TABLE III

COMPARISON OF CONDUCTIVITY DATA

Concn. of metal, moles/l. × 10^2			Equivalent conductivity		
Ethylenediamine	Methylamine[16]	Ammonia[6]	Ethylenediamine	Methylamine[16]	Ammonia[6]
0.228	0.222	0.260	68.4	46.77	790
.654	.605	.621	29.7	32.85	699
.768	.6171	.6935	26.8	32.17	642
	.92	.9185		27.82	605
1.18	1.05		20.8	25.28	
	1.24	1.255		23.77	558

serves that the roles of the electrons and monomer have been reversed as far as being the species of prominence is concerned.

Summary

The significant results obtained in this work are in accord with the model of Becker, Lindquist, and Alder for this system.

On the basis of the magnetic data showing the similarity of g-values to those of metal–ammonia solutions, the narrowness of the line observed in potassium solutions, the independence of the line width of concentration, and the absence of hyperfine structure coupled with the arguments assigning electrons as the paramagnetic species in liquid ammonia, we conclude that the paramagnetic species in metal–ethylenediamine solutions is the electron.

The absorptivity *vs.* specific conductivity curve, the value of the extinction coefficients, and the negative result found in the sodium, sodium iodide absorption experiment show that the absorbing and conducting species are different. The absorbing species in these solutions is either the monomer or the dimer, the monomer being the most likely.

Acknowledgments.—It is a pleasure to acknowledge the generous help of Dr. Leonard Yarmus, Physics Department, N.Y.U., in making the electron spin resonance measurements. Much of this work was supported by the Atomic Energy Commission under Contract AT-30-1-1837.

THE PHOTOCHEMICAL EVOLUTION OF HYDROGEN FROM AQUEOUS SOLUTIONS OF FERROUS IONS. PART I. THE REACTION MECHANISM AT LOW pH

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The photochemical oxidation of ferrous ion in 0.8 *N* H_2SO_4 was investigated in the absence and presence of O_2. The yields of H_2 and Fe^{3+} were determined and the dependence of the quantum yield on light intensity, Fe^{2+} and Fe^{3+} concentration, and on the concentration of O_2 was investigated. The post-irradiation effect due to H_2O_2 formation was followed. The inner filter effect due to the ferric ions formed in the reaction was taken into account. As a result, a mechanism accounting for the experimental facts could be derived. The excited state resulting on light absorption yields H atoms. H atoms oxidize ferrous ions in acid solution and also react with O_2, if present. The competition between O_2 and Fe^{2+} for the H atoms formed was investigated. It appears that the direct effect of O_2 on the excited state is relatively small.

The photochemically induced oxidation of ferrous ions in aqueous solution has been the subject of several investigations, since it enables one to gain insight into the mechanism of photochemical consequences of electron transfer processes in solutions. The light absorption by the ferrous ion and the photochemical liberation of hydrogen in the absence of O_2 were investigated by Potterill, Walker, and Weiss,[1] who interpreted their results by the Franck and Haber mechanism,[2] which postulated a dissociative electron capture process by a solvent molecule. Farkas and Farkas[3] concluded that the primary absorption act involves electron transfer from the ferrous ion to a molecule of water in the primary hydration layer and as a secondary act the dissociation of the water molecule may follow. This reaction was reinvestigated by Rigg and Weiss,[4] who reported that the quantum yield was pH dependent. However, their results were not confirmed by Lefort and Douzou.[5] Recently Hayon and Weiss[6] confirmed the pH dependence. In view of these contradictions, a complete reinvestigation of this reaction appeared to be desirable.

The effect of oxygen on this reaction is of interest since it may clarify the role of H atoms formed in the system and contribute to the establishment of the complete reaction mechanism.

Experimental

Light Source.—All irradiations were carried out with a low pressure spiral mercury lamp, manufactured by Messrs. Thermal Syndicate Ltd. The lamp was run at 30–80 ma. and was fed from a stabilized a.c. supply. Variations in current to give different light output were obtained by a variable transformer in the primary circuit of a transformer feeding directly into the lamp. During irradiation small fluctuations in light intensity were corrected by manual adjustment.

Irradiation Apparatus.—A cylindrical clear fused quartz reaction vessel of 5 cm. diameter was used. The solution was stirred by a small Teflon-coated magnetic stirrer. The position of the reaction vessel which was placed inside the spiral ultraviolet lamp was kept constant by aligning a mark

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(1) R. H. Potterill, O. J. Walker, and J. Weiss, *Proc. Roy. Soc.* (London), **A156**, 561 (1936).

(2) J. Franck and F. Haber, *Sitzber. Preuss. Akad. Wiss. Physik. Math. Klasse*, 250 (1941).

(3) A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

(4) T. Rigg and J. Weiss, *J. Chem. Phys.*, **30**, 1194 (1952).

(5) M. Lefort and P. Douzou, *J. Chim. Phys.*, **53**, 536 (1956).

(6) E. Hayon and J. Weiss, *J. Chem. Soc.*, 3866 (1960).

on the vessel with a mark on the supporting glass tube. The distance between the lamp and reaction vessel was about 0.5 cm. The lamp and the reaction vessel were immersed in a thermostat kept at 20 ± 0.2°. As preliminary experiments indicated that light at 1850 Å. photolyzed pure 0.1 *N* sulfuric acid, the liquid in the thermostat was 0.1 *M* NaCl in triply distilled water, which cut off all light below 2000 Å. The transmittance of this filter solution at 2536 Å. did not change after 20 hr. of exposure to ultraviolet light. Light intensity was monitored by a Photovolt photomultipler unit and was held constant in the region of ±2%.

Actinometry.—The relative output of the lamp in the 2200–4000 Å. region was determined by a photoelectric cell using the monochromator system of a Beckman DU spectrophotometer. It was found that 90% of the total output lies at 2536 Å. Actinometry was carried out in the reaction vessel. A 0.01 *N* uranyl oxalate actinometer solution was used.[7] The decomposition of the oxalate was held to less than 40%. The quantum yield at 2536 Å. was taken[7] as 0.60. Routine measurements of light intensity were taken after each set of experiments. It was found that the readings on the Photovolt unit were directly proportional to the lamp output as determined by chemical actinometry.

Gas Analysis.—The gas produced by photolysis was analyzed in a gas analysis instrument consisting of a modified McLeod gage. The gas ignition chamber was connected to the capillary of the gage by a stopcock. With the stopcock closed, the instrument is operated as a gage for the determination of the pressure of the gas formed. With the stopcock open, the instrument is operated as a Toepler pump to collect the gas in the ignition chamber. Hydrogen was estimated by combustion with pure oxygen on a heated platinum filament.

Procedure.—The reaction vessel was thoroughly cleaned with CrO_3-H_2SO_4, followed by nitric acid, and then finally with triply distilled water. It was stored full of triply distilled water and before irradiation it was rinsed with the solution to be irradiated. The experiments *in vacuo* were carried out when the whole system was pumped to a pressure of less than 10^{-5} mm. Twenty-five ml. of the solution was used for each irradiation. The solution was outgassed by cutting off the system from the pumps and opening the stopcock for about 30 sec. During the whole time the solution was vigorously stirred. This procedure was repeated until the uncondensable gas pressure above the solution was of the order of 10^{-5} mm. The outgassing was complete after approximately 2 hr. and losses due to evaporation were less than 0.5 ml. The reaction vessel surrounded by the lamp then was immersed in the thermostat for about 20 min. The lamp was lit preliminarily for 5 min. and afterward a metal sleeve on the vessel was lifted and the solution was irradiated. During irradiation the solution was stirred at a constant rate. After irradiation the stopcock was opened several times for about 30 sec., the water vapor was condensed in the trap, and the gas was analyzed. The reaction vessel then was disconnected and the solution analyzed.

Analysis.—Ferric ion was determined as the sulfate at 305 mμ with a Hilger Uvispek spectrophotometer. The extinction coefficient in 0.8 *N* H_2SO_4 was determined as 2175 l. mole^{-1} cm.$^{-1}$ at 24° in solutions containing less than 0.02 *M* $FeSO_4$. The temperature coefficient of the absorption was found to be 0.7% per degree, in good agreement with previous data.[8,9] The extinction coefficient depends on the total ferrous sulfate concentration and care was taken of this fact. The extinction coefficient is pH dependent. After irradiation at other acid concentrations, the final acid concentration was adjusted to 0.8 *N*.

Materials and Solutions.—Triply distilled water was prepared by redistilling distilled water from alkaline permanganate and from phosphoric acid. Ferrous ammonium sulfate, C.P., and "Analar" sulfuric acid were used without further purification. The initial ferric ion concentration of solutions containing 0.02 *M* ferrous ion did not exceed 10^{-5} *M*. Solutions at higher concentrations of ferrous ion were prepared by introducing a weighed amount of ferrous ammonium sulfate to the reaction vessel, followed by addition of the acid and immediate evacuation.

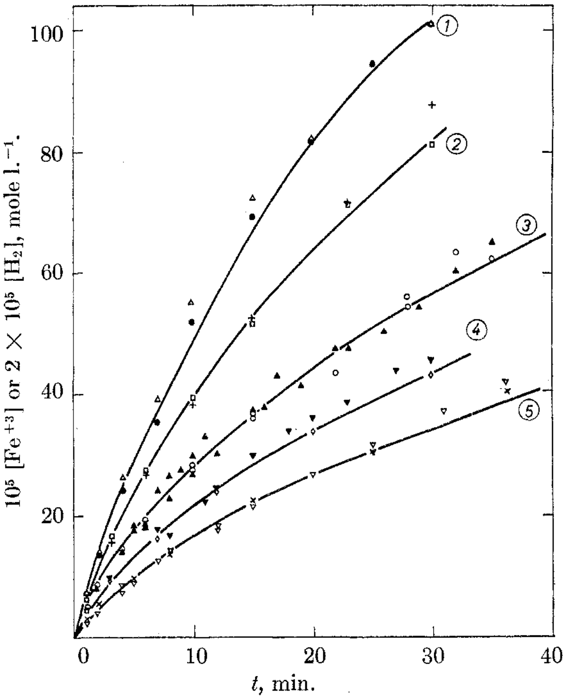

Fig. 1.—The dependence of the photoöxidation yield in evacuated solutions on [Fe^{2+}] concentrations and on light intensity: [H_2SO_4] = 0.8 *N*; (1) [Fe^{2+}] = 0.102 mole l.$^{-1}$; I_0 = 4.59 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, ●, Fe^{3+}; Δ, H_2. (2) [Fe^{2+}] = 0.051 mole l.$^{-1}$; I_0 = 4.59 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, □, Fe^{3+}; +, H_2. (3) [Fe^{2+}] = 0.0204 mole l.$^{-1}$; I_0 = 4.59 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, ○, Fe^{3+}; ▲, H_2. (4) [Fe^{2+}] = 0.0204 mole l.$^{-1}$; I_0 = 3.12 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, ◇, Fe^{3+}; ▼, H_2. (5) [Fe^{2+}] = 0.0204 mole l.$^{-1}$; I_0 = 1.84 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, ×, Fe^{3+}; ∇, H_2; curves calculated from eq. VI.

Results

Photochemistry in Air-Free Solutions.—The formation of ferric ion and hydrogen as a function of dose, initial ferrous ion concentration, and light intensity in 0.8 *N* H_2SO_4 solutions *in vacuo* is presented in Fig. 1. The experiments were carried out under conditions of total light absorption. The agreement with the relation $\Delta(Fe^{3+}) = 2\Delta(H_2)$ is satisfactory.

Dependence of Photochemical Yield on Irradiation Time.—The ferric yield *vs.* time plots suggest retardation by a product. As the amount of the dissolved hydrogen is negligible, the inhibition is due to Fe^{3+} ion.

The dependence of the oxidation rate on the initial ferrous ion concentration at relatively long irradiation periods (Fig. 1) suggests that a competitive reaction may be operative. In order to determine whether the rate depends on the total amount of iron oxidized or is determined by the concentration ratio of the ferrous and ferric ion, the plot of the fraction of iron oxidized against $t/[Fe^{2+}]_0$ is presented in Fig. 2, indicating that the rate depends only on the fraction of iron oxidized. It may be suggested that the fall-off of the reaction rate is due to the reduction of ferric ion by hydrogen atoms. This conclusion is not consistent with recent studies. Using ionizing radiations it was

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[7] E. J. Bowen, "Chemical Aspects of Light," Oxford University Press, 1946, p. 283.

[8] J. L. Haybittle, R. D. Saunders, and A. J. Swallow, *J. Chem. Phys.*, **25**, 1213 (1956).

[9] T. Rigg, W. Taylor, and J. Weiss, *ibid.*, **22**, 575 (1954).

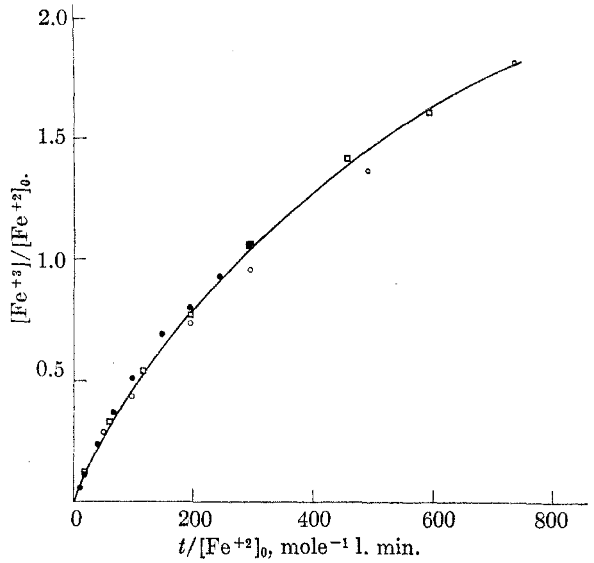

Fig. 2.—The plot of $t/[Fe^{2+}]_0$ against $[Fe^{3+}]/[Fe^{2+}]_0$ for various initial ferrous ion concentrations in evacuated solutions: ●, $[Fe^{2+}]_0 = 0.102$ mole l.$^{-1}$; □, $[Fe^{2+}]_0 = 0.051$ mole l.$^{-1}$; ○, $[Fe^{2+}]_0 = 0.0204$ mole l.$^{-1}$; curve calculated from eq. IV.

shown by Allen and Rothschild[10] that the ratio of the apparent reaction rates for reduction of ferric ion (present in various ionic forms) and oxidation of ferrous ion is 0.081 in 0.8 N H_2SO_4. Using hydrogen atoms, Czapski and Stein[11] obtained the value of 0.135 for this ratio at this pH. As in our experiments the fraction of iron oxidized did not exceed 4%, the effect of the reverse reaction is negligible in this pH region.

Since the falling off of the reaction rate is pronounced even after a relatively short irradiation period, it is very difficult to obtain reliable data for the initial photoöxidation rates. This problem was solved by Rigg and Weiss[4] by drawing the limiting slopes at $t = 0$. This method is sensitive to small experimental errors in the determination of the first experimental points on the curve. We attempt to present a full calculation of the shape of the kinetic curves and to propose a more reliable method for the determination of the initial rates.

The Inner Filter Effect.—The inner filter effect is observed when more than one absorbing species is present in the photochemical system. We attribute the decrease in the oxidation rate of the ferrous ion in 0.8 N H_2SO_4 to the inner filter effect of the ferric ion. The molar extinction coefficients at 2536 Å. in 0.8 N H_2SO_4 are $\epsilon_{Fe^{2+}} = 14.8 \pm 0.15$ l. mole^{-1} cm.$^{-1}$ and $\epsilon_{Fe^{3+}} = 2850 \pm 50$ l. mole^{-1} cm.$^{-1}$; thus, this effect is appreciable.

We denote by I_0 the total absorbed light intensity and by I_a the light intensity absorbed by the ferrous ions (both in einstein l.$^{-1}$ min.$^{-1}$). Under conditions of total light absorption by the system

$$I_a = \frac{I_0}{1 + (\epsilon_{Fe^{+3}}[Fe^{+3}]/\epsilon_{Fe^{+2}}[Fe^{+2}])} \qquad (I)$$

The Reaction Mechanism.—We assume that the primary photochemical process leads to the binding of the electron in an excited state, according to

$$Fe^{+2}_{aq} \xrightarrow{I_a} Fe^{+2}_{aq}{}^* \qquad (1)$$

This may be followed by deactivation

$$Fe^{+2}_{aq}{}^* \xrightarrow{k_2} Fe^{+2}_{aq} \qquad (2)$$

or by H atom formation.

$$Fe^{+2}_{aq}{}^* \xrightarrow{k_3} Fe^{+3}_{aq} + OH^- + H \qquad (3)$$

Here reactions 2 and 3 are schematic only, and the actual reaction mechanism may involve dependence on ferric, ferrous, and hydrogen ions.

The hydrogen atoms formed in acid solution act as oxidizing agents for the ferrous ion. The experimental evidence from radiation chemistry[10,12-14] and from experiments on the action of hydrogen atoms on acid solutions of ferrous sulfate[11,15] in favor of this reaction is conclusive. Without considering the actual reaction mechanism and the participating species, the reaction will be schematically presented by

$$Fe^{2+}_{aq} + H + H^+_{aq} \xrightarrow{k_4} Fe^{3+}_{aq} + H_2 \qquad (4)$$

The hydrogen atoms formed may reduce Fe^{3+}

$$Fe^{3+}_{aq} + H \xrightarrow{k_5} Fe^{2+}_{aq} + H^+_{aq*} \qquad (5)$$

or recombine

$$2H \xrightarrow{k_6} H_2 \qquad (6)$$

The possible photochemical reactions due to light absorption by the product Fe^{3+} have to be considered.[16] The amount of light absorbed by Fe^{3+} is $I_0 - I_a$

$$Fe^{3+}_{aq} \underset{k_7'}{\overset{I_0 - I_a}{\rightleftarrows}} Fe^{3+}_{aq}{}^* \qquad (7)$$

followed by the possible radical formation

$$Fe^{3+}_{aq}{}^* \xrightarrow{k_8} Fe^{2+}_{aq} + R \qquad (8)$$

As the reaction occurs in sulfuric acid the radical R may be OH, HSO_4, and SO_4^-, which probably all act as oxidizing agents in the reaction

$$Fe^{2+}_{aq} + R \xrightarrow{k_9} Fe^{3+}_{aq} + R^- \qquad (9)$$

As the reaction was investigated at relatively high ferrous ion concentration at relatively low rate of hydrogen atom formation and at high acidity, the recombination reaction 6 can be neglected. Taking into account reactions 1–5 and 7–9 for the stationary state we obtain

$$\frac{d[Fe^{3+}]}{dt} = \frac{2k_3I_a}{(k_2 + k_3)(1 + k_5[Fe^{3+}]/k_4[Fe^{2+}])} \qquad (II)$$

As was pointed out,[10,11] $k_5/k_4 = 0.1$ at pH 0.4; thus, at this pH the term $(k_5/k_4)[Fe^{3+}]/[Fe^{2+}]$ may be neglected under our experimental condi-

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(10) A. O. Allen and W. G. Rothschild, *Radiation Res.*, **7**, 591 (1957).

(11) G. Czapski and G. Stein, *J. Phys. Chem.*, **63**, 850 (1959).

(12) T. Rigg, G. Stein, and J. Weiss, *Proc. Roy. Soc.* (London), **A211**, 375 (1952).

(13) A. O. Allen, V. D. Hogan, and W. G. Rothschild, *Radiation Res.*, **7**, 603 (1957).

(14) W. G. Rothschild and A. O. Allen, *ibid.*, **8**, 101 (1958).

(15) (a) G. Czapski and G. Stein, *Nature*, **182**, 598 (1958); (b) T. W. Davis, S. Gordon, and E. H. Hart, *J. Am. Chem. Soc.*, **80**, 4487 (1958).

(16) (a) M. G. Evans and N. Uri, *Nature*, **164**, 404 (1949); (b) J. Sadlick and A. O. Allen, *J. Am. Chem. Soc.*, **77**, 1388 (1956).

tions. For 0.8 N H_2SO_4 solution, combining eq. I and II we obtain

$$\frac{d[Fe^{3+}]}{dt} = \frac{AI_0}{1 + (\epsilon_{Fe^{3+}}[Fe^{3+}]/\epsilon_{Fe^{2+}}[Fe^{2+}])} \qquad (III)$$

where $A = 2k_3/(k_2 + k_3)$
The general solution of eq. III is

$$(AI_0\, t/[Fe^{2+}]) = ([Fe^{3+}]/(Fe^{2+}]_0) - (\epsilon_{Fe^{3+}}/\epsilon_{Fe^{2+}})[([Fe^{3+}]/[Fe^{2+}]_0) + \ln(1 - [Fe^{3+}]/[Fe^{2+}])_0] \qquad (IV)$$

For low per cent of conversion, eq. IV is reduced to the form

$$AI_0t = [Fe^{3+}] + \frac{B}{2}\,[Fe^{3+}]^2 \qquad (V)$$

where

$$B = \frac{\epsilon_{Fe^{3+}}}{\epsilon_{Fe^{2+}}\,[Fe^{2+}]_0}$$

The general equation for the photoöxidation curve is thus

$$[Fe^{3+}] = \frac{(1 + 2BAI_0t)^{1/2} - 1}{B} \qquad (VI)$$

Determination of Initial Rates.—In order to solve eq. VI, the initial rate $AI_0 = (d[Fe^{3+}]/dt)_0$ has to be determined. The determination was carried out graphically transforming eq. V to the form

$$[Fe^{+3}] = (2AI_0/B)(t/[Fe^{+3}]) - \frac{2}{B} \qquad (VII)$$

The plot of the experimental results for the dependence of the photoöxidation rate on the ferrous ion concentration and light intensity is presented in Fig. 3.

The linear relationship is well fulfilled within the experimental error. The intersection of the straight lines thus obtained with the $t/[Fe^{3+}]$ axis yields the value of $1/AI_0$.

Dependence of Initial Photoöxidation Rate on $[Fe^{2+}]_0$.—The proposed mechanism does not include the possibility that the initial rate should be dependent on the initial ferrous concentration.

The experimental results are summarized in Table I.

TABLE I

DEPENDENCE OF INITIAL PHOTOÖXIDATION RATE ON $[Fe^{2+}]_0$

Temp., 20°; $I_0 = 5.9 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$

$[Fe^{2+}]_0$, mole l.$^{-1}$	B, l. mole^{-1} measd. (spectroscopically)	B, l. mole^{-1} calcd. from photochemical results	$AI_0 \times 10^{-5}$, mole l.$^{-1}$ min.$^{-1}$
0.0204	9450	10000	6.85 ± 0.2
.051	3780	3650	6.95 ± .2
.102	1900	1700	7.05 ± .2

A slight trend of increasing AI_0 with increasing $[Fe^{2+}]_0$ is observed. This effect may be due to the fact that the absorption of the incident light is somewhat less than 100% under our experimental conditions. These results indicate that the initial photoöxidation rate does not depend greatly on the initial $[Fe^{2+}]$ concentration up to 0.1 M.

Dependence of Initial Yield on Light Intensity.—The initial quantum yield was found to be independent of the light intensity over the region 1.5–9 × 10^{-4} einstein l.$^{-1}$ min.$^{-1}$, in agreement with the theoretical considerations. The recombination reaction may indeed be neglected. We obtain for the initial quantum yield in 0.8 N H_2SO_4 *in vacuo* the value of $A = 0.148 \pm 0.010$. Our results yield that the fraction of excited ions that dissociate in 0.8 N H_2SO_4 is $k_3/(k_2 + k_3) = 0.075$, indicating the relative high efficiency of the deactivation reaction at this pH.

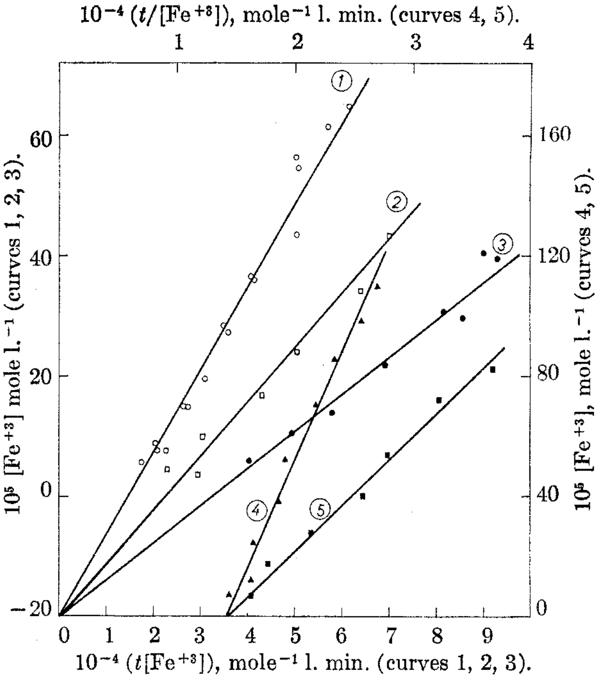

Fig. 3.—Determination of the initial photoöxidation rates in evacuated solutions: $H_2SO_4 = 0.8\,N$, according to eq. VII. (1) ○, $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$. (2) □, $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; $I_0 = 3.12 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$. (3) ●, $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; $I_0 = 1.84 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$. (4) ▲, $[Fe^{2+}] = 0.102$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$. (5) ■, $[Fe^{2+}] = 0.051$ mole l.$^{-1}$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$.

Photochemistry in the Presence of O_2.—The plot of the experimental results for the photoöxidation of aerated ferrous sulfate in 0.8 N H_2SO_4 solutions, under the conditions of total light absorption, is presented in Fig. 4. As in the case of deaerated solutions the rate depends on the fraction of iron oxidized. The results can be interpreted adequately by introduction of the correction for the inner filter effect, and can be presented by the equation

$$\frac{d[Fe^{+3}]}{dt} = \frac{A_{O_2}I_0}{1 + B\,[Fe^{+3}]} \qquad (VIII)$$

$A_{O_2}I_0$ is the initial rate in the presence of oxygen and $B = \epsilon_{Fe^{3+}}/\epsilon_{Fe^{2+}}[Fe^{2+}]$, as before.

The initial rate was determined by the graphical method outlined above.

The Ratio of Rates of Oxidation in Air and *in vacuo*.—Some results for the observed ratio of the initial oxidation rates in the presence and absence of oxygen are presented in Table II.

TABLE II

$[Fe^{2+}]_0$	10^4I_0, einstein l.$^{-1}$ min.$^{-1}$	10^5AI_0 *in vacuo*	$10^5A_{O_2}I_0$ in air	A_{O_2}/A
0.0204	4.59	6.85	13.15	1.92 ± 0.10
.051	4.59	6.95	13.15	1.89 ± .10
.0204	3.73	5.52	10.51	1.91 ± .10

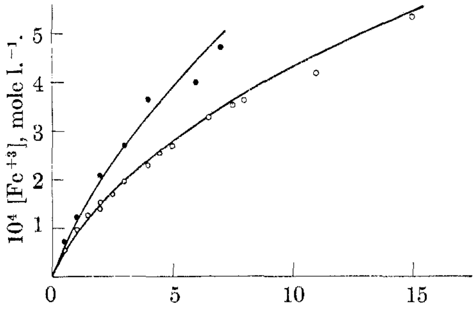

Fig. 4.—Photoöxidation curves in air saturated solutions: $[H_2SO_4] = 0.8\,N$; $I_0 = 4.59 \times 10^{-4}$ einstein l.$^{-1}$ min.$^{-1}$; ○, $[Fe^{2+}] = 0.0204$ mole l.$^{-1}$; ●, $[Fe^{2+}] = 0.051$ mole l.$^{-1}$; curves calculated from eq. VIII.

We proceed now to show that this ratio of the initial yields is in agreement with the theoretical expectations.

Kinetics of Photoöxidation in Aerated Solutions.—The application of the mechanism of Rigg, Stein, and Weiss[12] to the photochemical system can be carried out assuming that the mechanism of hydrogen atom formation is identical with that *in vacuo*, including reactions 1–3 discussed above.

The hydrogen atoms formed may oxidize ferrous ions according to reaction 4 or reduce O_2

$$H + O_2 \xrightarrow{k_{10}} HO_2 \qquad (10)$$

This leads to the oxidation of three Fe^{2+} ions

$$Fe^{+2}{}_{aq} + HO_2 + H^+ \xrightarrow{k_{11}} Fe^{+3}{}_{aq} + H_2O_2 \qquad (11)$$

$$Fe^{+2}{}_{aq} + H_2O_2 \xrightarrow{k_{12}} Fe^{+3}{}_{aq} + OH^- + OH \qquad (12)$$

$$Fe^{2+}{}_{aq} + OH \xrightarrow{k_{13}} Fe^{3+}{}_{aq} + OH^- \qquad (13)$$

In this treatment reaction 5 and

$$Fe^{3+}{}_{aq} + HO_2 \xrightarrow{k_{14}} Fe^{2+}{}_{aq} + H^+{}_{aq} + O_2 \qquad (14)$$

were not included, as it appears from radiation chemical evidence[10] that in 0.8 N H_2SO_4 their influence is negligible. Steady state treatment for the intermediates Fe^{2+*}, HO_2, H_2O_2, and OH yields the result

$$\frac{d[Fe^{3+}]}{dt} = AI_a\left[1 + \frac{1}{1 + (k_1[Fe^{2+}]/k_{10}[O_2])}\right] \qquad (IX)$$

In the limiting case when the concentration ratio of ferrous ion to oxygen tends to zero, the ratio of the initial rate of photoöxidation in air and *in vacuo* should approach the value of 2. The results of Table II are in agreement with this expectation.

However, it appeared that this result needed further verification. It was assumed that the presence of oxygen does not affect the mechanism of the hydrogen atom formation which is the same as *in vacuo*. The presence of oxygen may increase the yield of the hydroperoxy radicals by direct interaction of any oxygen molecule with the excited ferrous ion. Such a reaction may proceed by a charge transfer mechanism

$$Fe^{2+}{}_{aq}{}^* + O_2 \longrightarrow Fe^{3+}{}_{aq} + O_2^- \qquad (15a)$$

or by hydrogen abstraction

$$Fe^{2+}{}_{aq}{}^* + O_2 \longrightarrow Fe^{3+}OH^- + HO_2 \qquad (15b)$$

On the other hand, a deactivation process by the oxygen molecule may occur

$$Fe^{2+}{}_{aq}{}^* + O_2 \longrightarrow Fe^{2+}{}_{aq} + O_2 \qquad (16)$$

Including these two reactions in the kinetic scheme yields the result

$$\frac{d[Fe^{3+}]}{dt} = \frac{2k_3I_a}{k_2 + k_3 + k_{16}[O_2]}\left(1 + \frac{1}{1 + (k_4[Fe^{2+}]/k_{10}[O_2])}\right) + \frac{3k_{15}I_a[O_2]}{k_2 + k_3 + k_{16}[O_2]} \qquad (X)$$

In order to investigate the contribution of these reactions it has to be established whether the oxidation rate is dependent on the ratio $[Fe^{2+}]/[O_2]$ only or also on the oxygen concentration as such.

Effect of Variable Oxygen Concentrations.—The dependence of the initial rates in oxygen-containing solutions on the ferrous and oxygen concentrations was investigated by changing $[Fe^{2+}]$ in the region 0.02–0.08 M and the oxygen concentrations in the region 0–$2.3 \times 10^{-4}\,M$.

The oxygen concentration in 0.8 N H_2SO_4 solution was calculated from the solubility data[17] at 20°. A correction factor of 0.89 was introduced for solubility in 0.8 N H_2SO_4 relative to that in water.[10,17] The initial rate was obtained from the expression

$$A_{O_2}I_0 = \frac{1}{t}\left\{([Fe^{3+}]_t - [Fe^{3+}]_0) + \frac{B}{2}([Fe^{3+}]_t{}^2 - [Fe^{3+}]_0{}^2)\right\}$$

where t is the irradiation time, $[Fe^{3+}]_t$ the final ferric ion concentration, and $[Fe^{3+}]_0$ the initial Fe^{3+} concentration. The results are shown in Fig. 5 where $[Fe^{3+}]_c = A_{O_2}I_0t$, the ferric ion yield corrected for the inner filter effect.

It was found that the rate was determined solely by the concentration ratio $[Fe^{2+}]/[O_2]$. The experimental results were adequately represented by the equation

$$A_{O_2}/A = 1 + \frac{1}{1 + ([Fe^{2+}]/900[O_2])} \qquad (XI)$$

The comparison of the experimental results with the data calculated from eq. XI is in agreement within the range of ±10%. These results indicate that under the experimental conditions, the contribution of reactions 15 and 16 is negligible.

The rate constants for the competitive reactions of ferrous ion and oxygen for hydrogen atoms at 0.8 N H_2SO_4 is $k_{10}/k_4 = 900 \pm 300$. This value confirms within the range of experimental error the value of 1200 ± 300 obtained by Rothschild and Allen[14] from radiation chemical measurements in 0.8 N H_2SO_4 solution. For 0.4 M HCl solution, the results of Schwarz and Hritz[18] yield the value of $k_{10}/k_4 = 810$. There is thus agreement between the ratio of the rates obtained now from photochemistry and previously from radiation chemistry.

Post Irradiation Effect.—To verify the adequacy of the proposed mechanism we attempted to present independent evidence for the existence of H_2O_2 in solutions irradiated by ultraviolet light. At high

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[17] A. Seidell, "Solubilities," D. Van Nostrand Co., New York, N. Y., 1955, p. 1355.

[18] H. A. Schwarz and J. M. Hritz, *J. Am. Chem. Soc.*, **80**, 5636 (1958).

(0.02 *M*) ferrous ion concentration the steady state treatment for the H_2O_2 concentration probably is justified and leads to the result for the steady state concentration of H_2O_2

$$[H_2O_2]_s = \frac{AI_a}{2k_{12}[Fe^{2+}](1 + k_4[Fe^{2+}]/k_{10}[O_2])} \quad (XII)$$

The rate constant of reaction 12 is relatively small[9,19] (k_{12} = 47 l. mole^{-1} sec.$^{-1}$, at 20°). Inserting the known values of $k_2I_a/k_2 + k_3$ and k_4/k_{10} for aerated solutions containing 0.02 *M* Fe^{2+}, we obtain $[H_2O_2]_s = 6 \times 10^{-7}$ *M*. At these high iron concentrations this amount of H_2O_2 cannot be directly identified.

The presence of hydrogen peroxide in ferrous sulfate solutions of concentration about 10^{-5} *M* irradiated with X-rays was demonstrated in the work of Dainton and Sutton.[20] Similar effects were observed in the present photochemical work. The experimental results were fitted to the second-order equation

$$k_{12}t = \frac{2.303}{b - a} \log \left(\frac{b}{a} \times \frac{a - x}{b - x}\right) \quad (XIII)$$

where *b* is the initial $[Fe^{2+}]_0$ after irradiation, $a = [Fe^{3+}]_\infty - [Fe^{3+}]_0$ = initial concentration of oxidant in eq./l., and $x = \Delta[Fe^{2+}]$.

The experimental results were in good agreement with the second-order kinetic plots. The data of Table III clearly demonstrate the kinetics of this system to be identical with that of the ferrous ion + hydrogen peroxide system.

The steady state treatment which is adequate for high ferrous ion concentrations has to be substituted by the equations

$$(d[H_2O_2]/dt) = (AI_a/2) - k_{12}[Fe^{2+}][H_2O_2] \quad (XIVa)$$

$$-(d[Fe^{2+}]/dt) = AI_a + 2k_{12}[Fe^{2+}][H_2O_2] \quad (XIVb)$$

$$\frac{d([Fe^{3+}] + 2[H_2O_2])}{dt} = 2AI_a \quad (XIVc)$$

Under the conditions of feeble light absorption, the inner filter effect can be neglected and I_a is proportional to $[Fe^{2+}]$. There is no general solution which can conveniently be applied to the experimental results and an approximate solution was used. Assuming that the ferrous ion concentration is constant, integration of eq. XIVa yields the result

$$\frac{AI_a}{2} = \frac{k_{12}[H_2O_2]_0[Fe^{2+}]}{1 - e^{-k_{12}[Fe^{2+}]t}} = [H_2O_2]_p \quad (XV)$$

where *t* is the irradiation time and $[Fe^{2+}]$ the mean concentration of ferrous ion during irradiation. $[H_2O_2]_p$ is the total amount in concentration units of H_2O_2 produced during irradiation, and $[H_2O_2]_0$ the amount presented at the end of the irradiation.

Hence we calculated the value of $[Fe^{3+}]_p$, the amount of Fe^{3+} produced by reactions 3 and 11

$$[Fe^{3+}]_p = [Fe^{3+}]_\infty - 2[H_2O_2]_p \quad (XVI)$$

The values of $[Fe^{3+}]_p/[H_2O_2]_p$ are presented in Table III. These results are consistent with the mechanism proposed for H_2O_2 formation from the HO_2 radical.

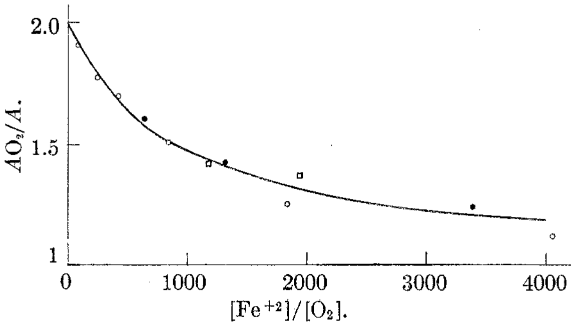

Fig. 5.—The dependence of the yield ratio AO_2/A on the concentration ratio $[Fe^{2+}]/[O_2]$; $[H_2SO_4]$ = 0.8 *N*: □, Fe^{2+} = 0.0816 mole l.$^{-1}$; ●, Fe^{2+} = 0.0408 mole l.$^{-1}$; ○, Fe^{2+} = 0.0204 mole l.$^{-1}$; curve calculated from eq. XI.

TABLE III

POST IRRADIATION EFFECT IN $FeSo_4$ SOLUTIONS IRRADIATED WITH ULTRAVIOLET LIGHT

Temp., °C.	*t*, min.	$10^5[Fe^{2+}]$ initial, *M*	$10^5[Fe^{2+}]$ after irradiation, *M*	k_{12} obsd.	k_{12} (kinetic data)	$\frac{[Fe^{3+}]_p}{[H_2O_2]_p}$
20°	6.0	6.0	5.02	43 ± 5	47	2.05
26°	6.0	2.4	1.81	64 ± 4	66	2.0

Throughout the whole treatment it was assumed that the light absorption by the hydrogen peroxide present can be neglected. The molar absorption coefficient of hydrogen peroxide[21,22] at 2536 Å. is ϵ = 19.6 mole^{-1} l. cm.$^{-1}$; thus, the inner filter effect of H_2O_2 will be unimportant even at low Fe^{2+} concentration.

Discussion

The results presented in this paper indicate that under our experimental conditions the major contribution to the retarding effect of the ferric ion is due to the inner filter effect. The theoretical curves, according to eq. V and VIII for evacuated and aerated solutions, were calculated using the spectroscopic values of *B* and the initial rates obtained by application of eq. VII. The calculated curves fit quite well with the experimental results. These conclusions are consistent with recent studies of the chemistry of hydrogen atoms in 0.8 *N* H_2SO_4. Another effect of the ferric ion which may be considered in the photochemical system is an electron transfer reaction from the excited ferrous ion to a ferric ion.

$$Fe^{2+}{}_{aq}{}^* + Fe^{3+}{}_{aq} \longrightarrow Fe^{3+}{}_{aq} + Fe^{2+}{}_{aq}$$

and

$$Fe^{2+}{}_{aq}{}^* + Fe^{3+}OH^- \longrightarrow Fe^{3+}OH^- + Fe^{2+}{}_{aq}$$

leading to the deactivation of the excited state. However, no evidence for such retarding effect of the ferric ion could be observed in our work.

The quantum yield is independent of the ferrous ion concentration up to 0.1 *M* Fe^{2+}, indicating that in this concentration region the excited state does not interact appreciably with another ferrous ion by the possible reactions

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[19] T. J. Hardwick, *Can. J. Chem.*, **35**, 428, 437 (1957).

[20] F. S. Dainton and H. C. Sutton, *Trans. Faraday Soc.*, **49**, 1011 (1953).

[21] R. B. Holt, C. McLane, and O. Oldenberg, *J. Chem. Phys.*, **16**, 225 (1948).

[22] J. Jortner and G. Stein, *Bull. Res. Council Israel*, **A6**, 239 (1957).

deactivation reaction: $Fe^{2+}_{aq}{}^{*} + Fe^{2+}_{aq} \longrightarrow 2Fe^{2+}_{aq}$

molecular hydrogen formation: $Fe^{2+}_{aq}{}^{*} + H^{+}_{aq} + Fe^{2+}_{aq} \longrightarrow 2\,Fe^{3+}_{aq} + H_2 + OH^-$

Besides, the reaction of the "molecular" formation of hydrogen is not consistent with the oxygen effect on the reaction mechanism.

The pronounced effect of oxygen on the rate of the photochemical oxidation is important for the elucidation of the primary photochemical process. This effect may be applied as a diagnostic criterion for hydrogen atom formation by the dissociation of the excited state. As in the case of the radiation-chemical oxidation of the ferrous ion, it appears that the photochemical system fulfills the prediction of the free radical theory where competitive scavenging reactions of the hydrogen atoms by two different solutes occur. The quantitative agreement between the photochemical and radiation-chemical results provides an additional support for the proposed mechanism. Comparison with the reactions of atomic hydrogen[11] indicates that in both systems in acid solution H atoms as such are involved.

Kinetic data derived from radiation-chemical and photochemical experiments may be compared. The application of a homogeneous kinetic treatment is justified at relatively low rates of radical formation and moderately low scavenger concentrations. This assumption is consistent with some experimental kinetic data on the reactions of hydroxyl radicals in aqueous solutions.[14,23,24]

The investigation of the photochemistry of oxygen-containing solutions yields the result that at relatively low O_2 concentrations (up to $\sim 10^{-4}$ *M*) the direct effect of oxygen on the excited state of the ferrous ion is negligible.

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[23] T. J. Sworski, *J. Am. Chem. Soc.*, **79**, 3655 (1957).

[24] F. S. Dainton and T. J. Hardwick, *Trans. Faraday Soc.*, **53**, 333 (1957).

THE PHOTOCHEMICAL EVOLUTION OF HYDROGEN FROM AQUEOUS SOLUTIONS OF FERROUS IONS. PART II. EFFECT OF CHANGING pH

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The photochemistry of the ferrous ion in the presence and in the absence of oxygen was investigated in the pH region 0.35–3.0. The pH dependence of the initial quantum yield up to pH 2.5 in the presence and absence of oxygen is interpreted as arising from the dependence on H^+ ion concentration of the rate of introduction of H atoms into the bulk. This results in the dependence of the quantum yield on $\sqrt{[H^+]}$. A mechanism to account for this is proposed. Another pathway leading to the pH independent formation of H atom also is postulated. The oxidation and reduction processes of the H atoms thus formed are investigated and it is shown that the oxidation of Fe^{2+} by H atoms may proceed by way of a hydride intermediate. Specific velocity constants are derived. The results of the photochemical experiments are correlated with those obtained in radiation chemistry.

In Part I the photochemistry of aqueous Fe^{2+} solutions at a constant low pH was investigated. It was shown that the excited state of the ferrous ion yields H atoms. However, the mechanism of this photochemical formation of hydrogen atoms in ionic solution is not yet well established, and the role of H^+ ions in this process is still a matter of controversy.[1–4]

The evidence in favor of the oxidation of ions such as Fe^{2+} [5,6] or Cr^{2+} [4] by H atoms is conclusive. Again the actual oxidation mechanism is not yet finally established. The results of Rigg and Weiss[7] on the pH dependence of the quantum yield in the photoöxidation of the ferrous ion were interpreted as due to the participation of the H_2^+ molecule ion in the oxidation of the ferrous ion by H atoms.[8] These results were not confirmed by Lefort and Douzou.[9] Recently the pH dependence of the initial quantum yield in the photoöxidation of the chromous ion was demonstrated[4] and for Fe^{2+}, it was reconfirmed.[8]

As the basic oxidation mechanism by H atoms still is in doubt, further work on this subject appeared desirable.

Results

The experimental technique was described in Part I. The evaluation of the initial photoöxidation rates was facilitated by the introduction of the correction for the inner filter effect. The pH dependence of the molar extinction coefficient of the ferric ion and the values of *B* in H_2SO_4 solutions are given in Table I. The absorption of the ferrous ion was found to be independent of pH. When 0.02 *M* Na_2SO_4 was added to each of these solutions *B* remained unchanged.

Photochemistry of Aerated Solutions.—The photoöxidation of aerated ferrous sulfate solutions was investigated at different values of pH. From these experimental results the values of $[Fe^{3+}]_c$—the concentrations of the ferric ion corrected for the inner filter effect—were obtained from the relation

$$[Fe^{3+}]_c = [Fe^{3+}]_t + \frac{B}{2}\,[Fe^{3+}]_t^2 \qquad (I)$$

These data are presented in Fig. 1. From Fig. 1

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[1] A. Farkas and L. Farkas, *Trans. Faraday Soc.*, **34**, 1113 (1938).

[2] J. Franck and R. L. Platzman, "Farkas Memorial Volume," Jerusalem, 1952, p. 21.

[3] J. Franck and R. L. Platzman, *Z. Physik*, **138**, 411 (1954).

[4] E. Collinson, F. S. Dainton, and M. A. Malati, *Trans. Faraday Soc.*, **55**, 209 (1959).

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