Kinetics and Mechanism of Replacements in Pentacyano(ligand)ferrate(II) Ions

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The kinetics of replacement of the ligand in the pentacyano(ligand)ferrate(II) ions have been examined for the leaving ligands *NN*-dimethyl(*p*-nitroso)aniline, nitrosobenzene, sulphite, and water, respectively, and for the entering ligands nitrosobenzene, 3-cyanopyridine, *NN*-dimethyl(*p*-nitroso)aniline, thiocyanate, nitrite, cyanide, and sulphite. Limiting reaction rates, at sufficiently large concentrations, of entering ligand have been observed with all the leaving ligands, except water, where the replacements obey the second-order rate law $-d[Fe(CN)_5OH_2^{3-}]/dt = k_Y[Fe(CN)_5OH_2^{3-}][Y]$. When the entering ligand Y bears no electrical charge, the k_Y values are very similar and in the range 200—300 l mol^{-1} s^{-1} at 25 °C and 1M ionic strength. For singly negatively charged anions $k_Y \simeq$ 40—60, and for the doubly charged SO_3^{2-} ion k_Y = 3·3 l mol^{-1} s^{-1}. The variations in k_Y are interpreted as being due to variations in diffusion rates since the reactions of the intermediate $[Fe(CN)_5]^{3-}$ with the ligands are diffusion controlled.

IN previous papers[1,2] we have shown that the replacement of X (X = PhNO or SO_3^{2-}) by CN^- in the $[Fe(CN)_5X]$ ion is a dissociative process, and a limiting S_N1 mechanism has been proposed. The $[Fe(CN)_5]^{3-}$ intermediate exhibited selective reactivity as shown by the competition factor $k_{CN^-}/k_{SO_3^{2-}} = 8{\cdot}76 \pm 0{\cdot}53$. Previously, a very low reactivity towards the intermediate was ascribed to the water molecule,[1] but from the work of Toma and Malin [3] it can be inferred that the reactivity of water is comparable with that of other reagents. The general reaction scheme can be written as in equations (1) and (2), where *m* and *n* are electrical charges of X and Y, respectively.

$$[Fe(CN)_5X]^{(3+m)-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + X^m \qquad (1)$$

$$[Fe(CN)_5]^{3-} + Y^n \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} [Fe(CN)_5Y]^{(3+n)-} \qquad (2)$$

Malin and his coworkers [3,4] observed that the pentacyano-intermediate is quite insensitive to the nature and electrical charge of the attacking reagent, and they concluded that this was consistent with a highly reactive intermediate for which the k_2 step is diffusion controlled. On inspection of the authors' results,[3,4] one can find that when the reagent Y was a neutral molecule ($n = 0$) the replacement rates of water in the aquapentacyanoferrate(II) ion were almost equal and less than when Y was the *N*-methylpyrazinium ion (mpz). This led us to postulate that the competition factor $k_{CN^-}/k_{SO_3^{2-}} = 8{\cdot}76 \pm 0{\cdot}53$, observed previously,[2] is primarily influenced by the difference in electrical charges of these reagents. In order to examine this supposition, we studied the kinetics of replacement with Y being nitrosobenzene (PhNO), 3-cyanopyridine (3-CNpy), *NN*-dimethyl(*p*-nitroso)aniline (dmna), thiocyanate, nitrite, cyanide, and sulphite, and the leaving ligand being dmna, PhNO, SO_3^{2-}, and H_2O, respectively. It can be shown that the greatest difference in the rate constants is between mpz (k_{mpz^+}) and SO_3^{2-} reacting with $[Fe(CN)_5]^{3-}$ for which $k_{mpz^+}/k_{SO_3^{2-}} = 167$.

RESULTS

If in the reaction scheme [equations (1) and (2)] the reverse of reaction (2) is neglected, because of the relative stability of the final reaction product ($k_{-2} \simeq 0$), the application of the steady-state approximation for the intermediate $[Fe(CN)_5]^{3-}$ gives (3). With the exception X^m = solvent,

$$k_{obs.} = \frac{k_1k_2[Y^n]}{k_{-1}[X^m] + k_2[Y^n]} \qquad (3)$$

limiting rates were observed in all cases as shown in Figure 1 for X^m = dmna and Y^n = CN^- and 3-CNpy, respectively.

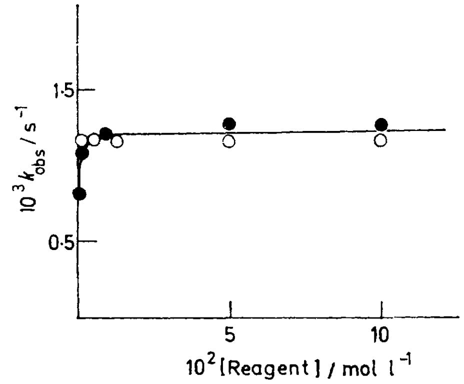

FIGURE 1 Dependence of $k_{obs.}$ on [Reagent] in the replacement of dmna by CN^- (●) and 3-CNpy (○), respectively, in $[Fe(CN)_5(dmna)]^{3-}$ [(2·5—6) × 10^{-5}M] at 25 °C, pH 10·8 ($Na_2B_4O_7,10H_2O$–NaOH buffer), and 1M ionic strength (maintained with $NaClO_4$) in aqueous solution

Plots of $1/k_{obs.}$ against 1/[Reagent] gave straight lines with gradient $k_{-1}/(k_1k_2)$ and intercepts $1/k_1$ and the ratios of gradient : intercept gave the competition factors k_{-1}/k_2 (see Table 1). For details of this method see previous work.[2] The rate constant k_1 is equal to $k_{obs.}$ at reagent concentrations which correspond to the limiting reaction rates.

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

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

[3] H. E. Toma and J. M. Malin, *Inorg. Chem.*, **1973**, **12**, 2080.

[4] H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 1973, **12**, 2084.

When the reacting complex was the aquapentacyanoferrate(II) ion $k_{-1}[H_2O] \gg k_2[Y^n]$, equation (3) was reduced to (4), and second-order kinetics were observed, as recently

$$k_{obs.} = k_1k_2[Y^n]/k_{-1}[H_2O] \qquad (4)$$

described by Malin and his co-workers.[3,4] By plotting $k_{obs.}$ against reagent concentration $[Y^n]$, straight lines were obtained with the gradient $k_Y = k_1k_2/k_{-1}[H_2O]$, as shown in Figure 2 for 3-CNpy, SCN^-, NO_2^-, CN^-, and SO_3^{2-}. Variations in the gradients of these straight lines were caused by variations in k_2, *i.e.* in the reactivity of the intermediate $[Fe(CN)_5]^{3-}$ with these reagents. These replacements in the aqua-complex were very fast under the experimental conditions studied, and stopped-flow spectrophotometry was used. Table 1 summarizes our kinetic results and some of the results of Toma *et al.*[4] on the aqua-complex. The third column of Table 1 shows what the leaving ligand (X^m) was, and its starting concentration as achieved by the extra addition of this ligand. The fourth column analogously shows the reagent (Y^n) and the range of its concentrations used.

TABLE 1

Rates of replacement in $[Fe(CN)_5X]^{(3+m)-}$ ions. The leaving ligand is X^m and the entering ligand is Y^n, m and n being the electrical charges. The specific rates k_1, k_{-1}, and k_2 are defined by equations (1) and (2), and $k_Y = k_1k_2/k_{-1}[H_2O]$. Uncertainties are standard deviations of the mean of five kinetic runs at 25 °C, ionic strength 1M (maintained with $NaClO_4$), and pH 10·80 ($Na_2B_4O_7,10H_2O$–NaOH buffer). Abbreviations: dmna = *NN*-dimethyl(*p*-nitroso)aniline, PhNO = nitrosobenzene, py = pyridine, 3-CNpy = 3-cyanopyridine, 4-Mepy = 4-methylpyridine, dmso = dimethyl sulphoxide, and mpz = *N*-methylpyrazinium ion

System	$[Fe(CN)_5X^{(3+m)}]$/ mol l^{-1}	X^m, mol l^{-1}	Y^n, mol l^{-1}	10^3k_1/s^{-1}	k_{-1}/k_2	k_Y/l mol^{-1} s^{-1}
(1)	5×10^{-5}	SO_3^{2-}	PhNO, 0·0001—0·001	0·057		
(2)	3×10^{-5}	dmna	3-CNpy, 0·0003—0·1	1·15		
(3)	$(3—6) \times 10^{-5}$	dmna, 0·0004	CN^-, 0·0005—0·1	1·18 ± 0·02	9·21 ± 0·05	
(4)	4×10^{-5}	dmna, 0·0004	PhNO, 0·0003—0·002	1·25 ± 0·05	1·30 ± 0·011	
(5)	6×10^{-5}	dmna, 0·0004	PhNO, 0·0003—0·002	1·85 ± 0·07	1·31 ± 0·11 [a]	
(6)	6×10^{-5}	dmna, 0·0004	PhNO, 0·0002—0·005	0·99 ± 0·03	0·65 ± 0·04 [b]	
(7)	2×10^{-5}	dmna, 0·0004	PhNO, 0·0002—0·005	0·60 ± 0·01	0·23 ± 0·01 [c]	
(8)	4×10^{-5}	dmna, 0·0004	PhNO, 0·0003—0·007	0·92 ± 0·01	0·39 ± 0·01 [d]	
(9)	6×10^{-5}	PhNO	CN^-, 0·01	0·00163		
(10)	3×10^{-6}	H_2O	SO_3^{2-}, 0·025—0·2			3·3
(11)	3×10^{-6}	H_2O	CN^-, 0·025—0·4			38
(12)	3×10^{-6}	H_2O	NO_2^-, 0·01—0·4			42
(13)	3×10^{-6}	H_2O	SCN^-, 0·025—0·4			64
(14)	3×10^{-6}	H_2O	dmna, 0·0004—0·0006			185
(15)	3×10^{-6}	H_2O	PhNO, 0·0006—0·0012			230
(16)		H_2O	dmso			240 [e]
(17)		H_2O	Isonicotinamide			295 [e]
(18)		H_2O	4-Mepy			354 [e]
(19)		H_2O	py			365 [e]
(20)	3×10^{-6}	H_2O	3-CNpy, 0·005—0·56			370
(21)		H_2O	Pyrazine			380 [e]
(22)		H_2O	mpz			550 [e]

[a] In unbuffered solution and no addition of $NaClO_4$. [b] In 80 v/v % MeOH. [c] In 80 v/v % EtOH. [d] In 80 v/v % acetone.
[e] Results from ref. 4.

The results in Table 1 enable one to reach several interesting conclusions. The rate of dissociation of the PhNO ligand (10^3k_1 = 0·00163 s^{-1}) was *ca.* 730 times slower than the rate of dissociation of dmna ($10^3k_1 \simeq$ 1·2 s^{-1}) at 25 °C. Nitrosobenzene is bound to iron through the nitrogen atom of the nitroso-group.[5] The slow dissociation of PhNO can be interpreted as being due to substantial interaction between the pentacyanoferrate(II) moiety and the nitrogen atom of the nitroso-group. Such π-interactions have been extensively studied.[3,4,6,7] The π-bonding stabilizing effect is obviously reduced by the resonance effect of the dimethylamino-group which is able to take a position coplanar with the benzene ring.* The specific rate of dissociation of the dmna ligand (k_1) was independent of the nature of the entering ligand [Table 1, systems (2)—(4)]. In an unbuffered aqueous solution, 10^3k_1/s^{-1} = 1·85 ± 0·07. In 80% methanol and acetone the rate was about one half and in 80% ethanol about one third of that value [Table 1, systems (6)—(8)]. This is probably due to the reduced π-bonding stabilizing effect of the dimethylamino-group in solvents of reduced polarity.

The k_{-1}/k_2 factors for aqueous solutions show that uncharged dmna is a 9·2 times better competitor for the intermediate $[Fe(CN)_5]^{3-}$ than negatively charged CN^-, but only 1·3 times better than PhNO. The importance of the electrical charge of the competitor for the intermediate $[Fe(CN)_5]^{3-}$ is even better demonstrated by k_Y values in reactions of the $[Fe(CN)_5OH_2]^{3-}$ ion, which varied between 3·3 (for SO_3^{2-}) and 550 l mol^{-1} s^{-1} (for mpz) (see last column of Table 1). When the entering ligands bore no electrical charge k_Y values were very similar, though the basicity of these reagents is different. This was previously observed by Toma and

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* If groups larger than hydrogen occupy the *ortho*-position, coplanarity cannot be attained and activation of the ring is not possible. Thus it is expected that the ligand *NN*-dimethyl-2,6-dimethyl(*p*-nitroso)aniline will dissociate from the pentacyanoferrate(II) complex much slower than *NN*-dimethyl(*p*-nitroso)aniline, which is under investigation.

[5] I. Dézsi, B. Molnar, T. Szalay, and I. Jaszberényi, *Chem. Phys. Letters*, 1973, **18**, 598.

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

[7] R. E. Shepherd and H. Taube, *Inorg. Chem.*, 1973, **12**, 1392.

Malin [3,4] and led them to the conclusion that k_2 is very near to the diffusion-controlled limit. The competition factors k_{-1}/k_2 can be also obtained with less accuracy from the ratios of the respective reagents' k_Y values. Thus, $k_{Y(dmna)}/k_{Y(CN^-)} = 185/38 \simeq 5$, which roughly agrees with $k_{-1}/k_2 = k_{(dmna)}/k_{CN^-} = 9{\cdot}2$ (Table 1, columns 6 and 7).

The diffusion-controlled rate constant is given by Smoluchowski's equation, but if two reactants are both ions the equation must be modified to take account of the interionic forces.[8] For reactions between oppositely charged ions, the diffusion-controlled rate constant is increased,[8] as compared with that of neutral species, by a factor up to *ca.* 10, depending on the ' reaction distance ' (= diameter of the reacting particles treated as spheres). Analogously the diffusion-controlled rate constant for equally charged ions is decreased so that the variations in k_Y from 3·3 (for SO_3^{2-}) to 550 l mol^{-1} s^{-1} (for mpz) are roughly what one would expect. Table 2 shows that there was no correlation between k_Y and the basicity of the reagents.

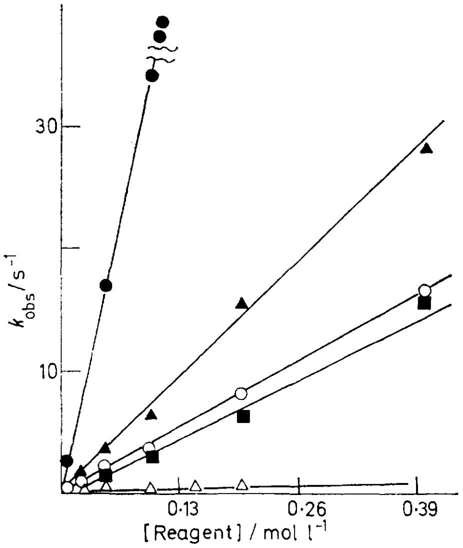

FIGURE 2 Dependence of $k_{obs.}$ on [Reagent] in the replacement of water in 3×10^{-6}M-$[Fe(CN)_5OH_2]^{3-}$ at 25 °C, pH 10·8 ($Na_2B_4O_7,10H_2O$–NaOH buffer), and 1M ionic strength (maintained with $NaClO_4$) in aqueous solution. Reagents: (●), 3-CNpy (the last two points of this line are plotted schematically, the actual parameters being $k_{obs.}/s^{-1} = 70$ and 200 at 0·15 and 0·53M-reagent); (▲), SCN^-; (○), NO_2^-; (■), CN^-; and (△), SO_3^{2-}

TABLE 2

Variation of pK_a and k_Y values for the reaction between Y^n and $[Fe(CN)_5OH_2]^{3-}$ at 25 °C. For experimental conditions see Table 1

Y^n	k_Y/l mol^{-1} s^{-1}	pK_a
CN^-	38	9·1 [a]
SO_3^{2-}	3·3	9·1 [a]
dmna	184	4·0 [b]
NO_2^-	42	3·4 [a]
3-CNpy	370	1·35 [c]
SCN^-	64	−0·7 [a]

[a] F. Basolo and R. G. Pearson, ' Mechanism of Inorganic Reactions,' 2nd edn., Wiley, New York, 1967, p. 140. [b] J. N. Pring, *Trans. Faraday Soc.*, 1924, **19**, 705. [c] A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, 1964, 3591.

DISCUSSION

The great body of data which has been recently accumulated on reactions of pentacyanoferrate(II) complexes [1-4] supports the dissociative mechanism. A dissociative mechanism has also been suggested [9] for monosubstitution in the complexes $[Fe(Hdpg)_2L_2]$ [Hdpg = diphenylglyoximato(1−); L = py or its derivatives, or PPh_3]. The question remains: do the kinetic data enable one to distinguish between *D* (dissociative) and I_d (interchange dissociative) mechanisms? [10] It has already been pointed out that variations in k_Y are determined by changes in k_2, which is the second-order rate constant for attack of the entering ligand on the five-co-ordinate intermediate. The I_d mechanism can explain equally well all the experimental data. In this case replacement of X^m by Y^n may be depicted by equations (5) and (6). This reaction scheme is also consistent with

$$[Fe(CN)_5X]^{(3+m)-} + H_2O \rightleftharpoons [Fe(CN)_5OH_2]^{3-} + X^m \quad (5)$$

$$[Fe(CN)_5OH_2]^{3-} + Y^n \rightleftharpoons [Fe(CN)_5Y]^{(3+n)-} + H_2O \quad (6)$$

the limiting rates observed at increased Y^n concentrations. Equation (6) can explain equally well the observed second-order kinetics for replacement reactions of the aqua-complex with various entering reagents. We may conclude that our kinetic results, including those in the literature, do not allow one to distinguish between the *D* and I_d mechanisms. Presently, all that we can do is to argue, as analogously done for substitution reactions in penta-amineaquaruthenium(II) complexes,[11] that if an I_d mechanism is operating and an entering ligand is positively charged, an outer-sphere complex with $[Fe(CN)_5OH_2]^{3-}$ will be formed, which should be reflected in a large change in k_Y, relative to the uncharged or negatively charged entering ligands. Table 1 shows that changes in k_Y exist, but they are probably too small for an I_d mechanism and we prefer to interpret the variations in k_Y as being due to variations in the diffusion rates of the intermediate and the entering ligands.

EXPERIMENTAL

Materials.—All chemicals were of Merck analytical purity, except sodium thiocyanate and 3-cyanopyridine (3-CNpy), which were twice recrystallized from water. Nitrosobenzene and *NN*-dimethyl(*p*-nitroso)aniline (dmna) were prepared as

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[8] P. Debye, *Trans. Electrochem. Soc.*, 1942, **82**, 265; M. Eigen, *Z. Elektrochem. Ber. Bunsengesellschaft Phys. Chem.*, 1960, **64**, 115; D. N. Hague, ' Fast Reactions,' Wiley–Interscience, New York, 1971, pp. 12—14.

[9] L. Vaska and T. Yamagi, *J. Amer. Chem. Soc.*, 1971, **93**, 6673.

[10] Symbolism given by C. H. Langford and H. B. Gray, ' Ligand Substitution Processes,' W. A. Benjamin, New York, 1965.

[11] R. J. Allen and P. C. Ford, *Inorg. Chem.*, 1972, **11**, 679.

described in the literature.[12] Trisodium amminepentacyanoferrate(II) was prepared according to the procedure of Kenney *et al.*[13] It was recrystallized several times from saturated ammonia solution at ice-bath temperature.[3] Trisodium pentacyano(nitrosobenzene)ferrate(II) was prepared according to the literature.[5] Trisodium pentacyano-[*NN*-dimethyl(*p*-nitroso)aniline]ferrate(II) dihydrate was prepared by mixing a cold aqueous solution of $[Fe(CN)_5NH_3]^{3-}$ and a saturated aqueous–ethanolic (1 : 1) solution of dmna. The ligand was in 50 times molar excess. The mixture was kept for *ca.* 3 h at ice-bath temperature and the reaction product was precipitated with cold ethanol, filtered off, quickly dissolved in a minimum amount of cold water, and recrystallized on addition of ethanol at −10 °C. The crystals were washed with chloroform in order to remove organic impurity. The i.r. spectra were recorded in KBr pellets: ν(CN) at 2 108w and 2 052vs cm^{-1} {Found: C, 33·95; H, 3·30; Fe, 12·85; N, 21·8. $Na_3[Fe(CN)_5(C_8H_{10}N_2O)],2H_2O$ requires C, 34·5; H, 3·10; Fe, 12·3; N, 21·65%}. The complex $Na_5[Fe(CN)_5SO_3],4H_2O$ was prepared as previously described.[2]

Kinetics.—The aquapentacyanoferrate(II) complex was freshly prepared [3] by dissolving $Na_3[Fe(CN)_5NH_3]$ in a previously thermostatted sodium perchlorate solution of 1M ionic strength at pH 10·80 (disodium tetraborate–sodium hydroxide buffer). The concentration of the complex was 6×10^{-6}M. Stopped-flow measurements were made in *ca.* 10—15 min, the time needed for the amino-complex to aquate to $[Fe(CN)_5OH_2]^{3-}$.[3] The aqua-complex, obtained in this way and being in such a small concentration, was stable for the period of time needed for stopped-flow measurements. When $[Fe(CN)_5OH_2]^{3-}$ was in a concentration larger than that cited, the polymerization process [14] became so extensive that the measurements were not reproducible.

The kinetic measurements of the rate of replacement of water with thiocyanate, cyanide, nitrite, and sulphite ions were followed at 434 nm, because that wavelength is the isosbestic point for conversion of $[Fe(CN)_5OH_2]^{3-}$ to binuclear $[Fe_2(CN)_{10}]^{6-}$. Reactions of $[Fe(CN)_5OH_2]^{3-}$ with 3-CNpy, PhNO, and dmna were followed at 414, 530, and 670 nm, respectively. The pseudo-first-order rate constants, $k_{obs.}$, were obtained by plotting ln $(A - A_t)$ against time, where A is the measured absorbance at time t. Each second-order rate constant k_Y reported in Table 1 was obtained from the gradient of a plot of $k_{obs.}$ against [Y].

Spectrophotometry.—Absorption spectra were recorded using a Cary 16 K spectrophotometer, and i.r. spectra on a Perkin-Elmer 457 grating spectrophotometer. Stopped-flow spectrophotometer Durrum-D-110 was used for following the fast replacements of water in $[Fe(CN)_5OH_2]^{3-}$.

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[12] A. I. Vogel, 'A Textbook of Practical Organic Chemistry,' 2nd edn., Longmans, London, 1951, pp. 550, 603, and 622.

[13] D. J. Kenney, T. P. Flynn, and J. B. Gallini, *J. Inorg. Nuclear Chem.*, 1961, **20**, 75.

[14] G. Emschwiller, *Compt. rend.*, 1969, **C268**, 694.