

Flash Photolysis of H₂O₂ Vapor in the Presence of D₂, Ar, and H₂ 18O

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J. Chem. Phys. **46**, 2450 (1967); 10.1063/1.1841066



uncertainty of the first-order RKR calculation, with the exception that the well depth is increased by a value of 10 cm^{-1} . This leads us to the conclusion that the original fit of V' vs V over the whole range of the curve gave second-order corrections to the potential curve of the correct order of magnitude, i.e., within the uncertainty of the first-order calculation except for the effect of V_{00} on the energy values.

ACKNOWLEDGMENTS

The authors are grateful to Dr. Stanley Weissman for his help in the earlier stages of these calculations. The computer time was supported by the National Aeronautics and Space Administration Grant NsG-398 to the Computer Science Center of the University of Maryland.

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Flash Photolysis of H_2O_2 Vapor in the Presence of D_2 , Ar, and $\text{H}_2^{18}\text{O}^*$

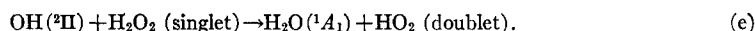
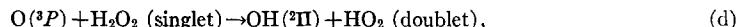
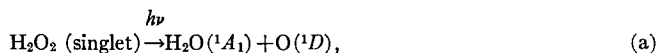
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(Received 14 February 1966)

The flash photolysis of H_2O_2 by itself, and in the presence of D_2 , Ar, and H_2^{18}O , was studied by the technique of kinetic absorption spectroscopy. The only observable primary products were $\text{OH}(^2\Pi_1)$ and $\text{OH}(^2\Pi_1)$. These ground-state levels were populated in a ratio of $\sim 1:1$, respectively, conforming to what is observed with the halogens.

The contribution of Reaction (a) to the primary process was shown in a direct way to be no more than 20% of that of (b). Reaction (c) followed by (d) was shown to make no significant contribution to the OH concentration during the time of our experiments ($< 200\mu\text{ sec}$):



Thus, this technique is a convenient one for directly observing reactions of OH. An upper limit to the rate constant of (e) at room temperature was determined to be $5.8 \pm 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$.

Conditions for generating vibrationally hot molecules in the primary photolytic step are discussed.

I. INTRODUCTION

IN the quartz uv, hydrogen peroxide has a large absorption coefficient and has long been considered to photolyze to two OH radicals, analogously to the photolysis of the halogens.¹ A good, brief, up-to-date review of the subject is given by Volman.² Only the steady-state photolysis has been studied to any great extent, and most of this at 2537 Å , so all of the conclusions about the primary step and subsequent reactions have been established indirectly through the values obtained for the quantum yield and the effect of various conditions on the net rate and final products.

Reactions of OH radicals independent of O atoms and the corresponding rates, are of great interest in the fields of combustion and detonation. A number of these reactions could be studied in terms of individual electronic-vibrational-rotational states by the technique of flash photolysis and high-resolution kinetic absorption spectroscopy.

We decided to study the photolysis of H_2O_2 by this technique to determine with greater certainty whether OH radicals, and only OH radicals, were produced in the primary step. In addition to settling this important question, information could be gained about the condition of the primary product, which indeed proved to be OH, with regard to population of the various vibrational-electronic states.

There are a number of possible mechanisms by which H_2O_2 may be photolyzed in the quartz uv ($\lambda \geq 2000\text{ Å} = 143 \text{ kcal mole}^{-1}$). If we assume that the HO-OH bond

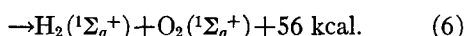
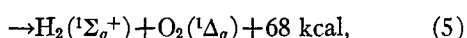
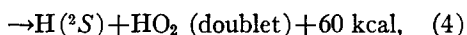
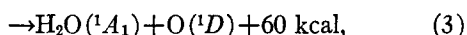
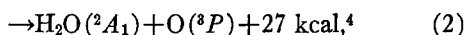
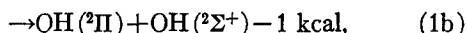
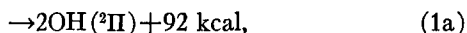
* This work was done under the auspices of the U.S. Atomic Energy Commission.

¹ H. C. Urey, L. H. Dawsey, and F. O. Rice, J. Am. Chem. Soc. **51**, 1371 (1929).

² D. H. Volman, Advan. Photochem. **1**, 69 (1963).

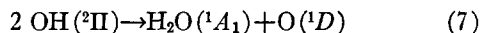
dissociation energy is 51 kcal/mole³ and that spin is conserved, the following reactions are possible:

H_2O_2 (singlet) + $h\nu$ ($\lambda = 2000 \text{ \AA}$)

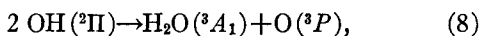


Reaction (1a) is generally accepted as the most probable one. The existence of (1b) was inferred from emission of the $\text{OH } ^2\Sigma^+ \rightarrow ^2\Pi$ (0, 0) band when H_2O_2 was photolyzed with a Zn spark at short wavelengths (2025–2138 \AA).¹ This explanation of the emission is doubtful now that the HO–OH bond energy is known to be near 51 kcal, rather than 39 kcal as believed earlier. A possible explanation may be that unsuspected light of $<1980 \text{ \AA}$ caused (1b).² Acetone, which absorbs from 2150 to 3100 \AA , was used to prevent wavelengths in this region of the Zn spark from entering the fluorescence vessel.¹ However, since the Zn 3076- \AA line evidently passed through the filter, the exact coincidence of a Zn-spark line with the R_{11}' OH absorption line at 3072.062 \AA suggests a reasonable alternate mechanism for the fluorescence. In this case it is not necessary to conclude that Reaction (1b) occurred.

The generation of oxygen atoms by photolysis of H_2O_2 in solution has suggested the occurrence of Reactions (2) and/or (3)⁵; however, Reaction (1), occurring in a solvent cage followed by



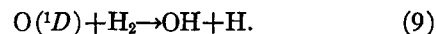
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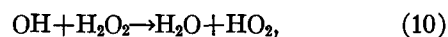
could easily account for the oxygen atoms detected.² Photolysis in the gas phase would eliminate the cage effect.

That the photolysis of H_2O_2 was unaltered by the presence of H_2 was taken as evidence of the non-

occurrence of (2) and (3).^{2,6} Recent studies, mentioned below, indicate that H_2 should not change the results if (2) and/or (3) were taking place. $\text{O}(^1D)$ has been shown to react very rapidly⁷ with H_2 according to (9):



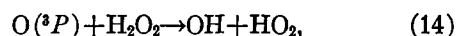
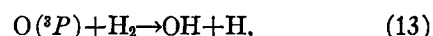
Both OH and H react rapidly with H_2O_2 according to (10) and (11)⁸:



The HO_2 could then react according to (12):



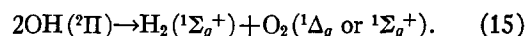
to give an over-all quantum yield of 2 (experimentally 1.7 ± 0.4).⁹ The relative rates of (13) and (14),



indicate that moderate amounts of H_2 would have the same effect as N_2 (i.e., an inert gas⁹) in a system where (2) was the primary process.^{8,10} The OH would then react with H_2O_2 according to (10) followed by (12), again resulting in a quantum yield of 2. In any case, any $\text{O}(^3P)$ that follows (13) also gives a quantum yield of 2 via a sequence analogous to that beginning with (9). Thus, the exclusion of (2) and (3) becomes doubtful on these bases.

The ineffectiveness of O_2 on the quantum yield appears to be good evidence that (4) does not occur to an appreciable extent.^{8,9} Reactions (5) and (6) are excluded by the quantum yield and the absence of H_2 in the products.⁹

Since flash photolysis is a good means for producing large momentary concentrations of reactive species, we thought this system might allow second-order reactions like (7), (8), and (15) to be detected in the gas phase



As is noted in Reactions (1)–(6), the fragments from the photolysis of H_2O_2 have quite large amounts of excess energy. Although the conclusion of Urey *et al.*¹ concerning fluorescence may be doubtful, their explanation suggests that the population of all $^2\Pi$ vibrational levels right up to the level of the $\text{OH } ^2\Sigma^+$ state may be possible in the primary process. It was of interest to see how much, if any, of this energy

³ W. C. Schumb, C. N. Satterfield, and R. L. Wentworth, *Hydrogen Peroxide* (Reinhold Publ. Corp., New York, 1955), p. 256.

⁴ This is based on the absorption of 3.4 eV of energy by H_2O from an electron beam. This type of energy absorption by various gases corresponds closely in many cases with known energy levels, transitions with change of multiplicity being allowed because of the electron's spin [see G. Schutz, *J. Chem. Phys.* **33**, 1661 (1958)]. Since no optical transition at 3.4 eV is known for H_2O , the energy level indicated here may well be the 3A_1 state of H_2O .

⁵ J. P. Hunt and H. Taube, *J. Am. Chem. Soc.* **74**, 5999 (1952); M. Auber, *Trans. Faraday Soc.* **57**, 971 (1961).

⁶ M. Tamres and A. A. Frost, *J. Am. Chem. Soc.* **72**, 5340 (1950).

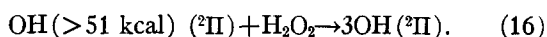
⁷ N. Basco and R. G. W. Norrish, *Proc. Roy. Soc. (London)* **A260**, 293 (1961).

⁸ S. N. Foner and R. L. Hudson, *J. Chem. Phys.* **36**, 2681 (1962).

⁹ D. H. Volman, *J. Chem. Phys.* **17**, 947 (1949).

¹⁰ F. Kaufman, *Proc. Roy. Soc. (London)* **A247**, 123 (1958).

appears as vibrational energy. A number of cases are on record where vibrationally excited molecules are produced in the primary photolytic step.^{11,12} Vibrational excitation is known to persist through many collisions and can modify the reactivity of molecules.¹²⁻¹⁴ If any OH from 1(a) had 51 kcal or more of excess vibrational energy, as is possible over most of the H₂O₂ absorption range, it could cause Reaction (16) to occur:

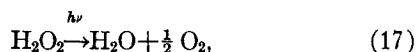


The occurrence of such reactions could require reinterpretation of quantum yields for such systems. The convenient absorption spectrum of OH makes it an especially attractive possibility for studying reactivity as a function of vibrational excitation.

Possible mechanisms which determine how the excess energy from photolysis is divided among the various degrees of freedom of the fragments have been commented on by Basco and Norrish.¹⁵ Flash-photolysis studies of H₂O₂ could give information about these proposed mechanisms.

II. EXPERIMENTAL

Commercially available 90% H₂O₂ was concentrated further by pumping off ~90% of the liquid at 0°C. The concentration of the remaining solution was >97%, as determined from its vapor pressure.³ We had hoped to obtain accurate analyses of H₂O₂+H₂O mixtures in the gas phase by photolyzing samples in a quartz bulb at 2537 Å with a Fuller lamp and observing the pressure rise with a dibutylphthalate manometer⁹ and traveling microscope. The pressure rise can be related to the H₂O₂ concentration by the net Reaction (17),



which occurs in steady-state photolysis.⁹ However, severe complications arose due to adsorption of H₂O₂ vapor on the walls of the bulb, making the analyses inaccurate and irreproducible. Even saturating the walls with H₂O had a very small effect on the adsorption rate. Neither silicone nor wax decreases the adsorption.⁶ However, the adsorption rate was slow enough so that vapor pressure could be measured reliably. We then used tables to determine the vapor composition from the liquid composition and temperature.³

The D₂ was 99.5% pure, with HD the major impurity, and the enrichment of the H₂¹⁸O sample was

¹¹ N. Basco, *Advan. Chem. Ser.* **36**, 26 (1962).

¹² G. M. Harris and J. E. Willard, *J. Am. Chem. Soc.* **76**, 4678 (1954).

¹³ M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.* **57**, 2176 (1961).

¹⁴ W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc. (London)* **A254**, 317 (1960).

¹⁵ N. Basco and R. G. W. Norrish, *Proc. Roy. Soc. (London)* **A268**, 291 (1962).

94.6%, both determined by mass spectrometry. Argon was research grade commercially available in Pyrex bulbs.

Care was taken to exclude mercury from the system, to eliminate Hg-sensitized reactions, by using all new glassware and the dibutylphthalate manometer to measure pressures.

The lamps, absorption cell, electrical circuitry, and spectrograph have been described elsewhere.¹⁶ Kodak 103aO plates were used to record the absorption spectra. Exposures were taken at delays of 4–200 μsec after the photolysis flash. The plate densities were measured on a Leeds & Northrup microdensitometer.

The relative populations of the various rotational states were determined in the following way. The intensity of light *I* for identical exposure times falling on a plate is related to the plate density *D* by Relation (18),¹⁷

$$\ln I = A + B \ln(10^D - 1), \quad (18)$$

where *A* and *B* are constants depending on plate type, development time, and presumably wavelength to some extent. Beer's Law states

$$I_t/I_0 = \exp(-CSP), \quad (19)$$

where *I_t* and *I₀* are transmitted light with and without absorption, *C* is a constant including the path length of the absorbing medium, *S* is the line strength, and *P* is the partial pressure of the absorbing species. From these relations we have for two absorption lines, 1 and 2,

$$\ln \left(\frac{P_1}{P_2} \right) = \ln \ln \left(\frac{10^{D_0} - 1}{10^{D_1} - 1} \right) - \ln \ln \left(\frac{10^{D_0} - 1}{10^{D_2} - 1} \right). \quad (20)$$

Use of this relation allows rotational temperatures (*T_{rot}*) and first-order reaction rate constants to be calculated without tedious plate calibrations as long as (18) is obeyed. For 103aO plates, this requires that 0.05 > *D* > 2.5 (see Ref. 17). The individual rotational lines were identified with the aid of an Fe hollow cathode lamp as a calibration source and the wavelength tables of Dieke and Crosswhite.¹⁸

III. RESULTS

Experiments were done on gas mixtures having the following compositions:

- (A) 0.8 mm H₂O₂ + 0.2 mm H₂O,
- (B) 1.4 mm H₂O₂ + 0.2 mm H₂O + 50 mm Ar,
- (C) 0.8 mm H₂O₂ + 0.2 mm H₂O + 1.0 mm H₂¹⁸O + 10 mm Ar,
- (D) 0.8 mm H₂O₂ + 0.2 mm H₂O + 10 mm D₂.

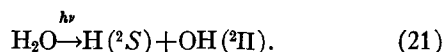
¹⁶ R. Engleman, Jr., *J. Am. Chem. Soc.* **87**, 4193 (1965); P. E. Rouse, Jr., D. L. Upham, R. Engleman, Jr., and H. M. Peek (to be published).

¹⁷ H. M. Crosswhite and G. H. Dieke, *Bumblebee Ser. Rept. No. 202*, Johns Hopkins University, 1953.

¹⁸ G. H. Dieke and H. M. Crosswhite, *Bumblebee Ser. Rept. No. 87*, Johns Hopkins University, 1948.

The average amount of H_2O_2 decomposed per flash was between 0.5% and 1.0% averaged over a number of flashes, determined by pressure rise and mass spectrometry, assuming Reaction (17) to hold. This small amount of decomposition still may not allow observation of (15); however, our rate of decomposition of H_2O_2 was 1.5×10^5 times that employed by Volman.⁹ This, together with rate constants derived later in this section, would allow the amount of H_2 produced by Reaction (15) to be 75 times greater in our system than in Volman's.

In our reaction products we observe an $[\text{H}_2]/[\text{O}_2]$ ratio of 0.02 ± 0.01 determined by mass spectrometry. We have determined that a small amount of the H_2O , which was always present, was photolyzed in our system. The photolysis of water ($\lambda < 1860$) follows (21)¹⁹



The most probable reaction for the H atom is Reaction (11), which could very well account for the H_2 observed. If Reaction (15) is to be observed, H_2O will have to be more thoroughly eliminated, and/or a larger rate of decomposition of H_2O_2 will have to be achieved.

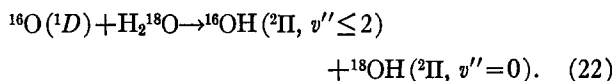
Analysis of the plates showed that in all cases the maximum of the OH concentration occurred at the time of maximum light intensity—that is, during the exposure taken at the 4- μsec delay. All of the observed OH was in the low rotational levels ($K \leq 7$) of the $v''=0$ level of the ground electronic ($^2\Pi$) states. The pressures employed here prevent appreciable Doppler broadening.

The plates taken with Systems (A) and (D) were good enough for the measurement of the intensities of all the observed lines of the P_1 , P_2 , Q_1 , and Q_2 branches ($0 < K < 7$), and a few lines of the R_2 branch. Conforming with what might be expected by analogy with the halogens, in Experiment A, the population of the $^2\Pi_{1/2}$ state was 1.0 ± 0.5 times the population of the lower $^2\Pi_{3/2}$ state, with the populations remaining equal throughout the experiment.

Experiment B was done both as a check of the method for determining rotational temperatures and as a means of determining the rate of disappearance of OH near room temperature. With this amount of inert gas present, the equilibrium temperature after photolysis can be no higher than 10°C above room temperature. The first-order rate constant for OH removal under these conditions was $2.6 \pm 0.8 \times 10^3 \text{ sec}^{-1}$. The three most probable reactions for OH removal are (7), (8), and (10), but since we do not know the absolute concentration of OH in our system with reasonable accuracy, we cannot assess the contributions of Reactions (7) and (8), both second order in OH. We then derive $5.8 \pm 1.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \cdot \text{sec}^{-1}$ as an

upper limit to the rate constant for (10), which is first order in both OH and H_2O_2 . The error limits are for a 99% confidence level.

The $^{16}\text{O}(^1D)$ atom is known to react on nearly every collision with H_2 according to (9) and with H_2^{18}O according to (22),^{7,16}



Mixtures (C) and (D) were photolyzed to determine the contribution of Reaction (3). A small amount of $^{18}\text{OH}(v''=0)$ was observed, but was found to be due to Reaction (21). No $^{16}\text{OH}(v''=1)$ was found, but, because of a smaller Franck-Condon factor²⁰ and a fast rate of relaxation, a ratio of

$$[^{16}\text{OH}(v''=1)]/[^{18}\text{OH}(v''=0)]$$

somewhat greater than 0.16 could go undetected. When Mixture (D) was photolyzed, no $\text{OD}(v''=0)$ was observed. From this last result we can conclude that $[\text{O}(^1D)]/[\text{OH}] < 0.10$, based on our faintest observable absorption lines.

IV. DISCUSSION

A. Experimental Results

No OH in the $v''=1$ level was detected. On the basis of the faintest observable lines, we can say that the $v''=1$ population was no more than 15% of the $v''=0$ population. Therefore, vibrational relaxation should not appreciably affect the $\text{OH}(v''=0)$ population. This result can also be taken as partial evidence that (1b) does not occur to a great extent. The lifetime of the $^2\Sigma^+$ state should be 1 μsec in the absence of quenching. Franck-Condon factors for emission to the $^2\Pi$ state are such that 10% of the molecules would end up in the $v''=1$ state, and thus be detectable. However, at the lowest pressure used by us, collisions occur on the average every 0.1 μsec or so, so quenching would probably be more important than fluorescence. In this case, 93 kcal of energy is available. Since the most probable collision partner is H_2O_2 , the weakest bond of which is 51 kcal, we would expect either the quantum yield to be increased by such quenching, or the OH to reserve some of this energy (at least 42 kcal) as vibrational energy, and thus be observable. Unfortunately, the quantum yield has been measured² only at 2537 Å. The production of $\text{OH } ^2\Sigma^+$ can take place only below 1980 Å. It would be of great value to measure the quantum yield for disappearance of H_2O_2 below 1980 Å, perhaps at 1849 Å.

It was of interest to estimate the possible contribution of (2) followed by (14) to the observed $[\text{OH}]_{4 \mu\text{sec}}$.

¹⁹ A. Y. M. Ung and R. A. Back, Can. J. Chem. **42**, 753 (1964).

²⁰ W. R. Jarman, P. A. Fraser, and R. W. Nicholls, Astrophys. J. **122**, 55 (1955).

A value for $[\text{OH}]_{4\mu\text{sec}} = 0.02$ mm could be estimated to within perhaps a factor of 3 from the absorption coefficient of the Q_{16} line,²¹ the relative resolving powers of the two spectrographs, and the estimated value of B in Eq. (21) for our plates. An upper limit of $k_{14} = 10^{-5}$ cm³ mole⁻¹·sec⁻¹ has been derived,⁸ which, with the net decomposition in these experiments (0.5%–1.0%) and the rate of disappearance of OH, allows an upper limit to the contribution of (2) + (14) to be calculated. We conclude that less than 0.5% of the OH observed could have been produced in this way.

To summarize the conclusions about the choice of primary process, we can conclude that no more than 20% of the H₂O₂ is photolyzed by (3), and that neither (2) followed by (14), nor vibrational relaxation, contributes significantly to the OH concentration. Therefore, this technique is a good one for observing reactions of OH radicals in the low rotational levels of the $v''=0$ state. Although the occurrence of (1b) and (2) cannot significantly affect the OH concentration during the time of our experiments, further work is necessary before their contributions to the primary process can be evaluated. Experiments are being attempted to determine the contribution of (2) to the primary process.

B. Vibrational Excitation from Primary Photolytic Processes

The first two mechanisms briefly considered here have been discussed in detail by Basco and Norrish.¹⁵

If we use as an example a linear molecule ABC and consider that the excess energy produces an instantaneous repulsive force between A and B, we can calculate the fraction of the excess energy (α) which will appear as vibration of BC as a result of conservation of momentum and the resulting compression of BC:

$$\alpha = m_A m_C / [(m_A + m_B)(m_B + m_C)], \quad (23)$$

where the m 's are the respective masses. It is easily seen that for the HO–O–H system this amounts to a mere fraction of one quantum of vibrational energy. Basco and Norrish have found that this mechanism underpredicts the excitation of NO from Cl–N–O. The fact that the repulsive force would be far from instantaneous, as required for (23) to hold, would further lower the amount of excitation to be expected from such a mechanism. Thus, the effectiveness of this mechanism may be generally questionable.

They also consider a more appealing process whereby the absorption of light causes the BC bond of ABC to

be excited vibrationally with an eventual redistribution of vibrational energy until the AB bond breaks. In most of such cases the BC bond would be expected to have a large part of the excess energy. We do not find this to be the case with H₂O₂. This suggests that the state from which H₂O₂ dissociates under our conditions is not predissociated.

In contrast to the first mechanism discussed, a third mechanism can be considered, whereby the upper state of the absorbing transition is repulsive with respect to the AB bond. But, because of the Franck–Condon principle, the configuration of ABC in the repulsive upper state will be nearly the same as in the ground state, and, because of the above-mentioned ineffectiveness of the repulsion to cause compression of BC, the BC bond will be left after decomposition in essentially the same condition as before absorption of radiation. This is what we found for OH from H₂O₂. This analysis suggests that the upper state from which H₂O₂ dissociates is repulsive with respect to the O–O bond.

We can now put down a tentative rule for deciding the suitability of a molecule ABC for producing a vibrationally excited fragment upon photolysis. If the state from which ABC dissociates is predissociated (i.e., if it is photolyzed in the diffuse but discrete region of its absorption spectrum), then the second mechanism should hold, and nearly all of the excess energy should appear in vibration of BC most of the time. If, on the other hand, photolysis takes place in a continuous region, as in the case of H₂O₂, the amount of vibrational excitation will depend on how much difference there is between the length of BC in the parent molecule and in free BC. In this case, the amount of excitation E of BC is given approximately by

$$E = D_e \{1 - \exp[-\beta(r_b - r_f)]\}^2 - \frac{1}{2}\omega_e, \quad (24)$$

where D_e is the dissociation energy of BC, r_b is the bond length of BC in ABC, r_f is the bond length of free BC, ω_e is the quantum of vibrational energy of free BC, and

$$\beta = 1.2177 \times 10^7 \omega_e (\mu/D_e)^{\frac{1}{2}}, \quad (25)$$

where μ is the reduced mass of free BC.²²

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