centration and a wide variation of the relative pressures of carbon monoxide and chlorine.

2. Simultaneous measurement of the alpha particle and photochemical reactions shows that the yield per ion pair is equal to the yield per quantum absorbed. This is also true in the presence of oxygen ($<10\%$) which inhibits the reaction.

3. With exceedingly weak radiation, yields as high as 85,000 molecules per ion pair were obtained: the more intense light radiations gave 5000 molecules per quantum absorbed.

4. The secondary steps in the phosgene synthesis involve an atomic chlorine chain mechanism and the above facts prove that this mechanism occurs independently of whether the primary step has been photochemical excitation or ionization by alpha particles.

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THE PHOTOCHEMICAL HYDROGEN-OXYGEN REACTION

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Several attempts have been made to elucidate the kinetics of the interaction of oxygen and hydrogen under influence of light. Andrejew[1] and Coehn and Grote[2] demonstrated the existence of a stationary state in the system water vapor-oxygen and hydrogen, illuminated by the short wave lengths of a mercury arc but did not investigate the details of the reactions involved. Tian[3] succeeded in showing the presence of hydrogen peroxide in illuminated hydrogen-oxygen mixtures and assumed that water is formed only through some intermediary steps involving hydrogen peroxide. Kistiakowsky[4] has shown that while at room temperature the quantum yield of water formation is not far from the value of two, reaction chains are set up in the temperature range where the thermal reaction becomes noticeable, the temperature coefficient of the photochemical water formation not following the Arrhenius equation. Reaction of hydrogen and oxygen photosensitized by mercury vapor has been studied by Marshall[5] and by Bates and Taylor.[6] It has been conclusively demonstrated that water is formed through a secondary decomposition of hydrogen peroxide. Bates and Taylor further noticed that in absence of mercury vapor only ozone is formed, hydrogen peroxide being completely

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[1] Andrejew, *J. Russ. Phys.-Chem. Soc.*, **43**, 1342 (1911).

[2] Coehn and Grote, "Nernst Festschrift," **1912**.

[3] Tian, *Compt. rend.*, **152**, 1012 (1911).

[4] Kistiakowsky, *Proc. Nat. Acad. Sci.*, **15**, 194 (1929).

[5] Marshall, *J. Phys. Chem.*, **30**, 34, 1078 (1926).

[6] Bates and Taylor, THIS JOURNAL, **49**, 2438 (1927).

absent. In these latter experiments mainly the mercury line 1842 Å. must have been photochemically active. The present work is concerned with the mechanism of the un-sensitized reaction of oxygen and hydrogen in light of two spectral regions: 1854–1862 Å., by which according to Birge and Sponer,[7] excited oxygen molecules are produced and the region of 1719–1725 Å., which dissociates oxygen molecules in one elementary act, a normal and excited oxygen atom resulting.[8]

The experimental set-up consisted of a condensed spark burning between aluminum electrodes and of a thin-walled quartz vessel of about 100-cc. capacity, through which the reacting gases were passed at measured rates of flow. The reaction vessel was placed at 4-cm. distance from the spark and the space between was filled with streaming air or purified nitrogen. Oxygen in an air layer 4-cm. deep absorbs the strong aluminum spark lines in the neighborhood of 1720 Å. completely[9] while the strong line group 1854–1862 Å. reaches the reaction vessel only very slightly weakened.[9] The correctness of this assumption is proved by the observation that substitution of nitrogen instead of air increased the reaction velocity more than ten-fold. Accordingly, with a layer of nitrogen, more than 90% of the reaction is due to the initial formation of oxygen atoms, while with the air layer only the lines in the band absorption region of oxygen are effective. In order to determine the course of reaction the exit gases were passed through a neutral potassium iodide solution and the liberated iodine was titrated on acidification. This gave the total amount of ozone and hydrogen peroxide formed, since better than 90% of the latter, as established by special experiments, was retained in the wash bottles containing potassium iodide and reacted with it on acidification. Hydrogen peroxide alone was determined colorimetrically with the aid of titanium sulfate solutions. To determine the absolute rate of the reactions involved use was made of the work of Warburg[10] and of Noyes,[11] which shows that the quantum yield of ozone formation in oxygen is, independently of wave length, equal to two. Warburg's experiments indicate further that the yield remains unchanged on dilution of oxygen with nitrogen. Accordingly, in the following experiments the reaction rates in the oxygen–hydrogen mixtures are referred to the rates of ozone formation in similar oxygen–nitrogen mixtures, measured in the same vessel and under identical conditions of illumination. In Fig. 1 are plotted yields of ozone in light of the line group 1854–1862 Å. against the rate of gas flow. Circles refer to a mixture containing 20% O_2 and 80% N_2,

[7] Birge and Sponer, *Phys. Rev.*, **28**, 259 (1926).

[8] Herzberg, *Z. physik. Chem.*, 4B, 223 (1929).

[9] *Cf.* Lyman, "The Spectroscopy of Extreme Ultraviolet," London, **1928**.

[10] Warburg, *Sitzb. Akad. Wiss. Wien*, 216 (1912); 872 (1914).

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

[12] Taylor and Marshall, *Trans. Faraday Soc.*, **21**, 560 (1925).

crosses to a mixture containing 80% H_2 instead of nitrogen. Determination of the hydrogen peroxide yield showed that this was formed at a rate of not more than 2×10^{-8} mole per minute (this being the sensitivity limit of the color test as here used) whether the gas flow was 700 or 30 cc./min. In calculating the points in Fig. 1 which were obtained with the highest rates of gas flow, averages have been taken of several experiments made. Since the effect on ozone yield of substitution of hydrogen for nitrogen is of importance for the discussion to follow, Table I presents complete data relating to this point.

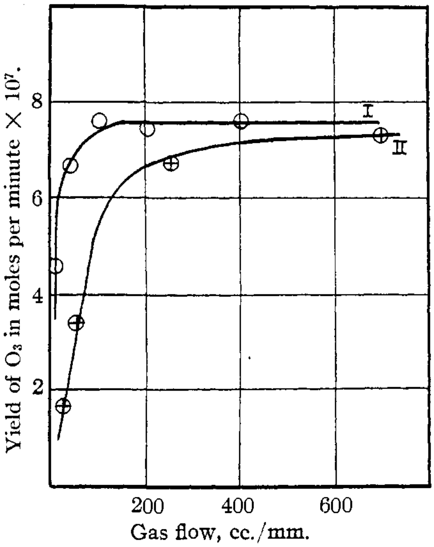

Fig. 1.—Yield of ozone in light of the (mean) wave length 1860 Å. Circles and Curve I, yields in the 1:4 oxygen–nitrogen mixture. Circles and Curve II, yields in the 1:4 oxygen–hydrogen mixture.

Figure 2 presents data obtained with the shorter wave lengths. Circles and Curve I represent ozone yields in the (1:4) oxygen–nitrogen mixture, crosses and Curve 2, ozone plus hydrogen peroxide yields in the (1:4) oxygen–hydrogen mixture, circles and Curve 3, finally, hydrogen peroxide yields alone. All points in Fig. 2 are averages of two or more experiments. The reproducibility of the results in the light of short wave lengths was not as good as in the experiments with the 1852–1864 Å. lines and can be best judged from Fig. 3, in which single experiments have been plotted. In this figure are plotted the relative yields of ozone (represented by circles) and of hydrogen peroxide (crosses) against the composition of the oxygen–hydrogen mixture, the ozone yields in the equivalent oxygen–nitrogen mixtures having been taken for 100%. The ozone yields in mixtures containing hydrogen were obtained by subtracting hydrogen peroxide yields from the total yield as determined by the iodine titration. All

TABLE I

OZONE YIELD

Gas mixture	Rate of gas flow, cc./min.	Ozone yield, moles per minute × 10^7							
20% O_2 + 80% N_2	400	7.62	7.67	7.73	6.60	6.88	6.54	6.60[a]	
20% O_2 + 80% H_2	700	7.62	7.16		5.85	6.88	7.00	6.48	6.88

[a] This second series of determinations has been made with a slightly changed apparatus and was not used in drawing Fig. 1.

these data were obtained with a gas flow of 2000 cc./min. with oxygen–hydrogen and 1500 cc./min. with oxygen–nitrogen mixtures.

Figures 1 and 2 show that with increasing rate of gas flow the yields tend to constant values which represent undoubtedly the maximum yields in absence of secondary photochemical decomposition of either ozone or hydrogen peroxide. In view of all earlier work, it may be further assumed—with a considerable degree of certainty—that the ozone yields, in the oxygen–nitrogen mixtures, are equal to two molecules per quantum of absorbed light energy, irrespective of the wave length. With oxygen–hydrogen mixtures the effect of the two spectral regions is considerably different. While with the 1860 Å. line group practically the same yield of ozone is obtained whether the mixture contain nitrogen or hydrogen, with the short wave lengths and in the presence of hydrogen, the ozone yield is only 25% of that in the presence of nitrogen, but an equal amount of hydrogen peroxide is formed in addition. As Fig. 3 shows, ozone yields in presence of hydrogen are—at least roughly—proportional to the relative concentration of oxygen, whereas the yields of hydrogen peroxide are proportional to the concentration of hydrogen. Since it is well established that in the light of the 1720 Å. spectral region oxygen atoms are primarily formed, one can consider somewhat more in detail their reactions, of which not many are possible.

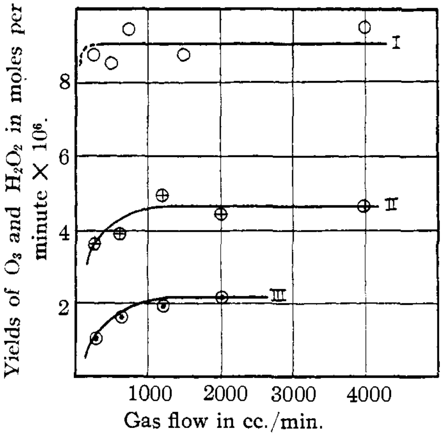

Fig. 2.—Yields of O_3 and H_2O_2 in light of the (mean) wave length 1720 Å. Circles and Curve I, O_3 in the 1:4 oxygen–nitrogen mixture. Crosses and Curve II, $O_3 + H_2O_2$ in the 1:4 oxygen–hydrogen mixture. Dots and Curve III, H_2O_2 alone in the 1:4 oxygen–hydrogen mixture.

$$O + O_2 + X = O_3 + X \tag{1}$$
$$O + H_2 + X = H_2O + X \tag{2}$$
$$O + H_2 = OH + H \tag{3}$$

X denotes here a molecule of oxygen or hydrogen. These three reactions are in qualitative agreement with the relations observed since they lead to an ozone yield which is proportional to the concentration of oxygen while the rate of the third reaction is proportional to the concentration of hydrogen. In this last reaction hydrogen atoms are produced, but, as was already suggested by Taylor and Marshall[12] and shown by Boehm and Bonhoeffer[13] hydrogen atoms react to form quantitatively hydrogen

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[13] Boehm and Bonhoeffer, *Z. physik. Chem.*, 119, 385 (1926).

peroxide. According to Marshall,[5] on the average not less than two molecules of this latter are produced by each hydrogen atom. While the first two reactions require three-body collisions and, therefore, should be relatively slow, the third reaction is free from this limitation and, being exothermic, should take place on every collision.[14] That this conclusion is incorrect is shown by the present experiments in which ozone yields equal to or in excess of hydrogen peroxide yields were obtained. Using data here recorded the probability of Reaction 3 can be estimated to 10^{-4} if, as the first approximation, the assumptions are made that all molecular diameters are equal ($\backsim 10^{-8}$ cm.) and that bimolecular collisions occur at atmospheric pressure 1000 times more frequently than termolecular ones (mean free path $\backsim 10^{-5}$ cm.). The only factor which might increase this value is the possibility that the three-body collisions leading to Reactions 1 or 2 occur more frequently than assumed, which means that the molecular effective cross sections are here larger than the kinetic values. The slowness of the reaction of oxygen atoms with hydrogen molecules finds a parallel in a similar reaction of chlorine atoms. By combining Bonhoeffer's[13] data on the reaction H + Cl_2 with calculations made by Trifonoff,[15] one finds that the probability of the reaction Cl + H_2 is somewhat less than 10^{-3} when water vapor is present and is presumably zero in completely dry gases. The hydrogen molecule shows thus a remarkable stability in reactions which should take place on every collision according to the theories of Herzfeld[14] and of others.

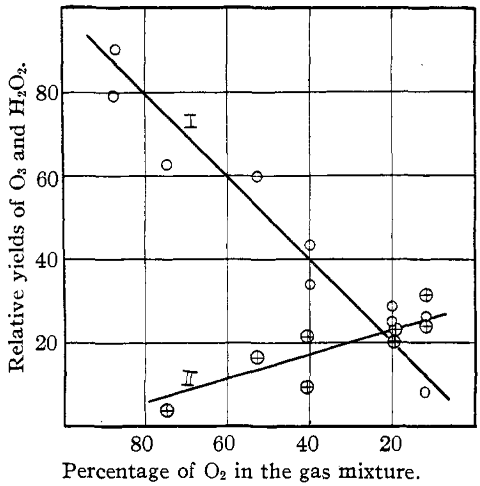

Fig. 3.—Dependence of the yields of O_3 and H_2O_2 on the composition of the gas mixture in light of the wave length 1720 Å. Circles and Curve I, O_3 yields. Crosses and Curve II, H_2O_2 yields.

In the dissociation of the oxygen molecule by light one of the oxygen atoms produced is in the normal ^3P state, whereas the other is, according to Herzberg,[8] in the ^1D metastable state, possessing some 30,000 cal. of excitation energy. The question is of considerable interest whether this difference in the energy levels influences the probability of reaction with hydrogen molecules. No definite answer can be obtained from the experiments with the short wave lengths alone. They can be accounted

[14] Herzfeld, *Ann. Physik*, **59**, 635 (1919).

[15] Trifonoff, *Z. physik. Chem.*, **3B**, 195 (1929).

for by assuming equal probabilities. However, the later discussion will show that the assumption is more helpful that the oxygen atoms in the normal quantum state react with hydrogen molecules more slowly than the excited ones, for which alone the above estimated probability of 10^{-4} would then hold.

The occurrence of Reaction 2 has been so far, left out of consideration. That either this reaction or, and this is less probable, a recombination of oxygen atoms does take place in the hydrogen–oxygen mixture is shown by the observation that there is a deficit in the ozone plus hydrogen peroxide yield as compared with the ozone yield in the oxygen–nitrogen mixtures. Several attempts have now been made to identify water among the primary reaction products by freezing out the products in a liquid-air trap and analyzing the contents on weighing. These attempts failed, due to low yields and the very high gas flow velocities required, but further work under changed conditions is planned. As an indirect proof of the occurrence of Reaction 2 the experiments of Farkas, Goldfinger and Haber[16] may be considered. They succeeded in exploding $O_2 + H_2$ mixtures by introducing oxygen atoms in fairly high concentration. Formation of either ozone or hydrogen peroxide is not exothermic enough to cause explosion and a strongly exothermic reaction of the type represented by Reaction 2, eventually leading to short chains, must have occurred in these experiments.

It remains now to consider results obtained with the 1860 Å. spectral region. These experiments are not quite in accord with the data already discussed. The essence of the results obtained is that with the long wave lengths practically no reaction occurs between hydrogen and oxygen, ozone being quantitatively formed. If the secondary process on excitation of an oxygen molecule is its dissociation into atoms on collision—there is enough energy for the process—this result would be quite incomprehensible. The other possible process is

$$O_2 + O_2 = O_3 + O \qquad (4)$$

the oxygen atom reacting then by 1, 2 or 3. But this scheme also requires a lower ozone yield and formation of hydrogen peroxide in presence of hydrogen even if the excited oxygen molecules do not react with hydrogen at all. In the 1:4 oxygen–hydrogen mixture one would expect (see Fig. 2) at most $50 + 25/2 = 62\%$ of ozone and at least $25/2 = 12\%$ of hydrogen peroxide as compared with the ozone yield in a similar oxygen–nitrogen mixture. The experiments show (Table I) that the sum of ozone and hydrogen peroxide formed is about 97–99%, while the hydrogen peroxide yield does not exceed 3%. This latter observation is, incidentally, in complete accord with the earlier mentioned results of Bates and Taylor. The difficulty in connection with the hydrogen peroxide yield is removed

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[16] Farkas, Goldfinger and Haber, *Naturwissenschaften*, **17**, 674 (1929).

if the suggestion be accepted that the probability of Reaction 3, which was calculated to 10^{-4} for excited atoms, is smaller in case of normal oxygen atoms, such as are produced in Reaction 4. But even with this assumption the excess of ozone yield over that calculated remains unexplained, since there are no reasons to assume that with normal oxygen atoms the ratio of the reaction velocities 1 and 2 is different than in case of excited atoms. This question, therefore, must be left open at present but it is hoped that further experiments now under way may bring a solution of this problem.

Summary

1. The oxygen–hydrogen reaction has been studied in light of the two spectral regions 1719–1725 Å. and 1854–1862 Å.

2. The effect of these spectral regions is markedly different. While the longer wave lengths produce only ozone in an amount equal to that produced in similar oxygen–nitrogen mixtures, in light of shorter wave lengths the yields of ozone in the presence of hydrogen are smaller but hydrogen peroxide is formed in addition.

3. The probable reaction mechanism has been discussed. The probability of the reaction $O + H_2 = OH + H$ has been estimated to 10^{-4}, a much smaller value than that predicted theoretically.

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[Contribution from the Chemical Laboratory of Harvard University]

THE VAPOR PRESSURE AND HEATS OF FUSION AND VAPORIZATION OF FORMIC ACID

By Albert Sprague Coolidge

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Introduction

In a recent paper[1] were given data on the density of formic acid vapor, together with some isolated vapor pressure data obtained in studying the process of purification. These data were obtained in order to make possible use of the Clapeyron equation in calculating heats of adsorption from equilibrium pressure data. The same equation should, of course, give the heats of evaporation of pure solid or liquid formic acid, when the corresponding vapor pressures are introduced. The case is interesting because of the wide deviation of the vapor from the perfect gas laws, produced by association. The only calorimetrically determined quantities by which the Clapeyron equation could be checked appeared to be the heat of vaporization of the boiling liquid, and the heat of fusion of the solid, which can be compared with the difference between the vaporization heats calculated for the solid and liquid at the triple point. Using

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[1] Coolidge, This Journal, **50**, 2166 (1928).