Kinetics of Oxidation of Transition-metal Ions by Halogen Radical Anions. Part I. The Oxidation of Iron(II) by Dibromide and Dichloride Ions Generated by Flash Photolysis

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The radical anions Br_2^- and Cl_2^-, generated by flash photolysis of the corresponding halide solutions or of the iron(III) complexes $FeBr^{2+}$ and $FeCl^{2+}$, oxidize iron(II) to iron(III). The product of the reaction between the ions Br_2^- and Fe^{2+} is the $FeBr^{2+}$ complex. The reaction proceeds by an inner-sphere substitution-controlled path with a rate constant of $(3{\cdot}6 \pm 0{\cdot}4) \times 10^6$ l mol^{-1} s^{-1} at 25 °C ($\Delta H^‡ = 25{\cdot}2 \pm 2$ kJ mol^{-1}; $\Delta S^‡ = -42 \pm 12$ J K^{-1} mol^{-1}). The reaction between the ions Cl_2^- and Fe^{2+} proceeds by two paths at 25 °C, an inner-sphere substitution-controlled path with a rate constant of $(4{\cdot}0 \pm 0{\cdot}6) \times 10^6$ l mol^{-1} s^{-1} ($\Delta H^‡ = 31{\cdot}5 \pm 4$ kJ mol^{-1}; $\Delta S^‡ = -21 \pm 15$ J K^{-1} mol^{-1}), and an outer-sphere path with a rate constant of $(1{\cdot}0 \pm 0{\cdot}2) \times 10^7$ l mol^{-1} s^{-1} ($\Delta H^‡ = 22{\cdot}7 \pm 4$ kJ mol^{-1}; $\Delta S^‡ = -42 \pm 15$ J K^{-1} mol^{-1}).

HALOGEN radical anions, Cl_2^-, Br_2^-, and I_2^-, originally proposed as intermediates in oxidation–reduction reactions of the halogens or halide ions,[1] have been directly observed in flash photolysis [2,3] and pulse radiolysis [4,5] experiments. Formation of the radical anions in the pulse radiolysis of aqueous halide-ion solutions by the reaction between hydroxyl radicals and halide ions has been the subject of extensive investigations.[6,7] Langmuir and Hayon [3] measured the rates of reaction of Cl_2^-, Br_2^-, and I_2^- with a variety of oxidisable substrates, but the reactions of the halogen radical anions with transition-metal ions have not previously been investigated.

These radical anions are among the simplest oxidizing radicals in aqueous solution apart from the hydroxyl radical. Oxidations of aquated transition-metal ions by such ions provide a means of testing current theories of oxidative electron-transfer reactions of metal ions over a very wide range of substitution rate and free-energy change. Direct observation of the kinetics and mechanisms of reactions of this type also illuminates the mechanisms proposed for a variety of metal ion–halide-ion–halogen reactions or metal-ion catalysed reactions of halogens in which metal ion–halogen radical anion reactions have been proposed. Preliminary results on the reactions of Br_2^- with the ions Fe^{2+} and Mn^{2+} have already been reported.[8]

EXPERIMENTAL

Solutions of Fe^{II} were prepared from the perchlorate salt (G. F. Smith) and standardized by titration with $KMnO_4$. Traces of Fe^{III} in the solutions were removed by electrolytic reduction or by reduction with zinc amalgam. These reductions were carried out under an atmosphere of nitrogen or argon gas and the solutions were stored under these gases. Zinc(II) ions present in solutions reduced with zinc amalgam were shown to have no effect on the reactions of the radical anions since no reaction with Cl_2^- or Br_2^- could be observed in solutions containing zinc perchlorate (0·2M). The latter concentration was at least one order of magnitude greater than that in the reduced Fe^{II} solutions. After reduction the Fe^{II} solutions contained $<0{\cdot}005\%$ Fe^{III}. Solutions of Fe^{III} in perchloric acid (0·1—0·5M) were prepared from the perchlorate salt (Fluka) after recrystallization from $HClO_4$ and were standardized by titration with EDTA.

AnalaR sodium halides were used to prepare the halide-ion solutions. Acid concentrations and ionic strengths of the solutions were adjusted with perchloric acid (AnalaR) and sodium perchlorate (Fluka). All solutions were prepared in water distilled from alkaline potassium permanganate and acidified potassium dichromate.

The flash photolysis apparatus had a maximum energy input to the flash lamp of 1000 J at 20 kV. In most experiments 500 J flashes were used. The Xe/O_2 filled lamps produced a flash with a half-width at half-height of 8 μs. The spectrophotometric arrangement consisted of a 100 W Xe/Hg lamp, a Bausch and Lomb high-intensity grating monochromator, and an E.M.I. photomultiplier (9558 QB) followed by an integrated-circuit voltage follower. The

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[1] H. Taube, *J. Amer. Chem. Soc.*, 1946, **68**, 611; 1948, **70**, 3928; A. J. Fudge and K. W. Sykes, *J. Chem. Soc.*, 1952, 119.

[2] L. I. Grossweiner and M. S. Matheson, *J. Phys. Chem.*, 1957, **61**, 1089.

[3] M. E. Langmuir and E. Hayon, *J. Phys. Chem.*, 1967, **71**, 3808.

[4] (*a*) H. C. Sutton, G. E. Adams, J. W. Boag, and B. D. Michael, 'Pulse Radiolysis,' eds. M. Ebert, J. P. Keene, A. J. Swallow, and J. H. Baxendale, Academic Press, London, 1965, p. 61; (*b*) B. Čerček, M. Ebert, C. W. Gilbert, and A. J. Swallow, *ibid.*, p. 83.

[5] M. Anbar and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 3829.

[6] M. S. Matheson, W. J. Mulac, J. L. Weeks, and J. Rabani, *J. Phys. Chem.*, 1966, **70**, 2092.

[7] D. Zehavi and J. Rabani, *J. Phys. Chem.*, 1972, **76**, 312; D. Behar, *ibid.*, p. 1815, and references therein.

[8] A. T. Thornton and G. S. Laurence, *Chem. Comm.*, 1970, 443.

photomultiplier output was recorded on a Tektronix 564 storage oscilloscope. Absorbance changes could be recorded at sensitivities of 0·005 absorbance units per cm deflection using the voltage comparator–differential amplifier of the oscilloscope. The minimum time response of the system was 0·3 µs.

Solutions were photolysed in cylindrical Spectrosil quartz cells (10 cm long) at ambient temperature (22 ± 2 °C) or in 5 cm Spectrosil cells fitted with a quartz jacket through which water at constant temperature was circulated. The cells were sufficiently transparent at short wavelengths for micromolar concentrations of the radical anion Cl_2^- to be formed by flash photolysis of 10^{-2}M-Cl^- solutions. Solutions were manipulated, in the absence of oxygen, either in cells sealed to reservoirs (100 ml) which could be evacuated and filled with N_2 or Ar, or by an adaption of the Argonne syringe technique[9] using rubber serum caps to seal the cells.

The concentrations of the radical anions were conveniently followed by changes in absorbance at 366 nm. At this wavelength the Xe/Hg lamp has a large output and the signal-to-noise ratio is correspondingly high. The radical anions Cl_2^- and Br_2^- have absorption maxima at 340 (ε $1{\cdot}25 \times 10^4$)[5] and at 365 nm (ε $7{\cdot}8 \times 10^3$ l mol^{-1} cm^{-1})[6] respectively. Corresponding extinction coefficients at 366 nm are $1{\cdot}0 \times 10^4$ (Cl_2^-) and $7{\cdot}8 \times 10^3$ l mol^{-1} cm^{-1} (Br_2^-). The Fe^{III} complexes $FeCl^{2+}$ and $FeBr^{2+}$, formed by the reactions of Fe^{2+} with the radical anions Cl_2^- and Br_2^-, absorb in the same region of the spectrum (335 nm,[10] ε $2{\cdot}4 \times 10^3$; and 405 nm,[11,12] ε $7{\cdot}9 \times 10^2$ l mol^{-1} cm^{-1} respectively) and allowance was made for this absorbance in analysing the traces of absorbance against time. At least three such traces were analysed for each set of experimental conditions.

RESULTS

Production of the Radical Anions.—Several different techniques were used to generate the radical anions depending on the system under investigation. Absorption of the flash light by Br^- ion (10^{-3}—10^{-1}M) in the charge-transfer-to-solvent region produces Br atoms and hydrated electrons [equation (1)][13] and then Br_2^- radical anions. The

$$Br^-_{aq} \xrightarrow{h\nu} Br + e^-_{aq} \qquad (1)$$

$$Br + Br^- \rightleftharpoons Br_2^- \qquad (2)$$

forward reaction in (2) is very fast (*k ca.* 10^{10} l mol^{-1} s^{-1}) and the equilibrium constant is $2{\cdot}2 \times 10^5$ l mol^{-1}.[4b] In some experiments N_2O was added to scavenge e^-_{aq} and to double the Br_2^- yield [equations (3) and (4)]. In others,

$$e^-_{aq} + N_2O \longrightarrow N_2 + OH^- + OH \qquad (3)$$

$$OH + Br^- \longrightarrow OH^- + Br \qquad (4)$$

where the acid concentration was $\geqslant 10^{-3}$M, e^-_{aq} was scavenged by H^+ ions as in (5). The H atoms produced

$$e^-_{aq} + H^+ \longrightarrow H \qquad (5)$$

in this way were effectively scavenged by the added Fe^{2+} ions and had no effect on the reactions of the Br_2^- radical anions.

Flash photolysis of deaerated 10^{-2}M-Br^- in the presence of up to 10^{-2}M-Fe^{2+} at pH $\leqslant 3$ produced reasonable yields of the radical anion Br_2^- in our apparatus. The corresponding ion Cl_2^- was produced in 10^{-2}M-Cl^-, but on addition of Fe^{2+} ions an inner filter effect due to absorption by these ions drastically reduced the Cl_2^- yield and an alternative source of halogen radical anions was investigated. Langmuir and Hayon[3] produced halogen radical anions by flash photolysis of halogenomercury(II) complexes. The photolysis of halogenoiron(III) solutions to produce these ions was suggested by the work of Evans and Uri[14] who observed free-radical initiated polymerization on photolysing in the charge-transfer region solutions containing iron(III) complexes, FeX^{2+}, and monomers. We have found that flash photolysis of the complexes $FeBr^{2+}$ and $FeCl^{2+}$ produces the radical anions Br_2^- and Cl_2^-.

Flash Photolysis of $FeBr^{2+}$ *and* $FeCl^{2+}$ *Complexes.*—Deaerated solutions containing the ions Fe^{3+} (10^{-3}M), H^+ (0·1M), and Br^- or Cl^- (0·1M) were flash photolysed. Equilibrium concentrations of halogenoiron(III) complexes,

$$Fe^{3+}_{aq} + X^- \rightleftharpoons FeX^{2+} \qquad (6)$$

FeX^{2+} (X = Cl or Br), were between 5×10^{-5} and 3×10^{-4}M. Large transient absorbances in the 300—400 nm region were observed. Spectra of the transient absorbances immediately after the flash resembled those of the radical anions Br_2^- (ref. 6) and Cl_2^- (ref. 5) (Figures 3 and 7), but in fact represented the difference in the absorbance of the halogen radical anion produced and the halogenoiron(III) complex destroyed by the flash. The iron(III) complexes have absorption maxima at 405 ($FeBr^{2+}$) and 335 nm ($FeCl^{2+}$) and, in order to confirm that the transients were actually produced on light absorption by the complexes, the same solutions were photolysed with light from the flash lamp filtered through Pyrex glass (2 mm) which eliminates wavelengths <270 nm. The same transient absorbance was observed, indicating that the transient was not produced by photolysis of the halide ion (0·1M solutions of the ions Br^- or Cl^- did not produce Br_2^- or Cl_2^- when photolysed through Pyrex glass in our apparatus).

$$FeX^{2+} \xrightarrow{h\nu} Fe^{2+} + X \qquad (7)$$

$$X + X^- \rightleftharpoons X_2^- \qquad (8)$$

Correction of the difference spectra, assuming a 1 : 1 stoicheiometry between X_2^- produced and FeX^{2+} destroyed (X = Cl or Br), showed that the photolysis products were the radical anions Br_2^- and Cl_2^-, but the results were subject to errors of up to 10% because the decay of the halogen radical anion by the disproportionation reaction (9) (X = Cl or Br) and the stray light from the flash

$$X_2^- + X_2^- \longrightarrow X_3^- + X^- \qquad (9)$$

lamp prevented precise measurement of the true initial yield of the ion X_2^-. Concentrations of the radical anions Br_2^- and Cl_2^- of 2—10µM were produced from the Fe^{III} complexes by filtered (λ > 270 nm) light from the flash.

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[9] E. J. Hart and E. M. Fielden, *Adv. Chem. Ser.*, No. 50, Amer. Chem. Soc., Washington, 1965, p. 253.

[10] Sister M. J. M. Woods, P. K. Gallagher, and E. L. King, *Inorg. Chem.*, 1962, **1**, 55.

[11] M. W. Lister and D. E. Rivington, *Canad. J. Chem.*, 1955, **33**, 1603.

[12] D. W. Carlyle and J. H. Espenson, *Inorg. Chem.*, 1969, **8**, 575.

[13] M. S. Matheson, W. A. Mulac, and J. Rabani, *J. Phys. Chem.*, 1963, **67**, 2613.

[14] M. G. Evans and N. Uri, *Nature*, 1949, **164**, 404; N. Uri, *Chem. Rev.*, 1952, **50**, 375.

Absorbance against time curves for the flash photolysis of both $FeBr^{2+}$ and $FeCl^{2+}$ complexes were similar to that shown in Figure 1 (broken line). At all wavelengths of interest, $\varepsilon_{X_2^-} > \varepsilon_{FeX^{2+}}$. The initial rise in absorbance during the flash (Figure 1) is due to production of Cl_2^- [equations (7) and (8); X = Cl]. The equilibrium between Cl atoms and Cl_2^- radical anions is very rapid (k_f *ca.* 10^{10} l mol^{-1} s^{-1}) and the equilibrium constant is large ($1{\cdot}0 \times 10^5$ l mol^{-1}) [15] so that all the Cl atoms are converted to Cl_2^- during the flash. Because of the reduction of an amount of $FeCl^{2+}$ complex equivalent to the Cl_2^- radical anion produced, equation (10) is applicable.

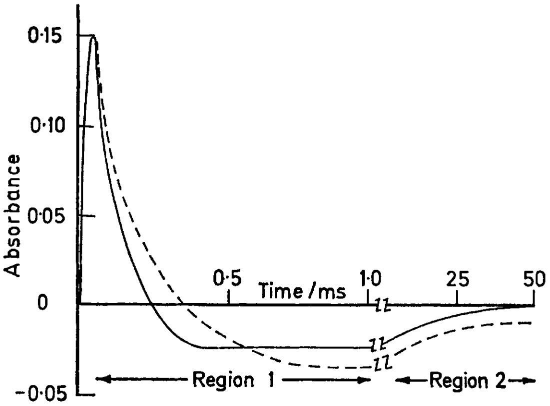

FIGURE 1 Absorbance against time curves for flash photolysed $FeCl^{2+}$ solutions (*ca.* 4×10^{-4}M-$FeCl^{2+}$, 0·1M-Cl^-, 0·1M-H^+, and 10^{-3}M-Fe^{III}) at 366 nm; (– – – –), no Fe^{2+} ions added; (——), 2×10^{-3}M-Fe^{2+} added. Absorbances are relative to that of the solution before the flash. The change in timescale after 1 ms is to be noted

$$\Delta(\text{Absorbance}) = (\varepsilon_{Cl_2^-} - \varepsilon_{FeCl^{2+}})[Cl_2^-]_{\text{initial}} \qquad (10)$$

Moreover, the disproportionation reaction (9) (X = Cl) is much faster than the rate of oxidation of the Fe^{2+} produced in the flash.

Thus the initial fast decay of the absorbance (region 1, Figure 1) is due almost entirely to the disproportionation reaction. After about 500 μs the absorbance reached a minimum when all the Cl_2^- radical anions had decayed and then, to a good approximation, equation (11) is obtained.

$$\Delta(\text{Absorbance}) = -\varepsilon_{FeCl^{2+}}[Cl_2^-]_{\text{initial}} \qquad (11)$$

The Fe^{3+}–Cl^- system is however labile on the millisecond time scale and equilibrium (6) (X = Cl) adjusts to the new $[Fe^{3+}]_T$ and $[Cl^-]_T$ (region 2, Figure 1). At the end of this period (10—100 ms) this equilibrium has readjusted and the absorbance is less than it was initially. Finally at very long times ($\geqslant$100 s) reaction (12) brings the

$$Fe^{2+} + Cl_3^- \longrightarrow FeCl^{2+} + 2Cl^- \qquad (12)$$

system back to its initial conditions. A similar reaction sequence accounts for absorbance changes in the $FeBr^{2+}$ system.

We have measured the rates of the disproportionation reactions (9) in the $FeCl^{2+}$ and $FeBr^{2+}$ systems at 25 °C and an ionic strength of 0·2M ($k_9 = 5{\cdot}2 \times 10^9$ for Cl_2^- and $5{\cdot}3 \times 10^9$ l mol^{-1} s^{-1} for Br_2^-). These rates agree with our own measurements at the same temperature and ionic strength in systems in which the halogen radical anions are generated without simultaneous production of e^-_{aq} or H by flash photolysis of the trihalide ions Cl_3^- and Br_3^-.[15] The disproportionation rate for the Br_2^- radical anion is in good agreement with previously reported values,[4,6] but that for Cl_2^- is much smaller than the value reported [3] by Langmuir and Hayon, *i.e.* $1{\cdot}5 \times 10^{10}$ l mol^{-1} s^{-1}. There may have been a significant contribution to the disappearance of the Cl_2^- radical anion in Langmuir and Hayon's experiments from reactions (13) and (14), as we have

$$e^-_{aq} + Cl_2^- \longrightarrow 2Cl^- \qquad (13)$$

$$H + Cl_2^- \longrightarrow 2Cl^- + H^+ \qquad (14)$$

observed much higher disproportionation rates in systems in which these reactions can occur.

The very low quantum yields for photochemical reduction of the complexes $FeBr^{2+}$ and $FeCl^{2+}$, observed by Evans and Uri[14] in the absence of monomers were confirmed in our experiments where, after *ca.* 100 s, the system returned to the initial concentration of FeX^{2+}. The precision of our absorbance measurements was such that any permanent change produced by the light flash must have been $<1\%$ of the initial yield of the radical anion X_2^-.

Photolysis of the halogenoiron(III) complexes has a number of advantages over that of the halide ions as a source of radical anions for kinetic studies. Thus larger yields are obtained in the presence of ions such as Fe^{2+}, which absorb in the same region as Cl^-, and there is no simultaneous production of e^-_{aq} or H species which may interfere with subsequent reactions. Interference by the micromolar concentrations of Fe^{2+} ions produced was not a problem as the concentration of added Fe^{2+} was always $>10^{-4}$M, but the use of $FeBr^{2+}$ and $FeCl^{2+}$ complexes increased the complexity of the analysis of the absorbance changes in the 300—450 nm region because both the complexes and the radical anions absorb in this region.

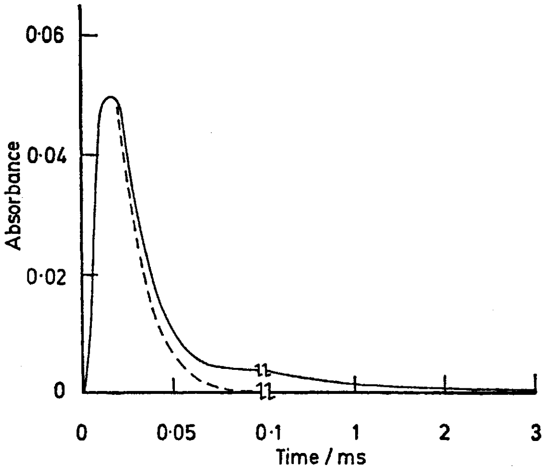

FIGURE 2 Absorbance against time curves for Br_2^-–Fe^{2+} systems at 405 nm: (——), 0·1M-Br, solution containing 0·1M-H^+ and 10^{-2}M-Fe^{2+}; (– – – –), *ca.* 5×10^{-5}M-$FeBr^{2+}$ solution (0·1M-Br^-, 0·1M-H^+, and 10^{-3}M-Fe^{III}) containing 10^{-2}M-Fe^{2+}. Absorbances are relative to that of the solution before the flash. The change in timescale after 0·1 ms is to be noted

Reaction of the Radical Anion Br_2^- *with the* Fe^{2+} *Ion*.—Deaerated solutions of the ions Br^- (0·1M) and H^+ (0·1M) containing Fe^{2+} (10^{-3}—10^{-2}M) were photolysed by light from the flash lamp and absorbance changes followed with time, usually at 366 nm or at the maximum absorbance

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[15] A. T. Thornton and G. S. Laurence, unpublished work.

of the FeBr^{2+} complex at 405 nm. Absorbance against time curves had the shape shown in Figure 2 (solid line) for wavelengths in the 350—420 nm region, where both the ions Br$_2^-$ and FeBr^{2+} absorb.

The initial absorbance in Figure 2 is due to the Br$_2^-$ radical anion produced by the flash from the Br$^-$ ion, and this disappears by the two reactions (9) (X = Br) and (15) with a half-life of 10—200 μs depending on the

$$Br_2^- + Fe^{2+}_{aq} \longrightarrow Fe^{III} + 2Br^- \qquad (15)$$

Fe^{2+} concentration. These reactions are complete within 1 ms and the slower decrease in absorbance which takes several milliseconds is attributed to dissociation of the complex FeBr^{2+} which is produced as a result of reaction (15) in excess of the equilibrium concentration. The spectrum taken after 500 μs is that of the complex FeBr^{2+} (Figure 3). The absorbance does not return to zero at long times because of the equilibrium concentration of this complex governed by reaction (6) (X = Br). The kinetic behaviour of the absorbance after 500 μs confirms the formation of the complex FeBr^{2+}. If the initial product of reaction (15) were the hexaquoiron(III) ion (Fe$^{3+}_{aq}$) then, in solutions containing 0·1M-Br$^-$, the complex FeBr^{2+} would be formed by reaction (6) and we would observe a growth in absorbance due to this complex until equilibrium was reached. Except in experiments with high [Fe^{2+}] (*ca.* 10^{-2}M), the stoicheiometric ratio between the radical anion Br$_2^-$ produced in the flash and the complex FeBr^{2+} is greater than 1 : 1 because some Br$_2^-$ disproportionates by reaction (9) to form the ion Br$_3^-$.

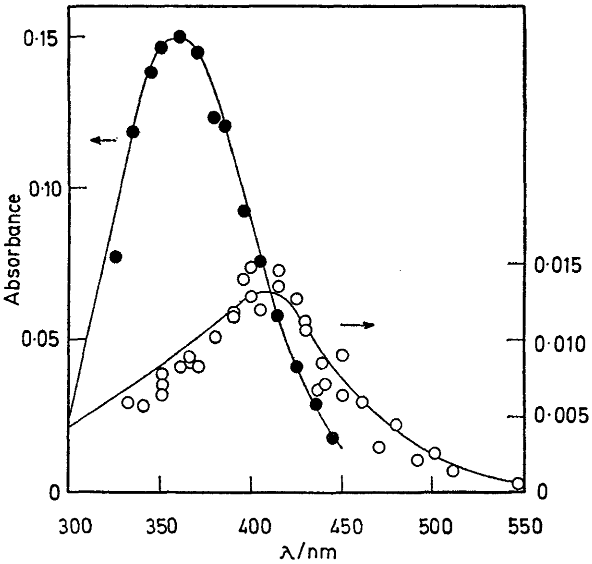

FIGURE 3 Spectra of transients observed after flash photolysis of 0·1M-Br$^-$, 0·1M-H$^+$, and 5 × 10^{-3}M-Fe^{2+} solutions: (●), 50 μs after the flash (the solid line is the spectrum of Br$_2^-$ [7]); (○), 500 μs after the flash (the solid line is the spectrum of the complex FeBr^{2+})

The slow decay of the absorbance due to the dissociation of the FeBr^{2+} complex was studied in experiments in which the [Fe^{2+}] was high and the initial yield of FeBr^{2+} correspondingly large. The decay obeyed first-order kinetics and plots of ln $(A_t - A_\infty)$ against time are shown in Figure 4. The observed first-order rate constant at 25 °C for an acid concentration of 0·1M, in the presence of 1·2 × 10^{-2}M-Fe^{2+}, was (9·0 ± 0·2) × 10^2 s^{-1}. The rate of establishment of equilibrium (6) (X = Br) has been investigated by Matthies and Wendt [16] and by Carlyle and Espenson.[12] The two studies are not in very good agreement and, at our acid concentration, we calculate from the data of the previous investigators that the rate constant for the first-order approach to equilibrium is (7 ± 2) × 10^2 s^{-1}. Our result is in reasonable agreement if the slow process we observe is dissociation of the complex FeBr^{2+} formed in reaction (15) to give the equilibrium concentration, and it is possible that at our [Fe^{2+}] there is a contribution due to an Fe^{2+} catalysed path similar to that observed in the FeCl^{2+} system by Sutin *et al.*[17]

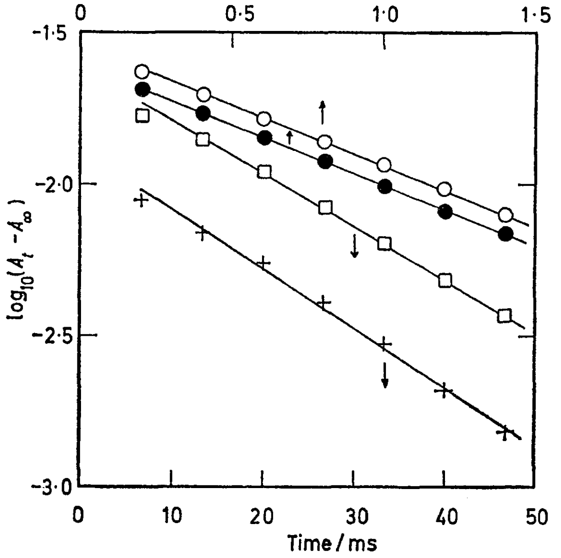

FIGURE 4 Relaxation kinetics of the complexes FeBr^{2+} and FeCl^{2+} after flash photolysis at 22 °C: FeBr^{2+} decay (0·1M-Br$^-$, 0·1M-H$^+$, 1·2 × 10^{-2}M-Fe^{2+}, and I = 0·2M) at 405 (○) and 366 nm (●); FeCl^{2+} growth (0·1M-Cl$^-$, 0·1M-H$^+$, 10^{-3}M-Fe^{III}, 1·2 × 10^{-2}M-Fe^{2+}, and I = 0·2M) at 334 (□) and 366 nm (+)

Flash photolysis of deaerated solutions containing *ca.* 5 × 10^{-5}M-FeBr^{2+} (0·1M-Br$^-$, 0·1M-H$^+$, and 10^{-3}M-Fe^{III}) and Fe^{2+} confirmed the initial product of reaction (15) as the complex FeBr^{2+}. Absorbance against time plots for these experiments had the shape shown in Figure 2 (broken line) at [Fe^{2+}] (*ca.* 10^{-2}M) high enough to scavenge all the Br$_2^-$ radical anions. The return of the absorbance to the initial value due to the FeBr^{2+} complex in 10—20 μs indicates that this complex cannot be formed from the relatively slow substitution of Br$^-$ into the ion Fe$^{3+}_{aq}$ and demonstrates that under these conditions no permanent change is produced in the solutions by flash photolysis; the overall stoicheiometry is expressed by reactions (7), (8), and (15) (X = Br) and the equilibrium concentration of the complex FeBr^{2+}, disturbed by the flash, is restored by the reaction of the Br$_2^-$ radical anion with the ion Fe^{2+} before equilibrium (6) has relaxed more than a few percent.

Because of the larger yields of the Br$_2^-$ radical anion from photolysis of the complex FeBr^{2+}, and the absence of

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[16] P. Matthies and H. Wendt, *Z. phys. Chem.* (*Frankfurt*), 1961, **30**, 137.

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

reducing species such as e^-_{aq} and H, kinetic data for reaction (15) were obtained from analysis of absorbance against time curves for the flash photolysis of deaerated solutions containing *ca.* 5×10^{-5}M-FeBr^{2+} (0·1M-Br$^-$, 0·1M-H$^+$, and 10^{-3}M-Fe^{III}) and 10^{-3}—10^{-2}M-Fe^{2+}. The absorbance was usually followed at 366 nm; in some runs monitored at 405 nm identical results were obtained. Reaction (15) was always pseudo first order in our experiments, where $[Fe^{2+}] \gg [Br_2^-]$, and the decay of the Br_2^- radical anion absorbance [equation (16)] was of mixed first [due to reaction (15)] and second order [due to reaction (9)]. A numerical integration

$$-d[Br_2^-]/dt = k_{15}[Fe^{2+}][Br_2^-] + k_9[Br_2^-]^2 \quad (16)$$

procedure was performed by a CDC 6400 computer, using the appropriate value of k_9, to obtain the pseudo-first-order rate constants for reaction (15). Second-order-rate constants for this reaction were obtained from gradients of plots of the pseudo-first-order rate constant against [Fe^{2+}]. Such plots at different temperatures are shown in Figure 5 and the second-order rate constants derived therefrom are given in Table 1. Activation parameters obtained from the data of Table 1 are given in Table 2.

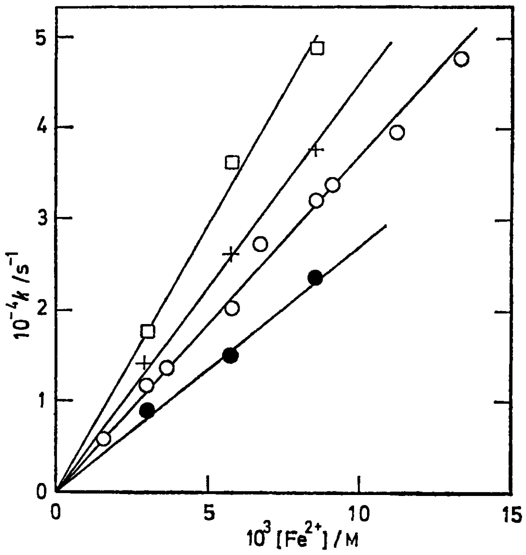

FIGURE 5 Dependence of pseudo-first-order rate constants on [Fe^{2+}] for the Br_2^-–Fe^{2+} reaction at (●), 15; (○), 25; (+), 30; and (□), 40 °C. The error in individual points is ±10%

TABLE 1

Variation of rate constants (l mol^{-1} s^{-1}) with temperature for $Fe^{2+} + X_2^-$ (X = Cl or Br) reactions: 0·1M-HClO$_4$; I = 0·2M

Temp./°C:	15	25	30	40
$Fe^{2+} + Br_2^-$, $10^{-6}\,k_{22}$	2·7 ±0·3	3·6 ±0·4	4·5 ±0·5	5·9 ±0·6
$Fe^{2+} + Cl_2^-$, $10^{-6}k_{17}$	9·6 ±1	14 ±1	17 ±2	23·5 ±2
$k_{18} : k_{19}$	0·37 ±0·02	0·40 ±0·03	0·45 ±0·03	0·57 ±0·05
$Fe^{2+} + Cl_2^-$, $10^{-6}\,k_{18}$	2·6 ±0·4	4·0 ±0·6	5·3 ±1	8·5 ±2
$Fe^{2+} + Cl_2^-$, $10^{-6}\,k_{19}$	7·0 ±2	10 ±2	11·7 ±2	15 ±3

Reaction of the Radical Anion Cl_2^- *with the* Fe^{2+} *Ion*.—Flash photolysis of deaerated solutions containing the ions Cl$^-$ (0·1M), H$^+$ (0·1M), and Fe^{2+} (10^{-4}—10^{-3}M) produced only small (<1 μM) concentrations of the radical anion Cl_2^-. Absorbance changes at 366 nm as a function of time are shown in Figure 6, and resemble those in solutions containing Br$^-$ ions. The initial absorbance in the Figure is due to the Cl_2^- radical anion produced in the flash, which disappears by the two reactions (9) (X = Cl) and (17),

$$Cl_2^- + Fe^{2+}_{aq} \xrightarrow{k_{17}} Fe^{III} + 2Cl^- \quad (17)$$

the half-life (10—200 μs) depending on [Fe^{2+}]. The spectrum of the species present after 500 μs is that of FeCl^{2+} (Figure 7). The decay of the FeCl^{2+} absorbance is due to the production by reaction (17) of FeCl^{2+} in concentrations greater than the equilibrium concentration determined by equation (6) (X = Cl).

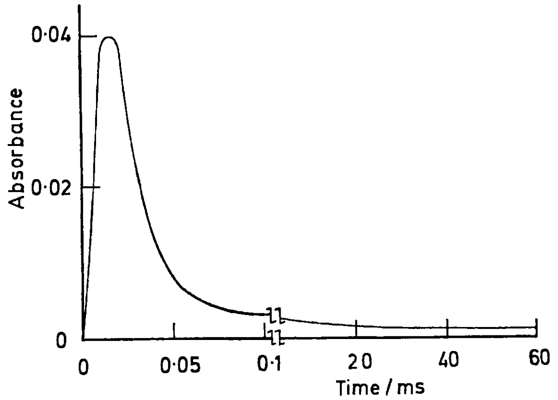

FIGURE 6 Absorbance against time curves observed in flash photolysed 0·1M-Cl$^-$, 0·1M-H$^+$, and $1{\cdot}2 \times 10^{-2}$M-Fe^{2+} solutions at 366 nm. Absorbances relative to that of the solutions before the flash. The change in timescale after 0·1 ms is to be noted

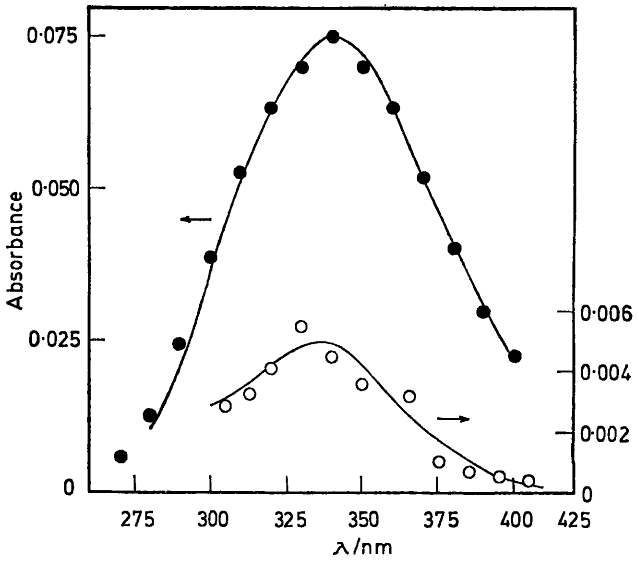

FIGURE 7 Spectra of transients observed after flash photolysis of 0·1M-Cl$^-$, 0·1M-H$^+$, and 10^{-3}M-Fe^{2+} solutions: (●), 50 μs after the flash (the solid line is the spectrum of the radical anion Cl_2^- [5]); (○), 500 μs after the flash (the solid line is the spectrum of the complex FeCl^{2+})

The concentrations of the Cl_2^- radical anion produced in these solutions were too small for good kinetic analysis and in most experiments Cl_2^- was produced by flash photolysis of deaerated solutions containing *ca.* 4×10^{-4}M-$FeCl^{2+}$ (0·1M-Cl^-, 0·1M-H^+, and 10^{-3}M-Fe^{III}). In the presence of Fe^{2+} (5×10^{-4}—5×10^{-3}M), after the flash, absorbance against time curves similar to that shown in Figure 1 (solid line) were obtained (366 or 330 nm). The shape of the curves differed significantly from those obtained in the equivalent $FeBr^{2+}$ system (Figure 2, dotted line) because the absorbance fell *below* that of the initial value during the first 10—500 µs and recovered with a half-life of several milliseconds. The initial change in absorbance observed is the difference between the absorbances of the Cl_2^- radical anion produced and that of the complex $FeCl^{2+}$ destroyed, and the rapid decrease is due to removal of Cl_2^- by reactions (9) (X = Cl) and (17). Because the absorbance at *ca.* 500 µs is below the initial absorbance due to the $FeCl^{2+}$ complex in the solution, reaction (17) apparently does not produce only $FeCl^{2+}$ as the initial product [unlike the corresponding reaction of Br_2^-, reaction (15)]. The slower return of the absorbance towards its initial value {the extent of this return depending on $[Fe^{2+}]$, *i.e.* on the relative importance of reactions (17) and (9) (X = Cl) in consuming the Cl_2^- radical anion} is then due to formation of a new equilibrium concentration of the complex $FeCl^{2+}$ from the Fe^{3+}_{aq} ions produced in reaction (17) and Cl^-.

The experiments described in the previous two paragraphs suggest two different initial products from reaction (17): in the first paragraph, from solutions containing only Cl^- and Fe^{2+} ions, the product is the $FeCl^{2+}$ complex; in the second, from solutions containing the complex $FeCl^{2+}$ and the ion Fe^{2+}, the product is at least partly the hexa-aquoiron(III) ion, Fe^{3+}_{aq}, but the stoicheiometry is not known for either set of experiments. Comparison of the results of both sets of experiments with those from the flash photolysis at the same flash intensity of deaerated solutions containing the complex $FeCl^{2+}$ (0·1M-Cl^-, 0·1M-H^+, and 10^{-3}M-Fe^{III}) without added Fe^{2+} ions showed that both $FeCl^{2+}$ and Fe^{3+}_{aq} are produced by reaction (17). Absorbance against time curves observed when no Fe^{2+} was present had the shape shown in Figure 1 (dotted line) and have already been discussed. The initial fall in the Cl_2^- radical anion absorbance was slower than that in the presence of Fe^{2+} ions because only reaction (9) (X = Cl) was removing Cl_2^-, but the absorbance at about 500 µs—1 ms was less than that when Fe^{2+} ions were present. Under these conditions, because reaction (9) is *ca.* 10^3 times faster than reaction (17), reaction (17) can be neglected, and the loss of absorbance measured after 1 ms represents the concentration of the complex $FeCl^{2+}$ reduced by the flash [equation (7); X = Cl]. Because this loss of absorbance was greater than those in experiments in which Fe^{2+} ions were present (Figure 1), we conclude that some $FeCl^{2+}$ complex is formed by reaction (17), in agreement with the experiments of the first paragraph for solutions containing only Cl^- and Fe^{2+} ions. However, the amount formed is less than that destroyed by the flash; some of the Fe^{2+} ions oxidized by reaction (17) therefore form Fe^{3+}_{aq} as the initial product. Reaction (17) must proceed by the two paths (18) and (19) to give the two products $FeCl^{2+}$ and Fe^{3+}_{aq}, and we can express the rate constant as equation (20).

$$Cl_2^- + Fe^{2+} \xrightarrow{k_{18}} FeCl^{2+} + Cl^- \qquad (18)$$

$$Cl_2^- + Fe^{2+}_{aq} \xrightarrow{k_{19}} Fe^{3+}_{aq} + 2Cl^- \qquad (19)$$

$$k_{17} = k_{18} + k_{19} \qquad (20)$$

The relative proportions of the two products, $FeCl^{2+}$ and Fe^{3+}_{aq}, were obtained from the flash photolysis of solutions of the complex $FeCl^{2+}$ with and without Fe^{2+} ions. The difference between the decrease in absorbance from the initial value before the flash (at 1 ms when all the Cl_2^- radical anion absorbance had decayed) for solutions with and without Fe^{2+} ions represents the amount of the $FeCl^{2+}$ complex formed by reaction (18). At high $[Fe^{2+}]$ (*ca.* 10^{-2}M) where reaction (9) can be neglected, the decrease in absorbance from the initial value after 1 ms represents the amount of the $FeCl^{2+}$ complex which is not reformed by reaction (18), *i.e.* the amount of the ion Fe^{3+}_{aq} formed by reaction (19). Measurement of the relative proportions of the $FeCl^{2+}$ and Fe^{3+}_{aq} products in this way, rather than from the ratio of the Cl_2^- radical anion produced by the flash to the complex $FeCl^{2+}$ formed by (18), had the advantages that effects of stray light from the flash on the measurement of the initial absorbance due to the Cl_2^- radical anion were eliminated, and that the ratio of the extinction coefficients of Cl_2^- and $FeCl^{2+}$ did not have to be known exactly. The relative yields of the products $FeCl^{2+}$ and Fe^{3+}_{aq}, which are proportional to the relative rates of reactions (18) and (19), were apparently independent of $[Fe^{2+}]$, but were dependent on temperature. Values of the ratio $k_{18} : k_{19}$ are given in Table 1.

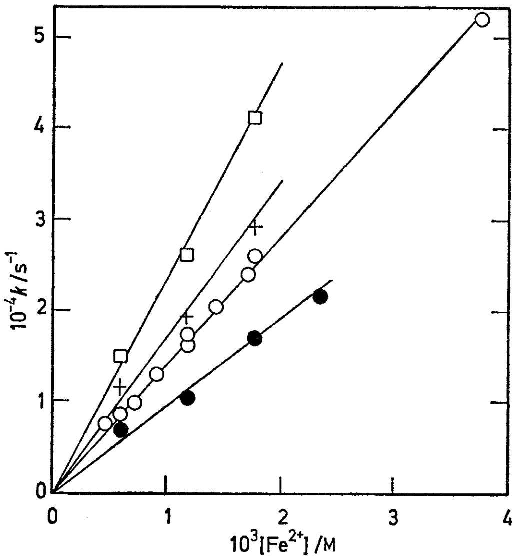

FIGURE 8 Dependence of pseudo-first-order rate constants on $[Fe^{2+}]$ for the Cl_2^-–Fe^{2+} reaction at (●), 15; (○), 25; (+), 35; and (□), 40 °C. The error in individual points is ±10%

The kinetics of reaction (17) were measured in solutions containing the complex $FeCl^{2+}$ and Fe^{2+} ions. The reaction was always pseudo first order, as $[Fe^{2+}] \gg [Cl_2^-]$, and the disappearance of the Cl_2^- radical anion was mixed first and second order [reactions (9) (X = Cl) and (17)]. Using our values of k_9 measured at the appropriate temperature,[15] numerical integration yielded pseudo-first-order rate constants for reaction (17). Second-order rate constants were obtained from straight-line plots of the pseudo-first-order rate constants against $[Fe^{2+}]$. The plots are shown in Figure 8 and the overall second-order rate constants, k_{17}, and rate constants for the two paths, k_{18} and k_{19}, are given in Table 1. Activation parameters obtained from the data of Table 1 are given in Table 2.

The slow readjustment of the $FeCl^{2+}$ equilibrium was investigated for solutions containing the complex $FeCl^{2+}$ and Fe^{2+} ions, in which $[Fe^{2+}] = 10^{-2}$M. The approach to equilibrium was first order because the perturbation of the equilibrium by the flash was $<1\%$. Plots of $\ln(A_\infty - A_t)$ against time are shown in Figure 5. The observed first-order rate constant at 25 °C in 0·1M-acid in the presence of $1{\cdot}2 \times 10^{-2}$M-Fe^{2+} was 41 ± 1 s^{-1} at an ionic strength of 0·2M. This value agrees very well with that of 37 s^{-1} calculated for the same concentrations from data of Moorhead and Sutin[18] for the acid dependence of the iron(II)-catalysed reaction between the ions $Fe^{3+}{}_{aq}$ and Cl^- at an ionic strength of 3·0M.

DISCUSSION

For electron-transfer reactions which proceed by an inner-sphere mechanism, electron transfer is preceded by a substitution step in which the inner co-ordination sphere of one of the reactants is penetrated, and new primary bonds are formed and old ones disrupted in the path up to and through the transition state. The maximum rate of the electron-transfer process cannot exceed the substitution rate at the determining metal centre and may be much slower than this rate. For electron-transfer reactions of the outer-sphere type, the primary co-ordination spheres of the reactants remain intact during the approach to electron transfer, although rearrangements of secondary solvation spheres and of ligand–metal bond lengths and geometries can occur. For reactions in which one oxidation state of one of the reactants is labile but the other is inert, if the reaction follows an inner-sphere path, it is possible to demonstrate experimentally that ligand transfer accompanies electron transfer and that the mechanism is indeed inner sphere.[19]

Although both the ions $Fe^{2+}{}_{aq}$ and $Fe^{3+}{}_{aq}$ are normally considered labile species, their substitution rates (*ca.* 10^6 l mol^{-1} s^{-1} for $Fe^{2+}{}_{aq}$ and *ca.* 10—10^2 l mol^{-1} s^{-1} for $Fe^{3+}{}_{aq}$) differ by a factor of ten thousand or more. For oxidation reactions of the $Fe^{2+}{}_{aq}$ ion with rate constants greater than *ca.* 10^4 l mol^{-1} s^{-1}, $Fe^{3+}{}_{aq}$ or Fe^{III} complexes can be considered as inert on the timescale of the oxidation reaction. It is then possible to distinguish between inner- and outer-sphere mechanisms for oxidation of the $Fe^{2+}{}_{aq}$ ion by using the same experimental criteria that were used in the classic investigations by Taube *et al.*[19] of the oxidation of the $Cr^{2+}{}_{aq}$ ion by inert cobalt(III) complexes. For the oxidation of the $Fe^{2+}{}_{aq}$ ion by an inner-sphere mechanism in which the ligand L substitutes into the $Fe^{2+}{}_{aq}$ inner-co-ordination sphere, the initial iron(III) product will be the $Fe^{III}L$ complex. This will aquate [equation (21)] at a rate (depending on pH and other conditions) of *ca.* 10—10^2 s^{-1}. In the oxidation of the $Fe^{2+}{}_{aq}$ ion by an outer-sphere process, the primary co-ordination sphere will remain unchanged during the oxidation and the initial iron(III) product will be the ion $Fe^{3+}{}_{aq}$. Substitution of the latter may then occur at a rate of *ca.* 10—10^2 l mol^{-1} s^{-1} if a suitable ligand is present in solution. The oxidation of the $Fe^{2+}{}_{aq}$ ion by Cl_2 has been shown in this way to occur predominantly *via* an inner-sphere reaction.[20] For oxidations of the $Fe^{2+}{}_{aq}$ ion with rates less than the rate of substitution of $Fe^{3+}{}_{aq}$ it is not possible to distinguish between inner- and outer-sphere mechanisms by observation of the type of oxidation product because the iron(III) substitution reactions will keep pace with the rate of oxidation.

$$Fe^{III}L + H_2O \rightleftharpoons Fe^{3+}{}_{aq} + L \qquad (21)$$

The oxidation reactions of $Fe^{2+}{}_{aq}$ by the radical anions Br_2^- and Cl_2^- are sufficiently rapid for the mechanism of the reactions to be established from observation of the initial iron(III) products. We have shown that the initial product of the reaction between the radical anion Br_2^- and the ion $Fe^{2+}{}_{aq}$ is the $FeBr^{2+}$ complex, and therefore reaction (15) must be written as in (22). The

$$Br_2^- + Fe^{2+}{}_{aq} \longrightarrow FeBr^{2+} + Br^- \qquad (22)$$

$FeBr^{2+}$ then aquates at the rate expected from previous measurements of the rate of the attainment of the $Fe^{3+}{}_{aq}$–Br^- equilibrium, reaction (6) (X = Br). Reaction (22) is inner sphere, but it is not possible to distinguish observationally between electron transfer in the inner-sphere complex ($Fe^{II}Br_2^+$) accompanied by simultaneous loss of Br^- ion [equations (23) and (24)],

$$Br_2^- + Fe^{2+}{}_{aq} \longrightarrow (Fe^{II}Br_2^+) \qquad (23)$$

$$(Fe^{II}Br_2^+) \longrightarrow Fe^{III}Br^{2+} + Br^- \qquad (24)$$

and electron transfer followed by rapid loss of Br^- ion from the iron(III) complex [equations (23), (25), and (26)]. Rates of formation and aquation of tetra-aquodihalogenoiron(III) complexes such as $FeBr_2^+$ are not known but are probably slightly greater than those for monohalogeno-complexes because the water-exchange rate increases by a factor of two for the addition of each chloro-group[21] in the series $Fe(OH_2)_6{}^{3+}$, $Fe(OH_2)_5Cl^{2+}$, and $Fe(OH_2)_4Cl_2{}^+$. It is probable then that the rate of loss of Br^- ion from the $FeBr_2^+$ complex is slower by at least a factor of 100 than the oxidation reaction (22), and the electron transfer and loss of Br^- ion from the ($Fe^{II}Br_2^+$) complex take place simultaneously.

$$(Fe^{II}Br_2^+) \longrightarrow Fe^{III}Br_2^+ \qquad (25)$$

$$Fe^{III}Br_2^+ \longrightarrow Fe^{III}Br^{2+} + Br^- \qquad (26)$$

Identification of an electron-transfer reaction as one of inner-sphere type is not sufficient to define the details

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of the intimate mechanism. Substitution in the inner-co-ordination sphere must precede electron transfer, but either the rate of substitution or the rate of the subsequent electron transfer may be the rate-limiting step. We can distinguish the two situations as *inner sphere–substitution controlled* and *inner sphere–electron-transfer controlled*. For the simple case of oxidation of a metal ion by an oxidizing ligand such as we have investigated, the two paths can be written as in equations (27) and (28). Reaction profiles for

$$M^{2+}_{aq} + L \xrightarrow{\text{slow}} M^{2+}L \xrightarrow{\text{fast}} M^{3+}L^- \qquad (27)$$

inner sphere–substitution controlled

$$M^{2+}_{aq} + L \xrightarrow{\text{fast}} M^{2+}L \xrightarrow{\text{slow}} M^{3+}L^- \qquad (28)$$

inner sphere–electron-transfer controlled

the two paths are shown in Figure 9 and it can be seen that direct observation of the substituted intermediate of the original oxidation state of the metal ion would provide unequivocal evidence that a reaction is of the inner sphere–electron-transfer controlled type.

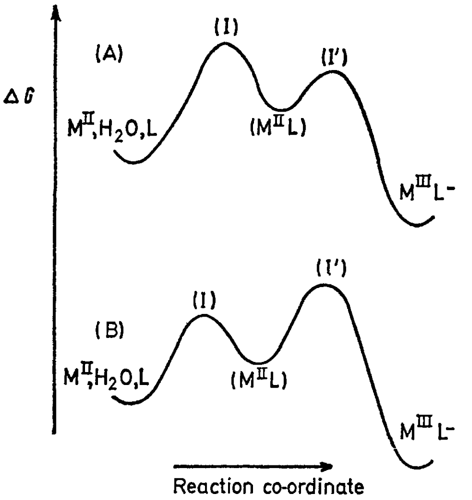

FIGURE 9 Free energy against reaction co-ordinate profiles for inner-sphere reactions between the ion M^{2+} and the ligand L leading to a $M^{3+}L^-$ product: (A), the inner sphere–substitution controlled case; and (B), the inner sphere–electron-transfer controlled case. (I) is the transition state for substitution, (I′) that for electron transfer. Initial ion-pair formation steps are omitted from both profiles. The substituted lower oxidation state metal ion ($M^{2+}L$) may be experimentally detectable if the reaction is electron-transfer controlled (B)

Unequivocal identification of the intimate mechanism is less easy for reactions which are inner sphere–substitution controlled, but the mechanism may be established by comparison of the substitution rate at the reactant metal centre with the rate of the redox reaction. If the rate of the observed inner-sphere reaction equals or very nearly equals that of substitution, we may infer that the reaction mechanism is inner sphere–substitution controlled. Even in the absence of direct observation of the substituted intermediate, if the rate of the inner-sphere redox reaction is much less than the substitution rate, we can infer that the reaction mechanism is inner sphere–electron-transfer controlled. Comparison of the activation parameters with those for substitution also provides a distinction between the two types of inner-sphere mechanism. If the enthalpy of activation is larger than that for substitution, the reaction must be inner sphere–electron-transfer controlled.

We have not been able to observe the possible substituted iron(II) intermediate, ($Fe^{II}Br_2^+$), in reaction (22). The intimate mechanism of this reaction may however be inferred from the observed rate constant and activation enthalpy. The rate constant, k_{22}, at 25 °C is $3{\cdot}6 \times 10^6$ l mol⁻¹ s⁻¹ and the water-exchange rate for the ion Fe^{2+}_{aq} at this temperature is $3{\cdot}2 \times 10^6$ s⁻¹.[22] Substitution reactions of bivalent transition-metal ions appear to be governed by the Eigen–Wilkins mechanism [23] in which ion-pairing precedes substitution and the rate of loss of a water molecule from the ion-pair is the rate-determining step [equation (29)]. The relationship

$$M^{2+}_{aq} + L \overset{\text{fast}, K_{IP}}{\rightleftharpoons} (M^{2+},H_2O,L) \xrightarrow{\text{slow}} M^{2+}L + H_2O \qquad (29)$$

between the observed substitution rate, k_0, the ion-pair constant, K_{IP}, and the water-exchange rate, k_{ex} [equation (30)] is well established for ions such as Ni^{2+}_{aq}.[24]

$$k_0 = K_{IP}k_{ex} \qquad (30)$$

If the substitution of the radical anion Br_2^- at the Fe^{2+}_{aq} ion follows the Eigen–Wilkins mechanism, the substitution rate constant will be the product of the Fe^{2+}_{aq} ion water-exchange rate and an ion-pairing constant K_{IP}. The magnitude of the latter is difficult to estimate, but probably lies between 0·1 and 10 l mol⁻¹. {If K_{IP} were much larger than 10, deviations from the linear dependence of the pseudo-first-order rate constant for reaction (22) on [Fe^{2+}] might have been detected. Such deviations have been observed by us in the reaction between the radical anion Cl_2^- and the ion Mn^{2+}_{aq}.} The rate of reaction (22) is therefore within the probable limits of the substitution rate on the ion Fe^{2+}_{aq} for the radical anion Br_2^- and we identify this reaction as inner sphere–substitution controlled. The activation enthalpy, $\Delta H_{22}^{\ddagger} = 25{\cdot}2 \pm 2$ kJ mol⁻¹, is lower than that for water exchange,[22] 35 ± 4 kJ mol⁻¹, and the difference is probably significant. Comparisons between activation energies for substitution and water exchange are made difficult by uncertainties in the measured activation parameters, but differences of 4—8 kJ mol⁻¹ are known for water exchange and substitutions on the ion Ni^{2+}_{aq}.[24] Such differences may be accommodated in the enthalpy

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change for ion-pairing, or may represent real reductions in the energy barrier for water exchange brought about by the ligand (ligand-assisted solvent exchange).

We have shown that oxidation of the ion $Fe^{2+}{}_{aq}$ by the $Cl_2{}^-$ radical anion proceeds by two parallel paths, one producing the complex $FeCl^{2+}$ as the initial product, (18), which must be the inner-sphere path, and one producing the ion $Fe^{3+}{}_{aq}$ as the initial product, (19), which is the outer-sphere path. Reaction (18) has the same rate constant as the inner-sphere reaction of the $Br_2{}^-$ radical anion with the $Fe^{2+}{}_{aq}$ ion (Table 2) and the reaction can be classified as inner sphere–substitution controlled, by the same argument. The activation enthalpy $\Delta H_{18}{}^‡$, 31·5 ± 4 kJ mol^{-1}, is larger than that for the $Br_2{}^-$ reaction and the increase may reflect either a difference in the energies of ion-pair formation for the radical anions $Cl_2{}^-$ and $Br_2{}^-$, or a difference in the activation energies for loss of water from the ion-pairs in the substitution step. The difference may not be significant because of larger errors in $\Delta H_{18}{}^‡$ which are due to the composite nature of the overall observed rate constant, k_{17} [equation (20)].

TABLE 2

Activation parameters for Fe^{2+}–$X_2{}^-$ reactions (X = Cl or Br) and for water exchange on the $Fe^{2+}{}_{aq}$ ion

Reaction	$\Delta H^‡$/kJ mol^{-1}	$\Delta S^‡$/J K^{-1} mol^{-1}	k(25 °C)
$Fe^{2+} + Br^{2-}$, k_{22}	25·2 ± 2	−42 ± 12	(3·6 ± 0·4) × 10^{6} l mol^{-1} s^{-1}
$Fe^{2+} + Cl_2{}^-$, k_{18}	31·5 ± 4	−21 ± 15	(4·0 ± 0·6) × 10^{6} l mol^{-1} s^{-1}
$Fe^{2+} + Cl_2{}^-$, k_{19}	22·7 ± 4	−42 ± 15	(1·0 ± 0·2) × 10^{7} l mol^{-1} s^{-1}
$Fe^{2+}{}_{aq}$–H_2O exchange [22]	35 ± 4	−13 ± 10	(3·2 ± 0·5) × 10^{6} s^{-1}

Kinetic parameters for the outer-sphere reaction (19) (Table 1) are not greatly different from those for the inner sphere–substitution controlled path, (18). The increased free-energy change for the oxidation of the Fe^{2+} ion by the $Cl_2{}^-$ rather than the $Br_2{}^-$ radical anion is apparently just sufficient to make the rates of the outer- and inner-sphere paths comparable. Although activation enthalpies for the two paths are uncertain by ±4 kJ mol^{-1}, the increase in the ratio of the inner-sphere product ($FeCl^{2+}$) to the outer-sphere product ($Fe^{3+}{}_{aq}$), *i.e.* the ratio $k_{18} : k_{19}$, with temperature (Table 1) is known more precisely and the activation enthalpy for the outer-sphere path is definitely less than that for the inner-sphere path. As might be expected, the reorganization energy required prior to electron transfer by the outer-sphere path (where the inner co-ordination sphere of the $Fe^{2+}{}_{aq}$ ion is intact) is less than that required for the substitution path. The activation entropy is more negative for the outer-sphere path and this may indicate the rather more precise adjustment of energy levels necessary prior to electron transfer by this mechanism. Energy requirements for the transition state of such a path for the labile ion $Fe^{2+}{}_{aq}$ and an anion would be expected to be less than those for electron transfer between ions such as $Co(NH_3)_6{}^{2+}$ and $Co(NH_3)_6{}^{3+}$, and current electron-transfer theories [25] suggest that the activation enthalpy will become smaller as the overall free-energy change for the reaction becomes more negative. For the reaction of the ion $Fe^{2+}{}_{aq}$ with the $Cl_2{}^-$ radical anion (but not for the corresponding reaction with $Br_2{}^-$), the overall free-energy change is such as to reduce the activation enthalpy of the outer-sphere path sufficiently for this path to be observed in competition with the inner-sphere path.

The reaction between Cl_2 and the $Fe^{2+}{}_{aq}$ ion apparently also takes place by both inner- and outer-sphere paths.[20] The observed rate constant, 80 l mol^{-1} s^{-1}, is much smaller than that for the corresponding reaction between the $Cl_2{}^-$ radical anion and $Fe^{2+}{}_{aq}$. We suggest that the reaction sequence is as in equations (31), (8) (X = Cl),

$$Cl_2 + Fe^{2+}{}_{aq} \longrightarrow Fe^{III} + Cl^- + Cl \qquad (31)$$

and (17). The iron(III) product was found to be predominantly (>70%) $FeCl^{2+}$. As our results show that the yield of the complex $FeCl^{2+}$ from reaction (17) is 30% at 25 °C, reaction (31) must be entirely inner sphere, and can be classified as inner sphere–electron-transfer controlled because the rate is so much slower than that of substitution, presumably due to energy requirements for Cl–Cl bond breaking in the electron-transfer step.

The rates of reaction of the $Fe^{2+}{}_{aq}$ ion with a number of free radicals of importance in the radiation chemistry of water have been reported previously. Rate constants for reactions (32)—(34) are: 2·1 × 10^{6};[26] 7·5 × 10^{6};[26]

$$HO_2 + Fe^{2+} \longrightarrow Fe^{3+}O_2H^- \qquad (32)$$

$$H + Fe^{2+}{}_{aq} \longrightarrow Fe^{3+}H^+ \qquad (33)$$

$$OH + Fe^{2+}{}_{aq} \longrightarrow Fe^{III} + OH^- \qquad (34)$$

and 3·3 × 10^{8} l mol^{-1} s^{-1}.* Both reactions (32) and (33) can be assigned inner-sphere mechanisms on the basis of observed transient absorbances attributed to the species $Fe^{3+}O_2H^-$ and $Fe^{3+}H^-$. The absorbance due to the former disappears by a first-order process with a rate constant of 8 × 10^{3} s^{-1}, probably due to aquation. The $Fe^{3+}H^-$ complex decays by reaction with H^+ ion to give Fe^{3+} ion and H_2. Reactions (32) and (33) have essentially the same rate constants as those for our inner-sphere paths, suggesting that the former reactions are also inner sphere–substitution controlled. Reaction (34) is significantly faster and is probably outer sphere, the free-energy change being sufficiently

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* The rate constant for reaction (34) was calculated from the ratio $k_{OH+H_2} : k_{OH+Fe^{2+}}$ obtained by Bunn *et al.*[27] and the value of k_{OH+H_2} reported by Thomas *et al.*[28]

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negative for such a path to be favoured. The standard reduction potential for the OH radical is more positive than that for the Cl_2^- radical anion by *ca.* 0·1 V, and this could account for the thirty-fold increase in rate between reactions (19) and (34).

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