Pulse Radiolysis Studies of Iron(I) in Aqueous Solutions

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The absorption spectrum and decay kinetics of the products of the reactions of iron(II) ions with hydrated electrons and hydrogen atoms have been studied in aqueous solution using pulse-radiolysis techniques. Iron(I) is formed by reaction with hydrated electrons and its absorption spectrum is reported and discussed. The formation of molecular hydrogen by reaction of Fe^+ with water is suppressed by other solutes present in the solutions. In acidic solutions containing $[SO_4]^{2-}$, the intermediates formed in the reaction with H atoms decay by a first-order process and produce molecular hydrogen, but the rate of their decay does not depend only on the oxonium ion concentration but also on intermolecular rearrangement in the $[FeSO_4\text{–}H]$ complex.

THE hydrated electron reduces the Fe^{2+} ion but there is no direct experimental evidence concerning the product, presumed to be Fe^+, formed in the reaction [1,2] [equation (1)]. On the other hand, the hydrogen atom acts as an oxidizing agent towards Fe^{2+} and is itself converted into molecular hydrogen [4] [equations (2) and (3)]. It is known that the hydrido-complex $[Fe^{2+}\text{–}H]$ is formed in this reaction.[4]

$$e^-(aq) + Fe^{2+} \longrightarrow Fe^+ + H_2O;\quad k_1 = 1.2 \times 10^8\text{—}3.5 \times 10^8\ \text{dm}^{-3}\ \text{mol}^{-1}\ \text{s}^{-1}\ (\text{ref. }3) \tag{1}$$

$$H + Fe^{2+} \longrightarrow [Fe^{2+}\text{–}H];\quad k_2 = 0.75 \times 10^6\text{—}2 \times 10^6\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ (\text{ref. }5) \tag{2}$$

$$[Fe^{2+}\text{–}H] + H^+ \longrightarrow H_2 + Fe^{3+};\quad k_3 = 1.06 \times 10^4\ \text{s}^{-1}\ (\text{ref. }4) \tag{3}$$

In the present study we have obtained direct evidence for the intermediates of the reactions of Fe^{2+} with the hydrated electron. In order to eliminate the very fast reaction [equation (4)] which can compete with reaction (1), we took special care to prepare $Fe[SO_4]$ solution with a small quantity of Fe^{3+}. An absorption spectrum of the intermediate formed in reaction (1) clearly indicates the Fe^+ ion and that its properties are different in many respects from those of the $[Fe^{2+}\text{–}H]$ complex. In addition, some steady-state γ-radiolysis studies were carried out in order to obtain more information about reactions in which molecular hydrogen is produced.

$$e^-(aq) + Fe^{3+} \longrightarrow Fe^{2+} + H_2O;\quad k_4\ ca.\ 5 \times 10^{10}\ \text{dm}^3\ \text{mol}^{-1}\ \text{s}^{-1}\ (\text{ref. }6) \tag{4}$$

EXPERIMENTAL

Materials.—Ferrous sulphate solutions were prepared by dissolving iron metal (B.D.H.) in 4 mol dm^{-3} H_2SO_4 at 60 °C under an argon atmosphere. The ferrous sulphate solutions were transferred, into 100-cm^3 all-glass syringes joined to the preparation vessel, by applying argon pressure and then diluted. The concentration of Fe^{3+} was monitored throughout. The pH of the solutions was adjusted with Na[OH]. Solutions were prepared from analytical grade chemicals (Merck or B.D.H.). Triply distilled water was used throughout.

Procedure.—For pulse radiolysis a Febetron 707 (Field Emission Corp.) electron accelerator with pulse duration of 20 ns was used, the operating conditions being similar to those described previously.[7] The total light path through the cell was 5.1 cm. The absorbed doses were in the range 0.5—9 krad pulse^{-1} † measured by using a potassium ferrocyanide dosimeter [8] and taking ε_{420} $[Fe(CN)_6]^{3-}$ = 1 000 dm^{-3} mol^{-1} cm^{-1} and $G[Fe(CN)_6]^{3-}$ = 5.6.

Steady-state irradiations were performed with a ^{60}Co γ source. The total absorbed doses were in the range 5—60 krad and the dose rate was 10 krad min^{-1}. Molecular hydrogen was determined by gas chromatography.[9] The pH of the solution was determined in an argon atmosphere. The measurements were accurate to within 0.01 pH unit and were recorded at 20 ± 1 °C.

RESULTS AND DISCUSSION

Absorption Spectrum of $Fe^+(aq)$.—Pulse radiolysis of concentrated and dilute solutions of $Fe[SO_4]$ allowed us to distinguish between the intermediates formed from reaction (1) and those from reactions (2) and (5). The results are presented in Figure 1(*a*).

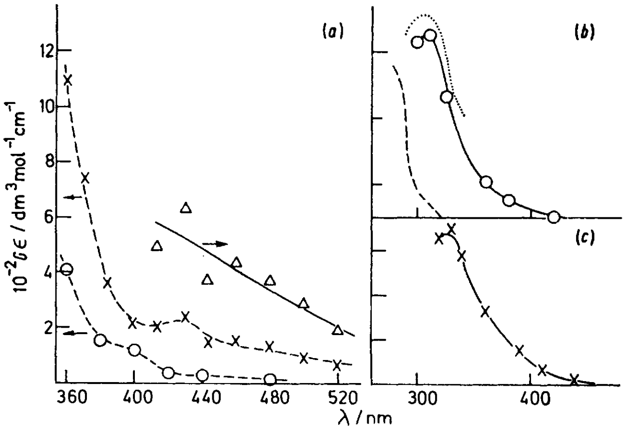

FIGURE 1 Absorption spectra of intermediates formed in aqueous iron(II) sulphate solutions. (*a*) Argon-saturated solutions: 3 × 10^{-3} mol dm^{-3} $Fe[SO_4]$, pH 2.65 (○); 0.4 mol dm^{-3} $Fe[SO_4]$, pH 3.65, measured 5 μs after the pulse (×); spectrum of Fe^+ intermediate (△). Absorbed dose 7.7 krad. (*b*) N_2O-saturated 3 × 10^{-3} mol dm^{-3} $Fe[SO_4]$, pH 3.2, measured 600 μs after pulse (○). Absorbed dose 6.9 krad. Broken and dotted lines represent the spectra of Fe^{3+} and $[Fe(SO_4)]^+$, respectively, taken from ref. 10. (*c*) Argon-saturated 4 × 10^{-2} mol dm^{-3} $Fe[SO_4]$, pH 0.55. Absorbed dose 6.9 krad

Since preparation of $Fe[SO_4]$ at higher pH always resulted in a much lower concentration of Fe^{3+} ions than in $Fe[ClO_4]_2$ solutions, we chose to work with $Fe[SO_4]$

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† Throughout this paper: 1 rad = 10^{-2} J kg^{-1}.

solutions to avoid reaction (4). However, in the presence of $[SO_4]^{2-}$ ions the build up of the $[Fe(SO_4)]^+$ complex from uncomplexed Fe^{3+} ions after the pulse was an additional factor in the interpretation of the kinetic data. The $[Fe(SO_4)]^+$ spectrum formed by reaction (6) is recorded at 600 μs after pulse and presented in Figure 1(*b*). The absorption of $[Fe(SO_4)]^+$ did not overlap the measured spectrum of reaction (1) intermediates up to 420 nm.

In dilute solution [Figure 1(*a*), lower curve] oxidation of Fe^{2+} occurs, equations (5) and (6), and $[Fe^{2+}\text{–}H]$

$$Fe^{2+} + OH \longrightarrow Fe^{3+} + [OH]^-; \quad k_5 = 3.5 \times 10^8\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 11)} \qquad (5)$$

$$Fe^{3+} + [SO_4]^{2-} \longrightarrow [Fe(SO_4)]^+ \qquad (6)$$

complexes are formed by reaction (2). Competition of reaction (2) with (7) takes place. Hydrogen atoms can be formed too, by reaction (8). Under these conditions

$$H + H \longrightarrow H_2; \ k_7 = 1.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 5) at pH 2—3} \qquad (7)$$

$$e^-(aq) + H^+ \longrightarrow H; \quad k_8 = 2.3 \times 10^{10}\ dm^3\ mol^{-1}\ s^{-1}\ \text{(ref. 6)} \qquad (8)$$

[Figure 1(*a*), lower curve] reaction of Fe^{2+} with $e^-(aq)$ does not take place. Reactions between H and OH, as well as recombination of OH radicals, can also be neglected. This means that H atoms react in reactions (2) and (7), and OH in reaction (5). The increase in absorption is attributed to $[Fe^{2+}\text{–}H]$ (8×10^{-6} mol dm^{-3}) and Fe^{3+} (2×10^{-5} mol dm^{-3}). We calculated the contribution due to Fe^{3+} by taking $G(Fe^{3+}) = G_{OH} = 2.6$. However, we estimated the $[Fe^{2+}\text{–}H]$ complex yield to be 1.0 on the basis of the complex concentration formed for the dose given. The concentration of the complex was calculated by equation (9), derived by Jayson *et al.*,[4] which takes into account competition between reactions (2) and (7) where H_0 represents the

$$[Fe^{2+}\text{–}H] = \frac{[Fe^{2+}]k_2}{k_7} \ln\left(1 + \frac{k_7 H_0}{k_2[Fe^{2+}]}\right) \qquad (9)$$

initial hydrogen-atom concentration, found to be 2.6×10^{-5} mol dm^{-3} $\{G(H) = G_H + G_{e^-(aq)} = 3.25\}$ under our experimental conditions.

The spectrum of $[Fe^{2+}\text{–}H]$ obtained in $Fe[SO_4]$ solution at pH 0.55, which is the same as that previously established in $Fe[ClO_4]_2$ solution,[4] is given in Figure 1(*c*) as an illustration.

In concentrated solutions at pH 3.65 [Figure 1(*a*), upper curve] reactions (1) and (5) are dominant and reaction (2) takes place to a lesser extent. The spectrum shows a weak broad band in the region 400—600 nm and absorption only decreases slightly, from 5 μs to several milliseconds. Corrections for the contributions of Fe^{3+} and $[Fe^{2+}\text{–}H]$, below 420 nm, are considerable [Figure 1(*a*), lower curve and Figure 1(*b*) and 1(*c*)] and there is further uncertainty concerning real values for G_{OH}, G_H, and $G_{e^-(aq)}$ due to spur scavenging in concentrated $Fe[SO_4]$ solution (0.4 mol dm^{-3}). For this reason the transient spectrum of Fe^+ was estimated above 420 nm where absorption of Fe^{3+} and $[Fe^{2+}\text{–}H]$ is very weak [Figure 1(*b*) and 1(*c*)] and the correction does not exceed 20%. These corrections were made by using the spectrum in dilute solution [Figure 1(*a*), lower curve], assuming that Fe^{3+} contribution is negligible, that $G_H = 0.55$ and that the yield of H, formed by reaction (8), is 0.54. The last value was calculated from the data presented in Figure 3. It should be mentioned here that the spectrum obtained in this way is exactly the same as that of the long-lived component recorded 10 ms after the pulse. The short-lived component ($\tau_{\frac{1}{2}} = 1.4 \times 10^{-4}$ s) seems to be the $[Fe^{2+}\text{–}H]$ complex present to a small extent as was confirmed by our observation of the kinetics of $[Fe^{2+}\text{–}H]$ decomposition.

Mechanism of Decomposition of $[Fe^{2+}\text{–}H]$.—For a better understanding of the kinetics of the intermediates formed by reaction of $e^-(aq)$ and H, we followed the decay of $[Fe^{2+}\text{–}H]$ at 420 nm at different $[H_3O]^+$ concentrations (2.5×10^{-4}—3×10^{-1} mol dm^{-3}). The results are presented in Figure 2. The kinetics of the decay were always first order, independent of $[SO_4]^{2-}$ concentrations. In $Fe[ClO_4]_2$ solution the decay rate depends linearly on $[H_3O]^+$ concentration. Similar behaviour has also been found for the $[Cr^{2+}\text{–}H]$ complex formed by reaction of Cr^{2+} with H atoms.[12,13] However, we have found a difference in the kinetics in $[ClO_4]^-$ and $[SO_4]^{2-}$ solutions. It seems that the process which controlled the rate of $[Fe^{2+}\text{–}H]$ decomposition is intermolecular rearrangement resulting in the formation of the $[Fe(SO_4)]^+$ complex, which was different from the formation of free Fe^{3+} ions in $[ClO_4]^-$ solutions. The decomposition most likely occurs according to the reactions (10) and (11). It has been found that the observed rate constant, $k_{obs.}$, depends on the $[H_3O]^+$ concentration (Figure 2) according to the expression $k_{obs.} = k_g +$

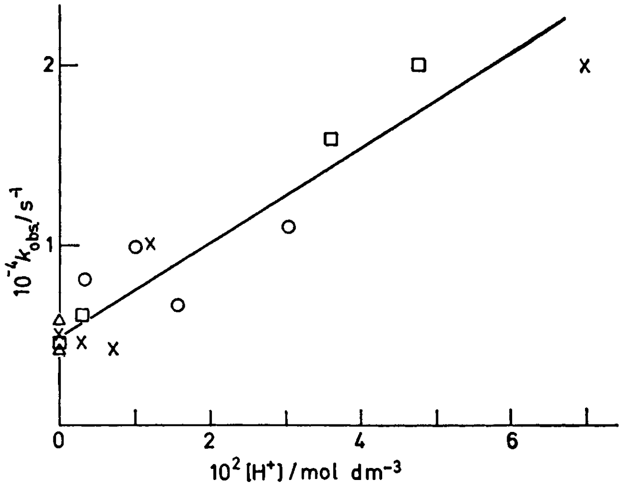

FIGURE 2 Decomposition rate constant of $[Fe^{2+}\text{–}H]$ as a function of oxonium ion concentration in the presence of various sulphate ion concentrations: 2.5×10^{-2}—7.8×10^{-2} (○); 0.2 (△); 1.2—1.45 (×); 0.4—0.6 mol dm^{-3} (□)

$[H_3O^+]k_{10}$. Therefore, we have measured $k_{obs.}$ at different $[H_3O]^+$ concentrations and calculated the rate constants $k_9 = 5 \times 10^3$ s^{-1} and $k_{10} = 2.6 \times 10^5$ dm^3 mol^{-1} s^{-1}.

Formation of Molecular Hydrogen.—Molecular hydrogen is formed in the reaction of the $[Fe^{2+}–H]$ complex [reactions (10) and (11)]. It has been found that $G(H_2)$ (= 3.9 at pH 1) does not depend on the absorbed

$$[Fe(SO_4)–H] + H_2O \longrightarrow H_2 + [Fe(SO_4)]^+ + [OH]^- \quad (10)$$

$$[Fe(SO_4)–H] + [H_3O]^+ \longrightarrow H_2 + [Fe(SO_4)]^+ \quad (11)$$

dose, dose rate, $Fe[SO_4]$ concentration, or the presence of Fe^{3+} ions. However, $G(H_2)$ decreases with increasing pH of the solution. This effect is related to the formation of Fe^+ ions in solutions. A similar effect has already been found for Ti^{2+} ions formed by reaction of e$^-$(aq) with $Ti_2[SO_4]_3$ which also do not give rise to molecular hydrogen.[14]

We have determined molecular hydrogen as a function of $[Fe^{2+}]/[H_3O^+]$ and the results are presented in Figure 3. Determination of molecular hydrogen provides the basis for determination of k_1/k_8 since H atoms formed in reaction (8) react with $Fe[SO_4]$ yielding H_2. In our calculation of k_1/k_8 we assumed that $G_{H_2} + G_H = 1$ [see equation (12), where $G(H_2)$ and G_{H_2} are the yields of hydrogen formed in all processes and in the primary radiation processes, respectively].

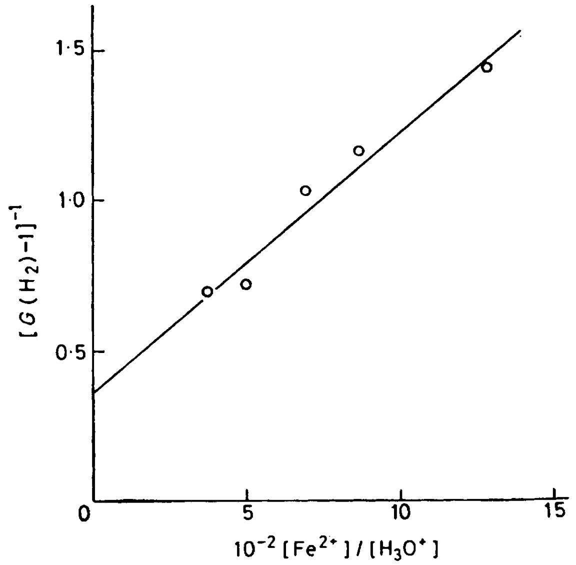

FIGURE 3 The competition between Fe^{2+} and $[H_3O]^+$ for e$^-$(aq) in the presence of 0.2 mol dm^{-3} $Na_2[SO_4]$

$$[G(H_2) - G_{H_2} - G_H]^{-1} = \{G_{e-(aq)}\}^{-1}\left(1 + \frac{k_1[Fe^{2+}]}{k_8[H^+]}\right) \quad (12)$$

In the presence of 0.2 mol dm^{-3} $Na_2[SO_4]$, $k_1/k_8 = 2.2 \times 10^{-3}$ was obtained. This value is lower than the ratio of the rate constants (0.52×10^{-2}—1.5×10^{-2}) previously obtained separately for reactions (1) and (8) at low ionic strength probably due to the greater effect of ionic strength on the decrease of the rate constant of reaction (1) than of reaction (8).

In γ-irradiated solutions of $Fe[SO_4]$ (0.4 mol dm^{-3}) at pH 3.7 the values of $G(H_2) = 1.12$ and $G(Fe^{3+}) = 5.5$ have been obtained. The hydrogen yield can be equated with $G_H + G_{H_2}$ and $G(Fe^{3+})$ with $G_H + G_{OH} + 2G_{H_2O_2} + fG_{e-(aq)}$, where $fG_{e-(aq)}$ represents the yield of reaction (8). It seems that neither H_2 nor Fe^{3+} is the main product of the decay of Fe^+. The reduction of water to molecular hydrogen by Fe^+ seems to be a very slow process which can easily be suppressed by the presence of other solutes in aqueous solutions. On the other hand, transient absorption of Fe^+ is very weak in the 420—600 nm region and the procedure used in this study does not permit unequivocal observation of Fe^+ reactions with other radicals or oxidizing agents. The reaction of Fe^+ with H_2O_2 may occur only partly since it competes with the reaction of Fe^{2+} with H_2O_2. However, two other reactions are also probable: the disproportionation, which was found to occur with other unstable univalent ions,[15] and the reaction with impurities.

Reduction of bivalent transition-metal ions, such as Co^{2+}, Ni^{2+}, Zn^{2+}, Cu^{2+}, Cr^{2+}, and Cd^{2+}, has been studied in detail.[12,15] In aqueous solutions all these metal ions are rapidly reduced by e$^-$(aq) to the corresponding lower valency state M^+, and show intense optical absorption bands in the ultraviolet region [15] and high reactivity towards oxidizing agents.[16,17] However, reduction of Fe^{2+} by e$^-$(aq) is not so fast. The obtained spectrum [Figure 1(*a*) upper curve] of Fe^+ shows a weak band in the visible region very similar to the second band of Ni^+ and Co^+ obtained in the same wavelength region.[15] The spectral similarities between these ions are not unexpected taking into account their electronic structures.

We have tried to see whether N_2O oxidizes Fe^+ as it does other univalent metal ions,[18] *i.e.* equation (13), and

$$Fe^+ + N_2O \longrightarrow N_2 + \text{product} \quad (13)$$

found that in γ-irradiated solutions of 2.2×10^{-2} mol dm^{-3} N_2O at pH 6, and in the solution of $Fe[SO_4]$ (0.4 mol dm^{-3}) in the presence of 4.4×10^{-4} mol dm^{-3} N_2O at pH 3.4, $G(N_2)$ decreases from 3.2 to 0.9. This indicates that reaction (13) takes place. $G(N_2)$ is less than the value expected for $G(Fe^+)$ according to the rate constants of reactions (1) and (8), probably due to the reaction of Fe^+ with impurities. Our observation was limited only to low N_2O concentrations since higher concentrations cannot be used without remarkable competition of N_2O for e$^-$(aq).

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