, $(1{\cdot}90 \pm 0{\cdot}15) \times 10^{-2}$, and $(2{\cdot}0 \pm 0{\cdot}1) \times 10^{-2}$ s^{-1} respectively, in agreement with the directly measured values of k_1 given in section (*c*).

(*ii*) When $X = H_2O$ and $Y = [Co(CN)_6]^{3-}$, the product of reaction was the binuclear species $[(CN)_5Fe^{III}(NC)Co^{III}(CN)_5]^{5-}$, the spectrum of which is shown in the Figure. The linkage isomer $[(CN)_5Fe^{III}(CN)Co^{III}(CN)_5]^{5-}$, which is formed by reaction of the ion $[Fe^{III}(CN)_6]^{3-}$ with $[Co(CN)_5]^{3-}$ followed by oxidation, has been reported previously.[13] The species $[(CN)_5Fe^{III}(CN)Fe^{III}(CN)_5]^{5-}$, formed by reaction of the ion $[Fe^{III}(CN)_6]^{3-}$ with $[Fe^{III}(CN)_5H_2O]^{2-}$, has also been reported.[14]

Under the conditions used in these experiments reaction (2) was essentially complete. Values of K_7k_{obs} were obtained by plotting the right-hand side of equation (9) against the appropriate value of t, and straight lines were obtained for values of K_7 within the limits 0—0·2. A value of K_7 of $0{\cdot}10 \pm 0{\cdot}05$ was obtained from reduction-potential data (Table 1). The rate of reaction was found to be dependent on the concentration of the ion $[Co(CN)_6]^{3-}$ and values of k_{obs} at 9·4 °C are given in Table 2. At the concentrations of the ion $[Co(CN)_6]^{3-}$ employed in these experiments, formation of the binuclear adduct was only 85% complete. This was allowed for in calculating the rate constant k_2 for this system. The mean value of k_2 was $3{\cdot}5 \pm 1{\cdot}8$ l mol^{-1} s^{-1}, compared with the value obtained directly for the substitution of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ by $[Co(CN)_6]^{3-}$ of $3{\cdot}43 \pm 0{\cdot}12$ l mol^{-1} s^{-1}. The large error in k_2 is due to uncertainty in the magnitude of K_7.

DISCUSSION

The results indicate that in reactions of the ion $[Fe^{III}(CN)_5NH_3]^{2-}$ with N_3^-, SCN^-, and OH^-, and $[Fe^{III}(CN)_5H_2O]^{2-}$ with $[Co(CN)_6]^{3-}$, where concentrations of $[Fe^{II}(CN)_5X]^{3-}$ are such that $c > 0{\cdot}01$, substitution occurs mainly *via* the catalytic path and direct substitution of $[Fe^{III}(CN)_5X]^{2-}$ by Y is insignificant by comparison. This conclusion is particularly relevant to systems where Y can act as a reducing agent. Our results indicate that iron(II) species are formed in reactions of the ion $[Fe^{III}(CN)_5NH_3]^{2-}$ with N_3^-, SCN^-, and OH^-. Significantly, this effect was not observed in the reaction between the ion $[Fe^{III}(CN)_5H_2O]^{2-}$ and $[Co(CN)_6]^{3-}$, where oxidation of the latter is unlikely. Hydrolysis of the ion $[FeCl]^{2+}$ has been shown to be catalysed by Fe^{2+}(aq).[15] The rate-determining step

---

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

[12] R. Strasiw and R. G. Wilkins, *Inorg. Chem.*, 1969, **8**, 156.

[13] A. Haim and W. K. Wilmarth, *J. Amer. Chem. Soc.*, 1961, **83**, 509.

[14] G. Emschwiller and J. Legros, *Compt. rend.*, 1971, **273**, 452.

[15] R. J. Campion, T. J. Conocchioli, and N. Sutin, *J. Amer. Chem. Soc.*, 1964, **86**, 4591.

for the catalytic path is an electron-transfer reaction which leads to a different rate expression to that reported in this paper.

Recently Espenson[1b] reported a kinetic investigation of the reaction between the ion $[Fe^{III}(CN)_5H_2O]^{2-}$ and SCN^-. The reaction appeared complicated. We repeated one of Espenson's experiments, initial concentrations being $[Fe^{III}(CN)_5H_2O]^{2-} = 2 \times 10^{-4}$, $[SCN^-] = 0{\cdot}08$, $[H^+] = 0{\cdot}0160$, and $I = 1{\cdot}0$M ($NaClO_4$) at 25 °C, and found that when Br_2 was added (*ca.* 4×10^{-4}M) the rate of substitution of the ion $[Fe^{III}(CN)_5H_2O]^{2-}$ did not exceed one sixth of that previously reported. We calculate that the rate observed by Espenson would require only the presence of *ca.* 0·01% iron(II) species ($c = 1 \times 10^{-4}$). This calculation was based on an estimate[12] of the second-order rate constant for substitution of the ion $[Fe^{II}(CN)_5H_2O]^{3-}$ by SCN^- of 10^4 l mol^{-1} s^{-1} at 25 °C; we assumed that rates of substitution by the ions N_3^- and SCN^- were similar.

We thank the S.R.C. for a grant (to A. D. J.).

[3/2106 *Received, 15th October,* 1973]