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

PHOTOCHEMICAL OZONIZATION AND ITS RELATION TO THE POLYMERIZATION OF OXYGEN

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It is a familiar fact that ozone is formed photochemically by irradiating oxygen gas with ultraviolet light. However, the assumption has always been made that this results from the absorption of radiation by the molecule O_2. The researches on photochemical ozonization, combined with related ones on the absorption of light by oxygen, afford evidence that the latter is not always the case, and that, rather, depending on the wave length used, the absorption may be due to another molecule, a polymer of O_2.

Most of our knowledge of this photochemical reaction has been gained through the quantitative researches of Warburg,[2] who studied ozonization at the wave lengths 2070 Å. and 2530 Å. in oxygen gas at high pressures, and measured the photochemical efficiency of ozonization for each of them. At wave length 2070 Å. he found conditions which nearly satisfied the photochemical equivalence equation, approximately two molecules of ozone being formed per quantum absorbed. This was not the case at 2530 Å. He concluded that the quantum corresponding to the former wave length was sufficient to dissociate the molecule O_2, and that this process was in reality the primary photochemical act.

The above wave lengths, however, lie to the red of the familiar ultraviolet absorption of oxygen at room temperature and ordinary pressures. The author has recently discussed the absorption of the O_2 molecule in relation to that occurring at 2530 Å. and 2070 Å. in oxygen at high pressure.[3] It does not appear that either of the two known electronic levels in the O_2 molecule can account for the absorption at 2530 Å. nor for the major part of that at 2070 Å. The absorption of oxygen gas at these wave lengths resulting in ozonization is thus evidence for the existence of another molecular species than O_2 in oxygen gas.

A second point directly related to the above is evidence in this same direction. It was originally assumed by Warburg that, in those cases where unit quantum efficiency is found in endothermic photochemical processes, the primary act is the dissociation of the absorbing molecule. The results of recent experiments have borne out Warburg's point of view.[4]

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[2] Warburg, *Berl. Ber.*, **1911**, 746; **1912**, 216; **1914**, 872; *Z. Elektrochem.*, **26**, 54 (1920); **27**, 133 (1921).

[3] Wulf, *Proc. Nat. Acad. Sci.*, **14**, 609 (1928).

[4] This does not mean necessarily that the longest wave length yielding unit quantum efficiency is a measure of the energy of dissociation of the molecule. In general it may be considerably greater, as discussed for instance in ref. 3.

Where it has been possible to test this experimentally, it appears to be true, and stoichiometrical considerations make it plausible. Thus we know today that the primary act in the photochemical dissociation of hydrogen bromide and of hydrogen iodide is indeed dissociation of the molecule,[5] and these are classical illustrations, as a result of Warburg's researches,[6] of reactions in which the conditions of the photochemical equivalence equation are apparently met. Yet so far as we now know, neither of the two wave lengths used by Warburg are sufficient to dissociate the molecule O_2, the most probable value for its dissociation energy being 7 volts,[7] corresponding to a quantum of wave length 1751 Å. Here, then, is further indication that there exists in oxygen gas a molecular species other than O_2, which is actually absorbing the light, and for which in the absorption of wave length 2070 Å. the primary act is dissociation of the molecule.[8]

Professor G. N. Lewis[9] has given evidence that there is polymerization in oxygen and from the data on the magnetic susceptibility of oxygen at low temperatures has computed a value for the change in heat content accompanying this polymerization. He concludes that at the temperature of liquid air, or at room temperature and a pressure of several hundred atmospheres, a considerable fraction of the oxygen is in the form of the molecule O_4.

A series of researches on the absorption of light in gaseous oxygen at high pressures and in liquid oxygen bear out this point of view. These have been enumerated, and discussed in part, by the author in the articles mentioned under references 3 and 8. New absorption enters whose character and behavior with changing pressure indicate that it is not due to the molecule O_2. It increases in intensity more nearly as the square of the pressure, rather than directly as the pressure. Its character and position afford evidence that in the region of 2400 Å. the molecule O_4 is undergoing dissociation by the absorption of light into the components O_3 and O. Calculation of the energy of this dissociation supports the point of view; and at the same time a plausible explanation is afforded of the

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[5] Coehn and Stuckardt, *Z. physik. Chem.*, **91**, 722 (1916); Bonhöffer and Steiner, *ibid.*, **122**, 287 (1926); Tingey and Gerke, THIS JOURNAL, **48**, 1838 (1926); Bernard Lewis, *J. Phys. Chem.*, **32**, 270 (1928); Bonhöffer and Farkas, *Z. physik. Chem.*, **132**, 235 (1928).

[6] Warburg, *Berl. Ber.*, **1916**, 314; **1918**, 300.

[7] Hogness and Lunn, *Phys. Rev.*, **27**, 732 (1926); Birge and Sponer, *ibid.*, **28**, 259 (1926).

[8] The author has recently discussed, *Proc. Nat. Acad. Sci.*, **14**, 614 (1928), the estimations of the heat of dissociation of oxygen that have been made from Warburg's data on photochemical ozonization. See Born and Gerlach, *Z. physik.*, **5**, 433 (1921), and Warburg, *Z. Elektrochem.*, **26**, 58 (1920).

[9] Lewis, THIS JOURNAL, **46**, 2027 (1924).

results of Warburg's quantum efficiency measurements. The wave length 2530 Å., which is to the red of this limit, would not be expected to give conditions approximating the equivalence equation, as has been discussed above, and indeed Warburg found that it did not, while λ 2070 Å., which is well to the short wave length side of this limit, did give conditions approximating the equivalence equation.

Thus there is evidence that the molecule O_4 is the absorbing molecule in photochemical ozonization at wave lengths 2530 Å. and 2070 Å., and that in the region of 2400 Å. a continuous absorption begins and stretches to shorter wave lengths, representing the dissociation of O_4 molecule into O_3 molecule and oxygen atom.

The behavior of this absorption with changing pressure is further evidence that it is due to the molecule O_4, and affords the possibility of making a quantitative estimate of the degree of polymerization. It is evident that the existence of the equilibrium between O_4 and O_2 gives at once a qualitative explanation of the tendency for this absorption to increase more rapidly than as the first power of the pressure. For low total pressures there would be predicted an increase proportional to the square of the pressure, as was recorded by early investigators. Liveing and Dewar suggested two possible explanations: (1) the existence of the molecule O_4 in equilibrium with O_2; and (2) an alteration of the O_2 spectrum by the influence at high pressures of neighboring molecules on those absorbing. Quantitative absorption measurements made by Warburg will now be considered.

For the two wave lengths 2070 Å. and 2530 Å., Warburg[10] measured the absorption over a range of pressures, in the case of the first wave length extending from 27.5 kg./cm.^{2} to 392.5 kg./cm.^{2}, and both for 95% oxygen and for air. Wave length 2530 Å. lies in the discontinuous spectrum,[3] that is, in the midst of the band progression that precedes the continuous spectrum. The change of the absorption of this wave length with pressure might be complicated by the pressure broadening of the band spectrum. Wave length 2070 Å., however, lies in the continuous spectrum, and the assumption that the absorption due to it is proportional to the number of absorbing molecules will probably be approximately true even to fairly high pressures. Warburg found that the absorption increased more rapidly than the pressure, but somewhat more slowly than the square of the pressure. He believed that there was sufficient evidence against polymerization as a possible explanation; at least this appears to be the case from a previous paper[11] in which he considered this absorption in liquid oxygen. Nernst had pointed out, for instance, that oxygen obeyed Trouton's rule and that this was evidence against the

[10] Warburg, *Berl. Ber.*, **1915**, 230.

[11] Warburg, *Verhandl. deut. physik. Ges.*, **17**, 194 (1915).

opinion[12] that liquid oxygen was appreciably polymerized.[13] Warburg felt rather that this failure of oxygen to obey Beer's law showed that the molecular absorption was influenced by neighboring molecules, an effect which Ångstrom[14] had ascribed to the action of collisions. Warburg treated his results entirely from this point of view.[15]

In view of the considerable amount of evidence pointing to the existence of the polymer O_4, it is our purpose to apply the idea of the polymerization to Warburg's results. Before passing to the calculation of the equilibrium constant, however, it must be mentioned that, as had been noticed by earlier observers, Warburg also found there was a considerable difference between the absorption of the oxygen in compressed air and that in compressed oxygen, the former being approximately two-fold greater than that in 95% oxygen for the same partial pressure. It seems probable, however,

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[12] See, for example, Hunter, *J. Phys. Chem.*, **10**, 330 (1906); Dolezalek, *Z. angew. Chem.*, **222**, 2460 (1909); *Z. physik. Chem.*, 71, 191 (1910).

[13] The argument with regard to Trouton's rule would apply, however, only if the degree of polymerization in the liquid state were considerable and if the change in heat content accompanying depolymerization were large. At the normal boiling point oxygen appears to be about one-quarter polymerized, and Lewis (ref. 9) finds the change in heat content accompanying depolymerization to be 128 calories. The molal heat of vaporization of oxygen at the normal boiling point is 1632 cal.. Dana, *Proc. Amer. Acad.*, **60**, 241 (1925).

[14] K. Ångstrom, *Arkiv. Mat. Astron. Fysik*, Bd. 4 (1908).

[15] A brief discussion regarding this type of explanation seems necessary. According to it, the molecule acquires the ability to absorb through the influence of impacts by other molecules, this dying away with time after each impact. Thus this absorption depends not only on the number of molecules of this kind present, but also upon the number of times they are struck per unit of time. There is some similarity between such an explanation and the idea of polymerization. It would seem, however, that the new absorption, as it decays with time, might reasonably be expected to change not only in intensity but also in character, reverting toward that of the unstruck molecule. This new absorption in oxygen, while somewhat diffuse, as would be expected of any absorption at high pressures, bears the characteristics of clear-cut molecular absorption. It would seem more in keeping with present ideas to attribute it to some definite molecular species having a definite electronic configuration of its own, and in this way polymerization seems a more acceptable explanation. In long paths of oxygen the new spectrum appears at relatively low pressures and its general form is preserved even into the liquid state. That this absorption is some of the known absorption of O_2 in a displaced or distorted form appears not to be the case. The character of this spectrum has been discussed by the author under reference 3. There is also a little evidence against the collisional point of view in the observation of Liveing and Dewar that this new absorption of oxygen appeared if anything to be slightly weakened in passing from normal temperature to 100°. The number of impacts per unit of time increases as the square root of the temperature, and thus, barring other complications, this would lead to a slight increase in the absorption from the point of view of Warburg's treatment. On the basis of the second suggestion of Liveing and Dewar, which depended on the average proximity of the molecules, no change would be expected, while from the point of view of polymerization one would predict a slight decrease in the O_4 concentration and hence in the absorption.

that the equilibrium $O_4 \rightleftarrows 2O_2$ may be considerably different in a solvent. At the highest pressure used by Warburg the concentration of nitrogen is less only by a factor of six than that of the solvent in water solution. That there is a difference in the amount of O_4 in pure oxygen and in air containing oxygen at the same partial pressure is not out of accord with the idea of polymerization.

Using Warburg's absorption data, the author had calculated the equilibrium constant in terms of partial pressures.[16] However, the assumption upon which the entire calculation rests is that the absorption is proportional to the number of O_4 molecules present. The absorption being thus employed as a measure of concentration (which is not proportional to partial pressure at these high pressures), it is evidently consistent to use units of concentration in the calculation and to express the equilibrium constant as

$$K_\rho = \frac{\rho_2^2}{\rho_4} = \frac{(\rho - \rho_4)^2}{\rho_4} = \frac{16c_2^2}{c_4}$$

where ρ_2, ρ_4 and ρ are the densities of O_2, O_4 and of the mixture, respectively in grams per cc., and the c's indicate concentrations in moles per cc. In the region where ρ_4 is small compared to ρ_2, one may write as a close approximation

$$\rho_4 = \frac{\rho^2}{K_\rho + 2\rho}$$

but above this, where the degree of association is appreciable, the expression is

$$\rho_4 = \frac{1}{2}\,(K_\rho + 2\rho - \sqrt{K_\rho^2 + 4\rho K_\rho})$$

The absorption observations at the lower pressures are at higher concentrations than the pressure would indicate on the basis of perfect gas behavior, while just the reverse is true concerning the observations at the highest pressure, these being at a lower concentration than the pressure would indicate. Both these facts tend to raise the value of the constant compared with that calculated in terms of partial pressures and as will be seen make a very considerable difference in the final value.

For wave length 2070 Å. Warburg gives at seven different pressures the value of $z = \log_{10} J_0/J$ for 95% oxygen, where J_0 and J are the initial intensity and the intensity after passing through a length d of the gas. Assuming that Beer's law holds for the absorbing molecular species, O_4,

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[16] Wulf, *Proc. Nat. Acad. Sci.*, **14**, 356 (1928). Over this range of pressures oxygen shows considerable deviation from the perfect gas law, the pv product passing through a minimum in the vicinity of 150 atmospheres and at 400 atmospheres being appreciably greater than its value at one atmosphere. The calculation was looked upon, however, as an approximate estimation. The result $K_\rho = 531$ atm. or, in other units, $K_\rho = 0.35$ g./cc., appeared not unreasonable, even though this indicated a rather surprisingly large degree of polymerization, considering that assumptions had been made which could be only approximately true.

we may write

$$z = \log_{10}\frac{J_0}{J} = d\cdot\mu_4\cdot c_4\cdot\log_{10} e = \beta\cdot\rho_4$$

where μ_4 is the molal absorption coefficient of the molecule O_4 for this wave length, and c_4 is the number of moles of O_4 per unit volume. It is evident that values of z for two values of ρ will afford a determination of K_p and the proportionality factor β.

In the following table the first and fifth columns are taken directly from Warburg's paper. The third and fourth columns give the corresponding pv product and density of the gas mixture which the author has obtained from the available data on the pressure–volume relations in oxygen at 20°.[17] The last column contains the values corresponding to the absorption of pure oxygen.[18] These are plotted in the figure against the corresponding densities of the gas mixture.

Table I

Results

Pressure Kg./cm.^{2}	 Atm.	pv pv = 1 at 0° and 1 atm.	Density, g./cc.	z 95% O_2	z 100% O_2
27.5	26.6	1.056	0.0360	0.144	0.154
47.5	46.0	1.043	.0630	.382	.409
67.5	65.3	1.031	.0905	.736	.788
97	93.8	1.017	.132	1.30	1.39
195	188.6	1.014	.266	4.69	5.02
293.5	284.0	1.053	.385	9.84	10.53
392.5	380.0	1.127	.482	13.9	14.87

The curve inserted in the figure corresponds to the equation

$$z = \frac{\beta}{2}\left(K_p + 2\rho - \sqrt{K_p^2 + 4\rho K_p}\right)$$

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[17] Below 100 atm. there are recent data; above this the earlier measurements of Amagat have been used. The nearest temperature at which the latter measurements were made is 15.65°; but those also made by Amagat at 0 and 99.5° showed that above 100 atm. a linear interpolation would be quite justifiable and the values for pv at 100 atm. and above were so determined. These two sets of data do not meet exactly. The discrepancy is not great, however, and in the plotting of the 20° pv–p curve up to 500 atm. a smooth joining of the data has been made. The difference in the value of pv at 100 atm. as given by the two sources of data is only about 1%.

[18] Warburg deduced a formula to convert the absorption of 95% oxygen to the case of pure oxygen. This resulted in a uniform 7% increase at any pressure. Since in treating this work from the viewpoint of the polymerization we apply an equation of different form to Warburg's results than that which he used, it is evidently the experimentally observed absorption which we must consider rather than the equation which Warburg finally arrived at as expressing best his results on the basis of the theory mentioned in footnote 15. But it is advisable to apply the correction to the observed values, since the absorption for pure oxygen will be greater than for 95% oxygen at the same total pressure, and by an amount which is at least approximately given by the 7% correction.

with the values of K_ρ = 1.2 g./cc. and β = 133 cc./g. The percentage deviations of the observed from the calculated values about cancel one another. It should be noted that there is, however, a tendency for the values of z at low values of ρ to lie above the computed ones, while at high values of ρ the reverse is true. The cause of this is not evident. It may be due to deviations from the fundamental assumption of the proportionality between the absorption and the number of molecules of O_4 per unit volume. It may also be due to the fact that a small amount of absorption due to the molecule O_2 is also present at this wave length. If the curve were lowered somewhat in the vicinity of c = 0.1, holding the value at c = 0.4 as it is, for instance, this would result in an increase in the value of K_ρ. The reduction of the observations from 95% oxygen to pure oxygen by the factor 1.07 does not greatly affect the result.

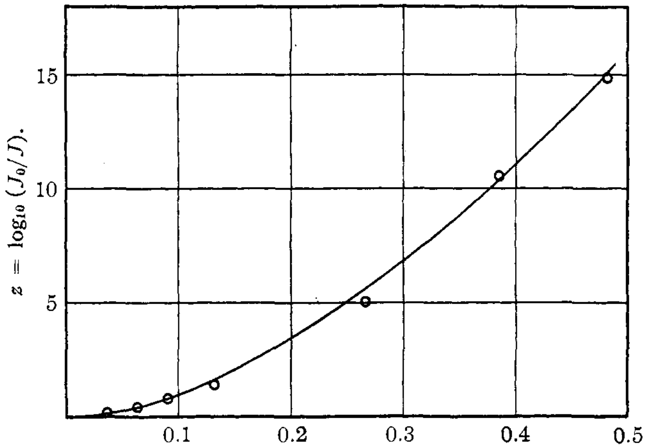

Fig. 1.

The value of the equilibrium constant obtained by Professor Lewis from the magnetic susceptibility measurements of Perrier and Onnes is K_ρ = 4 g./cc. Thus the value obtained in the present work is a little more than three-fold smaller, but the author feels that the agreement is satisfactory considering that assumptions which could only be approximately true have entered into this treatment of the absorption data. It may be that only the order of magnitude of the present result is significant.

The molal absorption coefficient of the molecule O_4 for this wave length may also be estimated. Warburg's values of z given in the table were for a thickness of gas of 1.72 cm. From the above

$$\mu_4 = \frac{\beta \cdot \rho_4}{d \cdot c_4 \cdot \log_{10} e} = \frac{\beta \cdot M_4}{d \cdot \log_{10} e} = \frac{133 \times 64}{1.72 \times 0.434} = 1.1 \times 10^4 \text{ cm.}^2 \text{ per mole}$$

It might be suggested that the extent of polymerization indicated above, although small, should make itself evident in the observed pressure–volume relations. A moment's reflection shows that in the absence of any knowledge of the independent behavior of O_2 and O_4, no quantitative conclusions can be drawn. It may be pointed out, however, that the *pv* value for oxygen falls markedly below that for nitrogen, and at high pressures by an amount that is of the order to be expected if the difference is due in a considerable degree to the decrease in the number of molecules. Furthermore, the constant *b* of the van der Waals equation is smaller for oxygen than for nitrogen, which is suggestive in view of a tendency for this quantity to increase with increasing molecular weight, within a series of molecules built of the same number of atoms. It is not meant to imply that the molecule O_2 should behave at high pressure just as the molecule N_2, but the difference might not be expected to be great and the observed difference is in the direction to be accounted for by the polymerization. It is true that the ratio of *pv* for nitrogen and oxygen varies very little from 500 atm. to 3000 atm. Yet at these pressures the concentration is no longer even approximately proportional to the pressure and the increase in the total gas concentration will be small, the composition of the mixture changing only slowly in the direction of being richer in O_4. But again, the molecular size determined from viscosity measurements also gives a value for oxygen smaller than for nitrogen, and it is not evident that this should be affected by the polymerization. The paramagnetism of oxygen is undoubtedly also a factor in conditioning its behavior. There appears, at least, to be nothing in the pressure–volume relations inconsistent with the idea of polymerization, while the latter affords a plausible explanation of some points. The present work rests upon the facts of photochemical ozonization in connection with the new absorption of oxygen, which appears in the liquid and in the gas at high pressures and which shows so striking a departure from Beer's law.

This work had its origin in discussion with Professor T. R. Hogness of this Laboratory, and the author gladly acknowledges his indebtedness to him for valuable suggestions.

Summary

The characteristics of photochemical ozonization at wave lengths 2070 Å. and 2530 Å. afford important evidence for the existence of a polymer of the molecule O_2 in oxygen gas.

Related experiments on the absorption of light by oxygen gas at high pressures and in liquid oxygen support this, and indicate that this polymer is the molecule O_4.

Qualitatively, the change of the absorption with the pressure agrees with the idea that the absorption is due to the molecule O_4. Quantita-

tively the data afforded by the absorption measurements of Warburg lead to a value of the equilibrium constant K_p = 1.2 g./cc. Probably this is significant only in order of magnitude owing to the approximations entering into the treatment of the data.

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THE INFLUENCE OF ACIDS AND BASES ON THE INHIBITORY EFFECT OF GELATIN UPON THE CATALYTIC DECOMPOSITION OF HYDROGEN PEROXIDE BY COLLOIDAL PLATINUM

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Introduction

Both Groh[1] and Iredale[2] have stated that the inhibitory effect of protective colloids upon the catalytic decomposition of hydrogen peroxide by colloidal platinum is approximately proportional to their protective properties as measured by Zsigmondy's "gold number." Tartar and Lorah[3] and later Reinders,[4] using proteins as protective colloids, investigated the influence of different degrees of acidity and alkalinity on the "gold number" and concluded that the variation of the protective action was in accordance with the known amphoteric character of the proteins.

The work presented herein is a study of the influence of different degrees of acidity and alkalinity on the inhibitory effect of gelatin upon the catalytic decomposition of hydrogen peroxide by colloidal platinum. It was undertaken in order to determine whether or not under these conditions the variation of the inhibitory effect is similar to that of the protective effect, as shown by Zsigmondy's "gold number."

Experimental Part

(a) **Preparation of Materials.**—The colloidal platinum was prepared by Bredig's arc method using a direct current, 110 volts and 8 amperes. The platinum was dispersed in a solution of 0.001 *M* potassium hydroxide as a peptizer. After standing for a few weeks in clean Pyrex flasks to permit the larger platinum particles to settle, the sol was carefully decanted and made uniform by mixing. The concentration then determined was 12.5 mg. of platinum per liter.

The gelatin ("Silver Label" brand) was purified and made isoelectric according to the procedure recommended by Loeb[5] and dried *in vacuo* at 65–70°. The gelatin sol used was prepared by adding 0.05 g. of gelatin to 100 cc. of water and heating the mixture

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[1] Groh, *Z. physik. Chem.*, **88**, 414 (1914).

[2] Iredale, *J. Chem. Soc.*, **119**, 109 (1921); *ibid.*, **121**, 1536 (1922).

[3] Tartar and Lorah, *J. Phys. Chem.*, **29**, 792 (1925).

[4] Reinders, *Chem. Weekblad*, **22**, 481 (1925).

[5] Loeb, "Proteins and Theory of Colloidal Behavior," McGraw-Hill Book Co., New York City, **1922**, p. 35.