rhombohedral form involves different processes from those involved in cooling face-centered-cubic carbon tetrachloride to the monoclinic form. A redetermination of the heat capacity and of related thermodynamic quantities of carbon tetrachloride, taking into account the results of our work, appears necessary.

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References and Notes

1. V. Goldschmidt, *Z. Krist.* **51**, 26 (1912); W. Wahl, *Proc. Roy. Soc. (London) Ser. A* **89**, 327 (1914); B. Post, *Acta Cryst.* **12**, 349 (1959).
2. C. Finbak and O. Hassel, *Z. Physik. Chem. B* **36**, 301 (1937).
3. A. Dunlop, *J. Amer. Chem. Soc.* **77**, 2016 (1955).
4. J. Hicks, J. Hooley, C. Stephenson, *ibid.* **66**, 1064 (1944).
5. R. Rudman and B. Post, in preparation.
6. P. W. Bridgman, *Phys. Rev.* **3**, 153 (1914).
7. This work has been supported by the Air Force Office of Scientific Research under grant AF-AFOSR-248-63.
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2 September 1966

Photochemical Evolution of Oxygen from Certain Aqueous Solutions

Abstract. *Illumination of aqueous solutions containing ferric ions and hydrogen peroxide leads to evolution of O_2 by way of a chain reaction. The photochemically active intermediate is the complex between Fe^3 and HO_2^-. The effects of* p*H and concentration of the reagent on the quantum yield (chain length) are reported.*

The catalytic decomposition of H_2O_2 by Fe^{3+} ions in a thermally activated dark reaction was shown (by parallel kinetic and spectrophotometric measurements in acid solutions of hydrogen peroxide and ferric perchlorate) to proceed by the following mechanism (*1–3*):

$$H_2O_2 \rightleftharpoons H^+ + HO_2^- \quad (1)$$

$$Fe^{3+} + HO_2^- \rightleftharpoons \{Fe^{3+}\,HO_2^-\} \quad \text{complex I} \quad (2)$$

$$Fe^{3+}HO_2^- \rightarrow OH^- + \{Fe^{3+}O\} \quad \text{complex II} \quad (3)$$

$$Fe^{3+}O + HO_2^- \rightarrow Fe^{3+}OH^- + O_2 \quad (4)$$

This involves complex formation between ferric ion and the anion of hydrogen peroxide (*4–6*). Electron transfer does not take place within this complex, as had been assumed (*7*). The first complex must be transformed (*1*), in the slow rate–determining step (reaction 2), into complex II, in which O is covalently bound to iron; in this step OH^- ions are displaced into the solution (*3*). Steps 1 to 3 thus result in elimination of a molecule of water from the reactants. Complex II may then react with a second HO_2^- to produce evolution of O_2 by hydride transfer. Elucidation of the reaction mechanism required work with solutions containing $\sim 10^{-3}M$ Fe^{3+} and $10^{-2}M$ (or less) H_2O_2.

Details of the reaction mechanism, the relation to cocatalysis by copper, and the extension of these concepts to the decomposition of hydrogen peroxide by haemin were elaborated by Kremer (*3, 8*); the mechanism is closely related to that resulting from the work of Jones, Wynne-Jones, and coworkers with more-concentrated peroxide solutions—higher than $1M$ (*9*). Jones and Wynne-Jones (*10*) also support the view that such a mechanism may be applicable to the catalase-induced decomposition of hydrogen peroxide.

Light of greater wavelength than 300 nm is not significantly absorbed by either Fe^{3+} or H_2O_2 alone in solutions comparable to those employed by the workers mentioned; mixtures of these components do absorb at greater wavelength because of the formation of the intermediate complexes. Absorption by the $Fe^{3+}OH^-$ complex (*6*) also must be considered. Complexes I and II have different absorption spectra, that of complex I extending further into the visible and near-ultraviolet (*1*). As the reaction mechanism indicates, absorption due to complex II can be observed only at low concentrations of peroxide; at higher concentrations of H_2O_2, the dominant absorption is due to complex I. Complex I was observed by Evans, George, and Uri (*4*), who assigned the band, with $\lambda_{max} = 350$ nm, to an ion-pair complex between Fe^{3+} and HO_2^-. This assignment is supported, and the light-absorption process is interpreted (*2*) as electron transfer from HO_2^- to Fe^{3+} (in the inner hydration sphere which it has entered), by correlation with energetic data. These data show (*2*) that HO_2^- itself, in aqueous solution, possesses a charge-transfer-to-solvent absorption band (*11*). In the presence of Fe^{3+} the new absorption band observed fits the energetic correlation that holds (*12*) for the anion-to-Fe^{3+} electron transfer of other anions having charge-transfer-to-solvent bands.

If the reaction mechanism proposed for the catalytic dark reaction holds, so that electron transfer does not occur within complex I, and O_2 evolution must await the slow rearrangement to complex II, it may be possible to cause photochemical evolution of oxygen from such solutions, under conditions in which the thermal reaction is slow, by light-induced electron transfer from HO_2^- to Fe^{3+} in the absorption band of complex I. In this case, free-radical formation, which does not take place in the dark catalytic mechanism proposed, may indeed occur.

This determination required experiments to be carried out in solutions at H_2O_2 concentrations that assured sufficient absorption of light at wavelengths greater than 300 nm, but which were low enough to enable one to determine reliably the difference in H_2O_2 concentration in the course of the reaction. This requirement necessitated the use of solution in the range between the low concentrations employed by Kremer and Stein and the high concentrations used by Jones and Wynne-Jones. Such experiments were performed (*13*) in the temperature range 5° to 27°C at H_2O_2 concentrations between 0.01 and $1M$. Rate constants obtained, in good agreement with the results in the lower and higher ranges, showed the general applicability of the catalytic mechanism.

In our photochemical experiments, high-purity ferric perchlorate, perchloric acid, and hydrogen peroxide were used with specially purified water in a

Table 1. Derivation of the rate constant of the light-induced reaction, from results of mixed decompositions (thermal and photo) at various temperatures; $[Fe^{3+}]$, $5.36 \times 10^{-3}M$; $[H_2O_2]_{initial}$, $0.24M$; *p*H, 2.10.

T (°C)	Combined reactions—thermal and photo ($10^3 \times k_{(t+p)}$, min^{-1})	Photoreaction alone, calc. ($10^3 \times k_p$, min^{-1})
14.0	16.4	2.4
10.0	13.1	3.8
5.0	7.4	3.4

Table 2. Quantum yield at ~ 365 nm; T, 5.5°C: $[Fe^{3+}]$, $5.36 \times 10^{-3}M$.

$[H_2O_2]_0$ (M)	*p*H	Quantum yield (ϕ)
Dependence on initial $[H_2O_2]$		
0.556	2.06	7.42
.290	2.06	5.17
.160	2.06	3.31
Dependence on p*H*		
0.290	2.06	5.17
.279	1.50	6.22
.274	1.22	7.78

manner described (*1*); also described are the analytical methods (*1, 8*). Experiments were carried out in the temperature range 5° to 27°C at temperatures held constant within 0.1°C. Evolution of oxygen was followed gasometrically. Photochemical experiments were performed by use of either (i) the light output of a medium-pressure Hg-vapor lamp at wavelengths greater than 310 nm (light of lesser wavelength being removed by a glass filter); or (ii) (particularly for the establishment of quantum yields) a Mazda-ME/D high-pressure mercury lamp, the collimated light beam being filtered by a Chance glass filter (No. OX1a) and 1 cm of a 125-g/liter solution of $CuSO_4 \cdot 5H_2O$; at 365 and 366.3 nm this transmits 65 percent of the incident light, but only 3 percent at the weaker line at 313.5 nm and 5 percent at 405 nm. The collimated beam then passed the thermostated, cylindrical quartz reaction vessel (with a light path of 5 cm), in series with the identical actinometer cell containing uranyl oxalate actinometer solution (*14*).

Light absorption in the reaction vessel was not total; it changed during the reaction with change in concentration of the complex. This change, at the concentrations of reactants employed, proved to be directly proportional to concentration of H_2O_2. Accordingly, light absorption was determined by difference between actinometer results of experiments in which the photolysis cell was filled with either distilled water or experimental solution. The integrated value of light absorbed during an experimental run was determined from actinometer data, concurrently. The value for $\phi_{\text{actinometer}}$ at the wavelength used was taken to be 0.48 (*14*). When thermal, catalytic, dark, control experiments were run in the photochemical vessel at various temperatures, the rate constants and activation energy previously obtained (*1, 13*) were confirmed. Control experiments entailed illumination of solutions of hydrogen peroxide or ferric ion; no evolution of oxygen was observed.

The thermal dark decomposition at *p*H 2.10, in solutions containing concentrations of the order of 2 to 5 $\times$ $10^{-3}M$ Fe^{3+} and, initially, of the order of $0.2M$ H_2O_2, gave first-order reaction with respect to H_2O_2. When the thermal reaction was allowed to proceed, and at the same time the vessel was illuminated, the plot of log H_2O_2 versus t again gave strictly straight lines. Thus the combination of the two reactions appears to be of first order. Using the known activation energy, 20 kcal/mole, of the thermal reaction, and subtracting at every temperature the contribution of the thermal reaction alone (thus assuming that the two reactions proceed independently of each other), we could obtain the apparent rate constant of the light-induced reaction and its activation energy. The results (Table 1) show that when one uses this procedure the rate constant of the light-induced portion of the reaction appears to be independent of temperature within experimental error. This finding contrasts with results with the thermal reaction, which shows a large activation energy. Therefore the light-induced reaction becomes dominant with decreasing temperature. Accordingly, experiments to determine the quantum yield at $\sim$ 365 nm, and the effects on it of variations in *p*H and reactant concentration, were run at a constant low temperature of 5.5°C and at constant ionic strength of 0.25. The results (Table 2) show that the quantum yield, which is greater than 1, increases both with increase in initial concentration of H_2O_2 and with decrease in *p*H. Experiments with varying concentrations of Fe^{3+} (from 2.1 to 5.4 $\times$ $10^{-3}M$), at constant initial concentration of H_2O_2, indicate an increase in chain length with decrease in concentration of Fe^{3+}. The occurrence of the temperature-independent chain reaction thus observed is consistent with the occurrence of a light-induced free-radical mechanism initiated by

$$Fe^{3+}HO_2^- \xrightarrow{h\nu} Fe^{2+} + HO_2 \qquad (5)$$

(rather than by H_2O_2 or $Fe^{3+}OH^-$) and propagated by the reactions of Fe^{2+} with H_2O_2 (*7*) and of the radical intermediates with H_2O_2. The detailed mechanism and the effects of other factors, such as light intensity and radical scavengers other than H_2O_2, on the yields remain to be investigated.

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References and Notes

1. M. Kremer and G. Stein, *Trans. Faraday Soc.* **55**, 959 (1959).
2. ———, in *Proc. Intern. Congr. Catalysis 2nd Paris 1960*, vol. 1, p. 551; J. H. Wang, *J. Amer. Chem. Soc.* **77**, 4715 (1955).
3. M. Kremer, *Trans. Faraday Soc.* **58**, 702 (1962).
4. M. G. Evans, P. George, N. Uri, *ibid.* **45**, 224 (1949).
5. M. G. Evans, N. Hush, U. Uri, *Quart. Rev.* **6**, 186 (1952).
6. M. G. Evans and N. Uri, *J. Soc. Dyers Colourists* **1950**, 125 (1950).
7. J. H. Baxendale, *Advan. Catalysis* **4**, 31 (1952); J. Weiss, *ibid.*, p. 343.
8. M. Kremer, *Nature* **184**, 720 (1959); *J. Catalysis* **1**, 351 (1962); *Nature* **205**, 384 (1965); *Trans. Faraday Soc.* **61**, 1453 (1965).
9. P. Jones, in *Proc. Intern. Congr. Catalysis 2nd Paris 1960*, vol. 1, p. 556; J. Haggett, P. Jones, W. F. K. Wynne-Jones, *Discussions Faraday Soc.* **29**, 153 (1960); P. Jones, T. Kitching, M. L. Tobe, W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **55**, 79 (1959).
10. P. Jones and W. F. K. Wynne-Jones, *Trans. Faraday Soc.* **58**, 1148 (1962).
11. J. Jortner and G. Stein, *Bull. Res. Council Israel* **6A**, 239 (1957).
12. ———, A. Treinin, *J. Chem. Phys.* **30**, 1110 (1959).
13. I. Burak and G. Stein, unpublished; see *Report TN-2 [AF-61-(052)-563] SAM* (USAF European Office, Aerospace Res., 1962).
14. E. J. Bowen, *Chemical Aspect of Light* (Oxford Univ. Press, Oxford, ed. 2, 1946), p. 283.
15. Work sponsored by the USAF School of Aerospace Medicine [contract AF 61(052)-655] through the European OAR.

17 September 1966

Thermal Properties of Water: Discontinuities Questioned

Abstract. *Reports of discontinuities have been tabulated, and those dealing with vibrational spectrum and volume have been examined in detail. No evidence has been found of any discontinuity greater than experimental error.*

During the last thirty years there have been many reports (Table 1) that the physical properties of water show discontinuities at certain temperatures. The discontinuities, often described as

Table 1. Reports of thermal discontinuities for liquid water.

Temperature (°C)	Report
Vibrational spectra	
30–40, 65–75	Baistrocchi *et al.* (*8*)
37	Luck (*11*)
43	Ganz (*12*)
40	Magat (*13, 14*)
Volume and compressibility	
50	Antonoff *et al.* (*17*)
60	Tammann (*26*)
15, 30	Lavergne *et al.* (*20*)
13, 35, 60	Forslind (*22*)
10, 21, 29, 33	Qurashi (*28*)
Surface tension	
60	Tammann (*26*)
13	Forslind (*22*)
13	Timmermans *et al.* (*32*)
15, 30, 45, 60	Drost-Hansen *et al.* (*33*)
Viscosity	
35–45	Magat (*14*)
60	Tammann (*26*)
12, 35, 55	Forslind (*22*)
6, 11, 14, 19, 24, 30, 39 46, 53, 58, 66	Qurashi *et al.* (*34*)
46, 55	Antonoff *et al.* (*35*)
Other properties	
37	Magat (*14*)
60	Tammann (*26*)
35	Vlès (*6*)
15, 30, 45, 60	Drost-Hansen (*33*)
34	Franks and Ives (*1*)
30–40	Feates and Ives (*2*)
36	Othmer and Thakar (*3*)
30	Frontas'ev (*4*)