The VaporPhase Photo Decomposition of Hydrogen Peroxide

David H. Volman

Articles you may be interested in

Phase transition and chemical decomposition of hydrogen peroxide and its water mixtures under high pressures
J. Chem. Phys. **132**, 214501 (2010); 10.1063/1.3429986

Decomposition of solid amorphous hydrogen peroxide by ion irradiation
J. Chem. Phys. **124**, 104702 (2006); 10.1063/1.2171967

Phase transition and decomposition of 90% hydrogen peroxide at high pressures
J. Chem. Phys. **110**, 6836 (1999); 10.1063/1.478588

Arsenic passivation of silicon by photoassisted metalorganic vaporphase epitaxy
J. Vac. Sci. Technol. B **10**, 235 (1992); 10.1116/1.586340

Isotopic Composition of Oxygen in the Catalytic Decomposition of Hydrogen Peroxide
J. Chem. Phys. **20**, 961 (1952); 10.1063/1.1700657

The Vapor-Phase Photo Decomposition of Hydrogen Peroxide

DAVID H. VOLMAN

Division of Chemistry, College of Agriculture, University of California, Davis, California

(Received February 14, 1949)

The decomposition of hydrogen peroxide vapor initiated by light of wave-length 2537A was studied. The quantum yield of the reaction was found to be 1.7±0.4, essentially independent of pressure of peroxide and intensity of absorbed light. The reaction products were water and oxygen only. The rate of the reaction was found to be independent of temperature and was not affected by the addition of oxygen, nitrogen or water to the reaction mixture. The reaction scheme proposed is

$$H_2O_2 + h\nu \rightarrow 2\ OH$$
$$OH + H_2O_2 \rightarrow H_2O + HO_2$$
$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$$
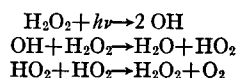
this leads to a maximum quantum yield of 2.

INTRODUCTION

FEW studies of the vapor-phase photo-chemistry of H_2O_2 have been made. This is somewhat surprising since H_2O_2 is, with the exception of H_2O, the only stable molecule containing H and O atoms exclusively, and is of considerable importance in problems associated with reactions in the system H_2-O_2. Moreover, the H_2O_2 molecule is comparatively simple. Experimental difficulties arising from the low vapor pressure of H_2O_2 at room temperature, thermal decomposition at moderate temperatures and reactivity with mercury have been deterrents to extensive studies.

The spectrum of H_2O_2 vapor has recently been studied by Holt, McLane, and Oldenberg.[1] This work summarizes and explains discrepancies in earlier investigations. It is clear that the absorption is continuous and without a maximum in the region studied (3100–1850A).

Urey, Dawsey, and Rice[2] consider three primary processes.

$$H_2O_2 + h\nu \rightarrow H_2O + O, \qquad (1)$$

$$H_2O_2 + h\nu \rightarrow 2\ OH, \qquad (2)$$

$$H_2O_2 + h\nu \rightarrow HO_2 + H. \qquad (3)$$
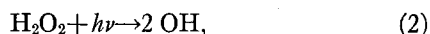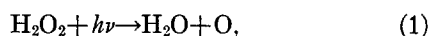
Of these equations, (1) appears to have a low probability and need not be further considered. The energy change for dissociation into two OH radicals, Eq. (2), has been approximated at 50.9 kcal. by thermochemical equations.[1] A simultaneous publication by Walsh[3] gives the dissociation energy of the OO bond in H_2O_2 as approximately 56 kcal. The recent data of Walsh also gives the dissociation energy of reaction (3) as 78 kcal. These values are somewhat higher than those calculated by Urey, Dawsey, and Rice.[2] However, the wave-length corresponding to an energy of 78 kcal. is 3670A which is well beyond the limit of absorption observed in the gas phase and near the limit of absorption by high concentrations in aqueous solution. Hence, sufficient energy

is available in absorbed light to effect either primary process (2) or (3) over most, if not all, of the absorption range.

Urey, Dawsey, and Rice[2] have demonstrated that H atoms are absent in the products of an electric discharge operating in H_2O_2 vapor. In these experiments the emission spectra of excited OH was observed. These authors reason that the inelastic collisional process is more probable if the optical transition is permitted by the selection rules, and, hence, the favored optical process should be a dissociation into OH radicals. Fluorescence studies by the same authors with absorbed light of 2000–2100A show that OH radicals are formed in the irradiated system. Work of von Elbe[4] on the reaction of radicals from H_2O_2 with H_2 and CO also indicates the formation of OH radicals. Although the evidence for the formation of OH is undisputable, evidence that process (3) does not occur is lacking. Sharma,[5] indeed, concludes that H atoms are produced since he has observed that cupric oxide is reduced in an absorption tube containing H_2O_2 under irradiation.

The work of Bates[6] and Volman[7] on the Hg sensitized reaction between H_2 and O_2 has shown that an important reaction is

$$H + O_2 \rightarrow HO_2, \qquad (4)$$

and that subsequently HO_2 radicals react to give H_2O_2,

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2. \qquad (5)$$
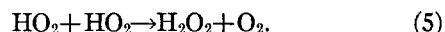
This sequence of reactions suggests that addition of O_2 to H_2O_2 should decrease the rate of over-all H_2O_2 decomposition if H atoms are produced by primary process (3), because the net result is no reaction. Experiments with added gases including oxygen are described below.

The products of the photo-decomposition of H_2O_2 in aqueous solution are only O_2 and H_2O.[8] It has been tacitly assumed that these are also the products in the

[1] Holt, McLane, and Oldenberg, J. Chem. Phys. **16**, 225 (1948).
[2] Urey, Dawsey, and Rice, J. Am. Chem. Soc. **51**, 1371 (1929).
[3] A. D. Walsh, J. Chem. Soc. 331 (1948).

[4] G. von Elbe, J. Am. Chem. Soc. **54**, 821 (1932).
[5] R. S. Sharma, Proc. Acad. Sci. (India) **4**, 51 (1934).
[6] J. R. Bates, J. Chem. Phys. **1**, 457 (1933).
[7] D. H. Volman, J. Chem. Phys. **14**, 707 (1946).
[8] G. Kornfeld, Zeits. f. wiss. Phot. **21**, 66 (1921).

gas phase.[9] However, no experiments directed at detecting H_2 in the products have been reported. It is evident that such information is of importance in establishing the decomposition mechanism. Thus H_2 could conceivably be formed not only from H atoms but also by the postulated mechanism[10,11]

$$OH+OH \rightarrow H_2+O_2. \qquad (6)$$
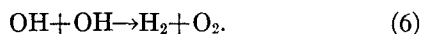
The author's experiments on the vapor phase reaction between ozone and hydrogen peroxide[7] also indicate the possibility of H_2 formation by this mechanism. Evidence for the non-formation of H_2 is presented here.

EXPERIMENTAL

Apparatus

The apparatus used to study the photochemical reaction is shown diagrammatically in Fig. 1. An aqueous solution approximately 90 percent by weight H_2O_2[12] was kept in storage vessel, A. This was stored usually at dry ice temperature to minimize decomposition and reaction with stopcock lubricant. The reaction was followed by measuring pressure changes with a manometer filled with dibutyl phthalate, M. In early experiments a glass "click" gauge was used to measure pressures, but comparative experiments established the fact that no complexities were introduced by use of the phthalate. The reaction tube, R, was a quartz jacketed vessel with quartz to Pyrex seals. Constant temperature water circulated in the outer jacket. The entire chamber was contained within a helical mercury resonance arc of the rare gas-mercury discharge type.

The effective absorbed light may be taken as 2537A since the resonance light source emits almost entirely 1849 and 2537A mercury emission lines. The quartz layers and liquid water barrier in the light path would eliminate 1849A radiation.

The H_2O_2 was outgassed by repeated warming, freezing and pumping out and introduced into the reaction tube while maintaining the storage vessel at about 19°C. The combined pressures of H_2O_2 and H_2O were
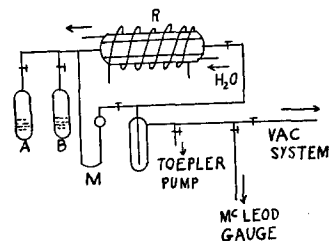

Fig. 1. Reaction system.

[9] G. K. Rollefson and M. Burton, *Photochemistry and the Mechanism of Chemical Reactions* (Prentice-Hall, Inc., New York, 1939), p. 178.

[10] Rodebush, Wende, and Campbell, J. Am. Chem. Soc. **59**, 1924 (1937).

[11] Rodebush, Keizer, McKee, and Quagliano, J. Am. Chem. Soc. **69**, 538 (1947).

[12] The hydrogen peroxide sample was kindly supplied by the Buffalo Electrochemical Company, Buffalo, New York.

adjusted to 1.62 mm Hg. As will be shown below, the H_2O_2 pressure was 1.23 mm.

Products of the Reaction

Analysis of the non-condensable decomposition products using a Blacet-Leighton gas microanalysis apparatus indicated that hydrogen was absent in the products. This point was checked by use of three experimental methods: the reaction of the gas with heated copper oxide; the combustion with oxygen over glowing platinum; and a determination that all of the non-condensable gas was O_2 by reaction with phosphorus. Although very small amounts of hydrogen would escape detection by these techniques, it seems safe to say that the upper limit of hydrogen gas cannot exceed about 0.2 percent and that it is probably completely absent.

Variation of Temperature

The temperature was varied by controlling the temperature of water in the jacket around the reaction tube. Figure 2 shows the course of the reaction over the temperature range covered. The curve in each case is the experimental curve derived from the 30° experiment, while the experimental points are for the indicated temperature. An attempt to follow the photo-chemical reaction at 75° was unsuccessful due to appreciable thermal decomposition.

It may be observed that in each case the pressure approaches a maximum. From the fact that no hydrogen is formed and the over-all decomposition equation

$$2 H_2O_2 \rightarrow 2 H_2O+O_2, \qquad (7)$$
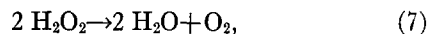
the initial H_2O_2 pressure may be calculated from the value of the maximum. This is the value referred to above.

Added Gases

The effect of adding O_2, N_2, and H_2O to the H_2O_2, H_2O gas mixture was studied at a single temperature, 30°. In Fig. 3 the results are represented graphically by comparison of each experiment with the experiment at 30° without added gas, represented by the curve. The experimental points are the ones obtained for the experiments with added gas.

The Quantum Yield

The quantum yield of the reaction was determined by using acetone as an actinometer. Acetone vapor was introduced into the reaction vessel at 70°C and the initial photo-chemical rate was determined on the basis of pressure increase in the system. At 70°C the decomposition of acetone[13] may be expressed by the over-all equation

$$(CH_3)_2CO+h\nu \rightarrow C_2H_6+CO. \qquad (8)$$
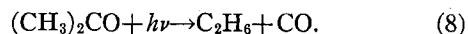
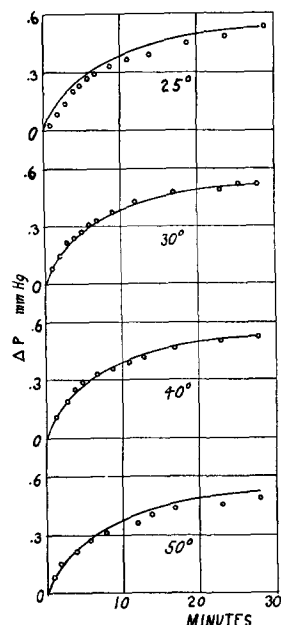[13] D. S. Herr and W. A. Noyes, Jr., J. Am. Chem. Soc. **62**, 2052 (1940).

FIG. 2. Course of the reaction at various temperatures. The curve is in each case the 30° experimental curve. The experimental points are for the indicated temperature.
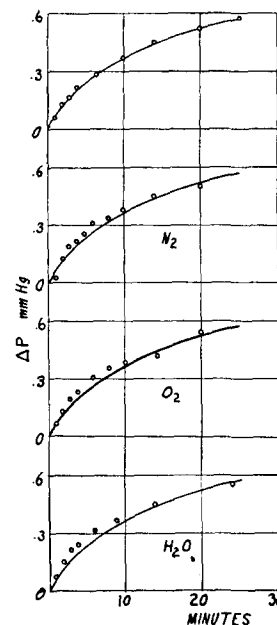

FIG. 3. Course of the reaction with added gases at 30°. The curve is in each case the 30° experimental curve without added gas, top curve. The experimental points are for the indicated added gas.

Herr and Noyes[13] have shown that above 60° the ratio of C_2H_6/CO is unity.

The acetone pressure was 2.16 mm Hg. At this low pressure, the absorption may be expressed by the first term of the logarithmic expansion

$$I_0 - I/I_0 = \epsilon cl. \tag{9}$$

Using this expression also for H_2O_2, the geometry of the system need not be considered and the quantum yield of H_2O_2 decomposition may be calculated from the quantum yield of acetone photolysis, Φ_a, the absorption coefficients of acetone and H_2O_2, ϵ_a and ϵ_p, the initial concentrations of acetone and H_2O_2, c_a and c_p, and the rates of decomposition of acetone and H_2O_2, n_a and n_p.

$$\Phi_p = n_p/I_p, \tag{10}$$

$$\Phi_a = n_a/I_a, \tag{11}$$

$$\Phi_p = (n_p I_a/n_a I_p)\Phi_a, \tag{12}$$

$$\Phi_p = (n_{pa}c_a/n_{ap}c_p)\Phi_a. \tag{13}$$

The absorption coefficient for H_2O_2 is calculated as 19.6 at 2537A from the Eq. (14) for c in moles per liter,

$$\log_{10}(I_0/I) = \epsilon cl, \tag{14}$$

using the absorption data of Holt, McLane, and Oldenberg.[1] The absorption coefficient of acetone for the same wave-length is 7.0.[14] Φ_a is dependent on concentration and intensity of absorbed light but at 70°C is rapidly approaching unity for all conditions and is certainly between 0.6 and 1.0.[13] Taking Φ_a, therefore, as 0.8 ± 0.2, the value of Φ_p is calculated as 1.7 ± 0.4.

DISCUSSION

In Fig. 4, the curves of Figs. 2 and 3 are represented on a $\log p$ vs. t plot. Deviation from linearity is not very serious until almost three-fourths of the peroxide has been decomposed. Since the quantity of light absorbed varies continuously with the pressure of H_2O_2, the incident light being constant, this does not imply that the reaction is unimolecular. Rather, it may be explained on the linear relationship between the quantity of light absorbed and concentration of absorbing species at the low pressures used. Mathematically then the decomposition rate may be expressed by the equation,
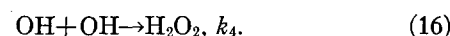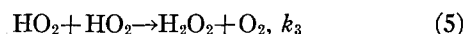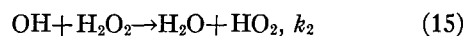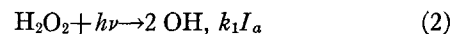
$$-\{d[H_2O_2]/dt\} = kI_{abs.}, \tag{15}$$

and, since $I_{abs.}$ is directly proportional to the pressure,

$$-\{d[H_2O_2]/dt\} = k'[H_2O_2], \tag{16}$$

for a constant I_0. Since this equation is moderately well followed, it may be concluded that the quantum yield of the reaction is, in fact, independent of both the pressure of H_2O_2 and $I_{abs.}$.

Since the experiments with added O_2 indicate that H atoms are absent, the primary process is as represented by Eq. (2), and the entire mechanism is adequately explained by the set of reactions.

$$H_2O_2 + h\nu \rightarrow 2 \ OH, \quad k_1 I_a \tag{2}$$

$$OH + H_2O_2 \rightarrow H_2O + HO_2, \quad k_2 \tag{15}$$

$$HO_2 + HO_2 \rightarrow H_2O_2 + O_2, \quad k_3 \tag{5}$$

$$OH + OH \rightarrow H_2O_2, \quad k_4. \tag{16}$$

Reaction (15) has been used by Taube and Bray[15] to maintain the chain in the reaction between H_2O_2 and

[14] C. W. Porter and C. Iddings, J. Am. Chem. Soc. 48, 40 (1926).

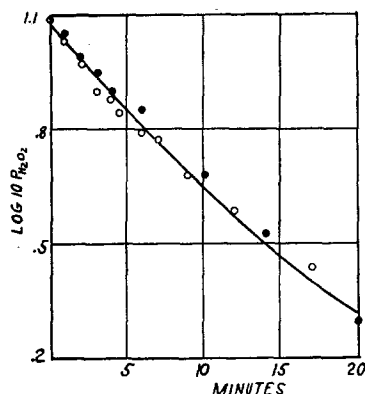[15] H. Taube and W. C. Bray, J. Am. Chem. Soc. 62, 3357 (1940).

FIG. 4. Log of H_2O_2 pressure *versus* time for duplicate experiments at 30°.

ozone. ΔF for this reaction is given as -25.3 kcal. Reaction (5) has proven useful in discussions involving systems of H atoms and oxygen.[6,7] ΔF for this reaction may be calculated from the data of Yost and Russell[16] as -30.0 kcal. Recombination of OH radicals to form H_2O_2, reaction (16), may be involved at the lowest pressures as shown in the following argument.

Using the steady state treatment for the concentration of free radicals, the sequence (2), (15), (5) leads to the kinetic equation

$$-\frac{d[H_2O_2]}{dt} = 2k_1 I_{abs.}. \tag{17}$$

This sequence would lead to a maximum quantum yield of 2.0 which is consistent with the experimental deter-

mination. A quantum yield of less than 2.0 and deviation from linearity in Fig. 4 may be accounted for by Eq. (16). If this reaction is used, the kinetic equation becomes

$$-\frac{d[H_2O_2]}{dt} = k_2[H_2O_2]\frac{-k_2[H_2O_2]+(k_2{}^2[H_2O_2]^2+16k_1k_4 I_{abs.})^{\frac{1}{2}}}{4k_4}.$$

A reaction such as (16) might be expected to be a 3 body or wall reaction. The observation that adding gases to the reaction mixture does not appreciably affect the reaction indicates that (16) is not important.

The gases O_2 and H_2O added are also reaction products. Since they have no appreciable effect it may be concluded that equilibria involving the products are not involved.

The quantum yield of H_2O_2 decomposition in liquid water solution has been reported as varying between 1 and 500 depending upon experimental conditions.[17] The careful work of Heidt[18] has shown that at low concentrations the quantum yield is in the region 1–2 in agreement with the vapor phase value reported here.

The observation that the rate of the reaction is temperature independent over the range studied is additional evidence that the rate depends only upon the rate of radiation absorption. If the recombination reaction is eliminated, then the secondary reactions postulated effect a sequence independent of temperature.

[16] D. M. Yost and H. Russell, Jr., *Systematic Inorganic Chemistry* (Prentice-Hall, Inc., New York, 1944), p. 268.

[17] See reference 9, p. 379.
[18] L. J. Heidt, J. Am. Chem. Soc. 54, 2840 (1932).