hibit the same agreement in the *PVT* behavior of the ortho and para forms of the gas.

A recently published paper by Schäfer [*Z. physik. Chem.*, 36, 85 (1937)] describes a similar investigation of the data of state of normal and para hydrogen, his results agreeing very well with ours, although calculated differently.

Summary

The data of state of normal and 99.8% para hydrogen have been compared at low pressures, from the boiling point to 55°K.

The measurements show no essential differences in the *PVT* behavior of the two forms of gaseous hydrogen. The data also agree well with the accurate measurements of the Leiden Laboratory.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

The Formation of Water and Hydrogen Peroxide at Low Pressures

BY W. H. RODEBUSH, C. W. J. WENDE AND R. W. CAMPBELL

The reactions between hydrogen and oxygen and their various dissociation products have been studied over a wide range of experimental conditions and the literature is much too voluminous to be cited here. This work concerns itself with reactions of active species produced by the electrodeless discharge at low pressures. The reactions occurring under these conditions should be similar to those occurring in the photochemical reaction[1] at higher pressures, but they are not necessarily important in the explosive reaction at higher temperatures.

The formation of hydrogen peroxide in dissociated water vapor was studied extensively by Rodebush and Wahl.[2] Campbell and Rodebush[3] showed that hydrogen peroxide is only formed in appreciable quantities on a liquid air cooled surface. Oldenberg has studied the rate of disappearance of hydroxyl in dissociated water vapor by spectrographic methods.[4] The reaction between atomic hydrogen and molecular oxygen has been studied by Geib,[5] who found that peroxide is only formed at temperatures well below −80°. He concluded that the peroxide was formed by the direct combination of hydrogen atoms with oxygen on the walls of the trap.

A preliminary survey of this work was presented by one of the authors at the Princeton Symposium on Molecular Structure.[6] At that time the authors had not yet realized the importance of pressure as a variable. The results presented here were obtained in experiments in which the pressure was controlled carefully.

Experimental

The gas or vapor was dissociated by pumping it rapidly through an electrodeless discharge of high frequency.[7] From the discharge it was pumped rapidly to the reaction chamber and the products were frozen out in traps with various refrigerants. The apparatus was made of Pyrex glass. No stopcocks were used and the apparatus was cleaned with chromic acid and washed with water. The pressures were measured by a manometer filled with dibutyl phthalate and the percentage dissociation was determined by a Wrede[8] gage.

The Reactions of Dissociated Water Vapor.—Water vapor was drawn from a calibrated reservoir and passed through a length of capillary tubing into the discharge. The reservoir was kept in a thermostated bath, so that the rate of flow could be varied by changing the bath temperature over the range 10–45°.

The reaction may take three possible courses: water passed into the system may reappear in the trap as such; it may be converted into peroxide; or it may be lost as permanent gases. The results are given in terms of "per cent. conversions," that is, the percentage of the admitted water which undergoes each of the above reactions. It should be noted that on this basis two molecules of water are required to furnish one molecule of peroxide.

1. The Reaction in the Trap at −180°.—Dissociated water vapor was led directly into a liquid air trap. Per cent. conversions are plotted against pressure (in millimeters of mercury) in Fig. 1. Below 0.8 mm. pressure, the composition of the products was quite uniform, and the conversions were roughly: water, 40%; peroxide, 50%; and permanent gases, 10%. From 0.8 to 1.1 mm. the "loss" increased. This was probably due to a reaction on the walls of the connecting tube or on the walls of the trap near the surface of the liquid air. The sharp rise in the "water" curve above 1.1 mm. may be ascribed to a decrease in the efficiency of the discharge at higher pressures.

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(1) For references and discussion of the photochemical reactions between hydrogen and oxygen see J. R. Bates, *J. Chem. Phys.*, **1**, 457 (1933); M. G. Evans, *ibid.*, **2**, 726 (1934); H. A. Smith and G. B. Kistiakowsky, THIS JOURNAL, **57**, 835 (1935).

(2) W. H. Rodebush and M. H. Wahl, *J. Chem. Phys.*, **1**, 396 (1933).

(3) R. W. Campbell and W. H. Rodebush, *ibid.*, **4**, 298 (1936).

(4) O. Oldenberg, *ibid.*, **3**, 266 (1935).

(5) K. H. Geib, *Z. physik. Chem.*, **A170**, 1 (1934).

(6) W. H. Rodebush, *J. Phys. Chem.*, **41**, 283 (1937).

(7) W. H. Rodebush and W. C. Klingelhoefer, THIS JOURNAL, **55**, 130 (1933).

(8) E. Wrede, *Z. Physik*, **54**, 53 (1929).

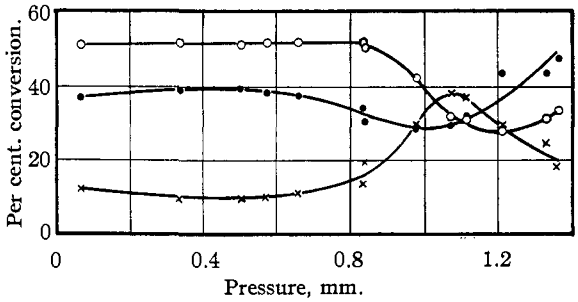

Fig. 1.—Conversion of water to hydrogen peroxide and permanent gases with a trap at −180°: ○, peroxide at −180°; ●, water at −180°; ×, "loss."

2. **The Reaction in the Trap at −80°.**—When dissociated water vapor was passed directly into a trap at −80° followed by a trap at −180°, the results of Fig. 2 were obtained. Any water vapor present as such should have condensed in the first trap, and any active species reaching the liquid air trap should have formed water and peroxide, in accordance with the results of the foregoing experiment. Figure 2 shows that the predominating reaction in the first trap led to the formation of permanent gases. Peroxide was found in the second trap only at the lower end of the pressure range, and the peroxide yields dropped sharply as the pressure was raised. Above 0.6 mm. the reaction took place entirely in the first trap.

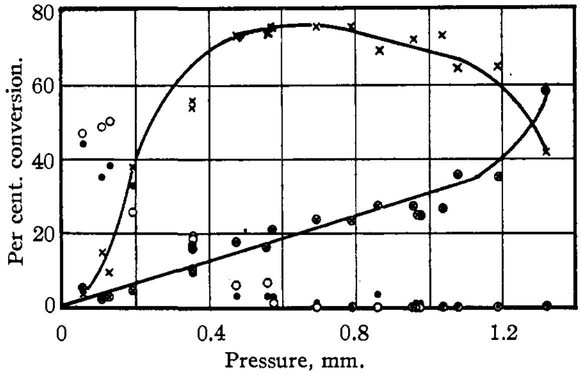

Fig. 2.—Conversion of water to hydrogen peroxide and permanent gases with a trap at −80° followed by a trap at −180°: ⊗, water at −80°; ○, peroxide at −180°; ●, water at −180°; ×, "loss."

The curve for water appearing in the first trap is approximately linear through most of the pressure range, with a sharp upturn at the upper end which is probably due to a decrease in the efficiency of the discharge. If this water be regarded as the undissociated fraction, it is apparent that the degree of dissociation in these experiments varied from nearly 100% at the lowest pressure to about 70% at 1.0 mm.

3. **The Reaction in a 5000-cc. Chamber.**—A reaction chamber consisting of a 5-liter Pyrex balloon flask was interposed between the discharge and the traps. With liquid air as the refrigerant on the first trap, the results of Fig. 3 were obtained. Again, peroxide formation was observed only at the lower pressures; but in this case the predominating reaction at higher pressures led to the formation of water. The surprising thing about this experiment was the appearance of a sharp peak in the "loss" curve at 0.2 mm. pressure. It might be expected that at this pressure the rate of diffusion to the walls and reaction thereon would become important, but the 65% conversion to permanent gases is hard to account for on this basis alone.

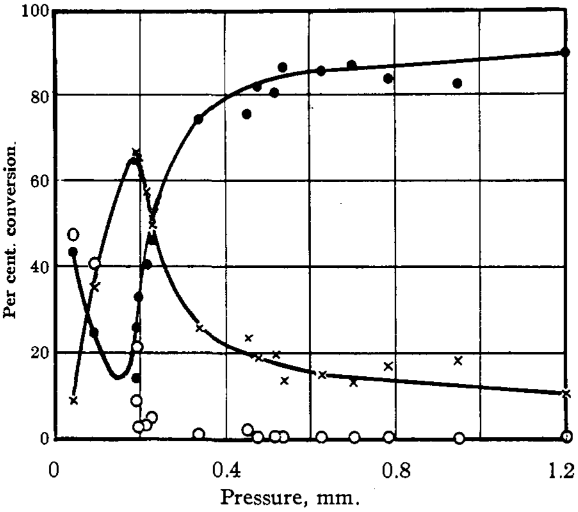

Fig. 3.—Conversion of water to hydrogen peroxide and permanent gases in a 5-liter reaction chamber: ○, peroxide at −180°; ●, water at −180°; ×, "loss."

The numbers of molecules of water ($\times 10^{-17}$) undergoing each reaction are plotted against pressure in Fig. 4.

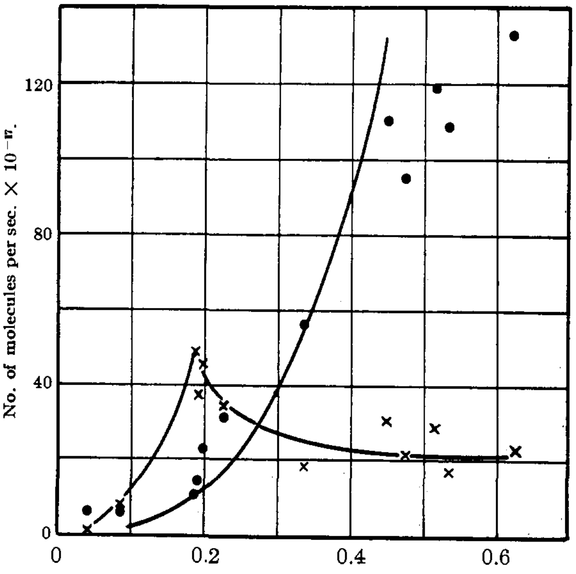

Fig. 4.—Conversion of water to hydrogen peroxide and permanent gases in a 5-liter reaction chamber: ●, water at −180°; ×, "loss."

This experiment was repeated with the first trap held at −80° and the second trap at −180°. The results are in general similar to those given above, with the exception that in this case the peak in the "loss" curve was 20% higher, due presumably to reaction in the first trap.

4. The Reaction in a Packed Chamber.—A reaction chamber having a volume of 700 cc. and a surface-volume ratio of 12.0 was constructed of a 45-mm. diameter Pyrex tube 80 cm. long. This was packed with 5-mm. Pyrex tubing and was used to test for the heterogeneous reaction at room temperature. The results obtained with this chamber are plotted as per cent. conversion against pressure in Fig. 5, and as numbers of molecules per second ($\times 10^{-17}$) in Fig. 6. The "loss" reaction predominated and water formation was comparatively small. Peroxide yields fell off sharply as the pressure was raised, indicating the disappearance of active species by permanent gas forming reactions on the Pyrex surface.

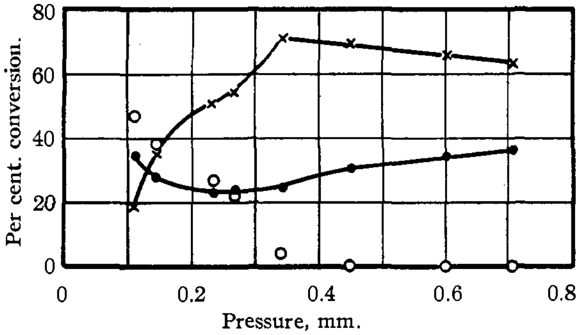

Fig. 5.—Products of dissociated water vapor in a packed chamber: ○, peroxide at −180°; ●, water at −180°; ×, "loss."

When the packed chamber was coated with potassium chloride, the composition of the products was fairly uniform throughout the pressure range: approximately 50% of the admitted water reappeared as such, and 50% was converted to permanent gases.

5. The Nature of the Products of Dissociation of Water Vapor.—The anomalous behavior of the pressure curves below 0.3 mm. (Fig. 3) suggested that the initial dissociation process might produce atomic oxygen at low pressures. Rodebush and Spealman[9] have shown that a strong afterglow is produced when atomic oxygen reacts with nitric oxide, and that this phenomeneon may be used as a sensitive test for oxygen atoms. Nitric oxide was admitted at various rates to the 5-liter reaction chamber while dissociated water vapor issued from the discharge. An afterglow was always present, but at pressures above 0.35 mm. it was confined to a volume of 100 cc. or less at the entrance to the chamber. As the pressure was lowered the glow spread through the flask, completely filling it at 0.2 mm. and below. This indicated that at the lower end of the pressure range considerable quantities of atomic oxygen were present.

This point was confirmed spectroscopically. A discharge tube having a quartz window in one end was fitted with supply lines for hydrogen, oxygen, or water vapor, and was connected to the pressure gage and pumping system. The spectrograph was a Bausch and Lomb instrument with quartz optical parts. Spectrograms of the emission spectra of water vapor, hydrogen, and oxygen were taken over a series of pressures. Comparison of the plates on water vapor with those on oxygen and hydrogen clearly indicated the presence of oxygen atoms in the discharge region at lower pressures.

6. Experiments with a Dehydrogenating Catalyst: the Oxidation of Carbon Monoxide.—The work of Jackson[10] indicated that the atomic hydrogen in dissociated water vapor could be destroyed selectively by a dehydrogenating catalyst such as platinum. If this were so, dissociated water vapor after passing over a platinum surface should consist mostly of H_2 and OH. These species are said to react together quite slowly[11] so that one might expect a reaction between hydroxyl molecules to take place. Either peroxide or water might be formed. In the latter case, oxygen atoms should be present, and these might presumably be detected by the nitric oxide test.

First, however, it was thought advisable to check Jackson's observations on the oxidation of carbon monoxide by dissociated water vapor. Carbon monoxide was admitted to the 5-liter reaction chamber by means of a small Hoke needle while dissociated water vapor was passing in from the discharge. In this experiment all traps were held at −80° to prevent the trapping out of carbon dioxide. Carbon dioxide formation was determined by collecting and analyzing the effluent gases.

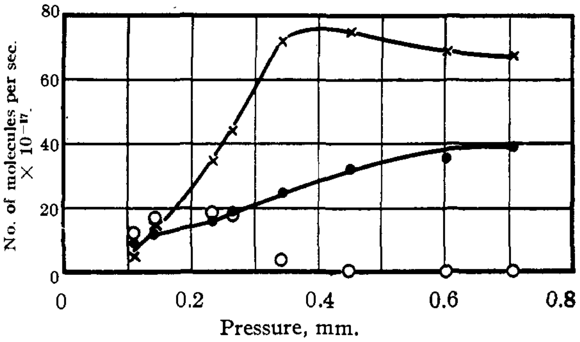

Fig. 6.—Products of dissociated water vapor in a packed chamber: ○, peroxide at −180°; ●, water at −180°; ×, "loss."

Average data for the two runs made are as follows: pressure, 0.6 mm.; reactants in millimoles per minute, H_2O, 0.86, CO, 0.56; per cent. conversions, water to water, 36%; CO to CO_2, 65%. These data indicate that the oxidation process was quite rapid. A platinum spiral was inserted in the system a short distance downstream from the discharge. When the discharge was turned on, the platinum glowed white hot and remained so throughout the run. Runs were made at 0.2 and 0.9 mm. pressure with only water vapor being admitted to the system. No peroxide was produced. About 60% of the water reappeared as such, and about 40% was converted to permanent gases. This high "loss" value suggested that hydroxyl molecules were being destroyed to give oxy-

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[9] W. H. Rodebush and M. L. Spealman, This Journal, **57**, 1474 (1935).

[10] W. F. Jackson, *ibid.*, **57**, 82 (1935).

[11] L. Farkas, F. Haber and P. Harteck, *Naturwissenschaften*, **18**, 266 (1930); G. von Elbe and B. Lewis, This Journal, **54**, 552 (1932); G. von Elbe, *ibid.*, **55**, 82 (1933).

gen atoms, possibly in the gas phase. The nitric oxide test was applied and found to give negative results.

Dissociated water vapor was led over the platinum spiral and mixed with carbon monoxide in the 5-liter chamber. The carbon dioxide yield was greatly reduced, as shown by the following data: pressure, 0.7 mm.; reactants in millimoles per minute: H_2O, 1.22; CO, 1.10; per cent. conversions: water to water, 72%; CO to CO_2, 14.6%.

It appeared that the discrepancy between the above data and the results of Jackson might be due to the fact that in these experiments the catalyst operated at a high temperature, so that activated adsorption of hydroxyl molecules might have occurred. To test this point, a water-jacketed catalyst chamber of 18-mm. Pyrex tubing, platinized on the inside, was interposed between the discharge chamber and the reaction vessel. Runs made with water vapor alone and with water vapor plus carbon monoxide were in general similar to the data obtained with the platinum spiral. In the latter case the loss was somewhat higher than before and the amount of carbon monoxide oxidized was zero.

7. The Reaction of Dissociated Water Vapor with Hydrogen.—If a fast water-forming reaction between OH and H_2 occurs, the mixing of dissociated water vapor with molecular hydrogen in the 5-liter chamber above about 0.6 mm. should increase the water yield. This experiment was performed, and it was found that the results were identical with those obtained when only water vapor was present.

8. The Reaction of Dissociated Water Vapor with Hydrogen–Oxygen Mixtures.—Dissociated water vapor was passed into an equal amount of a 1:1 mixture of hydrogen and oxygen and allowed to react in the 5-liter flask at pressures of 0.5–0.8 mm. In addition to the total amount of water originally introduced as such, there was trapped out an excess of 2–9% of water which must have been formed from the hydrogen and oxygen. The nitric oxide test was negative. It will be shown later that this suggests a reaction between hydroxyls, probably heterogeneous, by which water is formed.

The Reaction of Hydrogen Atoms with Oxygen Molecules.—"Dry" atomic hydrogen was produced by the method of Rodebush and Spealman;[12] the percentage dissociation was determined by a Wrede gage, and the gas was then passed through a constriction and into the reaction chamber. Dry oxygen was admitted to the chamber at a point several centimeters from the constriction. The products were trapped out and determined as before. Since the available pressure range from this experiment was limited, the most significant variable here was the ratio of admitted hydrogen atoms to oxygen molecules.

1. The Reaction in the Trap at −180°.—The mixture of oxygen and atomic hydrogen was passed directly into a liquid air cooled trap. Results appear in Table I in the order of increasing H/O_2 ratio. Inspection of the data for runs 8, 7, and 6 indicates that peroxide formation cannot be accounted for on the basis of a reaction involving two hydrogen atoms per molecule of peroxide. The peroxide-to-water ratio averaged about 1.75 for runs in which the H/O_2 ratio was less than unity, and about 1.2 for runs in which the H/O_2 ratio was large. This suggests that the excess atomic hydrogen converted part of the peroxide to water on the walls. It is interesting to note that when hydrogen atoms were present in excess the oxygen reacted almost quantitatively.

TABLE I

Run	Ratio H/O_2	P, mm.	Reactants H_2	Reactants H	Reactants O_2	Products H_2O	Products H_2O_2	Fraction H react.	Fraction O_2 react.
8	0.27	0.51	83.8	18.6	68.0	6.18	10.9	0.92	
7	.50	.25	51.0	28.8	57.1	7.90	13.8	.75	
6	.94	.22	46.7	64.8	68.8	17.7	31.2	.75	
1	2.65	.46	118.0	67.0	25.2	13.8	18.8	.49	1.01
2	5.40	.36	68.9	183.0	33.8	19.0	22.6		0.95
3	5.80	.38	74.0	189.0	32.6	19.1	20.6		.92
5	6.61	.31	146.0	212.0	32.2	14.8	22.4		.93
4	6.73	.40	157.0	232.0	34.5	25.7	25.0		1.09

2. The Reaction in a 100-cc. Chamber.—A reaction chamber of 25-mm. Pyrex tubing having a volume of 100 cc. and a surface–volume ratio of 1.6 was interposed between the oxygen inlet and the liquid air trap. The H/O_2 ratio was varied from 0.06 to 10.3 in the course of ten runs. In this case, the higher percentages of peroxide were obtained for H/O_2 ratios greater than unity. This fact indicates a disappearance of hydrogen atoms by a water-forming reaction in the chamber. When sufficient quantities of atomic hydrogen reached the trap, however, the cleanup of oxygen was complete (100% in the last five runs) and high percentages of peroxide were found.

3. The Reaction in a 1000-cc. Chamber.—A reaction chamber of 25-mm. Pyrex tubing having a volume of 1000 cc. and a surface–volume ratio of 1.6 was installed. This tube was about two meters long and was bent into a U shape. The H/O_2 ratio was varied from 0.67 to 4.4 in the course of seven runs. For low H/O_2 ratios, only about 50% of the atomic hydrogen reacted, and water was the sole product. With higher H/O_2 ratios, peroxide was formed in amounts that increased as the H/O_2 ratio was raised and the rate of flow was stepped up. Recombination on the walls reduced the efficiency of the reaction.

4. The Reaction in a 5000-cc. Chamber.—In order to reduce wall effects and to obtain some information as to the efficiency of the gas phase reaction, a 5-liter Pyrex flask was set up as a reaction chamber. The results are given in Table II. For low H/O_2 ratios, the sole product was water and more than 80% of the atomic hydrogen reacted, supporting the view that the inefficiency observed in preceding experiments was due to wall recombination. Higher H/O_2 ratios and higher rates of flow produced peroxide, as before.

TABLE II

Run	Ratio H/O_2	P, mm.	Reactants H_2	Reactants H	Reactants O_2	Products H_2O	Products H_2O_2	Fraction H react.	Fraction O_2 react.
3	0.42	0.48	95.6	58.1	139.0	49.5	Trace	0.85	
4	.51	.41	96.2	60.9	118.0	49.5	0.5	.82	
5	2.0	.36	119.0	159.0	78.5	85.5	4.1		0.60
1	2.5	.35	135.0	220.0	89.0	101.0	10.1		.69
2	2.7	.60	396.0	224.0	82.5	116.0	9.1		.81

5. The Reaction in a Trap at −80°.—Atomic hydrogen is known to pass through a trap held at −80° with a loss of

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[12] W. H. Rodebush and M. L. Spealman, THIS JOURNAL, **57**, 1010 (1935).

only 20% or so. Peroxide formation, however, does not occur at this temperature. If a mixture of oxygen and excess atomic hydrogen were passed through a trap at −80° and into one at −180°, one would expect to find a small amount of water in the first trap and a complete cleanup of oxygen in the second trap, with formation of both peroxide and water. The results of this experiment, shown in Table III, indicate that the principal reaction took place in the first trap. The column headed "H_2O^*" gives the water yields in the first trap; other headings have the same significance as before. Peroxide yields in the second trap increased with increasing H/O_2 ratio, as predicted, but the cleanup of oxygen was less than was expected. This points to a reaction in the first trap which destroyed atomic hydrogen or active species formed from it.

TABLE III

Run	Ratio H/O_2	P, mm.	Reactants H_2	Reactants H	Reactants O_2	Products H_2O^*	Products H_2O	Products H_2O_2	Fraction O_2 react.
1	1.8	0.43	100.0	77.0	43.0	15.9	0.28	0	0.19
3	3.0	.38	91.8	103.0	33.8	12.7	1.68	1.65	.26
2	5.9	.46	153.0	158.0	26.2	16.8	3.80	1.96	.47

6. **The Reaction in a 5000-cc. Flask; Trap at −80°.**—Three runs were made with the 5-liter chamber, with the first trap at −80° to substantiate the fact that water formation was completed in the flask. The results were in close agreement with the data of Table II.

7. **Test for the Formation of Pure Peroxide at Liquid Air Temperature.**—If all the water formed in the trap reaction experiments were due to the decomposition of peroxide, the admission of water vapor into the trap along with the reacting gases might be expected to favor the conversion of atomic hydrogen to peroxide, since peroxide on the walls would be diluted by the added water. The conditions of the runs at the bottom of Table I were reproduced and water vapor was passed into the trap during the reaction. The water and peroxide yields checked those of Table I within a few per cent., showing that water was not formed by the decomposition of pure peroxide. This fact, of course, is also substantiated by the observation of complete cleanup of oxygen for large H/O_2 ratios.

8. **Test for Gas-Phase Formation of Peroxide.**—Peroxide formed as an intermediate in the gas phase might have been destroyed by the atomic hydrogen present. If this were so, hydrogen peroxide should have appeared in a trap at −80° when small amounts of atomic hydrogen were allowed to react with large amounts of molecular hydrogen and oxygen in the 5-liter flask.

The apparatus was changed so that mixtures of hydrogen and oxygen could be swept past the nozzle of the discharge tube, from which issued small amounts of atomic hydrogen. Hydrogen and oxygen were admitted in roughly equal amounts. Atomic hydrogen was admitted in amounts less than one-tenth the amount of molecular hydrogen. The total pressure in the flask was 0.8–0.9 mm. Appreciable quantities of water were obtained in thirty-minute runs, but no peroxide was detectable.

9. **Test for the Presence of Oxygen Atoms in the H plus O_2 Reaction.**—Nitric oxide was passed into the 5-liter flask while the H plus O_2 reaction was taking place. The rates of flow of all gases were varied. An extremely faint afterglow could be seen if the room were darkened; but atomic hydrogen alone produced a slightly stronger afterglow. The admission of small quantities of oxygen through the discharge produced a brilliant afterglow. It therefore appears unlikely that any gas-phase reaction involving oxygen atoms occurs under these conditions.

The Reaction of Oxygen Atoms with Hydrogen Molecules.—Atomic oxygen was allowed to react with molecular hydrogen in the 5-liter chamber, and the products were frozen out in liquid air. Small amounts of water were obtained. The collision probability for a reaction between O and H_2 was found to be 10^{-8} at room temperature. This is in agreement with the result of Harteck and Kopsch.[13]

Discussion

From the experimental work that has been presented herewith it appears certain that water is formed in the gaseous phase by at least two different homogeneous reactions.

It seems certain that one may eliminate the homogeneous bimolecular reaction $H + O_2 = OH + O$ from consideration. This reaction cannot occur in the products from the discharge in water vapor because there is no molecular oxygen present. It would be the first mechanism to suggest itself in the case of the reaction between hydrogen atoms and molecular oxygen but here it is impossible to account for the amount of water produced by this mechanism and any which might follow in the gas phase. Furthermore, the nitric oxide test for atomic oxygen failed to show the presence of oxygen atoms and, finally, the reaction is probably endothermic by 10 cal., which makes it a very improbable reaction.

The only possible mechanisms therefore are those involving triple collision or reactions on the walls of the flask. Calculations show that the number of collisions occurring at the wall surface in the 5-liter flask is too small to account for any considerable amount of the water formed unless of course there is a considerable amount of adsorption. But the experiments in which a large ratio of surface to volume existed, indicate that the predominant heterogeneous reaction at 25° is not the formation of water at all. Hence one concludes that the primary mechanism involved in the formation of water in the gas phase must involve triple collisions. If one calculates the number of triple collisions occurring in the large chamber by the conventional method, using standard kinetic theory values for collision diameters, etc., he does not obtain a sufficient number of triple collisions to account for the amount of reaction. The uncertain factor in the conventional picture

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(13) P. Harteck and U. Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

of a triple collision is "ϑ" the mean path of the bimolecular "collision complex." It has ordinarily been assumed to have a value of 10^{-9} cm. and this is probably true in the case of the recombination of hydrogen atoms.[14] However, Kimball[15] has published recently a calculation of the mean life period of various bimolecular collision complexes. This mean life period is of course directly related to the mean path. Kimball infers that bimolecular condensations may occur when the resulting molecule is sufficiently complex. The most important result of Kimball's calculation, however, appears to us to be that because of the much larger value of ϑ permitted the number of triple collisions as calculated by the conventional method is greatly increased. It is possible to obtain by a calculation, using a value of 10^{-8} for ϑ, from 10 to 100 collisions per molecule of water formed. This is a larger probability of reaction per collision than one would wish to assume but at least one aspect of the matter is satisfactorily explained. Because of the larger value of ϑ the formation of water is a much more rapid reaction in the gas phase than the recombination of hydrogen atoms.

The reaction which takes place in the gaseous phase in dissociated water vapor is evidently

$$H + OH + M \longrightarrow H_2O + M \qquad (1)$$

This agrees with the conclusion of Frost and Oldenberg, who observed the rapid disappearance of hydroxyl at somewhat higher pressures under which conditions the number of triple collisions is large. It is of course impossible to decide from our data whether this reaction is second order or third. A calculation of the number of collisions shows however that the reaction probability is 10^{-8} for double collisions and 10^{-2} for triple collisions. Some additional evidence in support of this conclusion will be mentioned later.

The reaction between hydrogen atoms and molecular oxygen leads to the formation of water only at low pressures, provided the hydrogen atoms are all used up before reaching the trap. This is in marked contradiction to the results obtained at high pressures in the photochemical reaction where large yields of hydrogen peroxide have been reported. We shall not attempt to resolve this apparent contradiction of experimental results but shall limit ourselves to a discussion of the reaction by which water could be found at low pressures. The over-all reactions in this case must be

$$H + O_2 + H_2 \longrightarrow H_2O + OH \qquad (2)$$
$$H + OH \longrightarrow H_2O \qquad (3)$$

Reaction (2) may of course take place in steps. The first step may be

$$H + O_2 + M \longrightarrow HO_2 + M$$

but whether the molecule HO_2 has anything more than the fugitive existence calculated by Kimball cannot be demonstrated from our data. The second step then is apparently

$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (4)$$

At higher pressures in the photochemical reaction it has been assumed that this reaction is

$$HO_2 + H_2 \longrightarrow H_2O_2 + H \qquad (5)$$

thus accounting for the large yield of hydrogen peroxide. It is possible that (5) is occurring at low pressures and is then followed by the reaction

$$H_2O_2 + H \longrightarrow H_2O + OH \qquad (6)$$

This last reaction is known to take place[5] rapidly, and, with a high concentration of hydrogen atoms, might be expected to account for the disappearance of large amounts of hydrogen peroxide. Reaction (3) must take place also but since it involves triple collisions and is much slower it could not account for the disappearance of many hydrogen atoms. The recombination of hydrogen atoms is even slower so that it is possible that each hydrogen atom produced in (2) may eventually destroy one hydrogen peroxide molecule, thus accounting for the failure to obtain traces of hydrogen peroxide when conditions were such as to ensure the reaction of all the hydrogen atoms initially present, with oxygen. When the ratio of hydrogen atoms to oxygen molecules was large, hydrogen peroxide was obtained but in this case hydrogen atoms were reaching the trap and a heterogeneous reaction is indicated.

Assuming that the above reactions are taking place the disappearance of hydroxyl must be accounted for. Some of it undoubtedly disappears by a heterogeneous reaction with the walls of the chamber which will be discussed later. It must be assumed however that most of it disappears by reaction (3) with hydrogen atoms which have not yet reacted with molecular oxygen. Reaction (6) must be rapid as compared to reaction (3); otherwise, some hydrogen peroxide must escape destruction and reach the trap. At any rate under conditions in which the hydrogen atoms are all used up before reaching the trap no hy-

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[14] H. M. Smallwood, THIS JOURNAL, **56**, 1542 (1934).

[15] G. E. Kimball, *J. Chem. Phys.*, **5**, 310 (1937).

drogen peroxide was obtained and if it is formed as any intermediate product it must be completely destroyed. This fact seems rather surprising.

The Formation of Hydrogen Peroxide.—According to the calculations of Kimball the bimolecular complex formed from two hydroxyls should have a rather long life (10^{-10} sec.) and should therefore be likely to be stabilized by collision. A considerable amount of hydrogen peroxide should therefore be formed in the gas phase but it would perhaps be destroyed immediately by reaction with atomic hydrogen. At any rate the formation of hydrogen peroxide was only observed as a heterogeneous reaction on liquid air cooled surfaces. In dissociated water vapor hydrogen peroxide is undoubtedly produced by direct combination of hydroxyls adsorbed on the walls. In the experiments on the reaction between hydrogen atoms and oxygen molecules in a trap cooled with liquid air the yield of hydrogen peroxide is too large to be accounted for by a direct combination of hydrogen atoms with oxygen as suggested by Geib.[16] One may therefore postulate a heterogeneous chain mechanism

$$H + O_2 + H_2 \longrightarrow H_2O_2 + H \qquad (8)$$

Various attempts were made to alter conditions in such a way as to bring about hydrogen peroxide formation in the vapor phase. For example Jackson[10] has reported that platinum acts as a catalyst for the recombination of hydrogen atoms without destroying the oxidizing action of dissociated water vapor upon carbon monoxide. While we found that dissociated water vapor oxidizes carbon monoxide rapidly, we were unable to obtain the results reported by Jackson with a catalyst. Whenever the catalyst was used in a manner that was at all effective all activity of the dissociated water vapor was destroyed.

Other Heterogeneous Reactions.—When hydroxyl encounters a surface at a temperature of −80° or higher the reaction

$$OH + OH = H_2 + O_2 \qquad (9)$$

must take place as is indicated by experiments on dissociated water vapor with a packed chamber, or with a trap cooled with dry ice. At liquid air temperature of course hydrogen peroxide is formed. One may speculate as to the reason for this effect of temperature but it is not possible to obtain any experimental evidence to verify the speculations.

There is no evidence for a reaction

$$OH + OH \longrightarrow H_2O + O \qquad (10)$$

as suggested by Bonhoeffer and Pearson,[17] and the test for oxygen atoms with nitric oxide indicates that this reaction is not taking place. The formation of elementary hydrogen and oxygen in dissociated water vapor is illustrated by the curves in Figs. 4 and 5. A sharp peak appears in the curve at 0.2 mm. This peak is due to the superposition of two or more effects. Reaction (9) by which hydrogen and oxygen are produced on the walls of the reaction chamber is undoubtedly going on to a considerable extent. At low pressures the rate of this reaction should increase as the square of the pressure but at higher pressures the rate of diffusion becomes the slow stage of the process and reaction (9) ceases to be important as compared with the water forming reaction (1). It is interesting to note that, if the curves for the rate of formation of water and gases as a function of the pressure are compared, the rate of formation of water appears to depend upon the pressure to a higher power by one than the rate of formation of gases. This tends to confirm the notion that the formation of water is a third order reaction.

Another factor which must be taken into account in interpreting Fig. 4 is that a lower pressure of water vapor in the discharge is dissociated not into hydrogen and hydroxyl but into hydrogen and oxygen atoms. We have shown this both by spectrograms of the discharge which show the line spectrum of oxygen and also by making the nitric oxide test for atomic oxygen. Since as has been shown atomic oxygen does not react with hydrogen but recombines to form molecular oxygen, this results in the formation of permanent gases. With higher pressures the percentage of oxygen atoms produced in the discharge decreases markedly.

The experimental evidence indicates that the recombination of hydrogen atoms in a trap at −80° is accelerated by the presence of molecular oxygen. This is probably due to the adsorption of the molecule HO_2 resulting in the reactions

$$H + HO_2 \longrightarrow H_2 + O_2$$
$$HO_2 + HO_2 \longrightarrow H_2 + 2O_2$$

Summary

Water is formed by at least two different homo-

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[16] K. H. Geib, *J. Chem. Phys.*, **4**, 391 (1936).

[17] K. F. Bonhoeffer and T. G. Pearson, *Z. physik. Chem.*, **B14** 1 (1931).

geneous reactions at low pressures. One of these is undoubtedly $H + OH + M \longrightarrow H_2O + M$. The water-forming reaction between hydrogen atoms and oxygen may involve the formation of hydrogen peroxide as an intermediate but the failure to obtain any evidence of the formation of hydrogen peroxide in the gaseous phase is rather surprising.

The heterogeneous reaction of hydroxyl appears to result in the formation of hydrogen and oxygen. No evidence was obtained for a homogeneous reaction between hydroxyls.

There is no indication that the HO_2 molecule is anything more than a "collision complex" of very short life.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF STANFORD UNIVERSITY]

The Kinetics of the Pyrolysis of *n*-Propyl Iodide and *n*-Butyl Iodide

BY J. L. JONES AND R. A. OGG, JR.

In this paper are presented the results of the kinetic studies on the thermal decompositions of gaseous *n*-propyl and *n*-butyl iodides. The *n*-propyl iodide was studied in the temperature range of 584 to 627°K. and the *n*-butyl iodide in the temperature range of 590 to 624°K. The two compounds decomposed somewhat similarly, but the *n*-butyl iodide could not be treated quantitatively, for reasons which will be given later.

Two other papers will treat respectively the kinetics of the decomposition of isopropyl iodide and the equilibrium established between *t*-butyl iodide and its pyrolytic products, *e. g.*, isobutylene and hydrogen iodide. These three papers in conjunction with the two papers mentioned below constitute a more or less coherent series of studies on the thermal decomposition of the alkyl iodides which should facilitate a better understanding of the free radicals involved in such reactions and of the strength of the bonds affected by the pyrolysis.

The thermal decomposition of *s*-butyl iodide was investigated by Ogg[1] in the temperature range 238–276°. He found that the results were best fitted as a combination of a unimolecular reaction plus an iodine catalyzed decomposition of the iodide.

$$-\frac{d(C_4H_9I)}{dt} = k_1(C_4H_9I) + k_2(C_4H_9I)(I_2)^{1/2} \quad (1)$$

The activation energies for the two reactions were 39,420 and 35,220 cal., respectively. If the iodine catalyzed reaction was considered to occur between an iodine atom and a butyl iodide molecule, the activation energy of the reaction became 35,220 cal. minus one-half the heat of dissociation of an iodine molecule (*e. g.*, 18,400 cal.), or 16,820 cal.

The gas phase reaction between hydrogen iodide and methyl, ethyl and *n*-propyl iodides, respectively, was investigated by Ogg[2] in the temperature range 250–300°. The reaction proceeded exclusively by the over-all reaction

$$RI + HI \longrightarrow I_2 + RH$$

His kinetic studies indicated that the reactions proceeded by a common mechanism, which was the sum of a simple bimolecular metathesis, as above, and a complex rate expression, being given by

$$\frac{d(I_2)}{dt} = k_1(RI)(HI) + k_2\frac{(RI)(HI)}{(I_2) + (HI)} \quad (2)$$

k_2 has the dimensions of a unimolecular rate constant, *e. g.*, seconds^{-1}. The bimolecular reaction has an activation energy of 33,000, 29,800 and 29,200 cal. for the methyl, ethyl and *n*-propyl iodides, respectively, while the unimolecular reaction has an activation energy of 43,000 cal. for all three iodides. Much evidence[2] indicates that the dissociation energy of the C–I linkage is approximately equal to the activation energy of the above unimolecular reaction, *e. g.*, 43,000 cal.

Experimental Section

Preparation of Alkyl Iodides.—The *n*-propyl and *n*-butyl iodides were prepared by the method of Bogart and Slocum,[3] *e. g.*, by the action of red phosphorus and iodine on the *n*-alcohol. The dry *n*-propyl iodide employed boiled over the range of 102.5 to 102.8°. The *n*-butyl iodide had a boiling range of 128.0 to 128.2°.

Apparatus and Procedure.—The Pyrex reaction flask (about 800-cc. capacity) was contained in an electrically heated air thermostat provided with an efficient stirrer.

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(1) Ogg, *Trans. Faraday Soc.*, **31** 482 (1934).

(2) Ogg, THIS JOURNAL, **56**, 532 (1934).

(3) Bogart and Slocum, *ibid.*, **46**, 764 (1924).