whose relative intensities vary with the temperature have been studied in terms of energy level diagrams.

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[CONTRIBUTION FROM THE COBB CHEMICAL LABORATORY, UNIVERSITY OF VIRGINIA]

The Photodissociation of Hydrogen Peroxide in the Presence of Hydrogen and Carbon Monoxide and the Recombination of OH Radicals

BY GUENTHER VON ELBE[1]

The ultraviolet absorption spectrum of hydrogen peroxide in the gas phase has been determined by Urey, Dawsey and Rice.[2] The authors conclude that for every absorbed light quantum two hydroxyl radicals are formed according to the equation

$$H_2O_2 + h\nu = 2OH \qquad (1)$$

Hydroxyl radicals are also involved in Bonhoeffer and Haber's scheme of the hydrogen and carbon monoxide combustion[3]

$$H + O_2 + H_2 = H_2O + OH \qquad (2)$$
$$OH + H_2 = H_2O + H \qquad (3)$$
$$\text{or } OH + CO = CO_2 + H \qquad (4)$$

This scheme has been discussed by Frankenburger and Klinkhardt[4] who carried out experiments on the action of photochemically generated hydrogen atoms in hydrogen and oxygen mixtures. They propose that reaction (2) should be followed either by (3) or by

$$OH + OH + M = H_2O_2 + M \qquad (5)$$

and that reaction (3) should require an activation energy of not less than 14,000 cal. An activation energy of that order would keep the rate of (3) sufficiently small until about 400° to make (5) the predominant reaction. The formation of chains would thus be prevented until about that temperature, which is consistent with the observed behavior of hydrogen–oxygen mixtures.

In the present work, mixtures of hydrogen peroxide vapor with hydrogen or carbon monoxide were exposed to the light of a condensed zinc spark. A small but distinct reaction was observed in both cases, suggesting the occurrence of reaction (1) and (3) or (1) and (4). In view of Frankenburger and Klinkhardt's work, most of these experiments were made with hydrogen. If OH was formed, according to (1), these experiments should allow one to test the reaction scheme proposed by these authors. In the

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(1) Research Associate, University of Virginia.

(2) Urey, Dawsey and Rice, THIS JOURNAL, **51**, 1371 (1929).

(3) Bonhoeffer and Haber, *Z. physik. Chem.*, **137A**, 263 (1928).

(4) Frankenburger and Klinkhardt, *Trans. Faraday Soc.*, **123**, 431 (1931); *Z. physik. Chem.*, **15B**, 421 (1932).

first place, the observed rates of hydrogen consumption should correspond to an activation energy of not less than 14,000 cal. This is indeed the case,[5] but this fact alone is not sufficient for the test. The purpose may be achieved by varying the experimental conditions which influence the rate of hydrogen consumption. If the reaction scheme is right, one should be able to predict changes of this rate. If the observed changes do not check with those theoretically predicted within a reasonable limit, the scheme certainly would appear rather doubtful.

Experiments and Results

The apparatus consisted of a closed flow system filled with either hydrogen or carbon monoxide. The details will appear from the figure. The small bubbler within the thermostat contained a 95% hydrogen peroxide solution which was prepared as in the method of Rice, Reiff and Kilpatrick.[6] The liquid was sufficiently shielded against direct or stray radiation from the zinc spark. Oxygen within the system could be removed by passing the gas flow through a pyrogallol solution.

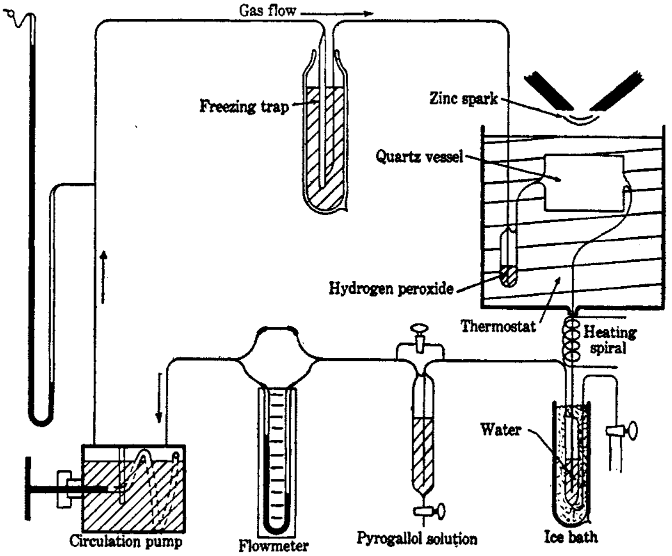

Fig. 1.—Apparatus for measuring photochemical reactions of hydrogen peroxide in the gas phase.

The data obtained are given in Table I. The first column shows the time for which the mixtures were exposed to ultraviolet light. The next three columns give the actual pressure changes effected by illumination. In some experiments, the oxygen was allowed to accumulate and afterward removed by pyrogallol. The fifth column contains the partial pressure of hydrogen peroxide in the mixture. It is calculated from the amount of hydrogen peroxide evaporated and the volume of hydrogen passing in a

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(5) Von Elbe and Lewis, THIS JOURNAL, **54**, 552 (1932).

(6) Rice, Reiff and Kilpatrick, *ibid.*, **48**, 3019 (1926).

given time. The latter is given in the next column. The hydrogen peroxide was caught in a water trap, except for the small amount which was used in the reaction. This amount was so small, indeed, that it did not appreciably change the hydrogen peroxide partial pressure. At the end of the run the contents of the ice water trap were removed and titrated with 0.1 *N* potassium permanganate. The seventh column shows the temperature of the thermostat. The last two columns show the number of hydrogen molecules disappearing and oxygen molecules formed during the illumination per sec. per cc. Since the reaction took place in the quartz vessel only, these last values were obtained by dividing the total number of molecules disappearing or formed per second by the volume of the quartz vessel which was 86 cc. The total amount of hydrogen and oxygen disappearing per sec. was obtained from the observed rate of pressure change, as given by the first four columns, the temperature and the total volume of the apparatus, namely, 218 cc.

The experiments can roughly be divided into two groups: those at 40° and a hydrogen peroxide pressure of 4 to 5 mm., and those at 28° and about 2 mm. hydrogen peroxide. It was not advisable to raise the temperature much above 40°, because the decomposition of hydrogen peroxide in the liquid phase then became appreciable. It was also not advisable to go lower than about 28°, because the rate of reaction was too small.

The number of light quanta entering the vessel per sec. was estimated in the following way. Mixtures of hydrogen and hydrogen bromide were passed through the quartz vessel, while the zinc spark was running, and the free bromine formed was measured. According to E. Warburg, for each *hν* absorbed one bromine is formed.[7] The results are shown as follows

H Br partial pressure (mm. Hg)	52	98	118
hν absorbed per sec. $\times 10^{-16}$	4.4	4.7	5.2

For the hydrogen bromide decomposition the same two line groups are responsible which cause the hydrogen peroxide decomposition, namely, the groups around 2070 Å. and around 2530 Å. However, they are absorbed at different percentages which can be calculated for hydrogen bromide from Warburg's data, and for hydrogen peroxide vapor from the work of Urey, Dawsey and Rice,[2] the length of the light path being, in the present case, 5 cm. In the above table, the apparent depending of the number of *hν* absorbed upon the hydrogen peroxide pressure may be attributed to changing absorption in the 2530 group. A calculation on this basis shows that the number of light quanta entering the vessel per sec. is 3.2×10^{16} in the 2070 group, and 2.4×10^{16} in the 2530 group. If the vessel is filled with hydrogen peroxide vapor at 5 mm., the first group will be absorbed to 26%, the other to 7%. The total absorption will amount to 1.0×10^{16} *hν* per sec. This yields 23×10^{13} OH radicals per sec. per cc.

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(7) Warburg, *Sitzb. preuss. Akad. Wiss.*, 314 (1916).

TABLE I

EXPERIMENTS WITH HYDROGEN

No.	Time of illumination, min.	Initial pressure, mm.	Final pressure with O_2	Final pressure without O_2	H_2O_2 partial pressure, mm.	Speed of gas flow cc./min.	Temp., °C.	Number of H_2 molecules disappearing per sec. per cc.	Number of O_2 molecules formed per sec. per cc.
1	70	712.5	Not measured	709.6	4.0	40	39.0	5.6×10^{13}	Not measured
2	50	711.1	Not measured	709.0	4.0	40	39.0	5.6	Not measured
3	53	729.0	Not measured	724.3	5.1	31	40.7	11.8	Not measured
4	37	725.7	Not measured	723.7	5.1	31	40.7	7.2	Not measured
5	55	735.9	Not measured	734.1	5.1	25	40.3	4.4	Not measured
6	60	784.6	Not measured	780.0	3.4	28	40.1	10.3	Not measured
7	30	723.9	726.5	722.7	5.1	31	40.5	5.4	17.1×10^{13}
8	54	722.7	725.5	721.2	5.1	31	40.5	3.8	10.8
9	55	715.6	721.2	712.8	5.1	25	40.5	6.8	20.5
10	55	701.1	Not measured	700.0	2.0	25	29.0	2.7×10^{13}	Not measured
11	62	772.4	Not measured	771.3	1.7	25	28.0	2.4	Not measured
12	60	772.4	Not measured	740.1	1.7	28	28.3	5.2	Not measured
13	55	697.3	700.6	695.6	2.0	23	27.5	4.2	12.4×10^{13}

EXPERIMENTS WITH CARBON MONOXIDE

								Number of CO molecules disappearing per sec. per cc.
15	60	706.0	Not measured	702.0	4.0		39.7	9.0×10^{13}
16	60	702.7	Not measured	700.4	2.0		26.8	4.6

Discussion

As mentioned before, reactions (3) and (5) provide a scheme for the reactions subsequent to the OH formation. If this scheme is true the disappearance of hydrogen would then be accounted for by (3), while a certain excess of OH should disappear unnoticed according to (5). The formation of oxygen requires some special consideration. One might consider the reactions

$$OH + OH = H_2O + O \qquad (6)$$

$$H_2O_2 + O = H_2O + O_2 \qquad (7)$$

$$O + O + M = O_2 + M \qquad (8)$$

of which (6) has been proposed by Bonhoeffer and Pearson.[8] This reaction (6) cannot be applied to the present experiment without interfering with Frankenburger and Klinkhardt's scheme. No way is left in their scheme for an appreciable consumption of OH according to (6), which means that collisions of OH among themselves must be largely ineffective, so ineffective that three-body collisions according to (5) dominate. This is perfectly consistent with the experimental facts of Bonhoeffer and Pearson.[5] Also in the present experiments reaction (6) cannot play a role if Frankenburger and Klinkhardt's scheme is true, because the hydrogen concentration and temperature were about the same as in their experiments and the relation between the number of two-body and three-body collisions must be the same as in their experiments.

Another reaction in which oxygen may be formed is

$$OH + OH + H_2O_2 = 2H_2O + O_2 \qquad (9)$$

But this reaction, however plausible, would not fit in the scheme either, because three-body collisions would occur much more frequently with hydrogen molecules than with hydrogen peroxide molecules since the concentration of the former is higher by the order of 10^2. Thus, reaction (5) would suppress reaction (9) completely.

As far as the author can see, all oxygen forming reactions are now disposed of[9] save those in which OH remains unaffected as, for example

$$OH + H_2O_2 = H_2O + O + OH \qquad (10)$$

This reaction, which would be analogous to the conversion of para to normal hydrogen by hydrogen atoms, would be endothermic, but there is an excess of energy of the dissociating light quanta, forming rather "hot" OH radicals. Another possibility might be

$$OH + H_2O_2 + H_2O_2 = 2H_2O + O_2 + OH \qquad (11)$$

The point is that by applying the Frankenburger–Klinkhardt scheme the oxygen formation in the present experiments must be considered as due to a kind of catalytic decomposition of hydrogen peroxide and not involving the disappearance of OH radicals. If the Frankenburger–Klinkhardt scheme holds, these radicals can only disappear according to (3) and (5).

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(8) Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).

(9) Compare the discussion of this subject in Bonhoeffer and Pearson's paper.

The rate of OH formation according to (1) per sec. per cc. can be symbolized by $+\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(1)}$, of OH disappearance according to (3) and (5) by $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(3)}$ and $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(5)}$. Then for the stationary state

$$\frac{+\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(1)} = \frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(3)} + \frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t}_{(5)} \qquad (12)$$

$+\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(1)}$ equals twice the amount of $h\nu$ absorbed per sec. per cc. and is, therefore, determined by the hydrogen peroxide concentration and the light intensity. $-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(3)}$ equals the number of hydrogen molecules disappearing per sec. per cc., or the number of successful binary collisions OH + H_2, given by the equation

$$\frac{-\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = Ze^{-Q/RT} = 2N_{\mathrm{H}_2}\, N_{\mathrm{OH}}\, \sigma^2_{1,2} \sqrt{2\pi RT\, \frac{M_1 + M_2}{M_1 \,.\, M_2}} \qquad (13)$$

N_{H_2} = number of H_2 per cc. = 22.1×10^{18} for $p_{\mathrm{H}_2} = 71$ cm., $t = 40$°C.
N_{OH} = number of OH per cc.
$\sigma_{1,2} = 2.3 \times 10^{-8}$ [4]
$R = 8.313 \times 10^7$

$-\mathrm{d}[\mathrm{OH}]/\mathrm{d}t_{(5)}$, the rate of recombination of OH to hydrogen peroxide, cannot be observed directly. It equals the number of ternary collisions (5) per sec. per cc., and is estimated by Frankenburger and Klinkhardt in the usual way (for atmospheric pressure) as 10^{-4} times the number of binary collisions OH + OH. The value is $2.77 \times 10^{-15}\, N^2_{\mathrm{OH}}$ binary collisions per sec. per cc. This (their) value can, therefore, be used here because the hydrogen concentration is about the same and the temperature dependency so small as to be negligible in this rough calculation.

For the following calculations an accuracy of a factor ten is quite sufficient for this value of the number of ternary collisions.

Equation (12) becomes

$$\frac{+\,\mathrm{d}[\mathrm{OH}]}{\mathrm{d}t} = 7 \times 10^9\, e^{-Q/RT}\, N_{\mathrm{OH}} + 2.77 \times 10^{-15}\, N^2_{\mathrm{OH}} \qquad (14)$$

and

$$7 \times 10^9\, e^{-Q/RT}\, N_{\mathrm{OH}} = -\,\mathrm{d}[\mathrm{H}_2]/\mathrm{d}t \qquad (15)$$

Taking experiment No. 9 as a specific example and assuming that 23×10^{13} OH are formed per sec. per cc., one obtains from (14)

$$23 \times 10^{13} = 7 \times 10^9\, e^{-Q/313\,R}\, N_{\mathrm{OH}} + 2 \times 2.77 \times 10^{-15}\, N^2_{\mathrm{OH}}$$

and from (15)

$$7 \times 10^9\, e^{-Q/313\,R}\, N_{\mathrm{OH}} = 6.8 \times 10^{13}$$

After elimination of N_{OH}, Q turns out to be 14,780 cal.

Now, if in experiment No. 9, the partial pressure of hydrogen peroxide were 2 mm. instead of 5.1 mm., the light absorption would be only $4.5 \times 10^{13}\, h\nu$ per sec. per cc. corresponding to 9×10^{13} OH formed per sec. per cc. If at the same time a temperature of 28° is assumed, instead of 40.5°, equations (14) and (15) change to

$$9 \times 10^{13} = 6.9 \times 10^9\, e^{-14{,}780/301\,R}\, N_{\mathrm{OH}} + 2 \times 2.77 \times 10^{-15}\, N^2_{\mathrm{HO}}$$

and

$$6.9 \times 10^9 e^{-14,780/301\,R} N_{OH} = -\,d[H_2]/dt$$

After elimination of N_{OH} and employing the value of Q derived above one obtains for the number of hydrogen molecules disappearing per sec. per cc. the value 1.87×10^{13}.

This value, which should be right for 28° and 2 mm. water pressure, is less than one-third of the value 6.8×10^{13} found experimentally for 40° and 5.1 mm. hydrogen peroxide pressure. This large difference holds not only for the above specific example but for all corresponding experiments in Table I. Furthermore, the result is only slightly dependent on assumptions concerning the three-body collision frequency and on errors in the assumed rate of OH formation. The three-body collision frequency might be wrong even by a factor ten without an appreciable change in the above result. The rate of OH formation might have been overestimated, but even if in the above example a value of 7.7×10^{13} instead of 23×10^{13} is taken—which would just be reconcilable with a value of 14,000 cal. for Q—the hydrogen consumption would be altered only to 2.5×10^{13} molecules per sec. per cc. It appears, therefore, that for the present experiments, if a change of the hydrogen peroxide pressure from 5 mm. to 2 mm. and of the temperature from 40 to 28° is made, the rate of hydrogen disappearance should decrease to one-third or less, if the proposed reaction scheme holds. This is obviously not in agreement with the facts. The above specific example, experiment No. 9, may properly be compared with experiment No. 13, because they were run one immediately after the other, thus, ensuring similar conditions. In No. 13 a rate of 4.2×10^{13} hydrogen disappearing was found, which corresponds to a decrease to two-thirds rather than one-third of the rate of No. 9. But besides this specific case, the decrease in the rate generally in all the experiments corresponds to certainly not more than a half, the mean value in group one being 7.2×10^{13} H_2 per cc. per sec. and in group two 3.6×10^{13} H_2 per cc. per sec.

From the above it can be concluded that the scheme consisting of reactions (1), (3) and (5) should be discarded. In the opinion of the author, the experiments and calculations are sufficiently accurate to justify this statement. On the other hand, it seems to be difficult to ascertain what has to be eliminated.

From the work of Urey, Dawsey and Rice it seems to be fairly well established that $H_2O_2 + h\nu = 2OH$. If this cannot be disputed, objections may be raised only against the occurrence of reaction (3) and (5). The reaction (3), ($OH + H_2 = H_2O + H$), however, seems to be most plausible for explaining the actually observed disappearance of hydrogen. It seems, therefore, that the reaction which is most probably at fault is reaction (5), $OH + OH + H_2 = H_2O_2 + H_2$. However, no other facts are published in the literature which might lead to objections against reaction (5) except this process of elimination. As already pointed out by von Elbe and Lewis[5] the paper of Bonhoeffer and Pearson does not contain any experimental material contradictory to Frankenburger and Klinkhardt's conclusions.

With reaction (5) discarded, an explanation for the formation of hydrogen peroxide is still to be sought. Marshall[10] some time ago proposed the intermediate formation of HO_2. While there is no experimental evidence for this, there is certainly no evidence against it.

In the present experiments the following scheme can be proposed

$$H_2O_2 + h\nu = 2OH \qquad (1)$$
$$OH + H_2 = H_2O + H \qquad (3)$$
$$OH + OH + H_2O_2 = 2H_2O + O_2 \qquad (9)$$

Perhaps this is a plausible scheme, as a rough calculation indicates. If for ternary collisions (9) a similar expression is used as for ternary collisions (5) previously, it follows that Q for reaction (3) equals 16,000–17,000 cal., and that the rates of hydrogen consumption and oxygen formation in both groups of experiments change by about one-half. It is hoped, however, that further experiments will allow more definite conclusions to be drawn on the subject.

Summary

1. Mixtures of hydrogen peroxide vapor and hydrogen or carbon monoxide were exposed to the light of a zinc spark. The kinetics of the reaction between the assumed product of dissociation—namely, OH—and hydrogen or carbon monoxide was studied at different partial pressures and temperatures.

2. The results do not sustain the reaction scheme of Frankenburger and Klinkhardt involving the recombination of two OH to hydrogen peroxide. However, there are no facts available which disturb the Bonhoeffer–Haber mechanism for the formation of water from hydrogen and oxygen.

CHARLOTTESVILLE, VIRGINIA

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[10] Marshall, *J. Phys. Chem.*, **30**, 1078 (1926).