Systematic Design of Chemical Oscillators. Part 56.† Kinetics and Mechanism of the Oxidation of Hexacyanoferrate(II) by Aqueous Bromine

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The kinetics and mechanism of the reaction between aqueous bromine and hexacyanoferrate(II) ion have been studied in the pH range 0.4—2.5. The stoicheiometry of the reaction is as in equation (i).

$$Br_2(aq) + 2[Fe(CN)_6]^{4-} \longrightarrow 2Br^- + 2[Fe(CN)_6]^{3-} \qquad (i)$$

The predominant ferrocyanide species in this range are $[HFe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{2-}$. The reaction is first order in the concentrations of both bromine and ferrocyanide. At 25.0 ± 0.1 °C and ionic strength 0.5 mol dm^{-3} ($NaClO_4$) the expression for the rate of appearance of $[Fe(CN)_6]^{3-}$ is (ii) where k_2 and k_3 are the bimolecular rate constants for the reaction of bromine with $[HFe(CN)_6]^{3-}$

$$\tfrac{1}{2}d[Fe(CN)_6{}^{3-}]/dt = (k_3 + k_2K_2/[H^+])[Br_2][Fe(CN)_6{}^{4-}]/(1 + K_{eq}[Br^-]) \qquad (ii)$$

and $[H_2Fe(CN)_6]^{2-}$, respectively, K_2 is the protonation equilibrium constant of $[HFe(CN)_6]^{3-}$, and K_{eq} is the equilibrium constant for tribromide ion formation. The values of k_2 and k_3 were evaluated as (1.7 ± 0.1) × 10^5 and (3.3 ± 0.4) × 10^3 dm^3 mol^{-1} s^{-1}, respectively. A mechanism consistent with the rate law is postulated in which the first step is formation of the $Br_2{}^{\bullet -}$ intermediate.

The hexacyanoferrate(II) ion is a one-electron reducing agent with a relatively stable octahedral co-ordination sphere.[1] Its oxidation by various oxidizing agents, however, has rarely produced simple kinetics.[2–6] The complex kinetics obtained in the oxidation of such an apparently simple complex can be attributed to some unique properties of the hexacyanoferrate(II) ion.

(*i*) *Protonation*.[7,8]—At low pH it is difficult to stabilize the −4 charge on the $[Fe(CN)_6]^{4-}$ ion. As a result, extensive protonation occurs in aqueous solutions. The different protonated forms of the complex do not react with an oxidizing agent at the same rate. It has been possible in some instances to work under pH conditions that can sustain only one or two protonated forms, hence yielding slightly simpler kinetics.

(*ii*) *Photochemistry*.[9–11]—The complex is very sensitive to light in the visible region of the spectrum. Exposure to normal fluorescent light leads to aquation of the co-ordination sphere, forming a pentacyanomonoaqua complex which exhibits kinetics different from those of the hexacyano complex.[12]

(*iii*) *The Iron*(II)—*Iron*(III) *Reaction*.—The product of the reaction, hexacyanoferrate(III), reacts rapidly with hexacyanoferrate(II) to form intense bluish green binuclear complexes.[13,‡] This reaction is more pronounced at low pH and in the presence of a stoicheiometric excess over the oxidant. The result of this process is inhibition of the ferrocyanide oxidation as more of the iron(III) complex is formed. This autoinhibition has also been observed in the oxidation of hexacyanoferrate(II) by iodate.[14]

(*iv*) *Air Oxidation*.—The reduction potential, 0.36 V, is very low,[1] and the complex is slowly oxidized by prolonged exposure to the atmosphere.[15]

The above four properties of the complex have been encountered in various kinetics studies. In the pH range 1.76—2.65 the oxidation of hexacyanoferrate(II) by iodate goes mainly through the unprotonated and the monoprotonated forms of the complex.[14] The oxidation by chlorite is inhibited by the product iron(III) complex,[1] while oxidation by hypochlorous acid is inhibited by both the iron(II) and iron(III) complexes.[3]

Hexacyanoferrate(II) is a major component of several pH-regulated chemical oscillators. The first such oscillator discovered, the Edblom–Orbán–Epstein (E.O.E.) oscillator, consists of iodate, sulphite, and ferrocyanide[16,17] ions and is a modification of the Landolt[18] reaction. The complex is necessary for the oscillations, since without hexacyanoferrate(II) the Landolt reaction is simply autocatalytic oxidation of sulphite by iodate.[18] In a variant of the E.O.E. oscillator, iodate is replaced by bromate.[19] Two other pH-regulated oscillators utilize ferrocyanide and hydrogen peroxide with[20] or without[21] sulphite ion.

Our initial interest in the oxidation of hexacyanoferrate(II) by aqueous bromine derives from the role played by this reaction in the bromate–sulphite–ferrocyanide oscillator.[19] A previous study of the bromate–hexacyanoferrate(II) reaction[22] found it to be partially autocatalytic and singled out bromine (formed from the reaction of bromate with bromide) as the autocatalytic species. Preliminary experiments suggested that

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[†] Part 55, K. Kustin, *Chemtech*, in the press.

[‡] Our reaction solutions turned bluish green at the end of the reaction when the complex was in stoicheiometric excess over the molecular bromine. The reaction that takes place must be analogous to the one that forms Prussian and Turnbull blue complexes (see ref. 1, pp. 856 and 865). A similar observation has been made by S. Asperger, I. Murati, and D. Pavlovic, *J. Chem. Soc. A*, 1969, 2044.

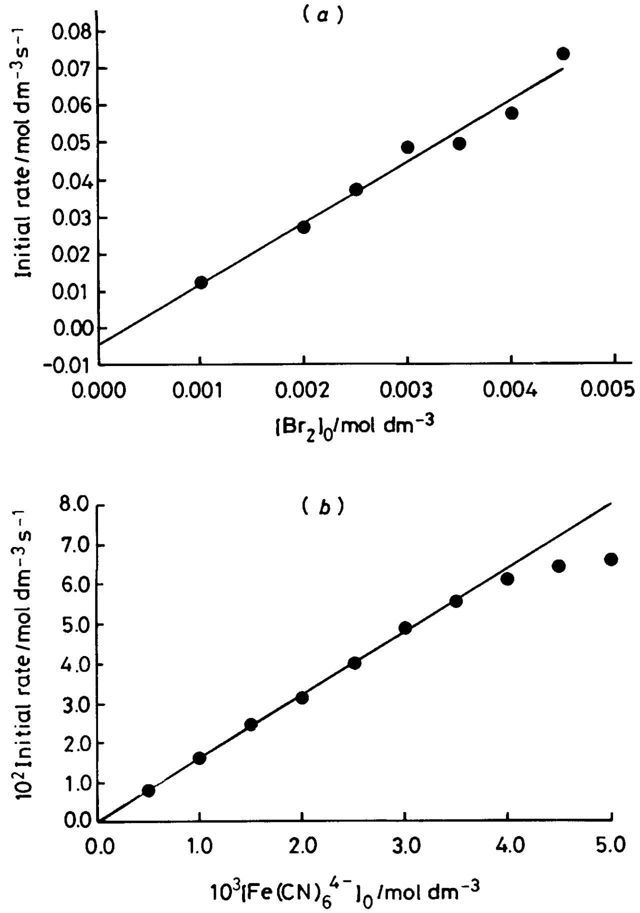

Figure 1. (*a*) Plot of initial rate against initial bromine concentration at $[H^+]_0 = 0.2$ and $[Fe(CN)_6{}^{4-}]_0 = 1 \times 10^{-3}$ mol dm^{-3}. (*b*) Plot of initial rate against ferrocyanide concentration showing the loss of linearity when $[Fe(CN)_6{}^{4-}]_0 > [Br_2]_0$; $[Br_2]_0 = 1 \times 10^{-3}$ and $[H^+]_0 = 0.3$ mol dm^{-3}

the bromine–ferrocyanide reaction is very fast, requiring rapid mixing techniques, *e.g.* stopped-flow, for a kinetics analysis.[22] A more recent study of the same reaction disputes the contention that bromine is the autocatalytic species.[23] A comparable study of aqueous iodine oxidation of ferrocyanide found an equilibrium mixture and a rate of reaction that was inhibited by one of the products, iodide.[24] Our aim in the present work was to study the bromine–ferrocyanide reaction over the pH range of the observed oscillations.

Experimental

Materials.—The following analytical grade chemicals were used without further purification: bromine (Aldrich), 70% perchloric acid, sodium bromide, sodium thiosulphate, potassium ferrocyanide, potassium ferricyanide, and potassium iodide (all Fisher). Stock solutions of sodium perchlorate (Aldrich) were filtered before use. Aqueous bromine solutions were standardized by adding excess of potassium iodide and titrating the liberated iodine against standard sodium thiosulphate with freshly prepared starch as indicator.* This standardization was used to evaluate the absorption coefficient of bromine as 165 dm^3 mol^{-1} cm^{-1} at 390 nm, the absorption co-efficient of potassium ferricyanide was found to be 1 080 dm^3 mol^{-1} cm^{-1} at 420 nm.

Methods.—Distilled water used to prepare reagent solutions was first bubbled through with argon to remove as much oxygen as possible. Absorbance measurements were performed on a Perkin-Elmer 552 u.v.–visible recording spectrophotometer. Reaction progress was followed by monitoring the absorbance of potassium ferricyanide at 420 nm on a Hi-Tech SF-3L stopped-flow spectrophotometer. The signal from the RCA 7268 photomultiplier tube was digitized *via* a Metrabyte A/D converter and interfaced to a Tandy HD-1200 microcomputer for analysis. Under conditions where $[Br_2(aq)]_0 > 7[Fe(CN)_6]^{4-}]_0$ the data were analysed for pseudo-first-order kinetics, otherwise the analysis used initial rate measurements. Each data point was averaged from at least ten replicate runs.

All preparations (except weighing) of standard ferrocyanide solutions were performed in the dark in the absence of both sunlight and fluorescent light. The final solutions were stored under argon in dark winchester bottles wrapped in aluminium foil. Freshly prepared ferrocyanide solutions were not used for at least 4 h and were discarded after 24 h. Our colleague, Dr. Gyula Râbai, has also found independently that freshly prepared ferrocyanide solutions give irreproducible kinetics results. We attribute this observation to the hexacyano–pentacyano equilibrium, which takes about 2 h to become fully established.

Aqueous bromine was found to have an absorption co-efficient of 145 dm^3 mol^{-1} cm^{-1} at 420 nm, which is too high to be neglected. Thus initial rate measurements were adjusted for the change in absorbance caused by the depletion of bromine [equation (1)]. After taking into account the stoicheiometry,

$$\Delta[A(\text{total})] = \Delta A(Br_2) + \Delta A[Fe(CN)_6]^{3-} \quad (1)$$

we calculated that the observed absorbance change of $[Fe(CN)_6]^{3-}$ is modified by 6.7% because of the contribution from the bromine, which was accounted for in all initial rate calculations.

The ionic strength was kept at 0.5 mol dm^{-3} ($NaClO_4$), and the temperature was maintained at 25 ± 0.1 °C. The pH was adjusted by adding perchloric acid standardized with standard (Fisher) sodium hydroxide and methyl orange as indicator.

Results

Stoicheiometry.—From absorbance measurements at 420 nm, the reaction stoicheiometry is as in equation (2). The initial

$$Br_2(aq) + 2[Fe(CN)_6]^{4-} \longrightarrow 2Br^- + 2[Fe(CN)_6]^{3-} \quad (2)$$

bromine concentration was kept constant while the ferrocyanide concentration was gradually increased in successive experiments. After taking into account the 6.7% correction factor for bromine, our results are in good agreement with stoicheiometry (2). When the initial ferrocyanide concentration was greater than twice the initial bromine concentration, however, the final absorbance observed was lower than that expected from equation (2). The final solution also turned bluish green (instead of yellow). Stoicheiometric amounts [equation (2)] of bromine and ferrocyanide gave a product whose spectrum is identical to that of ferricyanide. No other oxidation products are formed.

Reaction Kinetics.—The reaction is fast, typically going to completion in less than 0.1 s. For initial rate measurements the acid concentration was kept constant and high to reduce the number of variable concentrations. Figure 1(*a*) shows that the reaction is first order in the concentration of bromine. Varying

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* This is the indirect iodometric method. For examples see D. A. Skoog and D. M. West, 'Fundamentals of Analytical Chemistry,' Holt, Rinehart, and Winston, New York, 1963, p. 492.

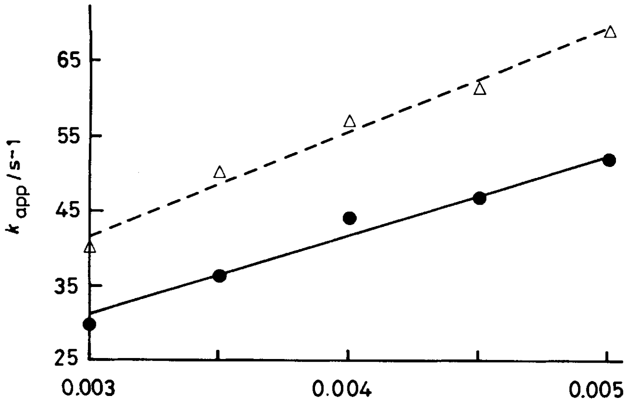


Figure 2. Dependence of the pseudo-first-order rate constant on initial bromine concentration at different acid concentrations (initial $[Br^-] \approx 0$). $[Fe(CN)_6{}^{4-}]_0 = 5 \times 10^{-4}$ mol dm^{-3}. $[H^+] = 0.2$ (△) or 0.3 mol dm^{-3} (●)

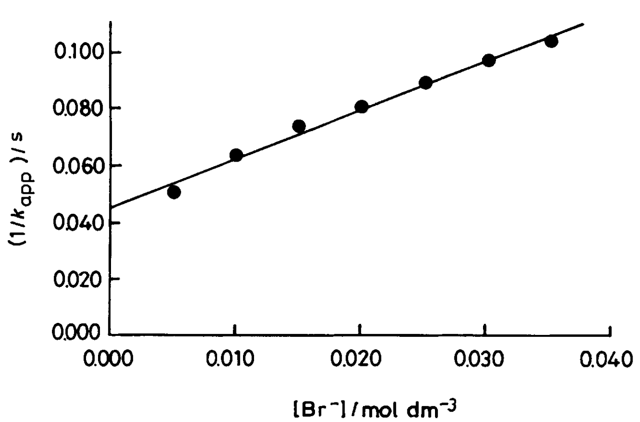


Figure 3. Bromide concentration dependence of the pseudo-first-order rate constant showing the observed inhibition, $[Fe(CN)_6{}^{4-}]_0 = 5 \times 10^{-4}$ and $[Br_2]_0 = 5 \times 10^{-3}$ mol dm^{-3}

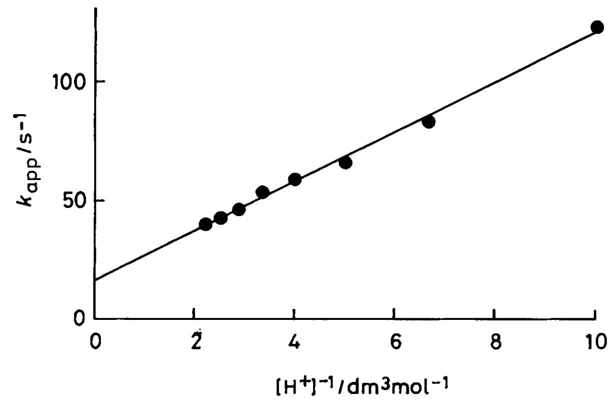
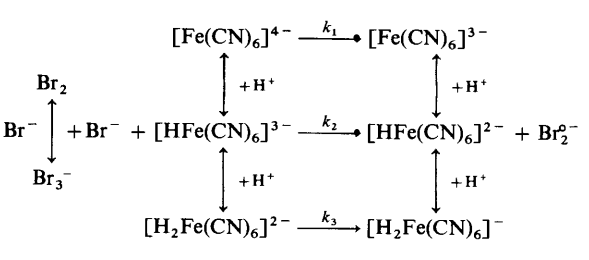


Figure 4. Inverse acid dependence of the pseudo-first-order rate constant, $[Fe(CN)_6{}^{4-}]_0 = 5 \times 10^{-4}$ and $[Br_2]_0 = 5 \times 10^{-3}$ mol dm^{-3}

the initial ferrocyanide concentration reveals that the reaction is also first order in ferrocyanide up to the stoicheiometric concentration [Figure 1(*b*)]. Further increases in $[Fe(CN)_6{}^{4-}]$ have little effect on the initial rate because of autoinhibition caused by ferricyanide, which reacts with the remaining ferrocyanide ions to form binuclear complexes. No pseudo-first-order kinetics were observed with $[Fe(CN)_6{}^{4-}]_0 \gg [Br_2(aq)]_0$.



Scheme.

Under these conditions the observed effect became very small at 420 nm because the reaction products do not absorb at that wavelength.

When $[Br_2]_0 > 7[Fe(CN)_6{}^{4-}]_0$, pseudo-first-order kinetics were observed in the rate of production of ferricyanide (Figure 2). The apparent rate constant, k_{app}, varies linearly with initial bromine concentration with an intercept indistinguishable from zero.

Addition of bromide ion retards the reaction, and the inhibition is strongest when $[Br^-]_0 \gtrsim [Br_2(aq)]_0$ (Figure 3). The apparent rate constant becomes less sensitive at low bromide concentrations.

Acid has the most profound effect on the reaction. In the pH range 0.4—2, acid significantly retards the reaction. Figure 3 shows two sets of experiments performed at different acid concentrations. The set with a higher acid concentration gives lower k_{app} values. A plot of k_{app} against $1/[H^+]$ gives a straight line with a positive intercept (Figure 4). Above pH 2 the reaction rate increased until at pH 3 it became too fast to measure on our stopped-flow spectrophotometer. We thus did not perform experiments above pH 2.5.

Treatment of Data.—For the protolytic equilibria, Jordan and Ewing[8] deduced the following equilibrium constants at 25 °C and zero ionic strength: $K_1 = 6.7 \times 10^{-5}$, $K_2 = 6 \times 10^{-3}$, and $K_4 > K_3 > 0.1$ mol dm^{-3}, where, *e.g.*, $K_1 = [Fe(CN)_6{}^{4-}][H^+]/[HFe(CN)_6{}^{3-}]$ and similarly for K_2, K_3, and K_4. Between pH 1 and 2 the predominant species are $[HFe(CN)_6]^{3-}$ and $[H_2Fe(CN)_6]^{2-}$. Tribromide ion formation can be significant at high bromide ion concentration, and equilibrium (3) must also be considered.

$$Br_2(aq) + Br^- \rightleftharpoons Br_3{}^-(aq);\ K_{eq} = 17\ \text{dm}^3\ \text{mol}^{-1} \quad (3)$$

A plausible mechanism for reaction (2) is one with rate-determining electron transfer between bromine and each of $[Fe(CN)_6]^{4-}$, $[HFe(CN)_6]^{3-}$, and $[H_2Fe(CN)_6]^{2-}$ to generate the bromine radical ion (see Scheme). From this mechanism the rate of reaction, *R*, should be given by, for example, $-d[Br_2]/dt = (1/2)d[Fe(CN)_6{}^{3-}]/dt$. Since rapid equilibrium (3) always prevails,[25] the rate actually measured is $-d([Br_2] + [Br_3{}^-])/dt$. The rate expression can be written in terms of *R* and the disappearance of Br_2 by incorporating equilibrium (3) into the rate expression. Then, utilizing the protolytic equilibria yields equation (4).

$$-d[Br_2]/dt = (k_1 + k_2[H^+]/K_1 + k_3[H^+]^2/K_1K_2)\ [Br_2][Fe(CN)_6{}^{4-}]/(1 + K_{eq}[Br^-]) \quad (4)$$

The total ferrocyanide concentration is given by equation (5).

$$[Fe(CN)_6{}^{4-}]_T = \left(1 + \frac{[H^+]}{K_1} + \frac{[H^+]^2}{K_1K_2}\right)[Fe(CN)_6{}^{4-}] \quad (5)$$

After assuming that $k_1K_1K_2 \ll k_2[H^+]K_2 + k_2[H^+]^2$ and that $[H^+] \gg K_2$ we obtain the final rate expression (6). It

$$-d[Br_2]/dt = (k_3 + k_2K_2/[H^+])\ \{1/(1 + K_{eq}[Br^-])\}[Br_2][Fe(CN)_6{}^{4-}]_T \quad (6)$$

follows that in a pseudo-first-order kinetics environment, where $[Br_2] \approx [Br_2]_0$ and $[Br_2]_0 \gg [Fe(CN)_6{}^{4-}]_0$, the rate of reaction R is given by equations (7) and (8).

$$-d[Br_2]/dt = k_{app}[Fe(CN)_6{}^{4-}]_T \quad (7)$$

$$k_{app} = (k_3 + k_2K_2/[H^+])\{1/(1 + K_{eq}[Br^-])\}[Br_2]_0 \quad (8)$$

The data in Figure 1(*a*) and (*b*) satisfy equation (6) by showing first-order dependences on bromine and total ferrocyanide concentrations. Values of k_3 and k_2 can be calculated from the slopes of these plots. The value of K_2 used is 1.2×10^{-2} mol dml^{-3}, which is appropriate to an ionic strength of 0.5 mol dm^{-3}.[8]

The data in Figure 2 agree with equation (8). The slope of the plot of k_{app} *vs.* $[Br_2]_0$ should be $(k_3 + k_2K_2/[H^+])/(1 + K_{eq}[Br^-])$. By running two sets of kinetic measurements at different acid concentrations one obtains two simultaneous equations which can be solved for k_2 and k_3 (see Figure 2).

The effect of bromide obtained in Figure 3 is consistent with equation (8), as is the hydrogen-ion dependence shown in Figure 4. A single plot in this case could give us k_2 and k_3 simultaneously. Values of k_2 and k_3 were evaluated from different sets of initial conditions and from either initial rate measurements [Figure 1(*a*) and (*b*)] or pseudo-first-order environments (Figures 2—4) and a statistical analysis performed. The final values are $k_2 = (1.7 \pm 0.1) \times 10^5$ dm^3 mol^{-1} s^{-1} and $k_3 = (3.3 \pm 0.4) \times 10^3$ dm^3 mol^{-1} s^{-1}.

Discussion

In the pH range investigated (0.4—2.0) we do not expect a significant concentration of unprotonated ferrocyanide ions. The acid dependence in Figure 4 implicates only two species. The observation that at pH > 3 the reaction becomes too fast to follow using our stopped-flow apparatus can be attributed to two possibilities: (*a*) if the unprotonated $[Fe(CN)_6]^{4-}$ reacts faster with bromine than with the protonated species, then an increase in pH would increase its concentration, thereby increasing the overall reaction rate; or (*b*) if HOBr reacts faster with ferrocyanide than does $Br_2(aq)$, then an increase in pH would speed up the reaction by shifting equilibrium (9)[26] to the right, thereby increasing [HOBr].

$$Br_2(aq) + H_2O \rightleftharpoons HOBr + Br^- + H^+ \quad (9)$$

We calculate that changes in $[Br_2(aq)]$ and [HOBr] between pH 0.5 and 3 are not as large as the observed increase in the rate of reaction and that within the same pH range $[Fe(CN)_6]^{4-}$ increases quite significantly. The concentration of HOBr is virtually negligible over the range encompassed by Figure 4. Furthermore, oxidation of ferrocyanide by HOBr should be a much slower reaction than oxidation by $Br_2(aq)$, because the outer-sphere one-electron jump from the complex to the oxidant is much more difficult to effect with HOBr. We thus conclude that the inverse acid dependence observed between pH 0.4 and 2 results from the changing degree of protonation of the ferrocyanide as the acid is varied.

Previous studies of ferrocyanide oxidation have implicated the pentacyanomonoaqua complex as a precursor to subsequent oxidation,[23] *e.g.*, equations (10) and (11) followed by

$$[Fe(CN)_6]^{4-} + H_2O \overset{h\nu}{\rightleftharpoons} [Fe(CN)_5(H_2O)]^{3-} + CN^- \quad (10)$$

$$[Fe(CN)_5(H_2O)]^{3-} \overset{\text{oxidant}}{\rightleftharpoons} [Fe(CN)_5(H_2O)]^{2-} \quad (11)$$

$$[Fe(CN)_6]^{4-} + [Fe(CN)_5(H_2O)]^{2-} \rightleftharpoons [Fe(CN)_6]^{3-} + [Fe(CN)_5(H_2O)]^{3-} \quad (12)$$

(12). Reaction (10), however, is too slow[14] to play a role in the system under study here. In our experimental procedures, we rigorously excluded light, making the photochemical reaction much less likely. The spectrum of our products was clean, with no trace of any product other than $[Fe(CN)_6]^{3-}$.

The formal reduction potential, E_0, of $[Fe(CN)_6]^{3-}$ is 0.36 V[1] [equation (13)]. In 1 N sulphuric acid, however, the reduction potential is 0.69 V.[27] For our experiments the real

$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-} \quad (13)$$

value lies in between these two figures. Using pulse radiolysis data for half-reaction (14)[28] and standard potentials, it is

$$Br_2{}^{\bullet -} + 1e^- \longrightarrow 2Br^-; \quad E_0 = 1.67 \text{ V} \quad (14)$$

possible to estimate the one-electron reduction potential of aqueous bromine [equation (15)]. As long as the first step

$$Br_2(aq) + e^- \longrightarrow Br_2{}^{\bullet -}; \quad E_0 = 0.51 \text{ V} \quad (15)$$

(10) produces at least an equilibrium mixture of $Br_2{}^{\bullet -}$ and $[Fe(CN)_6]^{3-}$ * the driving force will be provided by the reaction of $Br_2{}^{\bullet -}$ with more ferrocyanide to give the final products [equation (16)].

$$Br_2{}^{\bullet -} + [Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + 2Br^- \quad (16)$$

In the presence of sufficient light, it is also possible to produce bromine radicals, which can then oxidize ferrocyanide [equations (17) and (18)]. Steps (17) and (18) are unlikely to

$$Br_2(aq) \overset{h\nu}{\rightleftharpoons} 2Br^{\bullet}(aq) \quad (17)$$

$$Br^{\bullet}(aq) + [Fe(CN)_6]^{4-} \longrightarrow Br^- + [Fe(CN)_6]^{3-} \quad (18)$$

occur appreciably in our reaction because, except for the 420-nm radiation used to determine the ferricyanide concentations, the experiments were performed in the dark.

The data in Figure 3 suggest that $Br_3{}^-$ is unreactive toward the ferrocyanide species. We have been able to correlate the inhibition by bromide with the equilibrium constant of the formation of $Br_3{}^-$ from Br_2 and Br^-. In similar studies in which iodine is the oxidant, $I_3{}^-$ is also inert.[29] In most of our experiments tribromide ion inhibition did not interfere with the reaction progress. In pseudo-first-order kinetics environments the amount of bromide formed is very low and, with no bromide added initially, $1 + K_{eq}[Br^-] \approx 1$. In our initial rate measurements we used only the first 5% of the reaction when the concentration of bromide is still very low.

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* Even taking the extreme value of 0.69 V for the ferrocyanide–ferricyanide couple yields an equilibrium constant for the initial electron-transfer process of 1×10^{-3}. The actual situation will certainly be more favourable.

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