Photo-oxidation of Iron(II) in Water between pH 7.5 and 4.0

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Photo-oxidation of $[Fe(H_2O)_6]^{2+}$ proceeds at $\lambda < 300$ nm with formation of a solvated electron. At pH > 6.5, however, the photochemistry is dominated by the species $[Fe(OH)]^+(aq)$, which is photo-oxidised to Fe^{III} even by filtered light of $\lambda > 400$ nm, without formation of solvated electrons. The compound γ-FeO(OH) is precipitated throughout the range, even in the presence of 0.56 mol dm^{-3} NaCl. The effect of pH on the mechanism is discussed, as are the implications for CO_2 fixation.

It has been known for many years that iron(II) solutions in water are oxidised by u.v. light to give iron(III) species and hydrogen [equation (1)].[1] The process has been thoroughly

$$2\,Fe^{II}(aq) \xrightarrow{h\nu} 2\,Fe^{III}(aq) + H_2 \qquad (1)$$

investigated in aqueous sulphuric acid, and the quantum yield shown to depend on the concentrations of acid,[2-4] falling at pH >3 towards a limiting value,[4] and of sulphate.[5] The detailed mechanism of the reaction has remained obscure, with the intermediacy of the familiar solvated electron discussed inconclusively by some authorities[6] and explicitly denied by others.[7]

The reaction is difficult to study at pH >3.5. Oxidation by any dissolved O_2 is far more rapid,[8,9] and Fe^{III}, formed either by this process or photochemically, undergoes a series of deprotonation processes which change the pH, generate strongly absorbing iron(III) hydroxy-species, and lead eventually to precipitation. Inorganic buffers generally interact with Fe^{III}, while non-complexing organic buffers[10] cannot be guaranteed inert to highly reactive photochemical intermediates. For these reasons, presumably, no prior photochemical studies of near-neutral solutions of hydrated Fe^{2+} have appeared, although Stuglik and Zagórski[11] have described the radiolysis of such systems.

We were, however, particularly interested in the reactions at higher pH. Early Precambrian sediments contain massive deposits of banded iron formations, presumed to have formed through the precipitation of iron(II), dissolved in seawater, by oxidation to iron(III). This oxidation had been ascribed to low levels of atmospheric oxygen derived from u.v. photolysis of water vapour and/or CO_2,[12] or to biological activity.[13] Clearly there are major implications here for conditions on the early Earth and for the evolution of life.[14] We wished to test a null hypothesis: that sunlight alone, acting directly on dissolved iron(II), would have been a sufficient precipitating agent.[15] (As we shall show elsewhere, the results reported here give strong support to that hypothesis.) Preliminary accounts of parts of this work have already appeared.[16,17]

Experimental

Gases were scrubbed of residual oxygen by passage over finely divided copper (BASF R3-11) at 160 °C; mass spectrometry showed less than 1 p.p.m. residual oxygen. Purification and recrystallisation were carried out in a nitrogen-purged glovebox. Samples for photolysis were prepared by dissolving $K_2Fe(SO_4)_2\cdot 6H_2O$ in argon-flushed 10^{-3} mol dm^{-3} H_2SO_4, and transferred to the photolysis cell using a specially designed glass line, after which the system was flushed with argon and the pH adjusted by injection of argon-saturated 0.1 mol dm^{-3} NaOH. The photolysis cell, and all glassware in which solutions were stored, were first silanised with $SiMe_3Cl$ and then steamed out to reduce pH drift. The salt $K_2Fe(SO_4)_2\cdot 6H_2O$ (BDH) was purified by stirring in *ca.* 10^{-3} mol dm^{-3} H_2SO_4 with iron powder (Ventron Puratronic) for 12 h to remove Fe^{III} and Cu^{II}. The material was then filtered, twice recrystallised from hot water, and dried in a silica gel desiccator. Dissolved copper (colorimetric, as neocuproin complex[18]) was negligible, and the effective absence of Fe^{III} was confirmed spectroscopically both directly at 245 nm[19] and, more conclusively, as thiocyanate at 480 nm.[20] [Solutions showing more than 0.5 p.p.m. Fe^{III}, uncorrected for reagent background, were rejected, and the iron(III) level in most runs was decidedly less than this.]

Samples of solutions for spectroscopy were withdrawn directly from near the base of the photolysis cell through Teflon stopcocks *via* vacuum glassware into an evacuated quartz 1-cm cell. Samples for colorimetric analysis were obtained similarly, after the solution in the cell had been acidified with argon-purged dilute sulphuric acid and left to stand for at least 30 min.

We found it necessary to clean all glassware in which iron(II) solutions had been handled, by successive acidification with dilute HCl and soaking in neutral sodium dithionite solution. The removal of Fe^{III} from the absorption cell was routinely verified spectroscopically. Neglect of these precautions leads rapidly to the formation of mechanically robust films and to spurious spectra.

For continuous photolysis, solutions (between 2×10^{-2} and 10^{-3} mol dm^{-3} Fe^{2+}) were irradiated from above through a Suprasil II window using light from a Hanovia UVS 220 medium-pressure mercury lamp 25 cm above the solution. The light was filtered by passage through 5 cm of distilled water in a Suprasil cell, as well as, on occasion, through Schott glass filters. The solution depth was typically 30 mm, and the pH and temperature were continuously monitored for all runs, using a pH combination electrode (Probion SR217), a gold or platinum redox electrode, and a Beckman platinum resistance thermometer. Data were collected on a custom-built multichannel recorder [W. A. Scott (Scientific Instruments) Ltd.] (temperature remained fairly constant at 22 ± 0.5 °C). In several runs, total Fe^{III} was determined as thiocyanate,[20] while the gas evolved was examined in a Micromass MM601 mass spectrometer.

The lamp output of light absorbed by $[Fe(H_2O)_6]^{2+}$ was estimated from the value of 0.142 implicit in Jortner and Stein's findings[4] for the quantum yield of reaction (1) in 0.26 mol dm^{-3} H_2SO_4; our yield, like theirs, was corrected by integrating over time for the inner-filter effects of Fe^{III}. Lamp output at 366 nm was estimated by ferrioxalate actinometry[21] using a 331-nm cut-off filter together with a cobalt glass filter. Precipitates were examined by electron diffraction and transmission using a JEOL 100C electron microscope.

Flash-photolysis experiments were carried out in an apparatus described in detail elsewhere[22] using a frequency-quadrupled neodymium glass laser (up to 20 mJ cm^{-2} output at 265 nm; pulse length 25 ns), or a frequency-doubled ruby laser (400 mJ cm^{-2} output at 347 nm; pulse length 30 ns). Quantum yields of the transient ascribed (see below) to $e^-(aq)$ were estimated by the comparative method[23] using the naphthalene and anthracene triplet absorption in cyclohexane as standard,[24] and literature values[25] for $\varepsilon[e^-(aq)]$.

Results and Discussion

Most of the experiments described here were carried out in 0.56 mol dm^{-3} NaCl (because of our interest in Precambrian sea-water), but results in water were similar. Dark reactions were negligible in all cases.

Photolysis of $[Fe(H_2O)_6]^{2+}$ *in the Range* pH 6.2—4.—(*a*) *Overall reaction.* As expected, iron(III) was produced in accord with equation (1), and hydrolysed rapidly according to the well studied[26] equilibria idealised in equations (2)—(4). There was no pH drift before illumination, but after illumination the pH drifted downwards, typically for an hour or two, and the solutions become turbid [equation (5)].

$$Fe^{3+}(aq) \rightleftharpoons [Fe(OH)]^{2+}(aq) + H^+(aq) \qquad (2)$$

$$[Fe(OH)]^{2+}(aq) \rightleftharpoons \tfrac{1}{2}[Fe_2(OH)_4]^{2+}(aq) + H^+(aq) \qquad (3)$$

$$\tfrac{1}{2}[Fe_2(OH)_4]^{2+}(aq) \rightleftharpoons Fe(OH)_3(aq) + H^+(aq) \qquad (4)$$

$$Fe(OH)_3(aq) \longrightarrow FeO(OH)\ (s) \qquad (5)$$

The ratio of protons generated (as measured by pH change) to Fe^{III} formed was itself a function of pH and photolysis time, but for clear solutions was around 1 : 1 at pH 5. This is as expected from the known features[26] of equilibria (2)—(4). The quantum yield for iron(III) formation was 0.06 ± 0.03. The main sources of scatter here were fluctuations in precipitation kinetics, and electrode drift. No correction was applied for internal filtering; thus our value is a lower limit. The turbid solutions cleared within a very few hours, casting a granular precipitate identified by transmission electron microscopy as γ-FeO(OH). This was in the form of thin, highly crumpled plates. The measured ratio of protons to Fe^{III} formed rose at the precipitation stage to 2.20 ± 0.05 : 1, in fairly good agreement with the overall reaction (6).

$$Fe^{2+}(aq) \xrightarrow{h\nu} \gamma\text{-}FeO(OH) + 2H^+(aq) + \tfrac{1}{2}H_2 \qquad (6)$$

The formation of γ- rather than β-FeO(OH) even in the presence of 0.56 mol dm^{-3} Cl$^-$ is presumably a consequence of the high pH, rather than of the method of oxidation, since γ-FeO(OH) is also the reported[9] product of oxygenation for $Fe^{2+}(aq)$ in 0.5 mol dm^{-3} NaCl.

Hydrogen gas was evolved during the reaction, together with HD and D_2 when the solvent contained D_2O. Gold redox electrodes became more positive throughout the photolysis, as expected. Platinum electrodes, after an initial rise in potential, became much more negative; this effect is ascribable to chemisorbed hydrogen and was removed by flushing with nitrogen for 30 min. In view of the complexity of the equilibria, no attempt was made to analyse the redox data.

(*b*) *Effect of gases and other additives.* Experiments were routinely performed under argon. Substitution of methane or hydrogen made no measurable difference. The pH drift appeared to be slightly slower under nitrogen (suggesting the possibility of interference by nitrogen fixation). Dinitrogen oxide (N_2O) was without effect on rates. 2-Propanol (0.5 mol dm^{-3}) retarded the reaction by a factor of 2.6 ± 0.6, implying the quenching of an intermediate. The rate in 0.56 mol dm^{-3} NaBr was the same as that in 0.56 mol dm^{-3} NaCl, but that in water was some 20% lower; this is presumably a simple medium effect. Dissolved amorphous silica (Mallinckrodt silicic acid dissolved in alkali and neutralised) had no effect either on the reaction rate or on the identity of the precipitate.

(*c*) *Flash photolysis.* Irradiation at 265 nm of N_2-saturated solutions of pH 4.8—6.0, containing 0.02 mol dm^{-3} Fe^{2+} and 0.56 mol dm^{-3} NaCl, produced a broad transient absorption, peaking between 700 and 800 nm, approximately halving in intensity when the pulse energy was halved, and completely quenched on our detection time-scale in N_2O-saturated solution. We assign this signal to monophotonically produced $e^-(aq)$. The quantum yield for the process was 0.06 ± 0.03, and the signal half-life was 400 ns.

The only effective scavengers for the solvated electron in our system are $Fe^{2+}(aq)$ and $H^+(aq)$, so that the first-order rate constant for disappearance for $e^-(aq)$ is given by equation (7).

$$k_{obs.} = k(Fe^{2+} + e^-_{aq})[Fe^{2+}] + k(H^+ + e^-_{aq})[H^+] \qquad (7)$$

Literature values[25] for $k(Fe^{2+} + e^-_{aq})$ and $k(H^+ + e^-_{aq})$ are 1.2×10^8—3.5×10^8 and 2.3×10^{10}—2.4×10^{10} dm^3 mol^{-1} s^{-1} respectively. Thus, under our conditions, but not at lower pH, quenching by $Fe^{2+}(aq)$ (to give Fe^I) should dominate and the overall half-life should be 100—300 ns. This agrees tolerably well with our findings.

(*d*) *Mechanism.* Our electron-ejection process occurs well within 25 ns of excitation, since the $e^-(aq)$ signal reaches its full value within the duration of the pulse. The quantum efficiency is small compared with the familiar[27] electron-ejection processes of $[Fe(CN)_6]^{4-}$ in the charge transfer-to-solvent region. The photon energy required is in excess of that calculated (see Appendix) for formation of $[Fe(H_2O)_6]^{3+}$ and a solvated electron, or even a mobile electron[28] which subsequently achieves solvation. Each electron ejection must lead to the ultimate conversion of two Fe^{2+} ions into Fe^{III}, and recombination of ejected electrons or their decay products with Fe^{III} must be insignificant, otherwise N_2O would have caused an increase in rate. As already implied, the main secondary product from $e^-(aq)$ in these experiments is Fe^I. It follows that each Fe^I gives rise to one Fe^{III}. The quenching effect of 2-propanol is most probably the interception of a hydrogen atom,[29] generated from Fe^I and a proton. [We cannot of course rule out direct interaction between iron(I) and 2-propanol, but there is no reason to invoke such a novel process.] There is no significant reaction between the $(CH_3)_2\dot{C}OH$ radical and Fe^{II}, since such reaction would have negated the role of 2-propanol as quencher. Iron(I) has previously been reported as a product of electron capture following radiolysis, but its fate has remained obscure.[30]

We thus arrive at the reaction sequence (8)—(19). Reaction

$$Fe^{2+}(aq) \xrightarrow{h\nu} A^* \qquad (8)$$

$$A^* \longrightarrow Fe^{3+}(aq) + e^-(aq) \qquad (9)$$

$$e^-(aq) + H^+ \longrightarrow H^\cdot \qquad (10)$$

$$e^-(aq) + Fe^{2+}(aq) \longrightarrow Fe^+(aq) \qquad (11)$$

$$Fe^+(aq) + H^+ \longrightarrow Fe^{2+} + H^\cdot \qquad (12a)$$

or

$$Fe^+(aq) + H^+ \longrightarrow [FeH]^{2+}(aq) \qquad (12b)$$

$$\mathrm{Fe^{2+}(aq) + H^{\bullet} \rightleftharpoons [FeH]^{2+}(aq)} \qquad (13)$$

$$\mathrm{[FeH]^{2+}(aq) + H^{+} \longrightarrow Fe^{3+}(aq) + H_2} \qquad (14)$$

$$\mathrm{e^{-} + N_2O(aq) \longrightarrow N_2 + OH^{-} + OH^{\bullet}} \qquad (15)$$

$$\mathrm{Fe^{2+}(aq) + OH^{\bullet} \longrightarrow [Fe^{III}(OH)]^{2+}(aq)} \qquad (16)$$

$$\mathrm{H^{\bullet} + (CH_3)_2CHOH \longrightarrow H_2 + (CH_3)_2\dot{C}OH} \qquad (17)$$

$$\mathrm{Fe^{2+}(aq) + (CH_3)_2\dot{C}OH \not\longrightarrow Fe^{III}} \qquad (18)$$

$$\mathrm{A^{*} \longrightarrow Fe^{2+}(aq)} \qquad (19)$$

(9) represents the formation of a solvated electron, either directly or *via* a mobile electron, from the prompt excited species, and will be followed predominantly by reaction (10) at pH < 3.5. Under our conditions, however, the electron is scavenged according to equation (11). The partial quenching by 2-propanol arises from reaction (12a) followed by (17); we cannot say whether (12a) occurs directly, or as (12b) followed by the reverse of (13). 2-Propanol is therefore expected to reduce the rate by a factor of 2; the observed factor of 2.6 ± 0.6 may also include a medium effect, and/or some reduction of $\mathrm{Fe^{III}}$ by $\mathrm{(CH_3)_2\dot{C}OH}$ radicals. The reversible association (13) of $\mathrm{Fe^{2+}(aq)}$ and $\mathrm{H^{\bullet}}$ and the subsequent formation (14) of $\mathrm{Fe^{III}}$ and $\mathrm{H_2}$ are known reactions.[29] Equations (15) (which is valid either for mobile or for trapped electrons [31]) and (16) describe the role of $\mathrm{N_2O}$.

According to this scheme the quantum yield for $\mathrm{Fe^{III}}$ should be twice that for electrons. The correspondence between our values for these yields (0.06 ± 0.03 in each case) is merely accidental and reflects our rather high error limits. It is probably our value for the yield of $\mathrm{Fe^{III}}$ that is the less accurate due to the difficulty of extrapolating to zero internal filtering.

The pathway shown in our scheme need not necessarily be the only one in operation, and it is likely on other grounds (see below) that part of the photolysis proceeds by hydrogen loss [equation (20)] followed by reaction (13), *etc.* However,

$$\mathrm{A^{*} \longrightarrow [Fe^{III}(OH)]^{2+}(aq) + H} \qquad (20)$$

since reaction (20) would add to the yield of $\mathrm{Fe^{III}}$ but not to that for electrons, it cannot be the major pathway.

Photolysis of '$\mathrm{Fe^{2+}(aq)}$' *at* pH > 6.5.—Solutions of $\mathrm{Fe^{2+}(aq)}$ are in fact weakly buffered at pH > 6.5 according to the equilibrium (21) for which [26] $K = 3.2 \times 10^{-10}$ mol dm^{-3}, and

$$\mathrm{Fe^{2+}(aq) \rightleftharpoons [Fe(OH)]^{+}(aq) + H^{+}} \qquad (21)$$

the overall increase in $[\mathrm{H^{+}}]$ during photolysis must be corrected for this to obtain a true reaction rate. Reaction rates in the dark remained negligible, but the true light-induced rate was about 10-fold greater than at lower pH, and the threshold shifted to much longer wavelengths, light of $\lambda > 406$ nm still being effective. The reaction rate slowed down as the pH fell towards 6.4, and the ratio of protons released to $\mathrm{Fe^{III}}$ formed was about 2 : 1.

We infer that, although $\mathrm{Fe^{2+}(aq)}$ is still the main iron(II) species present, the photoactive species is $\mathrm{[Fe(OH)]^{+}(aq)}$. Ehrenfreund and Leibenguth [32] have reported an absorption shoulder at 320 nm, tailing to *ca.* 450 nm, which they ascribe to this species. Like them, we find a reproducible absorption tail in this region, stretching to at least 410 nm, although we would not claim quantitative agreement. This absorption was not ascribable to the small and variable traces (see Experimental section) of $\mathrm{Fe^{III}}$ that were sometimes present, being too reproducible, too intense (at least for $\mathrm{Fe^{III}}$), and distinct in shape from that of known iron(III) [19,33] and any iron(II)–iron(III) species.[34] The variation of intensity with pH, within the small range accessible before $\mathrm{Fe(OH)_2}$ began to precipitate, was as expected for $\mathrm{[Fe(OH)]^{+}(aq)}$. We could not ourselves observe any shoulder at 320 nm, but cannot be dogmatic about this since at $\lambda < 290$ nm absorption was dominated by $\mathrm{Fe^{2+}(aq)}$. Ehrenfreund and Leibenguth's value for the equilibrium constant of equation (21), however, is clearly in error,[26] and would indeed have implied a rate of proton production in our experiments, at pH *ca.* 7, greater by an order of magnitude than that of iron(III) formation. The absorption coefficient at 366 nm (the wavelength used to estimate quantum yield) was *ca.* 200 dm^3 mol^{-1} cm^{-1}. This is consistent with the non-appearance of this absorption in Staglik and Zagórski's spectra,[11] since even at pH 7 only *ca.* 0.3% of the $\mathrm{Fe^{II}}$ is hydrolysed. At pH > 6.5, $\mathrm{Fe^{III}}$ will mainly [26] be present as neutral species $\mathrm{[Fe(OH)_3(aq)}$, aggregates, and eventually $\mathrm{FeO(OH)]}$. Thus we write the process as in equations (21)—(23). The quantum yield for the

$$\begin{array}{ll} \mathrm{[Fe(OH)]^{+}(aq) \xrightarrow{h\nu} `Fe(OH)_3' + H^{+}(aq)} & (22) \\ \hline \mathrm{Fe^{2+}(aq) \longrightarrow `Fe(OH)_3' + 2H^{+}(aq)} & (23) \end{array}$$

process was estimated as 0.01—0.05; here, as in our earlier publication,[17] the value is based on the amount of light actually absorbed by our solutions at 366 nm.

The rather high uncertainty arises from the possible pH drift of our solutions during spectroscopic sampling, the very high sensitivity of the percentage light absorption to the pH of the solution, possible uncertainty as to the equilibrium constant of equation (21) in our medium, and the difficulty, inherent in our procedure, of estimating an initial rate from pH changes when the absorbance, and hence the rate, are themselves strongly dependent on pH. Very recently, Brimblecombe and Chang [35] obtained a value in the same range by direct analysis of iron(III) production at constant pH.

These data nevertheless unequivocally establish that $\mathrm{OH^{-}}$ effectively photosensitises the conversion of $\mathrm{Fe^{II}}$ into $\mathrm{Fe^{III}}$ in water, even by visible-near-u.v. light. Indeed, we have shown [17] that this process can more than account for the estimated annual deposition rate of iron in one of the most extensive banded iron formations, and presumably it would have been of major importance in any $\mathrm{Fe^{II}}$-containing Precambrian surface waters.

We turn now to the mechanism of this process. A careful search for solvated electrons using 0.02 mol dm^{-3} $\mathrm{Fe^{II}}$ and 0.56 mol dm^{-3} NaCl in the pH range 6.5—7.3, subjected to flash photolysis at 347 nm, was fruitless. Moreover, the calculated thermodynamic threshold for the hypothetical formation of $\mathrm{e^{-}(aq)}$ from $\mathrm{[Fe(OH)]^{+}(aq)}$ is *ca.* 390 nm (see Appendix). This is a shorter wavelength than the observed threshold, and in any case represents a very unlikely process, since solvated electrons are not expected to form directly in charge transfer-to-solvent (c.t.t.s.) processes but to be generated from mobile electrons [28] or other high-energy species. As expected, $\mathrm{N_2O}$ was without effect on the rate. 2-Propanol reduced the rate by a factor of 2.7 ± 0.8; this is evidence for the intermediacy of H atoms, formed either directly or by reaction of $\mathrm{Fe^{I}}$.

The reaction could conceivably involve such steps as (24) or (25). Of these, the threshold energy for (24) is clearly excessive (see Appendix); in any case, were the reaction to proceed

$$\mathrm{[Fe(OH)]^{+}(aq) \longrightarrow Fe^{+}(aq) + OH^{\bullet}} \qquad (24)$$

$$\mathrm{[Fe(OH)]^{+}(aq) \longrightarrow [Fe(OH)_2]^{+}(aq) + H^{\bullet}} \qquad (25)$$

according to equation (24), it would be totally suppressed by 2-propanol which is a good scavenger of hydroxyl radicals,[36] and also, as we have seen, for decay through Fe^{I}. We therefore suggest that (25) represents the reaction pathway. It may then be that the absorption step, both for $Fe^{2+}(aq)$ and for $[Fe(OH)]^{+}(aq)$, is a very similar c.t.t.s.(σ^*) process, but that in the former case only the c.t.t.s. state can lose an electron. Photosensitisation by hydrolysis is due in part to a lowering of the energy of the c.t.t.s. state (charge effect), and in part to the increased intensity of the c.t.t.s. absorption, resulting perhaps from the lowering of symmetry.

Comparison with Earlier Work.—All earlier published studies of reaction (1) refer to more strongly acidic ($pH < 3.5$) solution, under which conditions $e^{-}(aq)$ will rapidly generate H atoms. Quantum yields are dependent on conditions, with pH [2–4] and sulphate concentration [5] both affecting the results. Jortner and Stein,[4] under their conditions, found a rate law of the form (26) where α is the proportion of absorbed photons that lead to reaction, so that expression (27) is obtained.

$$\alpha = 0.038 + 0.63[H^{+}]^{\frac{1}{2}} - \text{other smaller terms in } [H^{+}] \qquad (26)$$

$$\varphi[Fe^{III}] = 2\alpha \qquad (27)$$

They equated the $[H^{+}]$-independent term with the proportion of hydrogen atoms that escaped unassisted from the primary reaction site, while the second and subsequent terms represent proton-assisted escape in competition with back-diffusion and recombination.

We found no evidence for back-diffusion of electrons, although, had it been present, it would have been detected in an *enhancement* of rate by N_2O. We therefore suggest that our electron-ejection process is responsible for at least the greatest part of Jortner and Stein's unassisted diffusion, in accord with our suggestion that the ejected electron is initially mobile. The proton-assisted part must then correspond to a second reaction mode. We therefore suggest the existence of such steps as (28)—(33) (e^{-}_{m} = mobile electron). Here reactions (28)

$$A^* \longrightarrow Fe^{3+}(aq) + e^{-}_{m} \qquad (28)$$

$$e^{-}_{m} \longrightarrow e^{-}(aq) \qquad (29)$$

$$A^* \longrightarrow B \qquad (30)$$

$$B \longrightarrow Fe^{2+}(aq) \qquad (31)$$

$$B \longrightarrow Fe^{III} + H^{\cdot} \text{ (unassisted)} \qquad (32)$$

$$B \longrightarrow Fe^{III} + H^{\cdot} \text{ (}H^{+}\text{ assisted)} \qquad (33)$$

and (29) together constitute (9), (30) and (31) together contribute to (19), (32), if real, contributes to Jortner and Stein's $[H^{+}]$-independent process, and (33) is their $[H^{+}]$-dependent process. It thus seems likely that B is not a single species but a pair, such as $[Fe^{III}(OH)]^{2+}(aq)$ and $H^{\cdot}$, created in close proximity. The photolysis of $[Fe(OH)]^{+}(aq)$, for which the quantum yield is probably relatively small, would then have its counterpart in (32). The excitations of $[Fe(OH)]^{+}(aq)$ and of $Fe^{2+}(aq)$ can then be regarded as closely related processes, although only the latter generates a state energetically capable of losing an electron.

Implications For CO_2 *Fixation.*—It has been known for some time [37] that photolysis of Fe^{2+} in acid solution in the presence of dissolved CO_2 generates a range of organic species. This is to be expected, given present knowledge, since CO_2 reacts rapidly both with $e^{-}(aq)$ [25] and with H.[36] The reaction has been re-examined by Åkermark *et al.*[38] who found that it led to a rather low steady-state concentration of formaldehyde, because of efficient interception of CO_2^{-} by $Fe^{3+}(aq)$. The reaction should therefore become more fruitful at higher pH, where Fe^{III} is removed by precipitation. Under primitive Earth conditions (pH *ca.* 7) there is the further interesting possibility that $[FeH]^{2+}(aq)$ could act as a reducing agent (hydride donor), although the insolubility of $FeCO_3$ would hamper laboratory tests of this hypothesis.

Appendix

Energy Thresholds.—We present highly approximate standard free energies for the actual and hypothetical processes discussed in this paper and infer threshold frequencies and wavelengths. In addition to total neglect of entropy changes, and of the possibility of endergodic photoreactions, this procedure assumes a reasonable Franck–Condon overlap between initial and final states. This condition will not always obtain, so that the energies correspond to lower limits. Energies are calculated in eV and cm^{-1} (wavelength inferred).

(*a*) *Electron loss from* $Fe^{2+}(aq)$ (29 400 cm^{-1}, 340 nm).

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^{-} \qquad -E^{\ominus} = 0.77\ V\ ^{39} \quad (A1)$$

$$\underline{e^{-} \longrightarrow e^{-}(aq) \qquad -E^{\ominus} = 2.87\ V\ ^{40}} \quad (A2)$$

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^{-}(aq) \quad \Delta G^{\ominus} = 3.64\ eV \quad (A3)$$

(*b*) *Loss of a mobile electron from* $Fe^{2+}(aq)$ (33 470 cm^{-1}, <296 nm). Webster [28] quotes −156.9 kJ mol^{-1} (−1.626 eV) as $\Delta G^{\ominus}$ for formation of $e^{-}(aq)$ from $e^{-}(g)$, and -1.2 ± 0.1 eV for the bottom of the conduction band in water, also relative to $e^{-}(g)$. Thus, loss of a mobile electron will require 0.42 ± 0.1 eV more than loss of $e^{-}(aq)$, corresponding to 32 800 ± 800 cm^{-1} (305 ± 8 nm).

(*c*) *Hydrogen-atom loss from* $Fe^{2+}(aq)$ (25 900 cm^{-1}, 387 nm).

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^{-}(aq) \quad \Delta G^{\ominus} = 3.64\ eV \quad (A3)$$

$$Fe^{3+}(aq) \longrightarrow [Fe(OH)]^{2+}(aq) + H^{+}(aq) \qquad \Delta G^{\ominus} = 0.13\ eV\ ^{26} \quad (A4)$$

$$\underline{e^{-}(aq) + H^{+}(aq) \longrightarrow H(aq) \quad \Delta G^{\ominus} = -0.564\ eV\ ^{40}} \quad (A5)$$

$$Fe^{2+}(aq) \longrightarrow [Fe(OH)]^{2+}(aq) + H(aq) \qquad \Delta G^{\ominus} = 3.20_{6}\ eV \quad (A6)$$

(*d*) *Electron loss from* $[Fe(OH)]^{+}(aq)$.

$$[Fe(OH)]^{+}(aq) + H^{+}(aq) \longrightarrow Fe^{2+}(aq) \qquad \Delta G^{\ominus} = -0.562\ eV\ ^{26} \quad (A7)$$

$$Fe^{2+}(aq) \longrightarrow Fe^{3+}(aq) + e^{-} \qquad -E^{\ominus} = 0.77\ V\ ^{39} \quad (A1)$$

$$\underline{Fe^{3+}(aq) \longrightarrow [Fe(OH)]^{2+}(aq) + H^{+}(aq) \qquad \Delta G^{\ominus} = 0.13\ eV\ ^{26}} \quad (A4)$$

$$[Fe(OH)]^{+}(aq) \longrightarrow [Fe(OH)]^{2+}(aq) + e^{-} \qquad -E^{\ominus} = 0.337\ V \quad (A8)$$

Whence, as in (*a*), loss of $e^{-}(aq)$ from $[Fe(OH)]^{+}(aq)$ requires 3.20(7) eV (25 900 cm^{-1}, 387 nm). The fortuitous coincidence with (*c*) reflects the almost equal proton acidities of Fe^{2+} (aq) and H(aq). Proceeding as in (*b*), loss of e^-_m requires 3.6 ± 0.1 eV (29 300 ± 800 cm^{-1}, 341 ± 10 nm).

(*e*) *Hydrogen atom loss from* $[Fe(OH)]^+$(aq) (22 850 cm^{-1}, 438 nm).

$$[Fe(OH)]^+(aq) \longrightarrow [Fe(OH)]^{2+}(aq) + e^-(aq) \qquad \Delta G^\ominus = 3.20_7\ \text{eV} \qquad \text{(A9)}$$

$$[Fe(OH)]^{2+}(aq) \longrightarrow [Fe(OH)_2]^+(aq) + H^+(aq) \qquad \Delta G^\ominus = 0.190\ \text{eV}\ [26] \qquad \text{(A10)}$$

$$\underline{e^-(aq) + H^+(aq) \longrightarrow H(aq) \quad \Delta G^\ominus = -0.564\ \text{eV}\ [40]} \qquad \text{(A5)}$$

$$[Fe(OH)]^+(aq) \longrightarrow [Fe(OH)_2]^+(aq) + H(aq) \qquad \Delta G^\ominus = 2.83_3\ \text{eV} \qquad \text{(A11)}$$

(*f*) *Hydroxyl loss from* $[Fe(OH)]^+$(aq). Little is known about Fe^+(aq), but it seems likely from this work that it could react in acidic solution to give hydrogen atoms.

$$Fe^{2+}(aq) + H(aq) \longrightarrow Fe^+(aq) + H^+(aq) \qquad \Delta G^\ominus > 0 \qquad \text{(A12)}$$

$$H^+(aq) + e^- \longrightarrow H(aq) \qquad -E^\ominus = 2.30\ \text{V}\ [40] \qquad \text{(A13)}$$

$$OH^-(aq) \longrightarrow OH(aq) + e^- \qquad -E^\ominus = 1.58\ \text{V}\ [41] \qquad \text{(A14)}$$

$$H^+(aq) + [Fe(OH)]^+(aq) \longrightarrow Fe^{2+}(aq) \qquad \Delta G^\ominus = -0.562\ \text{eV}\ [26] \qquad \text{(A7)}$$

$$\underline{H_2O \longrightarrow H^+(aq) + OH^-(aq) \qquad \Delta G^\ominus = 0.83\ \text{eV}} \qquad \text{(A15)}$$

$$[Fe(OH)]^+(aq) \longrightarrow Fe^+(aq) + OH(aq) \qquad \Delta G^\ominus > 4.15\ \text{eV} \qquad \text{(A16)}$$

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