[CONTRIBUTION FROM THE MALLINCKRODT CHEMICAL LABORATORY OF HARVARD UNIVERSITY]

The Photochemical Hydrogen–Oxygen Reaction

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Several years ago one of the authors of the present paper[1] reported an investigation into the direct photochemical hydrogen–oxygen reaction. He used ultraviolet light of the two spectral regions, 1854–1862 Å., by which excited oxygen molecules are produced on the absorption of light quanta[2] and 1719–1725 Å., which light dissociates oxygen molecules in one elementary act, a normal and an excited atom resulting.[3]

The present report concerns further investigation into the above-mentioned reaction using light of the same wave lengths, and employing apparatus designed not only to confirm earlier results, but also to make possible new measurements which may prove of some importance in the elucidation of the hydrogen–oxygen reaction.

Experimental

The light source employed in this work consisted of a condensed spark burning between two slowly revolving aluminum disks.[4] The gases to be illuminated were circulated at a high rate of flow through a thin-walled quartz vessel, and then through an ice-cooled absorption bubbler for removal of the reaction products. This bubbler was designed to make small amounts of absorbing liquid efficient for washing gases passing through it at high rates of flow, and was found to fulfil this requirement. After leaving the bubbler, the gases were dried, and returned to the reaction cell by means of an all-glass circulating pump.

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

Lyman[5] states that oxygen in an air column one centimeter long completely absorbs the strong aluminum spark lines in the neighborhood of 1720 Å., while the strong line group 1854–1862 Å. is only slightly weakened by passage through such a column.

In the present research this fact was applied in two ways. In the first place, the effect of the 1854–1862 Å. group alone was studied by keeping a layer of air about 1.5 cm. thick between the light source and the reaction vessel. Then a layer of oxygen-free nitrogen was substituted, and thus the total effect of the two could be observed. Secondly, two cells were used. The first cell was bulb-shaped, with the light-exposed side blown paper thin in order to allow passage of short ultraviolet waves. After entering the cell, the light passed through a column of gas about 3 cm. thick. This cell was used for extensive study with the longer wave length group. The second cell, employed for similar study of the shorter wave lengths, was of flat spiral design, and presented to the spark a gas layer of less than 1 cm. thickness. This thickness allowed almost complete absorption of the shorter waves entering the cell, while the absorption of longer wave lengths was slight.

The products of the reaction produced by the absorption of ultraviolet light by hydrogen–oxygen mixtures are ozone, hydrogen peroxide and water. The sum of the peroxide and ozone yields was determined by use of neutral 10% potassium iodide solution in the bubbler. Such a solution absorbs ozone quantitatively by chemical reaction while practically all of the hydrogen peroxide is retained in the bubbler, mainly by simple solution. After a run, sufficient sulfuric acid was added to the bubble liquid to make it three normal with respect to the acid, and the solution was then allowed to stand for about ten minutes. Under these conditions the dissolved peroxide reacts quantitatively with the potassium iodide.[6] The resulting solution was titrated with standard thiosulfate solution. The main error in this method is caused by oxidation of the acid solution by dissolved oxygen. This error was found to be considerably less than the errors due to variations of light intensity and other similar causes.

Hydrogen peroxide was determined alone in separate runs, by use of a solution of titanium sulfate in the bubbler. The amount of hydrogen peroxide absorbed was estimated by colorimetric comparison with another portion of the solution containing a known amount of hydrogen peroxide. The concentration of the hydrogen peroxide used in making up the reference colorimetric solutions was found by employing exactly the same analytical procedure as that previously described for the determination of ozone plus hydrogen peroxide. In this way both hydrogen peroxide and total oxidation yields were referred to the same standard.

When determining hydrogen peroxide separately it was found necessary to remove the ozone left in the gases before returning them to the reaction cell. This was done by passing them over some freshly precipitated manganese dioxide. Check runs made when the ozone was removed by means of a second bubbler containing potassium iodide solution gave the same results.

In order to determine the amount of water formed during a run, the volume of the system was cut down as much as possible. The bubbler was filled with neutral potassium iodide solution, and the pressure in the system was measured on a constant volume manometer. After a run, the temperature of the system was adjusted to its initial value and the change in pressure measured. Then the iodine set free in the bubbler was determined in the usual way, and the pressure change due to formation and absorption

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

(2) Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

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

(4) Wiig and Kistiakowsky, THIS JOURNAL, **54**, 1807 (1932).

(5) Lyman, "The Spectroscopy of the Extreme Ultra-violet," London, 1928.

(6) Treadwell and Hall, "Analytical Chemistry," 7th ed., Vol. II, p. 576.

of ozone and hydrogen peroxide was calculated. The difference between this value and the pressure change actually measured allowed the calculation of the amount of water formed during the run.

This method was checked using pure oxygen in the system. Since ozone is the only possible product formed in this case, the actual contraction can be calculated. The average discrepancy found in the four such determinations made was about 5%.

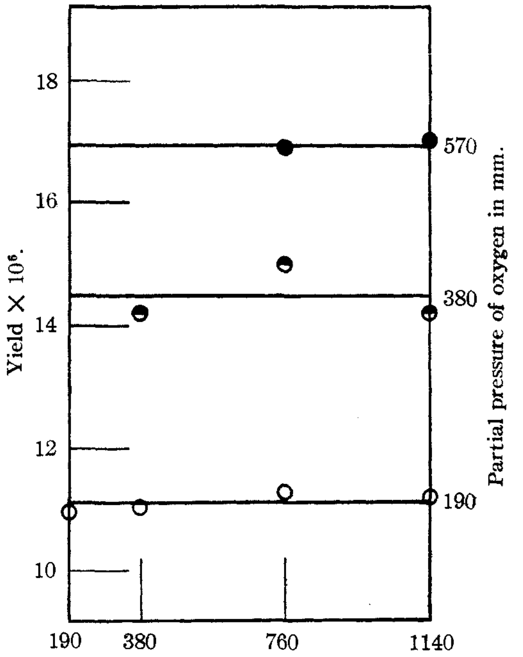

Fig. 1.—Yield of ozone in presence of nitrogen.

Earlier research[1,4] has already shown that, as the flow of gas through the cell is increased, the total quantities of ozone and hydrogen peroxide formed per unit illumination increase at first but soon approach a constant value. This result was confirmed, and in all cases the gas flow was made fast enough to have no effect on the amount of products obtained.

It seemed possible that some of the products obtained are formed in slow reactions after the gases leave the illuminated vessel. This was tested by interposing between the reaction flask and the bubbler volumes varying between 3 and 60 cc., so that the time between illumination and absorption varied from 0.005 to 0.1 second, but no difference could be observed in any of the products formed. Further, the extent of the glass surface exposed to the gases after they leave the reaction flask was varied by more than twenty-fold without any noticeable effect.

The light intensity of the spark was found to undergo slow changes, and also the transmission of the quartz vessels was gradually decreasing. To correct for errors arising from these sources, the quantity of ozone formed in a one to four oxygen–nitrogen mixture was determined shortly before or after all runs and the amounts of products obtained with other mixtures were reduced to constant incident light intensity using this reference determination.

Results

For the discussion of the results it is rather essential to establish that the quantity of ozone formed in the oxygen–nitrogen mixtures is proportional to the absorbed light energy, and independent of other factors. Some evidence in the matter is contained in earlier mentioned researches of Warburg[7] and Vaughan and Noyes.[8] Further confirmation is found in Fig. 1, which shows that the yield of ozone at constant oxygen pressure is entirely independent of the amount of nitrogen present. Together, all of these observations form a strong body of evidence that the quantum yield of ozone is constant, being independent of wave length (when it is shorter than about 2000 Å.) or of oxygen pressure, and is, therefore, presumably equal to two, as was found by Warburg, and by Vaughan and Noyes.

This being the case one should obtain the true quantum yields of different products in oxygen–hydrogen mixtures upon dividing the quantities obtained by the amounts of ozone found in oxygen–nitrogen mixtures containing corresponding partial pressures of oxygen and multiplying the results by two. This treatment has been applied to all results shown in the following figures.

Figures 2 and 3 show the effect of composition and of the wave length on the quantum yields in hydrogen–oxygen mixtures obtained with the large cell. The yields in short wave lengths have been corrected for the action of long wave length radiation present by deducting from the quantities found, amounts formed when the latter radiation alone was present. Although such procedure is possibly inexact, it should give sufficiently close approximation to the true correction.

Figures 4, 5 and 6 show the effect of pressure, and the water yields with the short wave lengths.

In general, the results as given in the graphs were found to be quite reproducible. The experimental points representing yields of hydrogen peroxide and ozone appear to be in error by less than 5%. In the case of water yields, the accuracy may not be greater than 10%, for determinations at one atmosphere total pressure, although the manner in which they fall on a smooth curve would tend to show that the accuracy is better. The water yields determined at low pressures were not nearly as reproducible

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(7) Warburg, *Sitzb. Akad. Wiss. Wien*, **216** (1912): 872 (1914).

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

as those at higher pressures, nor do the determined points fit a smooth curve very well. Still, the results are definite enough to show a decided increase of water yields with decreased pressure.

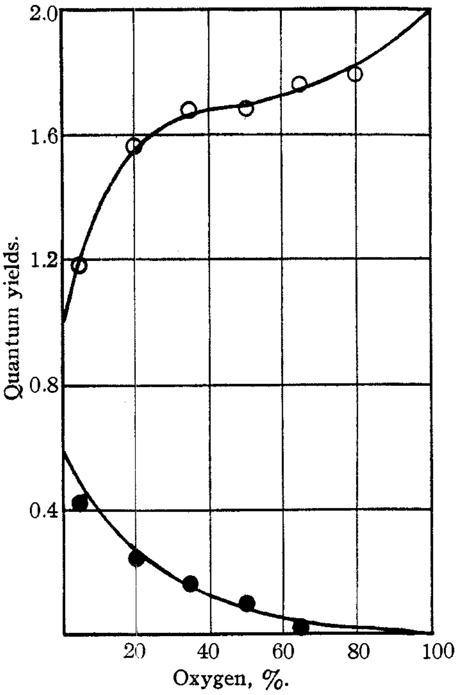

Fig. 2.—Quantum yields with 1854–1862 Å., using cell I, 1 atm. total pressure; O, ozone yields; ●, hydrogen peroxide yields.

If one examines the short wave length relative yields of ozone determined at one atmosphere total pressure, he finds a difference depending on which cell was used. This difference is probably partially due to the construction of the first cell.

Another factor which makes the results obtained by use of the spiral cell more accurate lies in the fact that the corrections for the effect of long wave lengths were smaller with this cell. With the first cell the corrections sometimes amounted to as much as 35% of the total yield, while with the spiral cell they amounted to only about 10%.

Some question might be raised as to the possibility that water in the gases might have had some effect on the reaction. The bubbler containing the absorbing liquid was always immersed in an ice-bath, and so the pressure of water vapor could never have risen above 4–5 mm. After the gases left the bubbler, they were usually passed through a calcium chloride tube for drying. Some experiments were made substituting first a tube of glass wool immersed in an acetone–carbon dioxide snow cooling mush, and, second, a large tube of dehydrite in place of the calcium chloride tube. In neither case was there any noticeable difference in the yields obtained.

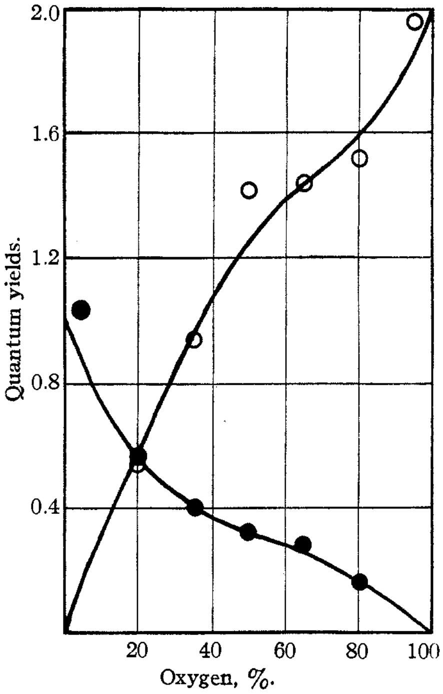

Fig. 3.—Quantum yields with 1719–1725 Å., using cell I, 1 atm. total pressure; O, ozone yields; ●, hydrogen peroxide yields.

Discussion

1854–1862 Å.—The results of the action of long wave lengths on hydrogen–oxygen mixtures, as now obtained, differ materially from the earlier results of one of us in that hydrogen peroxide, then reported as absent, has now been definitely observed. This is due to a more sensitive and accurate method now used for its determination. This yield of hydrogen peroxide is smaller than in light of short wave length, in fact is very nearly equal to one-half of it. The yield of ozone, under otherwise comparable conditions, is, on the other hand, larger. It appears as though one-half of all absorbed light of long waves was utilized to form ozone irrespective of composition of gases, whereas the other half gives rise to the same sequence of reactions as take place with illumination by short waves. If that is the case, a description of the observation is obtained by assuming that the primary action of light of about 1860 Å. wave length—in accordance with spectroscopic evidence—is the formation of excited oxygen molecules. These latter react then with oxygen molecules by

$$O_2^* + O_2 \longrightarrow O_3 + O \qquad (1)$$

but suffer only elastic collisions with hydrogen, so that the absorption of each energy quantum results in one ozone molecule and one oxygen atom.

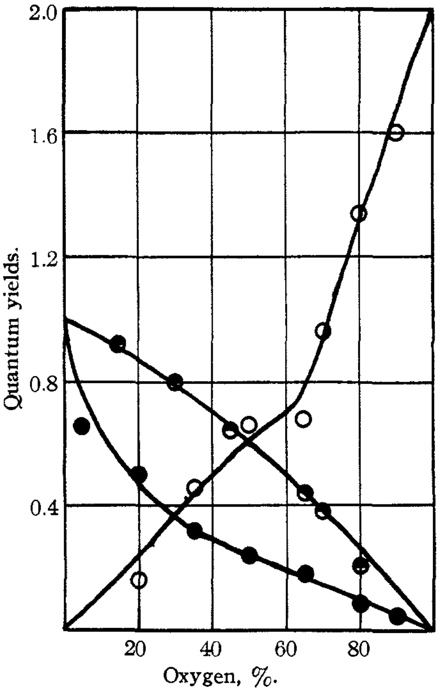

Fig. 4.—Quantum yields with 1719–1725 Å., using cell II, 1 atm. total pressure; O, ozone yields; ●, hydrogen peroxide yields; ◓, water yields.

This latter undergoes then the same reactions which will be discussed later in considering the action of short waves, and which result in formation of some ozone, hydrogen peroxide and water in proportions determined by composition of the reacting gases. The quantum yields of these products formed in long wave lengths are, however, only half as large as in light of short wave lengths, because only one atom results on absorption of each quantum, instead of two as in the latter case.

In this manner the correct balance of products is obtained. Some weaknesses are present in this mechanism. The assumption of elastic collisions with hydrogen is not a serious one, since the presence of electronic and vibrational excitation energy in the oxygen molecule does not necessarily preclude the need for some additional translational activation energy in order for reaction with hydrogen to take place. Such additional energy may be larger than for reaction (1). On the other hand, the assumption of an identical set of reactions for the oxygen atom formed in reaction (1) is not entirely supported by experiment, since (due to insufficient absorption of light) water formation has not been observed, thus making a complete quantitative comparison with the short wave reaction as yet not possible. Still, the explanation now advanced removes some of the difficulties discussed in the earlier paper and shows that there is no need to assume, as was done then, that oxygen atoms in the ^1D excited state have very different reactivity toward hydrogen molecules than have normal oxygen atoms.

1719–1725 Å.—In an attempt to set up a mechanism explaining the interaction of the oxygen atoms produced by absorption of short ultraviolet light with mixtures of hydrogen and oxygen, the following facts established by this work must be considered.

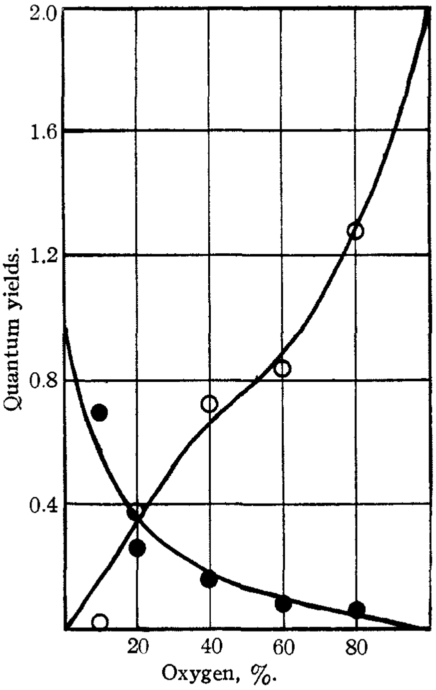

Fig. 5.—Quantum yields with 1719–1725 Å., using cell II, 0.5 atm. total pressure; O, ozone yields; ●, hydrogen peroxide yields.

(1) With increasing hydrogen concentration the yield of ozone decreases to zero, this decrease being independent of the total pressure.

(2) With increasing hydrogen concentration the yield of hydrogen peroxide increases, becoming approximately equal to unity in mixtures

very rich in hydrogen. This increase is also independent of the total pressure.

(3) The yield of water parallels closely that of hydrogen peroxide at high pressures. At lower pressures the yield of water increases, and this increase does not take place at the expense of ozone or hydrogen peroxide. Water is not formed by the interaction of ozone with hydrogen or hydrogen peroxide, unless such interaction is so fast that even the rapid gas flows employed in this research could not prevent it.

(4) Since in a 1:1 mixture the quantum yields of ozone and hydrogen peroxide are equal to about one-half their maximum value, the rates at which oxygen atoms react with oxygen or with hydrogen molecules are nearly equal.

All these observations (neglecting the increased yield of water at low pressures) can be formally represented by the following system of consecutive reactions

$$\begin{array}{rcll} O + O_2 & \longrightarrow & O_3 & (2) \\ O + H_2 & \longrightarrow & OH + H & (3) \\ H + O_2 & \longrightarrow & HO_2 & (4) \\ OH + OH & \longrightarrow & H_2O_2 & (5) \\ HO_2 + HO_2 & \longrightarrow & H_2O_2 + O_2 & (6) \\ OH + HO_2 & \longrightarrow & H_2O + O_2 & (7) \end{array}$$

This mechanism fits the experimental facts, if one accepts, as we do, the finding of Rodebush and Wahl[9] that hydroxyl radicals react to form hydrogen peroxide, a finding which is contradictory to the earlier work of Bonhoeffer[10] and of Harteck and Kopsch.[11] Water is considered as one of the primary products, since the reactions of ozone and hydrogen peroxide with hydrogen are too slow at room temperature to be of importance in this case.

In order to make this mechanism fit the experimental curves more exactly, another reaction may be introduced, namely

$$O + H_2 + O_2 \longrightarrow H_2O + O_2 \qquad (8)$$

When this reaction is included, the experimental inflection points in the yields of ozone and hydrogen peroxide and the slightly convex form of the water yield curve are represented.

Calculations involving this mechanism are omitted since very serious objections make it doubtful. Perhaps the main difficulty arises from a consideration of the fact that the quantum yields of ozone and hydrogen peroxide are independent of pressure. This implies that, since reaction (3) undoubtedly does not require triple collisions, the formation of ozone must also go via double collisions. This, on the other hand, is completely at variance with findings of Schumacher[12] and of Heidt and Forbes,[13] on the photochemical decomposition of ozone. Ritchie[14] also concludes that the formation of ozone proceeds via triple collisions. He has given an interpretation of the mechanism of the thermal decomposition of ozone from which he deduces that the formation of ozone by reaction between oxygen atoms and oxygen molecules requires about 5000 calories activation energy. This deduction is based on an erroneous assumption concerning the rate of diffusion of oxygen atoms to the walls. Using a more correct method provided by the diffusion equation of Smoluchowski, one finds that this activation energy is zero within the limits of error of the method and that reaction takes place on essentially every triple collision. This is consistent with the results of photochemical work, and on weighing all such evidence one is forced unavoidably to the conclusion that the formation of ozone proceeds via triple collisions.

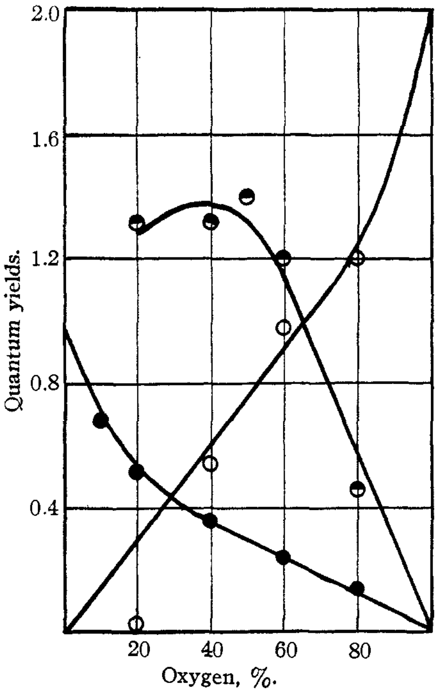

Fig. 6.—Quantum yields with 1719–1725 Å., using cell II, 0.25 atm. total pressure; ○, ozone yields; ●, hydrogen peroxide yields; ◓, water yields.

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[9] Rodebush and Wahl, *J. Chem. Phys.*, **1**, 696 (1933).

[10] Bonhoeffer and Pearson, *Z. physik. Chem.*, **14B**, 1 (1931).

[11] Harteck and Kopsch, *ibid.*, **12B**, 327 (1931).

[12] Schumacher, *Z. Elektrochem.*, **38**, 620 (1932).

[13] Heidt and Forbes, THIS JOURNAL, **56**, 2365 (1934).

[14] Ritchie, *Proc. Roy. Soc.* (London), **A146**, 848 (1934).

The same must be true then, also, for the primary reaction leading ultimately to the other products in the reaction here described, and reaction (3) of the first mechanism must be modified. This reaction was used by Harteck and Kopsch[11] to interpret their observations at low pressures. It is indeed possible that at the low pressures used by these authors reaction (3) is predominant. However, when pressures of the order of one atmosphere are employed, as was done in the present experiments, the triple collision appears to be the important one, for, as Harteck and Kopsch report, the collision yield of the bimolecular reaction is quite small, namely, 10^{-7} to 10^{-8}.

To arrive at a consistent, although somewhat arbitrary, representation of the experimental data, reactions (2), (3) and (4) may be replaced by the following

$$O + O_2 + O_2 \longrightarrow O_3 + O_2 \qquad (9)$$

$$O + O_2 + H_2 \longrightarrow OH + HO_2 \qquad (10)$$

reactions (5), (6) and (7) following these. To obtain approximately equal yields of water and of hydrogen peroxide it would be necessary to assume that the velocity constants of the last three reactions are all of the same magnitude. Also this scheme does not represent the inflection point in the yield of ozone unless one assumes slightly different velocity constants k_{10} for the ^3P and the ^1D oxygen atoms. Another difficulty is that it excludes reaction

$$O + H_2 + H_2 \longrightarrow H_2O + H_2 \qquad (11)$$

because its inclusion would give equations inconsistent with observations. At most the rate of this reaction must be small, something of the order of 10^{-2} of reactions (9) and (10). Furthermore, notwithstanding many efforts, we have been unable to include the increased water yields at lower pressures in this reaction mechanism. As will be seen from the experimental data, this increase is not obtained at the expense of ozone or hydrogen peroxide, and thus for instance the predominance of reaction (11) at low pressures must be excluded. It appears most likely that short chains, resulting in water formation alone, are set up at lower pressures, but are nearly absent at atmospheric pressure. There is a close analogy with thermal explosions of hydrogen–oxygen mixtures where also, as most investigators are now inclined to believe, oxygen atoms are responsible for the initiation of branched chains giving water, these latter being particularly enhanced at low pressures, while in general all three products, water, hydrogen peroxide and ozone are formed.

If these suggestions are correct, the study of the photochemical hydrogen–oxygen reaction initiated by oxygen atoms at somewhat elevated temperatures and at reduced pressures may prove to be of significance for the study of the mechanism of the thermal explosions. With our present outfit such work was not feasible.

Summary

The direct photochemical hydrogen–oxygen reaction has been reinvestigated using ultraviolet light of the two spectral regions 1719–1725 and 1850–1862 Å. Ozone, hydrogen peroxide and water were the products with the former lines, and ozone and hydrogen peroxide were found with the longer wave lengths. No attempt was made to determine water in the latter case.

The effect of pressure on this reaction has been studied.

Reactions which might be involved in the reaction mechanism have been discussed.

The work of Warburg, which showed that the yield of ozone from the reaction of oxygen atoms with oxygen molecules is not affected by the presence of nitrogen, has been confirmed.

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