merizes readily in solution, probably through rupture of a nitrogen–carbon bond, while this behavior is not shown by the azodicarbonate.

Consequently the actual increase in sensitivity to acid catalysis due to the double negative charge may well be much greater than shown by simple comparison of these two cases. It is significant that the positively charged hydrogen ion shows three times as great an increase in catalytic effect as the neutral water molecule. The effect of the charge of the catalyzing acid has been discussed in detail by Pedersen.[12]

The strength of azodicarbonic acid cannot be estimated easily, because of its instability and the nature of the decomposition products. It is almost certainly too strong to allow appreciable amounts of the acid ion or molecular acid to exist in the alkaline solutions used here. The general acid catalysis excludes spontaneous decomposition of traces of acid or acid ion as the mechanism of the reaction; but spontaneous decomposition of small amounts of equimolecular ion-acid compounds in equilibrium with the components would be indistinguishable from the bimolecular mechanism postulated. Neither mechanism accounts for the depressing effect of bases on the molar acid catalysis, found here for sucrose and in the diazoacetate decomposition for other acids.

The author is indebted to Mr. Lewis Appleton, who carried out some of the experimental work reported here.

Summary

The decomposition of azodicarbonate ion to give nitrogen, hydrazine and carbon dioxide or carbonate ion, has been found to be extremely sensitive to general acid catalysis. It is catalyzed by water, hydrogen ion and other acids in accordance with the equation $dx/dt = C_{N_2(COO)_2^{=}}(k_1C_{H_3O^+} + k_2C_{H_2O} + k_3C_{HA} + \ldots)$. That this equation does not completely explain the mechanism is shown by the fact that the molar catalysis by sucrose (and probably by other weak acids) is diminished by bases (hydroxyl ion, sucrate ion, etc.).

The molar catalysis constants as evaluated show good agreement with the Brönsted equation $k_m/p = G(q/pK^0_A)^x$ where $G = 7.40 \times 10^8$ and $x = 0.86$. This value of G is the highest yet found for acid catalysis; the value of x is similar to that found in several other cases.

WASHINGTON SQUARE COLLEGE
NEW YORK, N. Y.
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(12) Pedersen, *J. Phys. Chem.*, **38**, 581 (1934).

[CONTRIBUTION FROM THE WILLIAM H. CHANDLER CHEMISTRY LABORATORY OF LEHIGH UNIVERSITY]

The Photochemical Oxidation of Hydrogen[1]

BY HILTON A. SMITH AND A. NAPRAVNIK

There have been reported three earlier studies[2,3,4] of the photochemical oxidation of hydrogen by light of wave length 1719–1725 Å. The first of these papers dealt with the over-all temperature coefficient of the reaction, while the other two resulted from studies of the individual products obtained, and the quantum yields of these products at room temperatures. The present paper reports the quantum yields of the individual products at elevated temperatures as well as additional room temperature data.

Experimental

In the last of the papers mentioned above, it was demonstrated that the reaction products were ozone, hydrogen peroxide, and water. Analysis of this mixture was carried out by pumping the exit gases from the reaction cell through an analyzing bubbler, after which they were dried and returned to the cell. Three successive runs were made on each hydrogen–oxygen mixture. During the first run the bubbler contained titanium sulfate solution. The hydrogen peroxide formed was absorbed in this solution and determined colorimetrically. During the second run the bubbler contained neutral potassium iodide solution. This absorbed both hydrogen peroxide and ozone. The bubbler liquid subsequently was acidified and the liberated iodine titrated with sodium thiosulfate. The yield of ozone was calculated by subtracting from this result the yield of hydrogen peroxide determined in the first run. Finally, a much longer run was made, again using potassium

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(1) Presented at the Boston meeting of the American Chemical Society, September 12, 1939.

(2) Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

(3) Kistiakowsky, THIS JOURNAL, **52**, 1868 (1930).

(4) Smith and Kistiakowsky, *ibid.*, **57**, 835 (1935).

iodide in the bubbler. The pressure drop found during this run was corrected for ozone and hydrogen peroxide absorbed in the bubbler, and the water yields subsequently calculated.

A critical study of these procedures was undertaken. As a result it was possible to show that while either ozone or hydrogen peroxide may be determined individually by absorption in neutral potassium iodide, and subsequent titration of the iodine liberated in the acidified solution,[5] the two cannot be analyzed by simultaneous absorption in such a solution. In the presence of each other they are evidently catalytically decomposed.[6] It was shown that under conditions such that both ozone and hydrogen peroxide are formed in appreciable quantities, the apparent yield of ozone plus hydrogen peroxide was much less than that of hydrogen peroxide alone. For example, the yield of hydrogen peroxide obtained by passing a gas mixture of 50 mm. of oxygen and 710 mm. of hydrogen before the light source used in this research was 8.66×10^{-7} mole per minute. In this mixture the yield of ozone is approximately equal to that of peroxide. When the products obtained using this same mixture were passed through a bubbler containing neutral potassium iodide (2.5% solution), the yield of ozone plus hydrogen peroxide was only 1.95×10^{-7} mole per minute, a value less than one-fourth that of either product.

Further experiments established the fact that, if the mixture of ozone and peroxide were first passed through a bubbler containing titanium sulfate solution and then through neutral potassium iodide, the hydrogen peroxide was removed by the first bubbler, while the ozone was removed by the second. The passage of ozone through the titanium sulfate solution affects neither the ozone yields nor those of peroxide. This method of analysis was used in the work reported here.

The experimental set-up was similar to that previously employed.[4] The light source consisted of a condensed spark operating in a nitrogen atmosphere between two slowly revolving aluminum disks.[7,8] The gases to be illuminated were circulated at a velocity of 700 ml. per minute through a thin-walled quartz vessel of approximately 1 ml. volume (this time of light exposure was too short to cause photochemical decomposition of the products), and then through the two ice-cooled absorption bubblers. After the ozone and hydrogen peroxide had been removed, the gases were dried by means of a dehydrite tube, and returned to the cell through an all-glass circulating pump. This pump was a modification of the type described by Balsbaugh, Larsen, and Lyon.[9] It had two barrels, and the solenoids around these barrels were connected in quarter phase to the same motor. Thus, pumping action occurred four times per cycle. The pump operated at a speed of 80 cycles per minute. A section of capillary tubing between the pump and the cell evened out the gas flow so that it was quite regular when exposed to the light source. The whole circulating system was connected through a capillary tube to a constant-volume manometer.

The oxygen and hydrogen used were generated by the electrolysis of a solution of sodium hydroxide. Air or tank nitrogen was used in experiments dealing with nitrogen–oxygen mixtures.

The procedure employed in making a run was as follows. After the system was filled with the desired pressures of hydrogen and oxygen, the circulating pump was allowed to run for about fifteen minutes in order to assure temperature equilibrium with the surroundings. The pressure and temperature of the system were then taken. The pump was again allowed to run for a few minutes, and pressure readings repeated. This was continued until constant readings were obtained. Next, the gases passing through the reaction cell were exposed to the light source for a definite length of time, generally thirty minutes. After the illumination, the temperature was adjusted to its pre-run value, and pressure readings taken as before. The two bubblers were subsequently removed from the system, and ozone and peroxide yields determined. The pressure drop occurring during the run was corrected for the amounts of these products formed, and the water yield then calculated.

For runs at elevated temperatures, the thin-faced quartz cell was equipped with a thermocouple well which entered the cell from the gas-entrance side to a point just before that at which the reaction took place. Preceding the cell, and connected to it by a quartz to pyrex graded seal, was a short grill made from approximately four feet of pyrex tubing. The grill and cell were enclosed in a pyrex jacket to which was attached a long side arm, allowing entrance of the nitrogen into the cell jacket at a point behind the grill. The nitrogen emerged from the cell jacket through a round hole slightly less than one centimeter in diameter, this opening being directly between the thin face of the reaction cell and the spark. The cell jacket was insulated by placing it in a box packed with loose asbestos fibers, the front of the jacket emerging from the box for a distance of about one centimeter.

The side arm through which the nitrogen entered the cell jacket was wound with nichrome resistance wire. Heated nitrogen was blown over the pyrex grill at a rate of eight liters per minute, thus heating the gases passing into the reaction cell. Temperature equilibrium was established in the heat exchanger, and the temperature of the gases just before exposure to the light source was read by means of a copper–constantan thermocouple connected

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[5] *Cf.* Treadwell and Hall, "Analytical Chemistry," John Wiley and Sons, Inc., New York, N. Y., 8th edition, Vol. II, p. 573, and p. 576.

[6] *Cf.* Bray, This Journal, **60**, 82 (1938).

[7] Wiig and Kistiakowsky, *ibid.*, **54**, 1807 (1932).

[8] The authors are greatly indebted to Prof. G. B. Kistiakowsky for his generous loan of the sparker used in this research.

[9] Balsbaugh, Larsen and Lyon, *Ind. Eng. Chem.*, **28**, 682 (1936).

to a Leeds and Northrup potentiometer. During a run the temperature was kept constant to ±1°. Runs were made in the same manner as those performed at room conditions.

At the highest temperatures a number of experiments were tried without exposure to the light source. No dark reaction was detected.

As in earlier research,[4] each run with hydrogen–oxygen mixtures was preceded and followed by control runs made with air at atmospheric pressure in the system. The amounts of all products obtained were reduced to constant incident light intensity by means of these control runs. Since for experiments at elevated temperatures it was not feasible to cool the cell to room temperatures for the air runs, these were made under the same conditions as those of the corresponding hydrogen–oxygen runs.

A series of measurements of ozone yields in air at one atmosphere pressure and varying temperatures was made in order to study the effect of increased temperature on the yields of ozone. The results are given in Table I. They indicate clearly that in the mixture under consideration the amount of ozone formed is constant over the temperature range studied, and thus, that the control runs could be used without correction. This result is expected, since under the conditions of the runs, sufficient oxygen is present to absorb all of the light entering the cell. (Lyman[10] states that an air column one centimeter long completely absorbs the strong aluminum spark lines in the neighborhood of 1720 Å.)

Results

The quantum yields of the several products of each run were calculated by dividing such yields by the yield of ozone found in a mixture of nitrogen and oxygen containing the same partial pressure of oxygen as that of the hydrogen–oxygen run, and multiplying the resultant figure by two.[11] It has been demonstrated previously that neither reduction of total pressure nor dilution with nitrogen affects the quantum yield of ozone in the nitrogen–oxygen mixtures.[4] Table I indicates that the temperatures used in this research do not seriously alter its value.

TABLE I

EFFECT OF TEMPERATURE ON OZONE YIELDS IN AIR

T, °C.	Yields O_3 moles/min. $\times 10^6$
25	3.14
100	2.95
150	3.16
200	2.97
240	3.13
280	2.98

Quantum yields of ozone, hydrogen peroxide and water obtained at room temperatures using hydrogen–oxygen mixtures of total pressures varying from 1140 to 95 millimeters are given in the first five figures. In the case of runs made at 95 mm. pressure, it was difficult to obtain reproducible results, but the general trend of the curves is certainly correct.

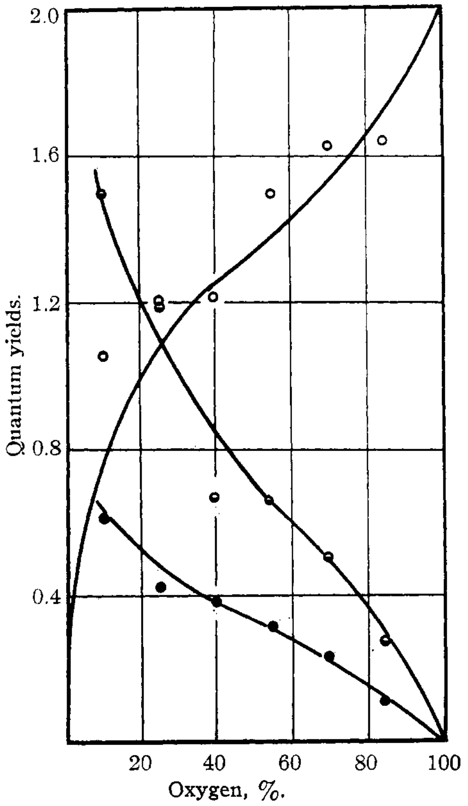

Fig. 1.—Quantum yields at 1140 mm. pressure: ○, ozone; ⊖, water; ●, hydrogen peroxide.

The quantum yields were not corrected for reaction due to absorbed light of wave lengths 1854–1862 Å., these corrections having been shown to be small in the case of a cell of the type used in this research.[4] This is particularly true at low pressures.

An examination of the figures shows the following:

1. With increasing oxygen content, the quantum yields of ozone increase, rapidly at first, and then more slowly, to a maximum value of two. The yields of water and hydrogen peroxide decrease quite regularly, the water yields always being greater than those of peroxide.

2. Pressure change from 1140 to 380 mm. has the following effect on the quantum yields of the three reaction products. The yields of both water and hydrogen peroxide increase, while that of ozone is decreased. These changes are minor

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(10) Lyman, "The Spectroscopy of the Extreme Ultra-violet," Longmans, Green and Co., London, 1928.

(11) *Cf.* Vaughan and Noyes, THIS JOURNAL, **52**, 559 (1930).

at high pressures, but become more pronounced at low pressures, as the results at 190 and 95 mm. total pressure indicate. The increase in water yields is much greater than that of peroxide yields, values as great as 14 having been found for water at 95 mm.

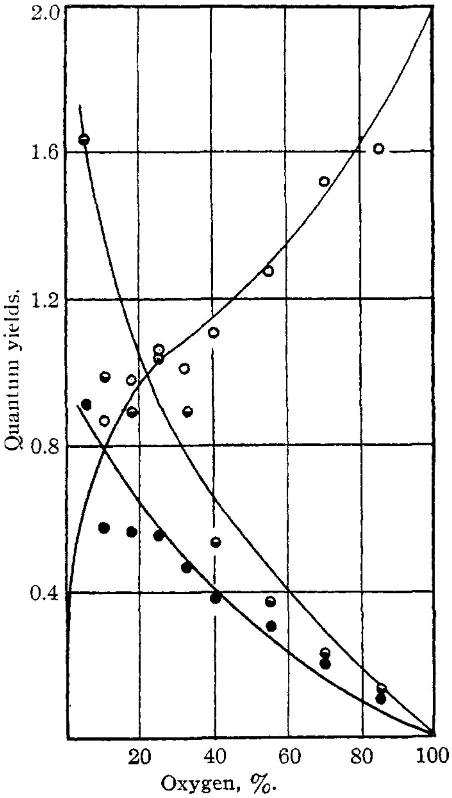

Fig. 2.—Quantum yields at 760 mm. pressure: ○, ozone; ⊖, water; ●, hydrogen peroxide.

The results found using hydrogen–oxygen mixtures of 190 mm. total pressure and temperatures from 25 to 280° are given in Figs. 6, 7, and 8. They indicate that the quantum yields of ozone fall off with increasing temperature until this product becomes undetectable at temperatures as low as 150° for mixtures containing 10% oxygen, and higher temperatures for mixtures containing larger percentages.

In the case of water and hydrogen peroxide, the quantum yields are greatly increased with rise in temperature, the increase being relatively small at first, but subsequently becoming very rapid. The hydrogen peroxide yields are always much smaller than those of water, but the changes in the curves parallel each other very closely.

Similar results were obtained at higher total pressures, although the region of rapid rise in the quantum yields of water and peroxide was not found in the temperature range studied.

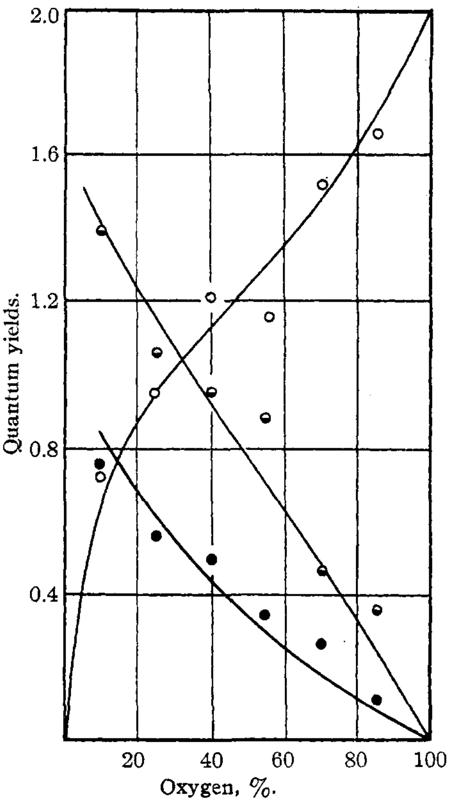

Fig. 3.—Quantum yields at 380 mm. pressure: ○, ozone ⊖, water; ●, hydrogen peroxide.

Discussion

In general, the above results are explainable through a rather simple mechanism. The primary reaction is unquestionably that of rupture of an oxygen molecule to form two oxygen atoms.[12]

$$O_2 + h\nu \longrightarrow 2O \qquad 2I_{abs.} \quad (1)$$

This is followed by interaction of the atoms formed with molecules of oxygen and hydrogen. There is good evidence[13] that the oxygen atom will react with oxygen molecules to form ozone on triple collisions only.

$$O + O_2 + M \longrightarrow O_3 + M \qquad k_2 \quad (2)$$

As to its reaction with hydrogen, two possibilities exist. The first is that the oxygen atom may combine with hydrogen in a triple collision to form water.

$$O + H_2 + M \longrightarrow H_2O + M \qquad (3a)$$

In order to explain the experimental results it is

(12) Herzberg, *Z. physik. Chem.*, **4B**, 223 (1929).

(13) *Cf.* Schumacher, THIS JOURNAL, **52**, 2377 (1930).

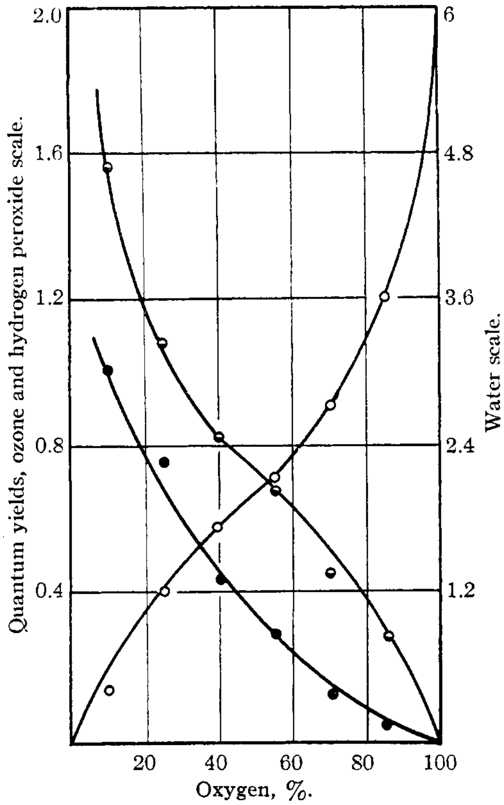

Fig. 4.—Quantum yields at 190 mm. pressure: O, ozone; ⊖, water; ●, hydrogen peroxide.

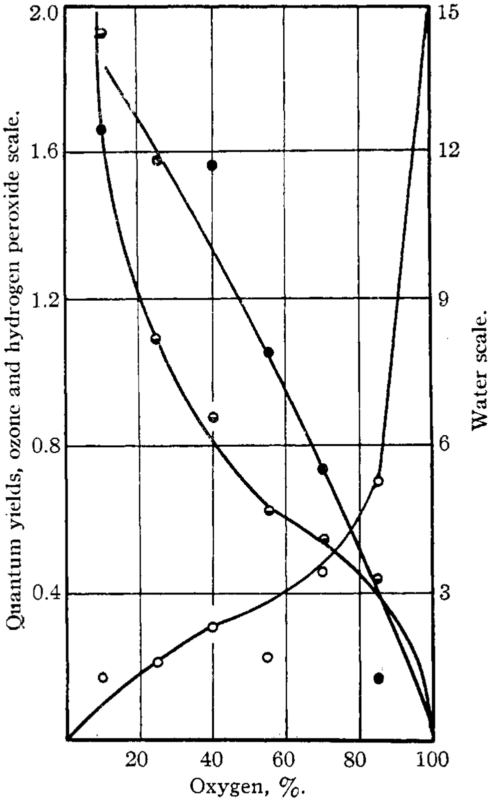

Fig. 5.—Quantum yields at 95 mm. pressure: O, ozone; ⊖, water; ●, hydrogen peroxide.

necessary to assume that in this reaction the third body is an oxygen molecule rather than a hydrogen molecule. However, it will be pointed out farther on that the possibility of hydrogen as the third body is not excluded.

$$O + H_2 + O_2 \longrightarrow H_2O + O_2 \qquad k_3 \quad (3)$$

The oxygen atoms may also react with the hydrogen molecules through a bimolecular collision.

$$O + H_2 \longrightarrow OH + H \qquad k_4 \quad (4)$$

The probability of this reaction is low,[14,15] but because other reactions require three-body collisions, the reaction is important, particularly at low pressures. The only logical fate of the OH radical is a reaction with hydrogen to form water and a hydrogen atom.

$$OH + H_2 \longrightarrow H_2O + H \qquad (5)$$

Finally, there is rather conclusive evidence that the sole result of the action of hydrogen atoms on a mixture of hydrogen and oxygen at room temperature and ordinary pressures is the formation of hydrogen peroxide.[16,17] The first step is the formation of the complex HO_2, which must take place by a triple collision mechanism.[18]

$$H + O_2 + M \longrightarrow HO_2 + M \qquad (6)$$

In order to explain the results of the mercury-sensitized reaction, Bates[19] postulated that HO_2 may react with hydrogen to form hydrogen peroxide and hydrogen atoms.

$$HO_2 + H_2 \longrightarrow H_2O_2 + H \qquad (7a)$$

This reaction is, however, energetically improbable at room temperatures. The logical fate of this radical is its reaction with another HO_2 either in the gas phase or on the walls to form hydrogen peroxide and oxygen; such a reaction was proposed by Bray[6] for the reaction in solution, and was also included in Bates' mechanism.

$$HO_2 + HO_2 \longrightarrow H_2O_2 + O_2 \qquad (7)$$

It should be noted, however, that the particular method by which hydrogen atoms react with the

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[14] Harteck and Kopsch, *Z. physik. Chem.*, **B12**, 327 (1931).

[15] Rodebush, Wende, and Campbell, THIS JOURNAL, **59**, 1924 (1937).

[16] Bates and Salley, THIS JOURNAL, **55**, 110 (1933).

[17] Bonhoeffer and Bohm, *Z. physik. Chem.*, **119**, 385 (1926).

[18] Cook and Bates, THIS JOURNAL, **57**, 1775 (1935). See also von Elbe and Lewis, *J. Chem. Phys.*, **7**, 710 (1939).

[19] Bates, THIS JOURNAL, **55**, 426 (1933).

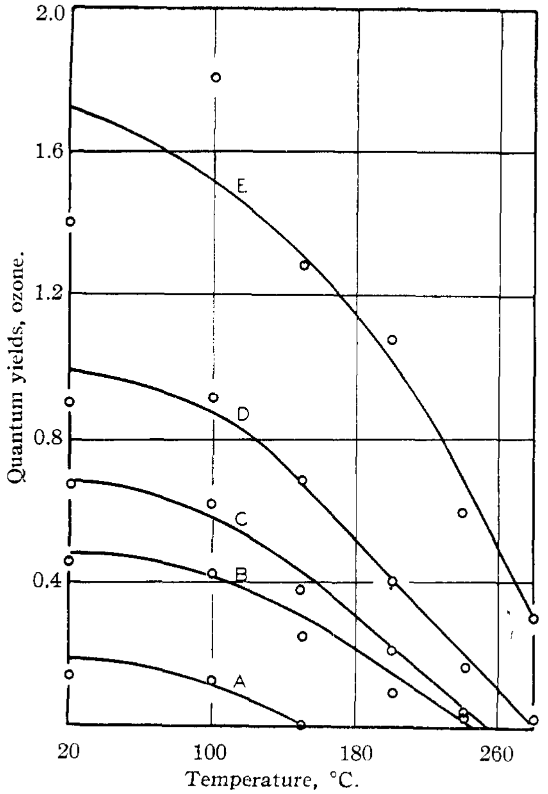

Fig. 6.—Quantum yields of ozone as a function of temperature, total pressure $H_2 + O_2$ = 190 mm.: A, 10% O_2; B, 30% O_2; C, 50% O_2; D, 70% O_2; E, 90% O_2.

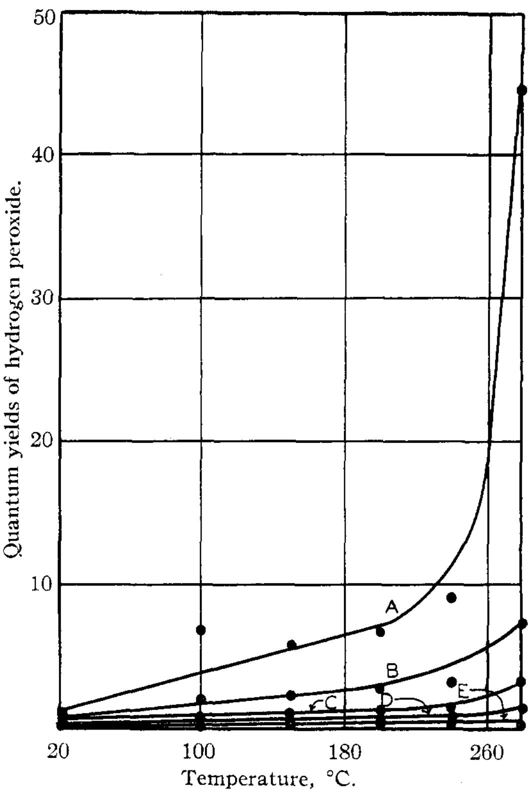

Fig. 7.—Quantum yields of hydrogen peroxide as a function of temperature, total pressure $H_2 + O_2$ = 190 mm.: A, 10% O_2; B, 30% O_2; C, 50% O_2; D, 70% O_2; E, 90% O_2.

gas mixture to form hydrogen peroxide may be altered without seriously affecting the resulting calculations.

Expressions for the quantum yields of the three products as calculated from the reaction mechanism given above are as follows

$$\Phi_{O_3} = \frac{2}{1 + k_3(H_2)/k_2(M) + k_4(H_2)/k_3(O_2)(M)}$$

$$\Phi_{H_2O_2} = \frac{2}{1 + k_3(O_2)/k_4 + k_2(O_2)(M)/k_4(H_2)}$$

$$\Phi_{H_2O} = \frac{8(O_2)/(M) + 2}{1 + k_3(O_2)/k_4 + k_2(O_2)(M)/k_4(H_2)}$$

Assuming that at one atmosphere total pressure $k_2 = k_3$ and $k_3(M) = 4k_4$, the above equations become

$$\Phi_{O_3} = \frac{2}{1 + (H_2)/(M) + (H_2)/4(O_2)}$$

$$\Phi_{H_2O_2} = \frac{2}{1 + 4(O_2)/(M) + 4(O_2)/(H_2)}$$

$$\Phi_{H_2O} = \frac{8(O_2)/(M) + 2}{1 + 4(O_2)/(M) + 4(O_2)/(H_2)}$$

Corresponding equations are easily derived for quantum yields at other pressures by introducing the appropriate factor into the ratio $k_4/k_3(M)$. The values obtained from such equations fit the experimental results quite well, except in the case of water at low pressures. Here it is clear that the high quantum yields can be accounted for only by the introduction of a chain mechanism which is negligible at higher pressures. In the preceding mechanism, the only reasonable change which will result in such increased water yields is a change in the reactions representing the formation of hydrogen peroxide from hydrogen atoms. One might suspect that the reaction

$$H + O_2 \longrightarrow OH + O \qquad (8)$$

is responsible for the low pressure results were it not for its high activation energy, and also for the fact that if it were sufficiently prominent to cause the increased water yields, the quantum yields of both ozone and hydrogen peroxide should be much larger than those actually observed.

Another possibility is the reaction

$$HO_2 + H_2 \longrightarrow H_2O + OH \qquad (9)$$

which might well compete with (7) at low pressures since it involves the reaction of HO_2 with a primary material rather than with another HO_2. This reaction followed by (5) and (6) readily accounts for increased water yields without affecting the yields of ozone or hydrogen peroxide, since the reaction of HO_2 by the chain of (9), (5), and (6) results in the formation of two molecules of water plus another HO_2 complex, and does not involve oxygen atoms. The chain would be broken by the formation of hydrogen peroxide.

Evidently there is some activation energy associated with (4), thus accounting for its probability of only 10^{-7} or 10^{-8}. As the temperature is increased, more molecules become sufficiently activated to react by (4), and this uses up oxygen atoms at the expense of (2) and also probably (3). While the yields of water and hydrogen peroxide do increase some as the ozone yields decrease, the sudden rapid rise in the formation of these two does not occur until a temperature considerably greater than that corresponding to the disappearance of ozone is reached. For instance, in a 10% H_2–90% O_2 mixture the formation of ozone is undetectable at 150°. The rapid rise in the water and peroxide yields does not occur until a temperature of some 220° is reached. Clearly, the disappearance of ozone is in no way connected with the appearance of long chains leading to water formation. Until the sudden rise in the water and hydrogen peroxide formation occurs, the course of the reaction is reasonably well described by the mechanism already outlined.

These sudden increases are probably due to the fact that the activation energy of (8) is overcome, allowing it to compete with (6). The result of the operation of this reaction is to cause a branching of the chain, forming two new chains of the type postulated in the room temperature mechanism. The new chains thus formed will be broken by the formation of hydrogen peroxide, and thus the simultaneous increase in water and peroxide yields is accounted for. Since the temperature at which chain branching becomes prominent is well above that at which (2) becomes negligible, no difficulty is offered by the fact that (8) does not cause increased ozone formation.

In order to check experimentally the fact that the results observed at elevated temperatures are caused by primary reactions rather than by the interaction of hydrogen and ozone, a run was made under the following conditions. A grill fashioned from 15 inches (38 cm.) of 6-mm. pyrex tubing and surrounded by a pyrex jacket was placed between the reaction cell and the absorption bubblers. A resistance wound side arm allowed admission into the jacket of air at any desired temperature. The grill was equipped with a thermocouple well for measuring the temperature attained by the reaction gases after passing through two-thirds of the pyrex tubing. The volume between the thermocouple and the gas exit approximated that of the reaction cell between the light source and the exit of the gases from the heated jacket.

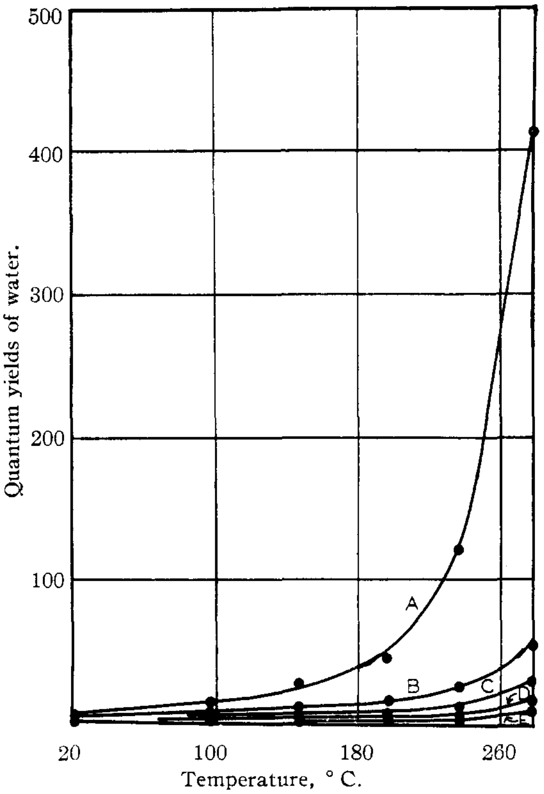

Fig. 8.—Quantum yields of water as a function of temperature, total pressure $H_2 + O_2 = 190$ mm.: A, 10% O_2; B, 30% O_2; C, 50% O_2; D, 70% O_2; E, 90% O_2.

A 30–70 oxygen–hydrogen mixture at 190 mm. total pressure was exposed to the light source. The quartz cell was kept at room conditions while the air passing around the grill between the reaction cell and the absorption bubblers was maintained at such a temperature that the thermocouple reading corresponded to 260°. Thus the reaction products were kept at a temperature above 260° for as long a period as in a regular run. Under these conditions in the regular cell, no ozone was found, while quantum yields of approximately 5 and 40 were found for hydrogen peroxide and water, respectively. On the other hand, in the room temperature runs the quantum yields were as follows: ozone, 0.5; hydrogen peroxide, 0.6; water, 2.8. The approximate quantum yields found with the cell at room conditions and the grill at 260° were: ozone, 0.1; hydrogen peroxide, 0.1; water, 3.5.

In order to bring the gas inside the grill to 260° the reaction products were necessarily exposed to more and hotter surface than in the regular runs. As a result, one would naturally expect some decomposition of the ozone and hydrogen peroxide on the walls of the grill. This accounts for the reduced yields of these products. The slight increase in the water yields is also readily attributed to decomposition of the peroxide. The fact that some ozone is still found after this treatment, while water and peroxide formation in no way compares to that found when the quartz cell was heated, indicates quite clearly that the reaction of hydrogen and ozone does not account for the results already presented.

Three objections may be raised to the proposed mechanism. The first of these lies in the fact that when the third body in (2) is a hydrogen molecule, reactions (2) and (3) involve identical reactants. If (2) takes place on nearly every triple collision as stated by Schumacher,[13] reaction (3) also must do so since $k_2 = k_3$. Accordingly, the theoretical yields of ozone must be decreased by an amount equal to the yields of water formed by (3). On the other hand, if only a small fraction of the triple collisions indicated by (2) are effective, this objection disappears. The probability of reaction (4) is estimated by Harteck and Kopsch[14] as 10^{-7}, and by Rodebush, Wende, and Campbell as 10^{-8}.[15] If these estimates are correct, reaction (2) cannot take place on nearly every triple collision, or else (4) could not compete with it, and no peroxide would be found.

A second objection results from the apparent exclusion of the hydrogen molecule as stabilizer in reaction (3). Actually this possibility is included in the proposed mechanism. If one combines (4) and (5) the result is

$$O + H_2 + H_2 \longrightarrow H_2O + H + H \qquad (10)$$

Since the reaction of an oxygen atom with a hydrogen molecule to form water is exothermic by some 117 kcal., while the heat of dissociation of the hydrogen molecule is only 102 kcal., it is readily understandable that reaction (10) might occur when a hydrogen molecule is the stabilizing body in the formation of water.

Finally, the absorption of light in the 1720 Å. region should produce a normal (^{3}P) and an excited (^{1}D) oxygen atom. No differentiation has been made between the two. Since the fastest possible reaction is evidently a three-body affair, it seems highly probable that collisional deactivation of the excited atom will take place before chemical reaction occurs.

Relation to the Mercury Sensitized Reaction.—The temperature coefficient of the mercury sensitized hydrogen–oxygen reaction was studied by Taylor and Salley.[20] These authors compared their results with those obtained for the direct photochemical reaction (2), and concluded as follows:

"The temperature coefficients of the mercury sensitized and the direct photochemical reactions of hydrogen and oxygen are shown to be comparable over the whole temperature range. It is suggested that the chain mechanism is the same whether initiated by atomic oxygen or atomic hydrogen."

The mechanism here proposed for the direct photochemical reaction would lead one to expect the complete similarity to the mercury sensitized reaction found by Taylor and Salley. The reaction responsible in both cases for the sudden rise in the temperature coefficient occurring at about 500° and approximately atmospheric pressure is reaction (8) which leads to chain branching.

Relation to the Explosion Reaction.—There is probably little doubt that the chains giving rise to large water yields in the photochemical reaction are the same as those involved in the explosion of oxy–hydrogen mixtures. For this reason it is of interest to examine mechanisms which have been presented in explaining the latter.

A rather satisfactory explanation of the explosive reaction is that proposed by Kassel and Storch[21] and modified by Lewis and von Elbe.[22] The present work would indicate that the explosion should follow reactions (4), (5), (6), and (9) for simple chain carrying reactions. However, (6) may result in chain breaking whenever (7) is more predominant than (9). Chain branching occurs by (8). The reaction as outlined by Kassel[23] includes four of the five equa-

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[20] Taylor and Salley, THIS JOURNAL, **55**, 96 (1933).

[21] Kassel and Storch, *ibid.*, **57**, 672 (1935).

[22] Von Elbe and Lewis, *ibid.*, **59**, 656 (1937).

[23] Kassel, *Chem. Rev.*, **21**, 331 (1937).

tions given above. In place of (9), however, he gives the reaction (7a). The arguments given by Kassel seem to apply equally well if (9) is substituted. If (7a) were important at elevated temperatures, the yields of hydrogen peroxide should not parallel the water yields as was found for the photochemical reaction, but should depend primarily on the activation energy of (7a).

The modification proposed by von Elbe and Lewis[22] is identical with that proposed here, except that it admits the possibility of (7a) as well as (9), and also includes a reaction

$$H + O_2 + H_2 \longrightarrow H_2O_2 + H \qquad (11)$$

in order to explain the explosion limits. The present work gives no indication that such a reaction is of importance.

Acknowledgment.—The authors are grateful to the Roy R. Hornor Fund of Lehigh University for financial aid.

Summary

The photochemical oxidation of hydrogen has been studied by exposing mixtures of hydrogen and oxygen at room temperature to light of wave length 1719–1725 Å. The total pressure of the reaction mixture was varied from 1140 to 95 mm.

In general, with increasing oxygen content, the quantum yields of ozone increase while those of hydrogen peroxide and water decrease. Lowering of the total pressure tends to increase the water and peroxide yields, apparently at the expense of the ozone. At pressures of 190 mm. and less, the formation of water shows chain characteristics.

The temperature coefficients for the formation of the individual products have also been studied over the range 25 to 280°. The formation of ozone has a negative temperature coefficient while those of water and hydrogen peroxide are positive. At total pressures of 190 millimeters and in a 10–90% oxygen–hydrogen mixture, the temperature coefficients of water and hydrogen peroxide formation increase with great rapidity at temperatures above 230°.

A mechanism has been offered which explains satisfactorily the experimental results.

The relation of the direct photochemical reaction to the mercury sensitized and the explosive reactions has been discussed.

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Thermodynamic Properties of Substances. III. Vapor Volumes as Functions of Reduced Temperature Alone

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In a previous article[1] we have shown that vapor volumes of chemically different substances can be expressed as a function of liquid volume and reduced temperature:

$$V_g = V_1 e^{k(1-\tau^2)^m/\tau^n} \qquad (1)$$

The same type of function was found to give correct values for vapor pressures of thirty liquids, including water, the parameters k', m', n', being very close in value to those of the above equation.[2,3]

$$P_s = P_{cr}\, e^{-k'(1-\tau^2)^{m'}/\tau^{n'}} \qquad (2)$$

An attempt was made[3] further to express vapor volumes as a function of reduced temperature alone by an analogous equation

$$V_g = V_{cr} e^{k''(1-\tau^2)^{m''}/\tau^{n''}} \qquad (3)$$

This equation was applied to water vapor and was found to hold for almost the entire saturation line (60–360°) with an average deviation under 0.2 volume per cent.

In view of the fact that equations (1), (2) and (3) represent the behavior of water and equations (1) and (2) apply to the various other substances as well, it seems reasonable to presuppose that equation (3) would also apply to the other substances; actual tests confirm this supposition in every one of the cases, as will be shown in detail in the following pages.[4]

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[1] H. A. Fales and C. S. Shapiro, THIS JOURNAL, **58**, 2418 (1936).

[2] H. A. Fales and C. S. Shapiro, *ibid.*, **60**, 794 (1938).

[3] H. A. Fales and C. S. Shapiro, *ibid.*, **60**, 784 (1938).

[4] After completing the test of equation (3) on all the various substances, we tried out (on water) the more general form

$$V_g/V_{cr} = \exp.\ k''[(1+\tau)^{s''}(1-\tau)^{m''}/\tau^{n''}] \qquad (4)$$

as was done previously for the vapor pressure of water.[3] This was done in the hope that it would improve the agreement at both extremes of the saturation line, namely, near the melting point and near the critical point. We found that both forms (4) and (3) fit water volumes equally well at every point in the interval 60–360°,