Kinetics and Mechanism of Replacement of Sulphite in the Pentacyano(sulphito)ferrate(II) Ion by Cyanide Ion

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The kinetics of replacement of sulphite by cyanide ion in $Na_5[Fe(CN)_5SO_3]$ in aqueous solution follow the rate law $-d\ln[Fe(CN)_5SO_3{}^{5-}]/dt = k_1k_2[CN^-]/(k_{-1}[SO_3{}^{2-}] + k_2[CN^-])$, which is consistent with reactions (i) and (ii).

$$[Fe(CN)_5SO_3]^{5-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + SO_3{}^{2-} \qquad (i)$$

$$[Fe(CN)_5]^{3-} + CN^- \xrightarrow{k_2} [Fe(CN)_6]^{4-} \qquad (ii)$$

At 43 °C, pH 10·80, and 1M ionic strength $k_1 = (9{\cdot}50 \pm 0{\cdot}21) \times 10^{-4}\ s^{-1}$. The $[Fe(CN)_5]^{3-}$ intermediate is sufficiently long-lived to exhibit selective reactivity toward different reagents as shown by the competition factor $k_2/k_{-1} = 8{\cdot}76 \pm 0{\cdot}53$. The kinetic data are considered as evidence for a limiting S_N1 mechanism. The competition factor has been interpreted in terms of free-energy changes resulting from desolvation processes of the competitors.

SUBSTITUTION reactions of octahedral complexes generally occur by a predominantly bond-breaking mechanism. In the case of extensive ion-pair formation distinction between the limiting S_N1 (or *D*) [1] mechanism and a dissociative-interchange [1] (or I_D) mechanism is extremely difficult, since the empirical form of the rate law will be the same for both mechanisms.[2] To avoid the complications of ion-pairing anionic aquopentacyanocobaltate(III) has been used [3] and it has been found that replacement of water by azide and thiocyanate ions occurs by a limiting S_N1 mechanism. Another very clear example [4] of the limiting S_N1 mechanism with no ion-pairing involves activation by $SO_3{}^{2-}$ in the systems *trans*-$[Co(CN)_4SO_3X]^{n-}$ ($X = CN^-, NCS^-, NH_3, OH^-, N_3{}^-, NO_2{}^-, SO_3{}^{2-}$). Recent reviews [2,5] cover the literature in this area.

In a previous paper [6] a limiting S_N1 mechanism was proposed for replacement of nitrosobenzene by cyanide ion in the pentacyano(nitrosobenzene)ferrate(II) ion. This reaction was not complicated by ion-pair formation either since CN^- does not form ion-pairs with the negatively charged complex. Kinetic studies of ligand replacements in a number of pentacyanoferrate(II) complexes of pyridine, pyrazine, and related aromatic nitrogen heterocycles have been recently reported and the data interpreted in terms of a limiting S_N1 mechanism.[7] Further support for the limiting S_N1 mechanism is now provided by showing that the pentacyano-intermediate is sufficiently long-lived to exhibit a selective reactivity toward different nucleophiles (cyanide and sulphite ions).

RESULTS

The kinetics of replacement of sulphite by cyanide ion in $Na_5[Fe(CN)_5SO_3]$ in aqueous solution was studied spectrophotometrically at 43 °C and 1M ionic strength (maintained with sodium perchlorate) at pH 10·80 (in $Na_2B_4O_7$–NaOH buffer). Figure 1 shows the change in absorption spectrum of the reaction solution during replacement, and the isosbestic point at 338 nm. The spectrum of the reaction solution after 10 half-lives was practically identical to that of $[Fe(CN)_6]^{4-}$ ion under the reaction conditions, showing that replacement of sulphite by cyanide ion is practically complete. The reaction rate was followed by measuring the change in absorption of the reaction solution at 370 nm, where the difference in absorption is large. It was found

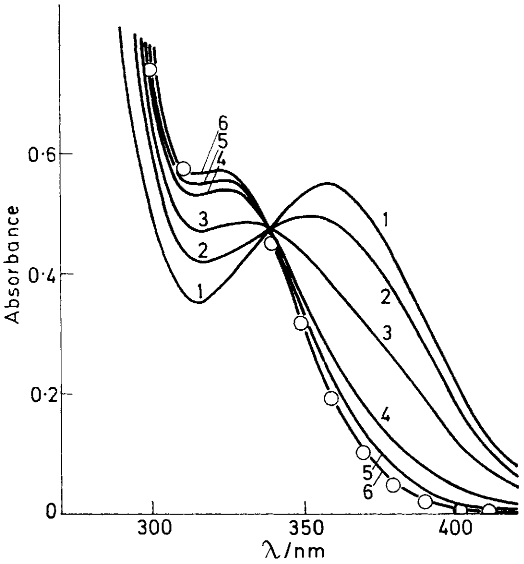

FIGURE 1 Absorption spectra at pH 10·80 (in $Na_2B_4O_7$–NaOH buffer), 1M ionic strength (maintained with $NaClO_4$) and 40 °C using 1 cm quartz cells: (1), 0·00175M-$Na_5[Fe(CN)_5SO_3]$ in absence of cyanide reagent; (2)—(5), complex solution, containing 0·0836M-NaCN, in the course of reaction; (6), 0·00175M-$[Fe(CN)_6]^{4-}$ ion under reaction conditions

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

[2] J. E. Byrd and W. K. Wilmarth, *Inorg. Chim. Acta, Rev.* 1971, **5**, 7.

[3] A. Haim and W. K. Wilmarth, *Inorg. Chem.*, 1962, **1**, 573; R. Grassi, A. Haim, and W. K. Wilmarth, *ibid.*, 1967, **6**, 237.

[4] D. R. Stranks and J. Yandell, *Inorg. Chem.*, 1970, **9**, 751.

[5] (*a*) A. M. Sargeson, *Pure Appl. Chem.*, 1973, **33**, 527; (*b*) C. K. Poon, *Co-ordination Chem. Rev.*, 1973, **10**, 1.

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

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

that the reaction was first order in complex and zero order in cyanide when the cyanide-ion concentration was greater than 0·005M (Figure 2).

The following reaction scheme involving a five-coordinate intermediate is proposed. The reverse of reaction

$$[Fe(CN)_5SO_3]^{5-} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} [Fe(CN)_5]^{3-} + SO_3^{2-} \qquad (1)$$

$$[Fe(CN)_5]^{3-} + CN^- \xrightarrow{k_2} [Fe(CN)_6]^{4-} \qquad (2)$$

(2) can be neglected since aqueous solutions of hexacyanoferrate(II) are very stable if not exposed to u.v. light or the catalytic action of metal ions.[8] The $[Fe(CN)_5]^{3-}$ intermediate is thermodynamically unstable and the steady-state approximation is applicable. The rate of disappearance of the pentacyanosulphito-complex is given by equation (3).

$$-d[Fe(CN)_5SO_3^{5-}]/dt = \frac{k_1k_2[CN^-][Fe(CN)_5SO_3^{5-}]}{k_{-1}[SO_3^{2-}] + k_2[CN^-]} \qquad (3)$$

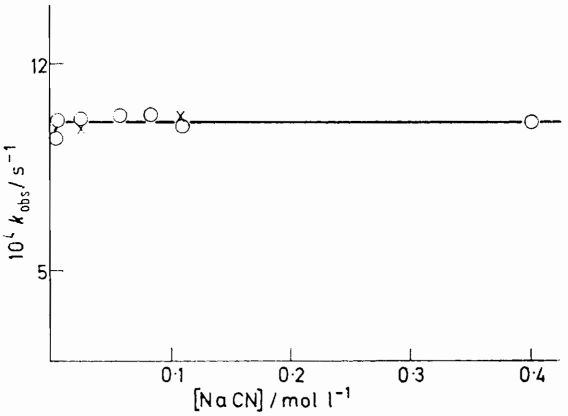

FIGURE 2 Cyanide-ion dependence of the rate of replacement of sulphite by cyanide ion in 0·000625 (×) and 0·0025M-$Na_5[Fe(CN)_5SO_3]$ (○) at 43 °C, pH 10·80, and I = 1M (maintained with $NaClO_4$)

Since k_2 is about nine times larger than k_{-1}, a small excess of CN^- over SO_3^{2-} makes $k_{obs} \simeq k_1$, *i.e.* independent of CN^- concentration, as in Figure 2. From rate law (3), equation (4) is obtained which shows that $1/k_{obs}$ is a linear

$$\frac{1}{k_{obs}} = \frac{1}{k_1} + \frac{k_{-1}}{k_1k_2}\cdot\frac{[SO_3^{2-}]}{[CN^-]} \qquad (4)$$

function of $1/[CN^-]$ if $[SO_3^{2-}]$ is made constant by addition of Na_2SO_3. Analogously by plotting $1/k_{obs}$ against $[SO_3^{2-}]$ for complex solutions containing excess of NaCN a straight line should be obtained. The procedure is essentially similar to that previously used[3,9] for a limiting S_N1 mechanism involving $[Co(CN)_5]^{2-}$ and $[Co(NH_3)_4SO_3]^+$ intermediates. The kinetic results are collected in Figures 3—5. It can be seen that good straight lines are obtained in all six cases. The three lines in Figure 3 have the same intercept, determined by the least-squares method, and the corresponding value of k_1 is $(9·55 \pm 0·29) \times 10^{-4}$ s^{-1}. From the gradients of the straight lines $k_2/k_{-1} = 9·15 \pm 0·69$ (uncertainties are standard errors of the mean). Analogously the data from Figure 4 gave $k_1 = (9·46 \pm 0·36) \times 10^{-4}$ s^{-1} and $k_2/k_{-1} = 8·25 \pm 1·22$. Average values of k_1 and k_2/k_{-1} from the seven straight lines are $(9·50 \pm 0·21) \times 10^{-4}$ s^{-1} and $8·76 \pm 0·53$ respectively.

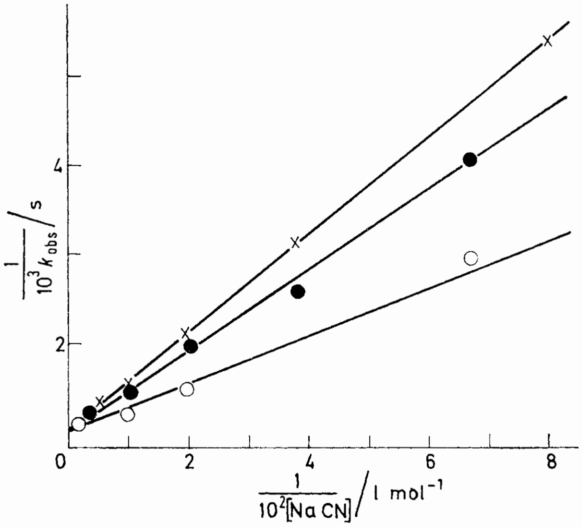

FIGURE 3 Dependence of $1/k_{obs}$ against $1/[CN^-]$ in the replacement of sulphite by cyanide ion in 0·000625M-$Na_5[Fe(CN)_5SO_3]$ at 43 °C, pH 10·80, I = 1M (maintained with $NaClO_4$), and constant sulphite-ion concentration: (○), 0·0220; (●), 0·0350; (×) 0·0509M-Na_2SO_3

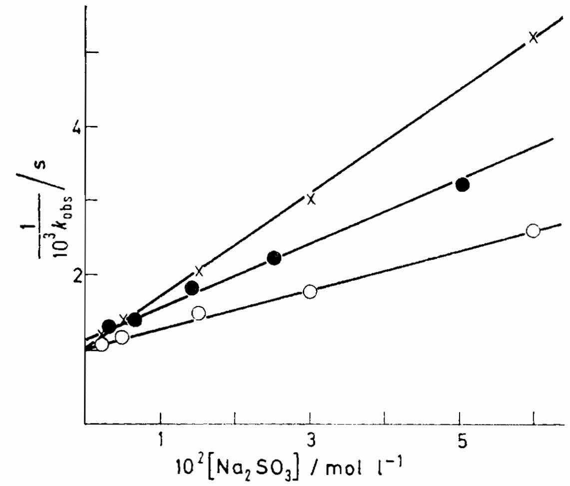

FIGURE 4 Dependence of $1/k_{obs}$ against sulphite-ion concentration in the replacement of sulphite by cyanide ion in $Na_5[Fe(CN)_5SO_3]$ at 43 °C, pH 10·80, I = 1M (maintained with $NaClO_4$), and constant cyanide-ion concentration: (○), [Complex] = 0·00085, $[CN^-]$ = 0·0055M; (●), [Complex] = 0·00125, $[CN^-]$ = 0·00275M; (×), [Complex] = 0·000625, $[CN^-]$ = 0·00196M

DISCUSSION

Legros[10] has studied the aquation of pentacyano(sulphito)ferrate(II) ion. The energy of activation, frequency factor, and entropy of activation at 20 °C were determined as 28 kcal mol^{-1}, 5×10^{17} s^{-1}, and 20·5

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[8] S. Ašperger, I. Murati, and D. Pavlović, *J. Chem. Soc.* (*A*), 1969, 2044.

[9] J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Amer. Chem. Soc.*, 1966, **88**, 2877.

[10] J. Legros, *J. Chim. phys.*, 1964, **61**, 923.

cal K^{-1} mol^{-1}. No final conclusion regarding the mechanism was made, but an S_N2 mechanism was favoured, though the positive entropy of activation could be better understood in terms of a *D* mechanism. Bimolecular solvolysis was also anticipated for the $[Fe(CN)_5SO_3H]^{4-}$ ion.[11] A dissociative mechanism has been recently proposed[12] for the reaction $[Fe(CN)_5(py)]^{3-}$ + $^{14}CN^-$ (py = pyridine) and it was suggested that the replacement reaction is accompanied by a ligand-exchange reaction in the very reactive $[Fe(CN)_5]^{3-}$ intermediate. Arguments in favour of a limiting S_N1 mechanism appeared inconclusive.

A competition factor $k_{CN^-}/k_{H_2O} = 1{\cdot}2 \times 10^4$ for reaction with the $[Fe(CN)_5{}^{3-}]$ intermediate has been previously determined.[6] From the competition factor at 43 °C $k_2/k_{-1} = k_{CN^-}/k_{SO_3{}^{2-}} = 8{\cdot}8$ it follows that the relative order of reactivity is $k_{H_2O} : k_{SO_3{}^{2-}} : k_{CN^-} = 1 : 7{\cdot}6 \times 10^4 : 6{\cdot}7 \times 10^5$. The competition factor $k_{CN^-}/k_{SO_3{}^{2-}}$ for the $[Co(CN)_4SO_3]^{3-}$ intermediate of *ca.* **13·4** at 25 °C (as calculated from competition factors for these anions and water[2]) is near to the value of 8·8 for the $[Fe(CN)_5]^{3-}$ intermediate. (The ratio 13·4 : 8·8 might change somewhat if the competition factors were determined at the same temperature.) If water is also considered as a competitor for the $[Co(CN)_4SO_3]^{3-}$ intermediate the order of reactivity is $k_{H_2O} : k_{SO_3{}^{2-}} : k_{CN^-} = 1 : 146 : 1\,960$. It has been suggested that competition factors in dissociative-type processes are mainly determined by free-energy changes resulting from desolvation processes of the competitors.[5a,12] Since the competition factors $k_{CN^-}/k_{SO_3{}^{2-}}$ for both $[Fe(CN)_5]^{3-}$ and $[Co(CN)_4SO_3]^{3-}$ intermediates are similar (8·8 and 13·4) it could be inferred that there is little bonding in the transition states of these intermediates with CN$^-$ and $SO_3{}^{2-}$. On the other hand the ability of water to compete is much better for $[Co(CN)_4SO_3]^{3-}$ than for $[Fe(CN)_5]^{3-}$. It is interesting to note that the competition factor k_{CN^-}/k_{H_2O} for carbonium ion[13] is *ca.* 3·5 × 10^5 at 23 °C, a value very near to that for the $[Fe(CN)_5]^{3-}$ intermediate[6] (6·7 × 10^5). It is possible that water behaves specially in the case of the $[Co(CN)_4SO_3]^{3-}$ intermediate due to hydrogen bonding to the sulphito-oxygen atoms which might help water to co-ordinate. Another possibility is that the $[Co(CN)_4SO_3]^{3-}$ intermediate is especially reactive and nucleophiles do not get a chance to exert their characteristics.

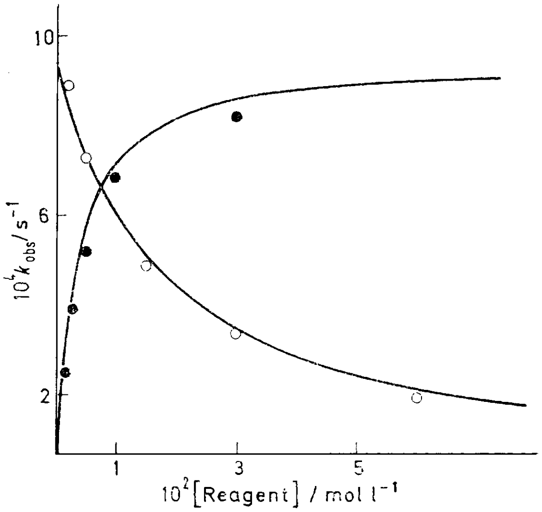

FIGURE 5 Dependence of k_{obs} on cyanide-ion concentration (●) at 0·035M-Na_2SO_3 (the full line has been drawn through the data points using values of the kinetic parameters) (reaction conditions as in Figure 3) and dependence of k_{obs} on sulphite-ion concentration (○) at 0·00196M-NaCN (the full line is the theoretical one) (reaction conditions as in Figure 4)

EXPERIMENTAL

All chemicals used were of analytical grade. Double distilled water was used throughout. The complex $Na_5[Fe(CN)_5SO_3],4H_2O$ was prepared according to Hofmann's procedure.[14] The crude product contained light yellow crystals of the complex and white crystals (mainly sodium sulphate). The method of purification of the complex was modified as follows. The white crystals were separated from crystals of the complex in a separating funnel using cold aqueous ethanol (75%). The crystals of the complex formed the 'upper layer.' The sedimentation process was repeated several times. The complex was dissolved in a minimum amount of cold water and precipitated as soon as possible with cold ethanol. The purification procedure through precipitation was repeated five times. The complex was dried over $CaCl_2$ *in vacuo* {Found: C, 13·15; H, 1·95; Fe, 12·25; N, 15·0. $Na_5[Fe(CN)_5SO_3],4H_2O$ requires C, 13·25; H, 1·80; Fe, 12·35; N, 15·45%}.

Kinetics.—A weighed quantity of the sulphito-complex, sodium cyanide, and, in competition experiments, sodium sulphite was transferred to a dry thermostatted calibrated flask at 43 ± 0·1 °C. In a separate flask disodium tetraborate–sodium hydroxide buffer solution was thermally equilibrated at the same temperature and quickly poured into the calibrated flask. The salt dissolved instantaneously. The reaction solution was quickly transferred to a thermostatted absorption cell of a Cary 16K spectrophotometer fitted with an automatic sample change. The thermostatted cell holder, in conjunction with a Hoepler ultra-thermostat, allowed temperature control of the reaction solution to within ±0·1 °C. The temperature of the reaction solution was measured with a thermometer immersed in a neighbouring absorption cell of the automatic sample changer.

Spectra.—Absorption spectra were obtained with a Cary 16K spectrophotometer (10 mm quartz cells) and i.r. spectra with a Perkin-Elmer 457 grating spectrophotometer using KBr pellets.

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