

## Direct Observation of Hydrated Electrons in the U.V. Photo-oxidation of $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$

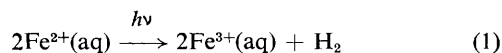
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Hydrated electrons are involved as intermediates in the photo-oxidation of  $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$  to  $\text{Fe}^{\text{III}}$  species in water at 265 nm.

Solvated electrons are well established intermediates in the u.v. photochemistry of some simple and complex anions,<sup>1,2</sup> and have been suggested but not observed as intermediates in the photo-oxidation of low valent hydrated transition metal cations, the detailed mechanism of which has remained obscure.<sup>2</sup> The photoconversion of  $\text{Fe}^{2+}$  into  $\text{Fe}^{3+}$  has been thoroughly studied in water at  $\text{pH} < 3.5$ , and shown to contain both  $[\text{H}^+]$ -dependent and  $[\text{H}^+]$ -independent components<sup>3</sup> but the intermediacy of a solvated electron ('in the normally accepted definition') in this reaction has been denied.<sup>1</sup> Our interest in photogeochemistry<sup>4</sup> has led us to examine the photolysis of  $\text{Fe}^{2+}$  ( $2 \times 10^{-2}$  to  $10^{-4}$  mol  $\text{dm}^{-3}$ ) in more nearly neutral solution ( $\text{pH}$  6–4.8), under rigorously purified Ar or  $\text{N}_2$ , irradiating from above (to minimise problems caused by solid product) with a heat-filtered Hg medium pressure discharge lamp. The net reaction [equation (1)] was monitored



continuously by pH change<sup>5</sup> due to the acidity of  $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$ , and overall by analysis for  $\text{Fe}^{\text{III}}$  (colorimetric, as thiocyanate,<sup>6</sup> after acidification) while formation of  $\text{H}_2$  ( $\text{HD}$  and  $\text{D}_2$  in the presence of  $\text{D}_2\text{O}$ ) was confirmed by mass spectrometry. The absorption spectra of our solutions, and the photolysis rates, were constant throughout the pH range, and reaction rates in the dark or with filtered ( $\lambda > 300$  nm) light were negligible.†

The addition of  $\text{N}_2\text{O}$  had no effect upon rates but the reaction was about 20% faster in saline.‡ Propan-2-ol (0.2 mol  $\text{dm}^{-3}$ ) reduced the photolysis rate by a factor of  $2.6 \pm 0.5$ . The quantum yield (using the well-studied<sup>3</sup> reaction in 0.26 mol  $\text{dm}^{-3}$   $\text{H}_2\text{SO}_4$  as reference) was  $0.06 \pm 0.03$ , in reasonable agreement with the literature value<sup>3</sup> of 0.08 for the  $[\text{H}^+]$ -independent component.

$\text{N}_2$ -Saturated saline solutions of  $\text{pH}$  4.8–6.0 containing  $2.0 \times 10^{-2}$  mol  $\text{dm}^{-3}$   $\text{Fe}^{2+}$  were subjected to flash photolysis from a frequency quadrupled Nd glass laser in the apparatus described by McVie<sup>8</sup> (pulse duration 25 ns, pulse energy up to 20  $\text{mJ cm}^{-2}$ ). A broad transient absorption was observed, peaking between 700 and 800 nm, which approximately halved in intensity when the laser intensity was halved and was completely quenched on our detection timescale in  $\text{N}_2\text{O}$ -saturated solution. We assign this absorption to monophotonic production of  $e^-(\text{aq})$ , and estimate the quantum yield for its formation as  $0.06 \pm 0.03$ , using the comparative method<sup>9</sup> with the naphthalene triplet absorption in cyclohexane<sup>10</sup> as standard, and literature values for  $\epsilon[e^-(\text{aq})]$ .<sup>11</sup>

The half-life for signal decay was around 400 ns, compared with a value of 300 ns calculated, from standard kinetic data,<sup>11</sup> for  $e^-(\text{aq})$  under our conditions. Scavenging by  $\text{Fe}^{2+}$  dominates the calculated decay in our pH range.

We infer that our steady state photolysis, flash photolysis, and the  $[\text{H}^+]$ -independent part of the low pH photolysis all proceed by initial formation of  $\text{Fe}^{3+}(\text{aq})$  and a hydrated

† At yet higher pH, however,  $[\text{FeOH}(\text{aq})]^+$  is formed and is photoactive even for  $\lambda > 400$  nm (ref. 7).

‡ In this communication, saline = 0.56 mol  $\text{dm}^{-3}$  NaCl in water.

electron, which in turn reacts to give  $H\cdot$ , either directly from  $H^+$  or indirectly *via*  $Fe^+$ , the second process becoming dominant at higher pH. The radical  $H\cdot$  then reacts with  $Fe^{2+}(aq)$ <sup>12</sup> to yield  $[Fe-H(aq)]^{2+}$  and hence a second  $Fe^{3+}(aq)$  ion. {Alternatively,  $Fe^+$  itself, or  $[Fe-H(aq)]^{2+}$  formed from  $Fe^+$  and  $H^+$ , must be propan-2-ol-quinchable.} The reaction of  $N_2O$  with  $e^-(aq)$  gives  $OH\cdot$ ,<sup>11</sup> which also oxidises  $Fe^{2+}(aq)$ ; this explains the ability of  $N_2O$  to quench  $e^-(aq)$  without affecting overall yields.

Our observation of  $e^-(aq)$  has been facilitated by its comparatively low<sup>11</sup> rate of reaction with  $Fe^{2+}(aq)$ , but we suspect its intermediacy in many other photo-oxidations of low-valent cations.

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