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Effects of Temperature and Wavelength on the Primary Process in the Photo-oxidation of Iron(II) Ion

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Experiments at 253.7 and 228.8 nm, each over a range of *ca*. 45 K, demonstrate that the primary quantum yield of photo-oxidation in deoxygenated acidic iron(II) solutions increases only very slightly with temperature, but that at the lower wavelength it is *ca*. 1.36 times greater. It is suggested that the excitation process involves the transfer of an electron to a shallow trap among the neighbouring solvent molecules, such that recombination of the electron with its geminate iron(III) ion is highly probable. It appears that temperature has little effect on the quantum yield because electron escape and recombination both depend on temperature to very similar extents and that the use of a higher-energy photon increases the quantum yield because then more and more distant traps are accessible for electron transfer.

The oxidation process effected by ultraviolet light on aqueous iron(II) ion has been studied[1] by various groups over a long period. Initially, the primary process was usually represented[2–5] in terms of eqn (1).

$$Fe^{2+} \cdot H_2O + h\nu = Fe^{3+} + H + OH^- . \qquad (1)$$

Later, on the evidence that when N_2O was added to an acidic solution containing iron(II) ion the quantum yield of N_2 increased and that of H_2 decreased, Airey and Dainton[6] asserted that the primary process was as follows:

$$Fe^{2+} + h\nu = Fe^{3+} + e^-_{aq} . \qquad (2)$$

They showed that the yields of these gaseous products varied with solute concentrations in the manner to be expected if reaction (2) occurred, followed by competition between reactions (3) and (5).

$$e^-_{aq} + H^+ \rightarrow H \qquad (3)$$

$$H + Fe^{2+} \rightarrow H_2 + Fe^{3+} + OH^- \qquad (4)$$

$$e^-_{aq} + N_2O \rightarrow N_2 + O^- \ (\xrightarrow{H^+} OH) \qquad (5)$$

$$OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (6)$$

More recently, the occurrence of process (2) has been confirmed[7] in laser flash photolysis experiments showing that an absorption attributable to the hydrated electron could be observed when iron(II) ion was excited with light of 265 nm. The proportionality of the absorbance to the pulse intensity indicated that the process involved was monophotonic.

Photolytic generation of the hydrated electron is a well known process,[8,9] that occurs with halide ions other than fluoride, some oxyanions (*e.g.* $S_2O_3^{2-}$, SO_4^{2-}), hydroxide ion, some anionic complexes of transition metals in lower oxidation states [*e.g.* $Fe(CN)_6^{4-}$] and with phenolate anions. The process appears to be related to the existence of charge-transfer-to-solvent (CTTS) excited states, whether, as in the halide case,[10,11] such a state is populated directly by quantum absorption or, as in the phenolate case,[12] there is no CTTS character to the excitation process.

For many such systems it has been found that the hydrated electron quantum yield increases appreciably with increasing temperature. This has been interpreted[13–15] in terms of two competing fates for the CTTS state: relaxation to the ground state or dissociation to yield the hydrated electron and the radical, where only the former process is influenced by temperature.

Examples of the photochemical generation of hydrated electrons from cations are very rare and the intermediacy of a CTTS state is not envisaged. However, it was desired to know in what way the primary quantum yield of process (2) varied with temperature. Reports[16] that it shows only a very slight dependence appear to be based on a comparison of the behaviour in solution at ambient temperatures with that in the solid at 77 K. It seemed desirable to investigate the effect of temperature using a range over which there occurs no change of phase. Also, since no data could be found in the literature for the quantum yield at a wavelength other than 253.7 nm, it was desired to make measurements using the cadmium line at 228.8 nm, to determine whether wavelength had any important effect on the quantum yield.

Experimental

AnalaR iron(II) ammonium sulphate and sulphuric acid were used, along with doubly distilled water. All glassware and the photolysis cells were carefully cleaned with permanganic acid followed by a hydrogen peroxide/nitric acid mixture and numerous rinsings with doubly distilled water.

The cells, of fused quartz, were cylindrical in shape with a side-arm attached. Irradiations were carried out in a thermostat bath, such that[14] the cell was located in a horizontal position where it was illuminated from above through a quartz window and while the contents of the cell were maintained homogeneous by a Teflon-enclosed magnetic follower, operated by an external magnetic stirrer.

The first light source was an Engelhard Hanovia low pressure mercury lamp, emitting predominantly at 253.7 nm. The 184.9 nm line was removed by interposing, between the lamp and the shutter above the quartz window, a quartz filter cell of 2 cm pathlength containing distilled water. Actinometry measurements were made at the time of each photolysis experiment using the ferrioxalate system,[17] where the quantum yield at 253.7 nm is known to be independent of temperature. Corrections for the actinic effect of the longer-wavelength lines (*ca.* 13% of the total) were determined by actinometric measurements with the water filter cell replaced by a similar one containing deaerated 10^{-2} mol dm^{-3} aqueous KI, which totally absorbed the 253.7 nm line but transmitted at the wavelengths of these other lines.

A Philips cadmium lamp was used as the source of the 228.8 nm radiation and was allowed at least 40 min to stabilise before use. The flux of 228.8 nm light entering the cell was determined at the time of each photolysis experiment by the technique described above,[14] since all the longer-wavelength lines from this lamp are transmitted by the KI filter solution.

The actinic effect of these lines was found to be *ca.* 69% of the total.

To minimise variations in the extent of dissociation of the bisulphate ion with temperature, the sulphuric acid concentration was kept fixed at 0.20 mol dm^{-3}, at which value the HSO_4^- ion, with a pK_a of 1.92 is only very slightly dissociated.[18] The iron(II) ion concentration was chosen so that more than 99% absorption of the incident light occurred within the 2 cm pathlength of the cell, and a correction was made for the very small amount transmitted.

In view of the rapid oxidation by dissolved oxygen of these fairly concentrated iron(II) solutions, the aqueous sulphuric acid was first de-oxygenated by boiling[3] while bubbling argon through it, before the weighed iron(II) salt was added. Alternative methods of sample preparation were used and yielded essentially the same results. In one case, a measured volume of the solution was degassed within a cell assembly by four freeze–pump–thaw cycles. For photolysis experiments above ambient temperature, *ca.* 400 Torr† of argon was then added as it was necessary to have an (inert) gas present, since not all the gas space of the cell assembly was to be immersed in the thermostat and vapour pressure varies with temperature. In the other case, using a different assembly, a measured volume of the solution was degassed by bubbling with argon using a rubber seal and two syringe needles.

In both cases, the growth of the concentration of iron(II) ion was monitored at 304 nm by putting the quartz cell end of the assembly into a special holder in the cell compartment of a Perkin-Elmer Lambda-5 spectrophotometer, using a custom-designed box to exclude light. Regardless of the temperature of irradiation, these measurements were made with the sample at 293 K.

Since the product iron(II) ion absorbs strongly at the wavelength of irradiation, it is necessary to make a correction for the consequent decrease in yield. Absorption by iron(III) causes[19] reduction to iron(II) ion,

$$Fe^{3+}\cdot H_2O \xrightarrow{h\nu} Fe^{2+} + H^+ + OH \qquad (7)$$

but this is of no account since in this system the reactions which follow negate step (7).

$$OH + Fe^{2+} \rightarrow OH^- + Fe^{3+} \qquad (8)$$

or

$$OH + H_2 \rightarrow H_2O + H \qquad (9)$$

$$H + Fe^{2+}\cdot H_2O \rightarrow H_2 + Fe^{3+} + OH^-. \qquad (10)$$

Thus the only significance of reaction (7) is that some fraction of the light entering the cell is not absorbed by iron(II) ion.

In correcting for light absorbed by iron(III) ion it was assumed that the magnetic follower kept the solution homogeneous, since the rate of production of this ion is not uniform through space and is highest at the upper face of the cell where the light flux is greatest.

Denoting by c_2 and ε_2 the concentration of Fe^{2+} ion and its absorption coefficient at the wavelength of irradiation, and using c_3 and ε_3 for the corresponding parameters of Fe^{3+} ion, the fraction of the incident light absorbed by iron(II) ion is given by $c_2\varepsilon_2/(c_2\varepsilon_2 + c_3\varepsilon_3)$. If the volume of the sample is V and I represents the flux of light, in Einstein s^{-1}, entering the cell, of which a fraction f is absorbed within it, then we have, for the rate of increase of iron(III) ion concentration.

$$\frac{dc_3}{dt} = \frac{\varepsilon_2 c_2}{\varepsilon_2 c_2 + \varepsilon_3 c_3} \frac{\phi(Fe^{3+})If}{V} \qquad (11)$$

where $\phi(Fe^{3+})$ represents the total number of Fe^{3+} ions formed per quantum of light absorbed by iron(III) ion. Integrating (and treating c_2 as a constant) we obtain

$$\phi(Fe^{3+}) = \frac{c_3 V}{Ift}\left(1 + \frac{\varepsilon_3 c_3}{2\varepsilon_2 c_2}\right) \qquad (12)$$

which is equivalent to the equation of Jortner and Stein,[5] and incorporates in the last term the necessary correction for the absorption of light by a product.

The usefulness of this relation as tested for both lamps to iron(III) concentrations much higher than those used in photolysis experiments and it was found that $c_3(1 + \varepsilon_3 c_3/2\varepsilon_2 c_2)$ increased linearly with the time of illumination. Since the primary process, reaction (2), will be followed in the acidic and deoxygenated solution by reactions (3) and (10), the primary quantum yield $\phi(e^-)$ was calculated as half the corrected quantum yield of iron(III) ion given by eqn (12).

Results and Discussion

Experiments using 0.07 mol dm^{-3} $FeSO_4$ in 0.2 mol dm^{-3} H_2SO_4 with 253.7 nm radiation found a very slight variation with temperature of the primary quantum yield, as shown in Table 1, where each value is the mean of at least five individual measurements. Since the slight rise is only just greater than the uncertainty of each value, it appears that there is genuinely an increase with increasing temperature, albeit a small one.

In another series of experiments using 0.05 mol dm^{-3} $FeSO_4$ with 228.8 nm light, a comparable rise was found, with greater uncertainty because with the cadmium lamp the actinic effect of the irradiating wavelength is a minor proportion of the total. Thus at this lower wavelength, where the quanta are more energetic by 0.53 eV, increasing the temperature has as little influence on the quantum yield as at 253.7 nm.

Studies[20] of the spectra of iron(II) solutions in aqueous H_2SO_4 suggest that ion pairing occurs to a negligible extent and that the bands in the UV are entirely due to absorption by hydrated iron(II) ions, $Fe(H_2O)_n^{2+}$. The process is sometimes written[20] as:

$$[Fe^{II}(H_2O)_n]^{2+} \xrightarrow{h\nu} [Fe^{III}(H_2O)_{n-1}]^{3+} + (H_2O)^- \qquad (14)$$

which would seem to imply that in the absorption process the electron is transferred totally to one water molecule in the salvation sphere of the ion.

Since the structure $(H_2O)^-$ may be expected to undergo immediate dissociation,

$$(H_2O)^- \rightarrow OH^- + H \qquad (14)$$

this conception of the excitation process appears totally inconsistent with the competition work of Airey and Dainton[6] in dilute acidic solutions and the laser flash photolysis work[7] at 265 nm in nearly neutral solutions, which

Table 1. Variation of the primary quantum yield with temperature and wavelength

	quantum yield, $\phi(e^-)$	
T/K	253.7 nm	228.8 nm
277	0.080 ± 0.003	0.111 ± 0.007
293	0.086 ± 0.003	0.117 ± 0.007
311	0.090 ± 0.003	—
318	—	0.119 ± 0.007
326	0.087 ± 0.003	—

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† 1 Torr = 101 325/760 Pa.

both showed that the species generated was the hydrated electron and not the H atom.

An alternative possibility is that the excited electron is transferred to a trap in the neighbourhood of the solvation sphere of the iron(II) ion, where a number of randomly oriented solvent molecules constitute a small potential well. This trap must be clearly distinguished from the potential well of CTTS transitions of reducing anions.[10,11] The latter is spherically symmetrical around the anion, whereas the proposed trap will be centred at some molecular diameters from the anion. Also, the potential well involved in CTTS excitations of an anion is much more substantial than that of this proposed trap, with a corresponding difference in the ease with which the electron might escape or move to another trap.

The smallness of the primary quantum yield detected for iron(II) ion, at either wavelength, must in terms of this proposal reflect the strong tendency for geminate recombination to occur between the trapped electron and the iron(II) ion. Any effect of temperature on the primary quantum yield must arise from the balance of its effects, on the one hand on this recombination process and on the other hand, on the diffusion and mutual escape of the geminate pair.

The former process resembles the reaction of the solvated electron with iron(III) ion, which is a very fast and virtually diffusion-controlled[21] chemical reaction with a rate constant of 6×10^{10} dm^3 mol^{-1} s^{-1}, so it is presumably accelerated to a modest extent by increasing temperature. The latter also involves diffusion, particularly of the electron as the more mobile of the geminate partners, as the solvent molecules around the electron undergo relaxation. It would thus seem that the effects of temperature on these competing processes should be fairly well balanced, and this is fully consistent with the experimental results, which show a very small rise over 40 or 50 K.

It may be helpful to show what effect of temperature on the primary quantum yield would be expected on the basis of the model[13–15] applicable to CTTS processes of anions. This would require an increase by a factor of *ca.* 1.25 over 10 K, or *ca.* 2.6 over 40 K. Clearly, at neither wavelength does the influence of temperature on the present system approach this magnitude.

In facilitating electron escape it would seem that increased quantum energy is much more significant than increased temperature. The explanation presumably is that at the shorter wavelength, where the quantum is more energetic and the absorption coefficient is substantially greater, the excitation process may utilise traps at an even greater distance from the iron(II) ion. Consequently, at the shorter wavelength, geminate recombination will become less probable, simply because, on average, the partners are already slightly further apart.

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