Direct Observation of Hydrated Electrons in the U.V. Photo-oxidation of $[Fe(H_2O)_6]^{2+}$

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Hydrated electrons are involved as intermediates in the photo-oxidation of $[Fe(H_2O)_6]^{2+}$ to Fe^{III} species in water at 265 nm.

Solvated electrons are well established intermediates in the u.v. photochemistry of some simple and complex anions,[1,2] 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.[2] The photoconversion of Fe^{2+} into Fe^{3+} has been thoroughly studied in water at pH < 3.5, and shown to contain both $[H^+]$-dependent and $[H^+]$-independent components[3] but the intermediacy of a solvated electron ('in the normally accepted definition') in this reaction has been denied.[1] Our interest in photogeochemistry[4] has led us to examine the photolysis of Fe^{2+} (2×10^{-2} to 10^{-4} mol dm^{-3}) in more nearly neutral solution (pH 6—4.8), under rigorously purified Ar or 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

$$2Fe^{2+}(aq) \xrightarrow{h\nu} 2Fe^{3+}(aq) + H_2 \qquad (1)$$

continuously by pH change[5] due to the acidity of $[Fe(H_2O)_6]^{3+}$, and overall by analysis for Fe^{III} (colorimetric, as thiocyanate,[6] after acidification) while formation of H_2 (HD and D_2 in the presence of D_2O) 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 N_2O had no effect upon rates but the reaction was about 20% faster in saline.‡ Propan-2-ol (0.2 mol dm^{-3}) reduced the photolysis rate by a factor of 2.6 ± 0.5. The quantum yield (using the well-studied[3] reaction in 0.26 mol dm^{-3} H_2SO_4 as reference) was 0.06 ± 0.03, in reasonable agreement with the literature value[3] of 0.08 for the $[H^+]$-independent component.

N_2-Saturated saline solutions of pH 4.8—6.0 containing 2.0×10^{-2} mol dm^{-3} Fe^{2+} were subjected to flash photolysis from a frequency quadrupled Nd glass laser in the apparatus described by McVie[8] (pulse duration 25 ns, pulse energy up to 20 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 N_2O-saturated solution. We assign this absorption to monophotonic production of $e^-(aq)$, and estimate the quantum yield for its formation as 0.06 ± 0.03, using the comparative method[9] with the naphthalene triplet absorption in cyclohexane[10] as standard, and literature values for $\epsilon[e^-(aq)]$.[11]

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

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

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

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

electron, which in turn reacts to give H•, either directly from H^+ or indirectly *via* Fe^+, the second process becoming dominant at higher pH. The radical H• then reacts with Fe^{2+}(aq)[12] 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-quenchable.} The reaction of N_2O with e^-(aq) gives OH•,[11] 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[11] 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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