964. *The Photo-oxidation of Water by Ferric Ion at 25°.*

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The action of ultraviolet light on pure ferric perchlorate solutions has been studied and shown to produce oxygen. Possible mechanisms are considered and the probable route involves two hydroxyl radicals reacting to give an oxygen atom. An upper limit for the rate constant of the reaction of a hydroxyl radical with a ferrous ion of 3×10^7 l. mole^{-1} sec.$^{-1}$ is suggested.

The possibility of the photo-oxidation of water by ferric ion has been under discussion for some time. Dain and Kachan [1] were the first to claim its occurrence, attributing it to absorption of light by the aquated ferric ion Fe^{3+},H_2O, since they found that the rate of production of permanent gas (assumed to be oxygen) decreased when the acidity was reduced from 5N to 1N. Evans, Uri, and their co-workers agreed [2,3] that production of oxygen was possible but associated the photo-reduction of ferric ion with absorption by the first hydrolysed species, $Fe(OH)^{2+}$. Under their conditions,[3] however, they considered that the permanent reduction of " pure " solutions of ferric ion on photolysis was due to the unavoidable presence of oxidisable organic impurities, the effect of which on the Fenton reaction has been proved.[4,5] Baxendale and Magee,[6] studying the oxidation of benzene in aqueous solution by the Fenton reagent, obtained a good oxidation–reduction balance; this was not so in the photo-oxidation,[7] a 10% excess of ferrous ion being noted. They were unable to define the cause of this discrepancy, but they considered it could not be due to impurities or to the reaction of hydroxyl radicals with themselves, since the effect was not sensitive to benzene concentration. All these workers agree that hydroxyl radicals are the primary product of photolysis.

Good and Purdon [8] photolysed solutions of ferric chloride and claimed to have identified oxygen in the products by combustion and by its ability to quench the phosphorescence of uranin adsorbed on silica gel. Their solutions were, however, incipientally colloidal, and they attributed the photoactivity to the more hydrolysed species. They did not report any kinetic data or suggest a mechanism.

Our interest in the phenomenon being to compare the reactivity of the hydroxyl radicals produced with those formed in the analogous Fenton system,[9] the occurrence of a side reaction yielding oxygen in the photochemical system is important as a complicating factor and we have investigated it extensively.

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[1] Dain and Kachan, *Doklady Akad. Nauk S.S.S.R.*, 1948, **61**, 471.

[2] Evans and Uri, *Nature*, 1949, **164**, 404; *J. Soc. Dyers and Colourists*, 1949, **95**, 709.

[3] Evans, Santappa, and Uri, *J. Polymer Sci.*, 1951, **7**, 243; Bates, Evans, and Uri, *Nature*, 1950, **166**, 869; *J. Amer. Chem. Soc.*, 1953, **75**, 2754.

[4] Barb, Baxendale, George, and Hargrave, *Trans. Faraday Soc.*, 1951, **47**, 462.

[5] Kolthoff and Medalia, *J. Amer. Chem. Soc.*, 1949, **71**, 3777.

[6] Baxendale and Magee, *Discuss. Faraday Soc.*, 1953, **14**, 160.

[7] Baxendale and Magee, *Trans. Faraday Soc.*, 1955, **51**, 205.

[8] Good and Purdon, *Chem. and Ind.*, 1955, **144**, 1594.

[9] Wilford and Williams, unpublished work.

EXPERIMENTAL

Materials.—Ferrous perchlorate was prepared by dissolving pure iron granules (British Chemical Standard No. 149) in " AnalaR " perchloric acid that had been twice redistilled, initially from silver oxide. Ferric perchlorate was obtained from the ferrous solution by oxidation with ozone. Distilled water was redistilled, in Leeds from alkaline permanganate, in Exeter from acid dichromate, the condensate in the latter case being used to feed a third distillation from alkaline permanganate. The stills were electrically heated and the distillates collected in such a way as to minimise contact with outside air. The still was of Pyrex glass, with as few cone-and-socket joints as possible. These joints were not greased and the condenser and receiver were cleaned regularly by steam generated from alkaline permanganate.

Light-source.—A 250-w compact-source mercury lamp was used, run off direct current. The current through the lamp was electronically stabilised and the light-output in a run was constant within $\pm 1\%$. Owing to the necessity of using the highest intensity available, the full output of the arc was used in all experiments, unless otherwise stated. The incident intensities on the reaction vessel of the photoactive spectral lines were measured by the use of the ferrioxalate actinometer, as described by Baxendale and Bridge,[10] with the quantum yields determined by Hatchard and Parker.[11] The filters used were: 365 mμ, OV1 and OX1 filter glasses (Chance Bros. Ltd.); 313 mμ, 2 cm. of 0·02% potassium chromate in dilute sodium hydroxide solution, together with an OX1 filter glass; 334 mμ (along with a known fraction of 313 mμ), 2 cm. of 41% nickel sulphate in 0·25M-copper sulphate, together with an OX1 filter glass; 302 mμ (along with known fractions of 313 mμ and 334 mμ), 2 cm. of 0·002% potassium chromate in dilute sodium hydroxide solution, together with an OX7 filter glass. Direct measurement showed that these four lines accounted for at least·99% of the total emission of the lamp below 400 mμ.

Reaction-cell.—The reaction-cell was a cylindrical quartz vessel, 7 cm. in diameter and 2 cm. in depth. This was attached to a standard deaeration vessel,[12] either through a graded seal or through a cone and socket, sealed with picein wax at its outermost end only, so that contact of the wax with the solutions was kept to a minimum. The cell and deaeration vessel were cleaned before each use as described elsewhere.[13]

Vacuum-line.—A standard arrangement was used for deaerating the solutions before use. A partial pressure of air in the deaeration vessel of less than 10^{-3} mm. was easily attained. After irradiation, the gas produced was pumped by a single-stage mercury pump into an integrating Toepler pump, measured, and analysed.

Analyses.—Initial and final concentrations of ferrous ion were determined colorimetrically as the 1,10-phenanthroline complex. Ferrous-ion concentrations at intermediate times were determined as the change in ferric-ion concentration, by measuring the optical density of the solution at the isosbestic point, 272 mμ. This was done by attaching a spectrophotometer cell to the deaeration vessel and tipping some of the solution into it at intervals during the run. Appropriate calibration demonstrated that this procedure was of sufficient accuracy. Initial ferric-ion concentrations were determined as ferrous ion after reduction with hydroxylamine. Hydrogen ion was determined by titration with barium hydroxide solution; it was necessary to subtract the contribution from the hydrolysis of iron, calculated from the constants given by Milburn and Vosburgh.[14] Permanent gas was analysed for oxygen by burning it with an excess of hydrogen. The condensable gas volatile at −78° was assumed to be carbon dioxide.

RESULTS AND DISCUSSION

Our findings at Leeds, with $[Fe^{3+}]_0 = 200$ μM, $[H^+] = 10^{-2}$M, and $\lambda = 313$ mμ, were that the sole gaseous product was carbon dioxide and that none of the many variations devised in the methods used to clean the vessels and purify the solutions altered this fact. Similar results were obtained initially at Exeter. Duplication of Good and Purdon's

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[10] Baxendale and Bridge, *J. Phys. Chem.*, 1955, **39**, 783.

[11] Hatchard and Parker, *Proc. Roy. Soc.*, 1953, **220***A*, 104; 1956, **235***A*, 518.

[12] Dainton and Hardwick, *Trans. Faraday Soc.*, 1957, **53**, 333.

[13] Bunn, Dainton, Salmon, and Hardwick, *Trans. Faraday Soc.*, 1959, **55**, 1762.

[14] Milburn and Vosburgh, *J. Amer. Chem. Soc.*, 1955, **77**, 1352; 1957, **79**, 537.

experimental conditions ($[Fe^{3+}]_0 = 1{\cdot}3$ mM, $[Cl^-] = 3{\cdot}9$ mM, pH = 3·0, full arc), however, gave oxygen in quantity, along with carbon dioxide (see typical data in Table 1); we are therefore able to confirm their result. These solutions, prepared from the " AnalaR " salt dissolved in water, had to be made up immediately before use as they became colloidal in a few hours. To test whether this incipient heterogeneity and the presence of chloride ion are requisites for the production of oxygen, chloride-free solutions of the same ferric iron concentration but of a range of acidities were prepared by slow addition of the appropriate amount of water to a more concentrated solution of ferric perchlorate in perchloric acid. These solutions, in which the ion product never approached the solubility product of ferric hydroxide during the preparation, were found to be stable indefinitely. The results (Table 1) indicate that neither chloride not incipient heterogeneity is necessary for oxygen production, while the effect of acidity confirms the view that the complex $Fe(OH)^{2+}$ is almost certainly the photoactive species.

TABLE 1.

Products of irradiation.

Full arc. Total $I_a \sim 3 \times 10^{-5}$ einstein/sec.

$[Fe^{3+}]_0$ (mM)	$[H^+]$ (mM)	Time (min.)	Products $[O_2]$ (μM) *	Products $[CO_2]$ (μM) *	Products $[Fe^{2+}]$ (μM)
Ferric chloride solutions					
1·3	(pH 3·0)	60	90	11	407
1·3	10	60	2	12	83
Ferric perchlorate solutions					
1·0	5	240	32	11	180
1·0	10	240	29	6	152
1·0	10	240	22	8	132
1·0	50	870	11	12	94

* These molarities refer to what they would have been if the gases had remained in solution.

The lack of oxygen production at Leeds, and initially at Exeter, was traced to two reasons. First, the ambient level of air pollution when the test solution is sealed into the reaction vessel is extremely important, the contaminants being trapped on the walls of the cold finger during deaeration and absorbed into the solution. Secondly, there was insufficient light-input. Any reasonable mechanism (see below) leading to production of oxygen results in a relation between rate of formation of ferrous ion and light intensity (I_a) approaching the second power in I_a, whereas if oxidation of impurity is the main cause of hydroxyl disappearance then the relation is a first-power one. Filters used to produce monochromatic light cut the absorbed intensity to about one-tenth, resulting in a much reduced possibility of detecting oxygen. Much more powerful light sources will be needed before definitive work on this reaction under monochromatic irradiation is possible.

If we accept the view that hydroxyl radicals are the primary product, it remains to decide what mechanism leads to oxygen. Two main alternatives appear possible; one (I) involves the production of atomic oxygen as the only precursor of molecular oxygen; the other (II) involves the formation of hydrogen peroxide; variations (IIa and b) are possible, depending on the nature of the step producing peroxide.

Mechanism I:

$$\begin{array}{rcll} Fe(OH)^{2+} & \longrightarrow & Fe^{2+} + OH\cdot & (\phi Ia) \\ \cdot OH + \cdot OH & \longrightarrow & H_2O + O\cdot & k_{1a} \\ \cdot OH + Fe^{2+} & \longrightarrow & FeOH^{2+} & k_2 \\ O\cdot + O\cdot & \longrightarrow & O_2 & k_3 \end{array}$$

Mechanism II:

$$\begin{array}{rll}
\mathrm{Fe(OH)^{2+}} \longrightarrow & \mathrm{Fe^{2+} + {\cdot}OH} & (\phi Ia) \\
\text{Either } \mathrm{{\cdot}OH + Fe(OH)^{2+}} \longrightarrow & \mathrm{H_2O_2 + Fe^{2+}} & k_{1b}\ (\textit{mechanism}\ \text{IIa}) \\
\text{or } \quad \mathrm{{\cdot}OH + {\cdot}OH} \longrightarrow & \mathrm{H_2O_2} & k_{1c}\ (\textit{mechanism}\ \text{IIb}) \\
\mathrm{{\cdot}OH + Fe^{2+}} \longrightarrow & \mathrm{FeOH^{2+}} & k_2 \\
\mathrm{{\cdot}OH + H_2O_2} \longrightarrow & \mathrm{H_2O + HO_2{\cdot}} & k_4 \\
\mathrm{HO_2{\cdot} + Fe^{2+}} \longrightarrow & \mathrm{HO_2^- + Fe^{3+}} & k_5 \\
\mathrm{HO_2{\cdot} + Fe_3^+} \longrightarrow & \mathrm{H^+ + O_2 + Fe^{2+}} & k_6 \\
\mathrm{H_2O_2 + Fe^{2+}} \longrightarrow & \mathrm{HO{\cdot} + OH^- + Fe^{3+}} & k_7
\end{array}$$

The rate constants (or their relative values) of several of the reactions listed are known under the conditions used in these experiments. Thus Barb *et al.*[4] give $k_2/k_4 = 33$, $k_5/k_6 = 1{\cdot}4$; Dainton and Hardwick[12] give $k_7 = 71$ l. mole^{-1} sec.$^{-1}$; Uri[15] has estimated $k_{1b} = 5 \times 10^5$ l. mole^{-1} sec.$^{-1}$. The rate of production of hydroxyl radicals (ϕI_a) was determined by saturating the ferric ion solution with carbon monoxide, in the absence of oxygen, and measuring the rate of production of ferrous ion under the standard irradiation conditions. With this substrate the rate of ferrous-ion production is effectively constant[9] for conversions up to 10% and is twice the rate of generation of hydroxyl radicals. For the conditions used the experimental result was (ϕI_a) = 3×10^{-6} mole l.$^{-1}$ sec.$^{-1}$ ($\phi_{\text{average}} = 0{\cdot}1$).

It appears reasonable to assign an upper limit to k_{1a} of 10^{10} l. mole^{-1} sec.$^{-1}$ by analogy with the recombination of iodine atoms in solution.[16] Since the minimum rate of formation of oxygen is known, it is possible to assign an upper limit for k_2 if mechansim (I) is correct and to calculate for each assumed value of k_2 the ambient peroxide concentration necessary to account for the rate of oxygen production by mechanism (II). Run C (Table 2), that of highest purity, was used for purposes of calculation, production of carbon dioxide virtually ceasing when $[\mathrm{Fe^{2+}}] = 100$ μM, $[\mathrm{Fe^{3+}}] = 900$ μM, $\mathrm{d[O_2]/d}t = 1{\cdot}7 \times 10^{-8}$ mole l.$^{-1}$ sec.$^{-1}$.

TABLE 2.

Progress of three irradiation runs.

$[\mathrm{Fe^{3+}}]_0 = 10^{-3}$M. $[\mathrm{H^+}] = 5 \times 10^{-3}$M.

Run A: Full arc; total I_a; ~3 × 10^{-5} einstein/l./sec.				
Time (min.)	60	120	240	480
$\mathrm{Fe^{2+}}$ (μM)	—	—	—	227
$\mathrm{O_2}$ (μM)	18·0	25·5	33·7	43·3
$\mathrm{CO_2}$ (μM)	19·8	23·0	24·6	24·6
Run B: λ = 313; I_a; ~3 × 10^{-6} einstein/l./sec.				
Time (min.)	10	40	150	515
$\mathrm{Fe^{2+}}$ (μM)	40	77	109	169
$\mathrm{O_2}$ (μM)	4·9	8·8	15·4	24·6
$\mathrm{CO_2}$ (μM)	4·5	8·2	10·4	11·9
Run C: Full arc; total I_a; ~3 × 10^{-5} einstein/l./sec.				
Time (min.)	10	20	80	200
$\mathrm{Fe^{2+}}$ (μM)	107	134	191	240
$\mathrm{O_2}$ (μM)	21·5	27·6	40·3	51·8
$\mathrm{CO_2}$ (μM)	8·5	10·1	11·8	13·2

Mechanism I. The steady-state equation for hydroxyl radicals is:

$$\phi I_a - 2k_{1a}[\mathrm{OH}]^2 - k_2[\mathrm{OH}][\mathrm{Fe^{2+}}] = 0,$$

whence

$$[\mathrm{OH}] = \{-k_2[\mathrm{Fe^{2+}}] + \sqrt{(k_2{}^2[\mathrm{Fe^{2+}}]^2 + 8\phi \mathrm{I}_a k_{1a})}\}/4k_{1a};$$

also

$$[\mathrm{OH}] = \sqrt{\{(2\mathrm{d[O_2]/d}t)/k_{1a}\}}.$$

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[15] Uri, *Chem. Rev.*, 1952, **50**, 393.

[16] Noyes, *J. Amer. Chem. Soc.*, 1958, **80**, 2410.

The value of k_2 fitting these equations under the conditions stated above is 3×10^7 l. mole^{-1} sec.$^{-1}$, and the expression gives rates of oxygen production agreeing with experiment over the range $[Fe^{2+}] = 100$—200 μM.

Mechanism II*a*. This mechanism cannot be treated completely by steady-state methods as the peroxide is not a transient intermediate. However, the rate of production of oxygen is given by

$$\begin{aligned} d[O_2]/dt &= k_6[HO_2][Fe^{3+}] \\ &= \frac{k_6[Fe^{3+}]}{k_6[Fe^{3+}] + k_5[Fe^{2+}]} \times k_4[H_2O_2][OH], \end{aligned}$$

where

$$[OH] = \frac{\phi I_a + k_7[H_2O_2][Fe^{2+}]}{k_2[Fe^{2+}] + k_{1b}[FeOH^{2+}] + k_4[H_2O_2]}.$$

Table 3 lists, for each value of k_2 assumed, the peroxide concentration that is needed to account for the observed rate of evolution of oxygen at two different concentrations of ferrous ion. At the lower concentration at least 20 μmole l.$^{-1}$ of peroxide is necessary even for the most favourable value of k_2. This quantity of peroxide should be easily detectable by the observation of an " after effect," the relatively slow oxidation of ferrous ion after irradiation has ceased. Table 4 lists the results of experiments made to test for the presence of peroxide. The control runs with added hydrogen peroxide establish that it is easy to detect as little as 10 μmole l.$^{-1}$ of peroxide under the experimental conditions. We believe that the minor differences between $[Fe^{2+}]_{t=0}$ and $[Fe^{2+}]_{t=5}$ for the irradiation runs are due to imperfect mixing in the cell during the necessarily rapid operations prior to the initial sampling. The results demonstrate that not more than 1 μ mole l.$^{-1}$ of peroxide can be present.

We conclude, therefore, that mechanism IIa cannot account for the observed rate of oxygen production. Similarly, mechanism IIb is also unsatisfactory, the rate equation for oxygen formation being the same as for mechanism IIa and requiring high concentrations of peroxide. Moreover, there are theoretical reasons [17] why the reaction of two hydroxyl radicals is unlikely to give peroxide; hence a value less than 10^{10} l. mole^{-1} sec.$^{-1}$ for k_{1c} would be expected in this instance, whereas a higher value is needed to account for the necessary rate of formation of peroxide. It appears, therefore, that mechanism I is the most likely route for formation of oxygen and that the maximum value for k_2 is 3×10^7 l. mole^{-1} sec.$^{-1}$.

TABLE 3.

Test of mechanism IIa.

k_2 (l. mole^{-1} sec.$^{-1}$)	$[H_2O_2]$ (μM)	$\frac{d[H_2O_2]}{dt}$ (10^{-9} mole l.$^{-1}$ sec.$^{-1}$)	$\frac{-d[H_2O_2]}{dt}$ (10^{-9} mole l.$^{-1}$ sec.$^{-1}$)	k_2 (l. mole^{-1} sec.$^{-1}$)	$[H_2O_2$ (μM)	$\frac{d[H_2O_2]}{dt}$ (10^{-9} mole l.$^{-1}$ sec.$^{-1}$)	$\frac{-d[H_2O_2]}{dt}$ (10^{-9} mole l.$^{-1}$ sec.$^{-1}$)
$[Fe^{2+}]$ 100 μM; $d[O_2]/dt = 1{\cdot}7 \times 10^{-8}$ mole l.$^{-1}$ sec.$^{-1}$.				$[Fe^{2+}] = 130$ μM; $d[O_2]/dt = 7{\cdot}5 \times 10^{-9}$ mole l.$^{-1}$ sec.$^{-1}$.			
10^9	21	9	170	10^9	13	6	124
10^8	22	63	175	10^8	13	47	128
10^7	24	540	190	10^7	14	400	139
10^6	59	2200	430	10^6	30	1900	281

Further, the value given by Uri for k_{1b} must be too high. Thus the rate of formation of peroxide by reactions 1b and 5 is

$$d[H_2O_2]/dt = k_{1b}[OH][FeOH^{2+}] + k_5[HO_2][Fe^{2+}],$$

while the rate of destruction by reactions 4 and 7 is

$$-d[H_2O_2]/dt = k_4[HO][H_2O_2] + k_7[H_2O_2][Fe^{2+}].$$

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[17] Weiss, *Trans. Faraday Soc.*, 1940, **36**, 856.

For each value of k_2 less than 3×10^7 l. mole^{-1} sec.$^{-1}$ the predicted rate of formation of peroxide exceeds the rate of destruction if peroxide is present at the concentration needed to give the observed rate of oxygen production. Since the presence of peroxide at all is doubtful, a value for k_{1b} at least ten-fold less is probable.

TABLE 4.

Test for production of peroxide after irradiation.

System	$[H_2O_2]$ added (μM)	Time of irradiation (min.)	Fe^{2+} (μM) at t min. after irradiation		
			$t = 0$	$t = 5$	$t = 60$
Pure $[Fe^{2+}]$; $[Fe^{2+}]_0 = 88\cdot5\mu$M	10	—	84·3	70·5	—
Synthetic mixture:					
$[Fe^{2+}]_0 = 116\mu$M; $[Fe^{3+}]_0 = 1\mu$M	10	—	116	102	99
Pure Fe^{3+}; $[Fe^{3+}]_0 = 1$mM (i)	—	8	102·3	99·0	—
		15	116·8	115·0	—
(ii)	10 *	8·5	93·9	90·5	—
		23	121·0	119·6	—

* Added immediately after start of irradiation.

From the results it appears that reaction Ia will compete with the reaction of hydroxyl with added substrates only if the latter are present in relatively low concentration and are relatively unreactive towards hydroxyl radicals and if the light intensity is high. None of these conditions is true for Baxendale and Magee's work on benzene; hence the discrepancy in the oxidation–reduction balance noted by them must be due to some other factor.

[*Note added September* 21*st*.]—Recently two other estimates of k_2 have been given,[18,19] 6×10^4 l. mole^{-1} sec.$^{-1}$ and 3×10^8 l. mole^{-1} sec.$^{-1}$. Neither appears to be reconcilable with our results. The explanation of these discrepancies may lie in the very different methods used to prepare the hydroxyl radicals; thus we have evidence [9] that hydroxyl radicals produced in the Fenton reaction differ markedly in reactivity from those produced photochemically, and it seems possible that the hydroxyl radical in solution may exist as different modifications, in a manner analogous to that now accepted for the hydrogen atom.

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[18] Baxendale, *Nature*, 1961, **192**, 622.
[19] Schwarz, *J. Phys. Chem.*, 1962, **66**, 255.