767. *Photochemical Decomposition of Water by Ferrous Ions.*

By E. Hayon and J. Weiss.

Re-investigation of the photochemistry of ferrous ions in aqueous solutions, with particular regard to the dependence of the initial quantum yields on the hydrogen-ion and ferrous sulphate concentrations, gave results in agreement with the mechanism previously proposed. This is confirmed by irradiation in the presence of a second solute (acrylic acid).

It is assumed that the primary process gives an excited ferrous ion which can lead to formation of a hydrogen atom. The pH-dependence is discussed from the point of view of the participation of H_2^+ in the reaction and interaction of the excited ferrous ions with hydrogen ions.

Irradiation of aqueous solutions of ferrous sulphate with light of the quartz ultraviolet region, in the absence of oxygen, leads to molecular hydrogen and ferric salt.[1] Rigg and Weiss [2] found that the quantum yield of oxidation of ferrous ions under these conditions depends on the hydrogen-ion concentration.

The present re-investigation had as objects to obtain more accurate data, particularly on the initial quantum yields, and to investigate the reaction over a wider range of ferrous sulphate and sulphuric acid concentrations.

The results confirm the pH-dependence of the quantum yields of the photochemical decomposition of water by ferrous ions.

Results

To obtain as nearly as possible the initial yields it is important to use the smallest practical amounts of radiation and to reduce to a minimum the traces of ferric salt present in solution before irradiation.

Fig. 1 shows the change in the yield of ferric salt with time of irradiation at different pH's, in de-aerated 0·1M-ferrous sulphate. Fig. 2 (circles) is a plot of the initial yields of photochemically produced ferric salt against pH, as obtained from the yield–dose curves (Fig. 1). Fig. 2 (top curve) shows also a corresponding plot of the initial yields in solutions after removal of the traces of ferric salt by reduction with spectroscopically pure iron before irradiation. In every case, a marked dependence of the initial quantum yields on pH was observed. The initial yields decreased with increasing pH, especially above pH 1·5, seemingly approaching zero. Elimination of the initial traces of ferric iron increases the initial quantum yield.

The quantum yields were found to depend also on the concentration of the ferrous sulphate, particularly at low pH's. Fig. 3 shows this dependence of the yields on the time of irradiation at pH 0·5 in the concentration range 0·1—1M-ferrous sulphate. The dependence of the initial yields on the ferrous sulphate concentration at different pH is more clearly shown again in Fig. 4.

The quantum yields also show some increase with increasing concentration of sulphuric acid. Fig. 5 gives the dependence of the initial quantum yields in solutions up to 10N-sulphuric acid, over the range of 0·1—1·0M-ferrous sulphate. In >4N-acid, experiments could only be carried out at the lower ferrous sulphate concentrations owing to the limited solubility of ferrous sulphate.

Some experiments were also carried out in the presence of a second solute, acrylic acid, which is known to be a good acceptor for hydrogen atoms. Above a certain concentration, acrylic acid might be expected to compete for the hydrogen atoms produced in the primary photochemical process, apart from other possible reactions which will be discussed below.

Fig. 6 shows the dependence of the quantum yield on time of irradiation, at different pH's in 0·1M-ferrous sulphate in the presence of 0·1M-acrylic acid. Fig. 7 shows the pH-dependence of the initial yields of ferric salt in the presence of acrylic acid: the yield of ferric iron is here appreciably reduced and decreases very rapidly with increasing pH.

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[1] Weiss, *Nature*, 1935, **136**, 794; (*b*) Potterill, Walker, and Weiss, *Proc. Roy. Soc.*, 1936, *A*, **156**, 561; (*c*) Weiss, *Trans. Faraday Soc.*, 1941, **37**, 463.

[2] Rigg and Weiss, *J. Chem. Phys.*, 1952, **20**, 1194.

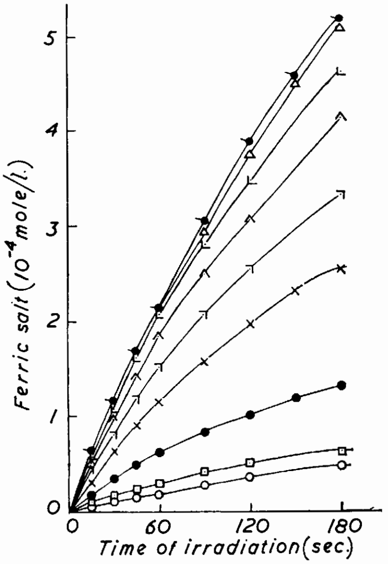


FIG. 1. *Photo-oxidation of de-aerated ferrous sulphate solutions* (0·1M). *Dependence of the relative yields of ferric salt on time of irradiation, at different* pH's, *at constant absorbed light intensity. The curves refer to* pH, *reading downwards, of* 0·2, 0·5, 0·75, 1·3—1·7, 2·0, 2·4, 2·7, 2·9, *and* 3·2.

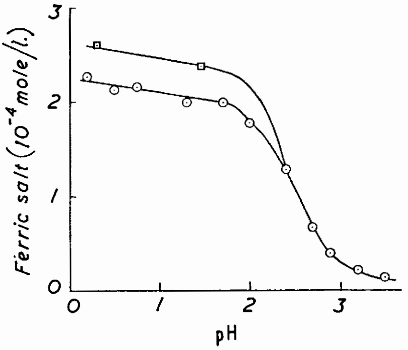


FIG. 2. *Photo-oxidation of de-aerated ferrous sulphate solution* (0·1M). pH-*Dependence of the relative initial yields of ferric salt, at constant absorbed light intensity. The upper curve was obtained after initial treatment of the ferrous solution with metallic iron.*

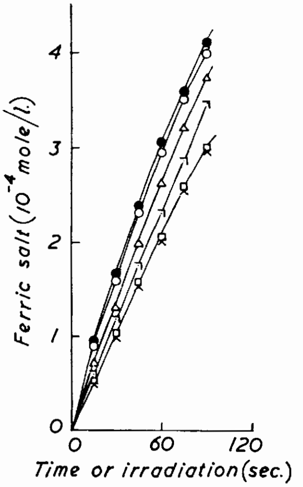


FIG. 3. *Dependence of the relative yields of ferric salt on the time of irradiation at different concentrations of ferrous sulphate, at* pH 0·5, *at constant absorbed light intensity.*

× 0·1M. □ 0·2M. ⌉ 0·4M. △ 0·6M.
○ 0·8M. ● 1·0M.

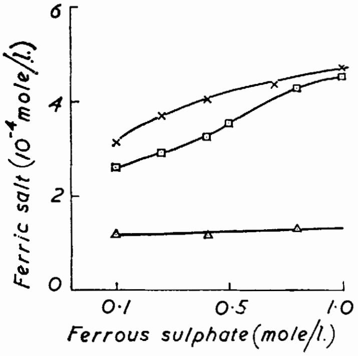


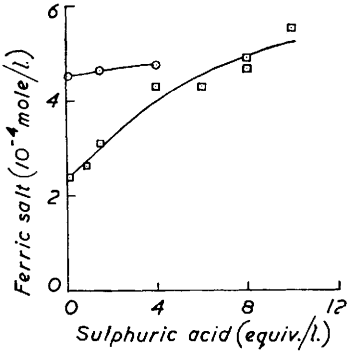
FIG. 4. *Dependence of the relative initial yields of ferric salt on ferrous sulphate concentration in the range* 0·1—1·0M-*ferrous sulphate, at constant absorbed light intensity.*

△ pH 2·4.
□ pH 0·5 (*after reduction by metallic iron*).
× *In* 0·5N-H_2SO_4 (*after reduction by metallic iron*).

DISCUSSION

The present work confirms the previous results, that the quantum yield of photochemical oxidation of ferrous ions in de-aerated aqueous solutions is strongly dependent on the hydrogen-ion concentration, contrary to the recent report by Lefort and Douzou.[3]

FIG. 5. *Photo-oxidation of de-aerated ferrous sulphate solution. Dependence of the relative initial yields of ferric salt on the concentration of sulphuric acid at constant absorbed light intensity. (Initial* Fe^{III} *removed by metallic iron.)*



□ 0·1M-$FeSO_4$. ○ 1·0M-$FeSO_4$.

FIG. 6. *Photo-oxidation of de-aerated ferrous sulphate solutions* (0·1M) *in the presence of acrylic acid* (0·1M). *Dependence of the relative yields of ferric salt on time of irradiation at different* pH's, *at constant absorbed light intensity.* pH *for the curves, reading downwards,* 0·2, 0·5, 0·65, 1·25, 1·4, 1·9, *and* 2·2.

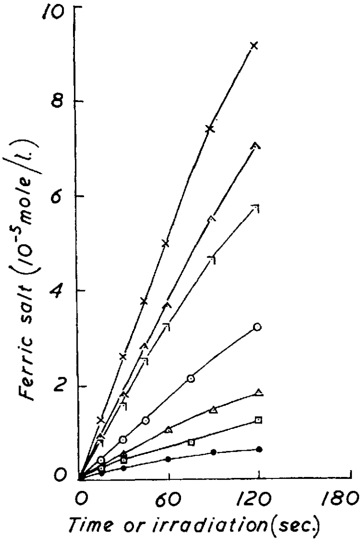


FIG. 7. *Photo-oxidation of de-aerated ferrous sulphate solutions* (0·1M) *in the presence of acrylic acid* (0·1M). pH-*Dependence of the relative initial yields of ferric salt at constant absorbed light intensity.*

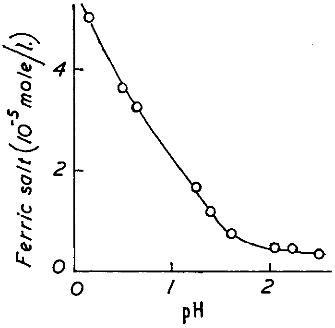


FIG. 8. *Silica irradiation cell.*

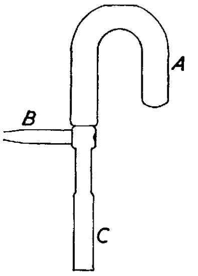
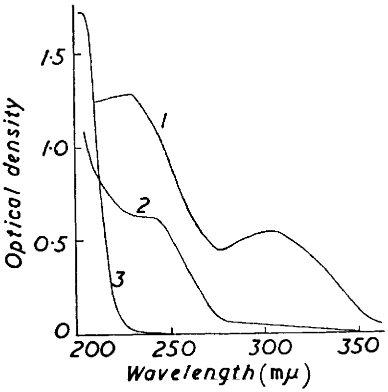


FIG. 9. *Absorption spectra of* (1) *ferric sulphate* (3 × 10^{-4}M *in* 0·01N-H_2SO_4), (2) *ferrous sulphate* (3 × 10^{-2}M *in* 0·1N-H_2SO_4), (3) *acrylic acid* (1·5 × 10^{-4}M).



Increase of pH up to 3·5 causes a continuous fall in the ferric yield, particularly above pH 1·5, tending towards zero (Fig. 2). The yield of molecular hydrogen measured under the same conditions follows a similar trend over the same pH range.

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[3] Lefort and Douzou, *J. Chim. Phys.*, 1956, **53**, 536.

The primary absorption of a light quantum has been stated to result in the formation of excited ferrous ion (Fe^{3+},H_2O^-). The assumption of a photoexcited complex, made first by Farkas and Farkas,[4] appears to be in general agreement with the results. Moreover, for positive ions, the existence of an excited state of finite life is also to be expected on theoretical grounds. The following primary processes [2] have been put forward to account for the results obtained:

Excitation: $(Fe^{2+},H_2O) + h\nu \longrightarrow \underset{\text{(Excited state)}}{(Fe^{3+},H_2O^-)} \cdots (I_a)$ . . . . . (1)

Deactivation: $(Fe^{3+},H_2O^-) \longrightarrow (Fe^{2+},H_2O) + \text{Energy} \cdots (k_2)$ . . (2)

Dissociation: $(Fe^{3+},H_2O^-) \longrightarrow Fe^{3+} + OH^- + H \cdots (k_3)$ . . . (3)

It has been assumed previously that reaction (3) is followed by formation of H_2^+ and oxidation of the ferrous ion:

$$H + H^+ \rightleftharpoons H_2^+ \cdots (k_4) \qquad (4)$$

$$H_2^+ + Fe^{2+} \longrightarrow H_2 + Fe^{3+} \cdots (k_5) \qquad (5)$$

The simple scheme (1—5) accounts formally and adequately for the experimental facts, at least qualitatively. It has now become apparent that the H_2^+ equilibrium is normally very much on the right-hand side, *i.e.*, that the spontaneous dissociation is relatively slow. The recent work by Eigen [5] on the rate of ionic dissociation would be in keeping with this. However, this may not be the only pH-dependent process involved. The excited ferrous ion may react with hydrogen ions:

Dissociation (*acid-catalysed*):

$$(Fe^{3+},H_2O^-) + H^+ \longrightarrow Fe^{3+},H_2O + H \qquad (3')$$

Our experiments show that the back-reaction involving ferric ions must be taken into account. This is essential, not only under the conditions of the experiments of, *e.g.*, Rigg and Weiss,[2] where irradiation covered a period of time, but also for the so-called initial yields, because even under the present conditions the ferric-ion concentration is sufficiently high for reactions such as:

$$H + Fe^{3+} \longrightarrow H^+ + Fe^{2+} \cdots (k_6) \qquad (6)$$

and, at higher pH's:

$$H + FeOH^{2+} \longrightarrow H_2O + Fe^{2+} \cdots (k_7) \qquad (7)$$

The species $FeOH^{2+}$ is present in the equilibrium:

$$Fe^{3+} + H_2O \rightleftharpoons FeOH^{2+} + H^+ \cdots (K_8) \qquad (8)$$

According to Fig. 5, increase in the sulphuric acid concentration from N to 10N increases the photochemical yield, probably owing to the increase in the hydrogen-ion concentration although in the concentrated solutions very little is known about the ionic species present. There is also some increase in the quantum yields in going from 0·1N to M-ferrous sulphate solution (Fig. 4). This is more marked at low pH's, although even under the most favourable conditions the dependence is relatively very weak which suggests that it may not be a first-order effect. It is significant that under the conditions where there is an appreciable concentration effect, the ferric yield, even at the lower ferrous sulphate concentrations, is relatively high. Calculation shows that under these conditions the " inner filter effect " of the ferric salt must have an appreciable influence, since the molar extinction coefficient of ferric is about 100 times greater than of the ferrous ions.

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[4] Farkas and Farkas, *Trans. Faraday Soc.*, 1938, **34**, 1113.
[5] Eigen, *Z. Elektrochem.*, in the press.

At the lowest ferrous sulphate concentration (0·1M) the first measurement corresponds to a ferric concentration of about 3×10^{-4} mole per l. of Fe^{III} which, under the conditions in question, would absorb about 30% of the incident radiation. When the ferrous sulphate concentration is finally increased to M, *i.e.*, by a factor of 10, the amount of light absorbed by the ferric relative to the ferrous is correspondingly decreased. In addition, there will be a second effect which varies with the ferrous sulphate concentration, namely, that the actual " reaction zone," in which the photochemical process takes place, " contracts " with increase in ferrous sulphate concentration, when light absorption occurs in an increasingly thinner layer at the frontal wall of the cell. This again must tend to minimise the " inner filter effect " of the ferric iron. It would be difficult to make an exact calculation of this effect which must depend upon the rate of diffusion and convection of the ferric salt formed in the reaction zone. There can, however, be no doubt that both these effects will operate and this should give an increased quantum yield with increasing ferrous sulphate concentration; the size of this concentration-dependence is fully compatible with the effect found experimentally.

Dependence on the ferrous-ion concentration appears directly in the kinetic equations if the reverse process of reaction (4) is taken into account. This has been done already in the previous work.[2] There the ferrous-ion concentration enters directly into the expression for the yield. In view of the " inner filter effect," it is difficult to decide the relative importance of these different contributions. Increase of the ferrous sulphate concentration may manifest itself also by a kinetic " salt effect."

In the presence of acrylic acid, the following type of reactions may have to be taken into account (A = acrylic acid):

$$A + H \longrightarrow AH \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

$$AH + Fe^{3+} \longrightarrow A + Fe^{2+} + H^+ \quad . \; . \; . \; . \; . \; . \quad (10)$$

The net result would be that the ferric yield is reduced and again tends to zero at high pH. Fig. 7 indicates the competitive nature of the reactions leading to the photochemical oxidation of ferrous sulphate in the presence of acrylic acid.

Other reactions may also play a part in the mechanism but under the conditions of stationary irradiation cannot be distinguished. Such are the reaction of the excited ferrous ion with any ferric present in solution:

$$(Fe^{3+},H_2O^-) + Fe^{3+} \longrightarrow Fe^{3+},H_2O + Fe^{2+} \quad . \; . \; . \; . \; . \quad (11)$$

which essentially is an additional deactivation process.

In the presence of acrylic acid, the latter may possibly react with hydrogen atoms, reaction (9), and/or with excited ferrous ions:

$$(Fe^{3+},H_2O^-) + A \longrightarrow Fe^{3+},H_2O + A^- \quad . \; . \; . \; . \; . \quad (12)$$

and possibly according to:

$$A + H_2^+ \longrightarrow AH + H^+ \quad . \; . \; . \; . \; . \; . \; . \; . \quad (13)$$

Inclusion of any or all of these processes in the mechanism would not change the qualitative picture, but would, of course, have an effect on the more detailed interpretation of the quantum yields.

The equation for the differential quantum yield of ferric salt in the photostationary state, according to reactions (1) to (9), is as follows: (I_a, light intensity absorbed per unit of volume)

$$\gamma = \frac{1}{I_a}\frac{d(Fe^{III})}{dt} = 2\left(\frac{k_3}{k_2 + k_3}\right)\frac{k_4(H^+)^2}{\{k_4(H^+)^2 + k_6(Fe^{3+})(H^+) + k_7K_8(Fe^{3+}) + k_9(A)(H^+)\}} \quad (14)$$

If the reactions (3′) and (11) of the excited ferrous ions with H^+ and Fe^{3+} respectively are taken into account, the first parenthetical term in equation (14) changes to:

$$\frac{\{k_3 + k_3'(H^+)\}}{\{k_2 + k_3 + k_3'(H^+) + k_{11}(Fe^{3+})\}} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \qquad (15)$$

In the presence of acrylic acid an additional term corresponding to reaction (12) might also enter into the denominator.

According to Fig. 2 the quantum yield shows a pH-dependence with a point of inflexion in the region of pH 2·5. This can be deduced from the mechanism given above: an equation corresponding to equation (14), of the general form $(H^+)^2/\{A(H^+)^2 + B(H^+) + C\}$ should give a point of inflexion in the pH diagram as it leads to a cubic equation which will have at least one real root. In the presence of acrylic acid the numerator remains unchanged, but in the denominator one or possibly more terms dependent on the acrylic acid concentration will appear: this means, in the first instance, a decrease of the quantum yields. Further analysis shows that, apart from this, the point of inflexion in the pH diagram moves towards lower pH values, as a direct consequence of additional terms in the denominator due to the presence of the acrylic acid, which again is in agreement with experiment (Fig. 7).

EXPERIMENTAL

The solutions were irradiated by a full-wave low-pressure mercury-discharge tube of ~500 w, used in conjunction with a Ferranti voltage-stabiliser. Unfiltered radiation was used under conditions of complete absorption. A spherical silica flask containing triply distilled water acted as a condenser and heat-filter. At the relatively short exposures used in this work the reaction vessel was always easily kept at 20° ± 1°.

Some experiments were carried out with a light-filter which transmitted only light below 3200 Å. The filter [6] consisted of an aqueous solution containing, per l., 240 g. of nickel sulphate hexahydrate and 45 g. of cobalt sulphate heptahydrate. 5 cm. thickness of this transmits ~50% of the incident light between 2400 and 3200 Å. The (initial) quantum yields of the photochemical oxidation of ferrous sulphate were the same as those obtained with unfiltered radiation; in all later experiments unfiltered radiation was used.

Water used was triply distilled—ordinary distilled water redistilled from permanganate and from dilute sulphuric acid.

The reaction vessel used was a Thunberg-type silica vessel incorporating a 1 cm. optical cell *C* (Fig. 8). The ferrous sulphate solution was $\nless$0·1M in order to ensure complete absorption of the incident radiation within the cell. To avoid autoxidation of ferrous sulphate, the appropriate amount was placed in compartment *A* (Fig. 8), 5 ml. of acidified water were placed in *C*, and the vessel evacuated (through *B*). After evacuation to 10^{-3}—10^{-4} mm. the ferrous salt was brought into solution by tilting and slight shaking. In this way, the initial concentration of ferric ions was considerably reduced, though it was still not less than about $0{\cdot}5 \times 10^{-4}$ mole/l. in a 0·1M-solution at pH 1·0.

Further to reduce the initial concentration of ferric salt, spectroscopically pure metallic iron pellets (Johnson, Matthey Ltd.) were added to *A* (Fig. 8) with the ferrous sulphate. After evacuation and mixing, the solutions were set aside for a few hours during which the ferric ions were reduced by the iron. Then the pellets were removed by lifting them into compartment *A* by a small magnet. The solution was re-evacuated to remove any hydrogen formed by reaction with the iron: the cell was then ready for irradiation. The rate of reduction of ferric by the iron pellets was very slow in solutions of pH >2.

Acrylic acid, supplied by Goodrich Chemical Co., was redistilled three times before use. All other reagents used were of " AnalaR " grade.

In all the experiments, ferric iron was determined spectrophotometrically at 304 mμ by placing the silica cell, after irradiation, inside a " Unicam " Spectrophotometer S.P. 500 (cf. Fig. 9). Absorption by acrylic acid is negligible above 220 mμ. Identical yields were obtained on irradiation of ferrous sulphate solutions in the presence of acrylic acid with and without the

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[6] Kasha, *J. Opt. Soc. Amer.*, 1948, **38**, 929.

light filter, showing that, under the conditions, the photochemical primary process was not affected by the absorption of light by acrylic acid in the wavelength region below 230 mμ. The molar extinction coefficient of Fe^{III} in 0·1N-sulphuric acid at 304 mμ was taken as 2100 at 20°. In 6N-acid it was 2285, in 8N 2570, and in 10N 2835.

All pH's were adjusted with sulphuric acid and measured on a Pye pH-meter. The pH measurements were carried out after dissolution of the ferrous sulphate in the acidified solutions.

Actinometry.—The light output for the low-pressure mercury-discharge tube was measured actinometrically by means of 0·5M-monochloroacetic acid, with 0·62 ± 0·04 as the quantum yield [7] of photolysis of monochloroacetic acid. The radiation absorbed was $2{\cdot}5 \pm 0{\cdot}3 \times 10^{-6}$ einstein $min.^{-1}$ in 5 ml. of solution in the silica cell used for these experiments.

King's College, University of Durham,
Newcastle upon Tyne, 1.

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[7] Kuechler and Pick, *Z. phys. Chem.*, 1939, *B*, **45**, 116.