Reinvestigation of the Reaction between Hexacyanoferrate(III) and Sulphite Ions

By Robin S. Murray, Department of Chemistry, The University of Hull, Hull HU6 7RX

A reinvestigation of the reduction of $[Fe(CN)_6]^{3-}$ by SO_3^{2-} has shown that the previously reported intermediate species is formed by reaction between $[Fe(CN)_6]^{3-}$ and $SO_3^{-\bullet}$ radical ions.

IN previous publications [1,2] the mechanism in Scheme 1 was proposed for reduction of $[Fe(CN)_6]^{3-}$ by SO_3^{2-} in aqueous solution. It was shown that under conditions

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \rightleftharpoons [Fe(CN)_5(CN{\cdot}SO_3)]^{5-} \qquad (1)$$

$$[Fe(CN)_6]^{3-} + [Fe(CN)_5(CN{\cdot}SO_3)]^{5-} \rightleftharpoons [Fe(CN)_6]^{4-} + [Fe(CN)_5(CN{\cdot}SO_3)]^{4-} \qquad (2)$$

$$[Fe(CN)_5(CN{\cdot}SO_3)]^{4-} + H_2O \longrightarrow [Fe(CN)_6]^{4-} + SO_4^{2-} + 2H^+ \qquad (3)$$

SCHEME 1

where $[Na^+]$ and $[SO_3^{2-}]$ are high (*ca.* 1M),† the rate of formation of $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ is much faster than its subsequent hydrolysis to $[Fe(CN)_6{}^{4-}]$ and SO_4^{2-} The results of further experiments indicated that the species $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ is formed by reaction of a $SO_3^{-\bullet}$ radical ion with $[Fe(CN)_6]^{3-}$ *via* the sequence in Scheme 2. The aim of this publication is to substantiate the latter mechanism.

$$[Fe(CN)_6]^{3-} + SO_3^{2-} \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} [Fe(CN)_6]^{4-} + SO_3^{-\bullet} \qquad (4)$$

$$[Fe(CN)_6]^{3-} + SO_3^{-\bullet} \xrightarrow{k_5} [Fe(CN)_5(CN{\cdot}SO_3)]^{4-} \qquad (5)$$

SCHEME 2

EXPERIMENTAL

With the exception of $K_3[Co(CN)_6]$ (B.D.H., laboratory reagent) and allyl alcohol (May and Baker; laboratory reagent, redistilled), all chemicals were AnalaR grade. Water used for kinetic experiments was triply distilled, and doubly distilled water was used for the experiments with allyl alcohol. Ethylenediaminetetra-acetic acid (H_4edta) (*ca.* 5×10^{-5}M) was added to all solutions to complex trace amounts of heavy metals.

Kinetic experiments were carried out on a Durrum D-110 stopped-flow spectrophotometer at 420 nm, the absorption maximum of $[Fe(CN)_6]^{3-}$ (ε 1 000 l mol^{-1} cm^{-1}). For the equilibrium studies with allyl alcohol, an appropriate allyl alcohol solution (1·0 cm^3) was mixed with a solution (5·0 cm^3) of $K_3[Fe(CN)_6]$ in 2·53M-KCl. Then a solution (5·0 cm^3) of Na_2SO_3 (0·433M) was added, the mixture shaken, and transferred to a 1 cm optical cell. Optical-density measurements were made on a Hilger and Watts Uvispek spectrophotometer at 370 nm within 2 min of mixing the solutions in order to minimise inaccuracies due to the slow hydrolysis [2] of $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ {ε 44 and 225 l mol^{-1} cm^{-1} respectively at 370 nm for $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$}.

RESULTS AND DISCUSSION

(a) *Retardation of the Rate of Reaction by Hexacyanoferrate*(II).—Swinehart [3] showed that the presence of $[Fe(CN)_6]^{4-}$ (0·010M) led to a reduction in rate, $-d[Fe(CN)_6{}^{3-}]/dt$, of *ca.* 12% under conditions where the initial concentration of $[Fe(CN)_6]^{3-}$ was $9{\cdot}6 \times 10^{-4}$M. It was pointed out that, although this could imply a radical mechanism, a retardation of this magnitude could also be due to medium effects.

The present work was carried out at a higher ionic strength and $K_3[Co(CN)_6]$ and KCl were used to compensate for changes in $[K^+]$ caused by the addition of $K_4[Fe(CN)_6]$ in the range 0·010—0·050M. It has been shown [3] that the rate of reaction in the absence of added $[Fe(CN)_6]^{4-}$ is directly proportional to the concentration of univalent metal ions (M^+). It was therefore desirable to minimise the changes in concentration of these ions in the investigation of the dependence of the rate of reaction on the concentration of hexacyanoferrate(II). Under the conditions chosen, where $[K^+] \simeq$ 1·0M, it may be assumed [3,4] that the primary association between K^+ and $[Fe(CN)_6]^{4-}$ is complete. A value for the second association constant for the equilibrium giving $K_2[Fe(CN)_6]^{2-}$ does not appear to have been reported, and this equilibrium was ignored in the following experiments. When $K_3[Co(CN)_6]$ was used to buffer changes in the concentration of K^+, $[K_3Co(CN)_6] + [K_4Fe(CN)_6] = 0{\cdot}050$M, whereas when KCl was used $[KCl] = 3\{0{\cdot}050 - [K_4Fe(CN)_6]\}$.

In the absence of any added $[Fe(CN)_6]^{4-}$, first-order plots of the decay of the $[Fe(CN)_6]^{3-}$ absorption at 420 nm were linear (Figure 1) {although slight negative curvature was observed in some runs when $K_3[Co(CN)_6]$ was present and this will be discussed below}. Values of k_4 [$= -2{\cdot}303 \times$ (Gradient)/2] are quoted in the Table. Swinehart showed that, in the absence of added $K_4[Fe(CN)_6]$, the reaction obeys rate law (6) where the

$$-d[Fe(CN)_6{}^{3-}]/dt = k_M[M^+][SO_3^{2-}][Fe(CN)_6{}^{3-}] \qquad (6)$$

specific rate constants k_M are equal to $0{\cdot}52 \pm 0{\cdot}02$ and $1{\cdot}15 \pm 0{\cdot}04$ l^2 mol^{-2} s^{-1} for Na^+ and K^+ respectively at 25 °C. Under conditions where both Na^+ and K^+ are present, $2k_4 = k_{Na}[Na^+] + k_K[K^+]$. Using this expression k_4 was calculated to be $0{\cdot}77 \pm 0{\cdot}03$ l mol^{-1} s^{-1} under the conditions quoted in the Table. The slight discrepancy between this value and that quoted in the Table of $0{\cdot}96 \pm 0{\cdot}02$ l mol^{-1} s^{-1} may be due to the effect of chloride ions; Swinehart worked in the absence of anions other than sulphite. Alternatively, the difference may be due to the higher ionic strengths used in this work. There was no significant difference between

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† 1M = 1 mol dm^{-3}.

[1] R. S. Murray, *Chem. Comm.*, 1968, 824.

[2] J. M. Lancaster and R. S. Murray, *J. Chem. Soc.* (*A*), 1971, 2755.

[3] J. H. Swinehart, *J. Inorg. Nuclear Chem.*, 1967, **29**, 2313.

[4] 'Stability Constants of Metal-Ion Complexes,' *Chem. Soc. Special Publ.* No. 25, The Chemical Society, 1971.

the values of k_4 found using 1·15M-KCl and 1·00M-KCl + 0·050M-$K_3[Co(CN)_6]$. However, (6) predicts that even if $K_3[Co(CN)_6]$ was completely converted to $K[Co(CN)_6]^{2-}$ under the conditions chosen this would lead to a reduction in rate of only 5%.

Figure 1 shows the effect of added $K_4[Fe(CN)_6]$ on first-order plots of the consumption of $[Fe(CN)_6]^{3-}$ with time. Marked curvature is evident which is more pronounced at higher concentrations of $K_4[Fe(CN)_6]$. Scheme 2 gives the rate expression (7). An integrated

$$\frac{-d[Fe(CN)_6^{3-}]}{dt} = \frac{2k_4k_5[Fe(CN)_6^{3-}]^2[SO_3^{2-}]}{k_5[Fe(CN)_6^{3-}] + k_{-4}[Fe(CN)_6^{4-}]} \quad (7)$$

form of (7) under conditions where $[SO_3^{2-}]$ and $[Fe(CN)_6^{4-}]$ are constant is (8).

$$k_{-4}[Fe(CN)_6^{4-}]/[Fe(CN)_6^{3-}]2{\cdot}303k_5 = \log [Fe(CN)_6^{3-}] + (2k_4[SO_3^{2-}]t/2{\cdot}303) + \text{constant} \quad (8)$$

Plots of $[Fe(CN)_6^{3-}]^{-1}$ against $\log [Fe(CN)_6^{3-}] + (2k_4[SO_3^{2-}]t/2{\cdot}303)$ for concentrations of $K_4[Fe(CN)_6]$ in the range 0·010—0·050M were linear in experiments where KCl was used to buffer changes in $[K^+]$ and the gradients of these plots, together with calculated values of k_{-4}/k_5, are given in the Table. From these data the order in $[Fe(CN)_6^{4-}]$ in (8) was found to be −(0·90 ± 0·06). In runs where $K_3[Co(CN)_6]$ was present, some curvature of plots of (8) was observed, although the gradients of these plots in the initial stages approached those containing KCl. It is possible that the curvature of these plots and the first-order plots for runs where $[Co(CN)_6^{3-}]$ = 0·050M may be due to competition of this ion with $[Fe(CN)_6]^{3-}$ and $[Fe(CN)_6]^{4-}$ for $SO_3^{-\bullet}$ radicals, perhaps leading to formation of a transient species $[Co(CN)_5(CN{\cdot}SO_3)]^{4-}$.

Kinetic data[a] at 25·0 ± 0·1 °C

Expt.	$10^4[K_3Fe(CN)_6]$/M	[KCl]/M	$[K_3Co(CN)_6]$/M	$[K_4Fe(CN)_6]$/M	10^2k_4/l mol^{-1} s^{-1}	$\frac{10^6k_{-4}[Fe(CN)_6^{4-}]/\text{mol l}^{-1}}{2{\cdot}303\,k_5}$	$10^4k_{-4}/k_5$
(1)	3·3	1·150			96 ± 2[b]		
(2)	3·6	1·150			98[c]		
(3)	3·3	1·000	0·050		88 ± 8[d]		
(4)	3·7	1·000		0·050		106 ± 1·5[e]	49 ± 1·5[f]
(5)	3·7	1·030		0·040		90·4 ± 1·8[e]	52 ± 2·0
(6)	3·5	1·075		0·0250		54·2 ± 0·5[e]	50 ± 3·0
(7)	3·7	1·100		0·0167		36·8 ± 0·8[e]	51 ± 3·5
(8)	3·1	1·120		0·0100		25·8 ± 0·7[e]	59 ± 4·0
(9)	3·5	1·000	0·0250	0·0250		60·1	56 ± 12
(10)	3·5	1·000	0·0400	0·0100		26·3	60 ± 16

[a] Dioxygen was excluded from the solutions; $[Na_2SO_3]$ = 0·197M. [b] A value of k_4 = 0·96 l mol^{-1} s^{-1} was used in the calculations for experiments (4)—(8). [c] The solution contained 0·147M-allyl alcohol. [d] A value of k_4 = 0·88 was used in the calculations for experiments 9 and 10. [e] From least-squares calculations. [f] Error includes the uncertainty in k_4.

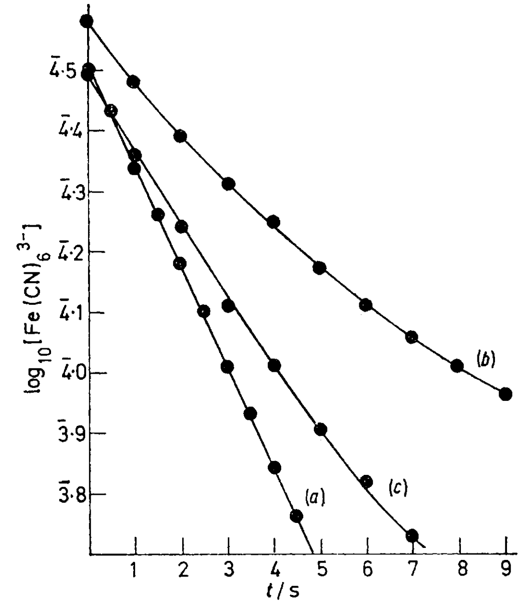

FIGURE 1 Effect of added $[Fe(CN)_6]^{4-}$ on the reaction rate at 25 °C and 0·197M-Na_2SO_3: (*a*), $[K_3Fe(CN)_6] = 3{\cdot}3 \times 10^{-4}$ and [KCl] = 1·50; (*b*), $[K_3Fe(CN)_6] = 3{\cdot}7 \times 10^{-4}$, [KCl] = 1·000, and $[K_4Fe(CN)_6]$ = 0·0500M; (*c*), $[K_3Fe(CN)_6] = 3{\cdot}1 \times 10^{-4}$, [KCl] = 1·120, and $[K_4Fe(CN)_6]$ = 0·0100M

Dioxygen had a slight retarding effect on the rate of reaction and the value of k_4 was reduced by *ca.* 5—7% in the presence of atmospheric amounts of the gas. The effect was much less than in the oxidation[5] of SO_3^{2-} by $[IrCl_6]^{2-}$ where the rate of reaction was reduced by a factor of 2. The mechanism of this reaction, which is also believed to involve formation of $SO_3^{-\bullet}$ radical ions, differs from the $[Fe(CN)_6]^{3-}$–SO_3^{2-} reaction in the second stage; the former is probably outer-sphere oxidation of the radical ion by $[IrCl_6]^{2-}$ to give SO_4^{2-}, whereas in the latter addition of the radical to $[Fe(CN)_6]^{3-}$ occurs.

Scheme 1, which leads to the same overall stoicheiometry as 2, predicts that, if the presence of $[Fe(CN)_6]^{4-}$ is to lead to a retardation in the rate of the reaction, addition of excess of $[Fe(CN)_6]^{4-}$ to mixtures of $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ should lead to formation of $[Fe(CN)_6]^{3-}$. In an experiment where a mixture of KCl (2·00), $[Fe(CN)_6]^{3-}$ (1·40 × 10^{-3}), and Na_2SO_3 (0·394M) was allowed to react to give $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ followed by addition of an equivalent volume of a solution of $[Fe(CN)_6]^{4-}$ (0·100M), no detectable $[Fe(CN)_6]^{3-}$ was produced.

(b) *Effect of Radical Scavengers on the Product Distribution.*—It has been suggested[3] that propan-2-ol is oxidised to propanone when present in a $[Fe(CN)_6]^{3-}$–SO_3^{2-} reaction mixture, and that this observation is consistent with radical formation. Here the effect of allyl alcohol on the relative concentrations of the

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[5] E. L. Stapp and D. W. Carlyle, *Inorg. Chem.*, 1974, **13**, 834.

products $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ was investigated under conditions where the rates of (4) and (5) are much faster than (3) ([KCl] = 1·15M and $[Na_2SO_3]$ = 0·197M). The data in the Table show that the presence of allyl alcohol has no effect on the rate of consumption of $[Fe(CN)_6]^{3-}$, and preliminary experiments indicated that the amount of $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ relative to $[Fe(CN)_6]^{4-}$ formed decreased with increasing concentration of allyl alcohol, (A). It is proposed that reactions (4) and (5) occur, together with those of (9)

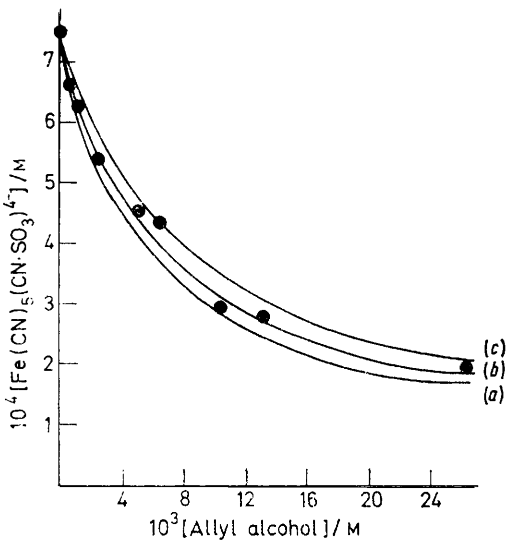

FIGURE 2 Effect of allyl alcohol on the reaction product distribution using $[K_3Fe(CN)_6] = 1{\cdot}50 \times 10^{-3}$, [KCl] = 1·15, and $[Na_2SO_3]$ = 0·197M, and k_9/k_5 = 0·10 (*a*), 0·083 (*b*), and 0·067 (*c*)

$$A + SO_3^{-\cdot} \xrightarrow{k_9} ASO_3 \qquad (9)$$

and (10). Since it has been shown that the amount of

$$[Fe(CN)_6]^{3-} + ASO_3 \xrightarrow{k_{10}} [Fe(CN)_6]^{4-} + A'SO_3 \qquad (10)$$

$S_2O_6^{2-}$ formed in the reaction is negligible [6] (except in the presence of catalysts [2]), the dimerisation reaction of $SO_3^{-\cdot}$ has been neglected. Calculations based on the value of k_{-4}/k_5 quoted in (a) showed that, in the absence of any added $K_4[Fe(CN)_6]$, the reverse of (4) may be also neglected. Under conditions where $k_4 \ll k_{-4} \ll k_9 < k_5 \ll k_{10}$, and where the concentrations of allyl alcohol and sulphite ions remain constant, the above scheme leads to expression (11). An integrated form of

$$\frac{-d[Fe(CN)_6{}^{3-}]}{d[Fe(CN)_5(CN{\cdot}SO_3)^{4-}]} = \frac{2k_5[Fe(CN)_6{}^{3-}] + 2k_9[A]}{k_5[Fe(CN)_6{}^{3-}]} \qquad (11)$$

(11) is (12), from which the theoretical dependence of

$$[Fe(CN)_6{}^{3-}]_0 - 2{\cdot}303(k_9/k_5)[A]\left\{\frac{\log\,[Fe(CN)_6{}^{3-}]_0}{(k_9/k_5)[A]} + 1\right\} = 2[Fe(CN)_5(CN{\cdot}SO_3)^{4-}]_\infty \qquad (12)$$

$[Fe(CN)_5(CN{\cdot}SO_3)^{4-}]_\infty$ on [A] may be calculated for particular values of k_9/k_5. Figure 2 shows plots of (12) for values k_9/k_5 of 0·100, 0·083, and 0·067, where $[Fe(CN)_6{}^{3-}]_0 = 1{\cdot}50 \times 10^{-3}$M. At concentrations of allyl alcohol less than 0·0133M, corrections were made to [A] in these calculations to allow for the consumption of this species during the reaction. In these cases the expression $2[A] = [A]_0 - [A]_\infty = \frac{1}{2}[Fe(CN)_6{}^{3-}]_0 - [Fe(CN)_5(CN{\cdot}SO_3)^{4-}]_\infty$ was used. The maximum correction (when $[A]_0 = 6{\cdot}7 \times 10^{-4}$M) was only 7·5% of the total initial concentration of A. Included in Figure 2 is a plot of the experimentally determined values of $[Fe(CN)_5(CN{\cdot}SO_3)^{4-}]_\infty$ against [A] and k_9/k_5 was estimated to be 0·083 ± 0·015. In experiments where $[Fe(CN)_6{}^{3-}]_0 = 3{\cdot}12 \times 10^{-3}$M and [A] = $6{\cdot}7 \times 10^{-3}$ and $1{\cdot}33 \times 10^{-2}$M, the observed concentrations of $[Fe(CN)_5(CN{\cdot}SO_3)]^{4-}$ were $1{\cdot}12 \times 10^{-3}$ and $9{\cdot}1 \times 10^{-4}$M respectively, compared to the calculated values (for k_9/k_5 = 0·083) of $1{\cdot}06 \times 10^{-3}$ and $8{\cdot}4 \times 10^{-4}$M respectively.

The nature of the product of the reaction between allyl alcohol and $SO_3^{-\cdot}$ radicals was not investigated, although a possible species is $[CH_2(OH){\cdot}CH(OH){\cdot}CH_2SO_3]$-Na. Acrylic acid and acrylamide were also found to react with the radical. However, due to the strong absorbances of the products of these reactions in the region 330—380 nm, quantitative investigations of these scavengers were not carried out.

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[6] J. Veprek Siska, D. M. Wagnerova, and K. Eckschlager, *Coll. Czech. Chem. Comm.*, 1966, **31**, 3287.