# THE REACTIONS OF OXYGEN AND HYDROGEN AT LOW PRESSURES<sup>1</sup>

#### W. H. RODEBUSH

Department of Chemistry, University of Illinois, Urbana, Illinois

#### Received October 6, 1936

The oxygen molecule is unique among the common elementary diatomic molecules. Chemists had always considered oxygen as a bivalent atom, but when they began to think in terms of the Lewis theory of valence this fact of paramagnetism naturally caused doubt as to whether the atoms in the oxygen molecule were linked by a double bond. Attempts were made to argue from the reactivity of the oxygen molecule as to the nature of the bonding. It never became necessary to point out that reactivity depends on factors which are not directly related to the strength of the bonding in a molecule, because the proponents of the argument could not agree as to the degree of reactivity to be attributed to the oxygen molecule. The reason for this difference of opinion lies, of course, in the erratic behavior of oxygen. If oxygen supported combustion with the same readiness that it supports respiration, all dry organic matter would doubtlessly be consumed in a short time. The reason for this erratic behavior is certainly to be found in the fact that the lowest energy state of the oxygen molecule is a triplet state, whereas the great majority of other molecules, including, of course, the products of combustion, exist in singlet states. The fact that the lowest energy state of the atom is also a triplet state undoubtedly adds to the peculiarities of the behavior of oxygen. Any reaction involving a change in multiplicity in the atom may be expected to proceed much more slowly than it would were the case otherwise. The factor is  $10^{-3}$  or less, so that such reactions may be regarded in many cases as not taking place at all.

It had occurred to the author and doubtless to many others that the explanation of the activity of oxygen in supporting respiration was to be sought in the paramagnetic character of the iron in hemoglobin. Recent work by Pauling and Coryell (6) appears to confirm this idea. Hemo-globin is paramagnetic, while the oxygen compound is diamagnetic.

<sup>1</sup> Presented at the Symposium on Molecular Structure, held at Princeton University, Princeton, New Jersey, December 31, 1936 to January 2, 1937, under the auspices of the Division of Physical and Inorganic Chemistry of the American Chemical Society. Another example of a rapid reaction, involving in this case the oxygen atom, is the reaction

$$O + NO_2 = NO + O_2$$

which was studied by Spealman and Rodebush (9). Here there is presumably no change in multiplicity, and a rapid reaction is to be anticipated. Aside from these reactions with molecules known to be paramagnetic, rapid reactions involving oxygen are likely to be rare. The direct oxidation of unsaturated molecules by addition of molecular oxygen is not a probable reaction. Most oxidations, as, for example, combustion reactions, are likely to involve chain reactions. These chains will presumably produce active species such as atoms or radicals. At higher temperatures, these exothermic reactions are likely to be rapid for various reasons, one of which is that oxygen atoms are likely to be produced in the higher energy singlet states.

Since we can produce the various active species of atoms and radicals in the laboratory by photochemical activation or electronic bombardment, it becomes possible to study the separate steps of the hypothetical chain reactions. In this paper will be reported some conclusions based on the study of the various activated species of oxygen and hydrogen produced by the electrodeless discharge at low pressures. This method of study has two advantages over the method of photochemical activation at higher pressures. It is possible to produce larger quantities of atoms or other activated species, and the mechanism of a homogeneous reaction can be established with certainty because of the infrequency of triple collision. There is one serious disadvantage in that seldom, and perhaps never, can the possibility of reactions occurring on the walls be entirely eliminated. Reactions on the walls will not take place to a considerable extent, however, unless one of the reactants is strongly adsorbed. But one who works at low pressures becomes more and more convinced of the truth of the old dictum that gaseous reactions occur only at surfaces. Certainly the homogeneous mechanisms which have been established for gaseous reactions are few in number.

One may, of course, argue that a study of reactions at low pressures will not give much information about what happens at high pressures. This is true to some extent, but negative evidence cannot be disregarded. On account of the great increase in the number of triple collisions, simple mechanisms are less likely to play a rôle at higher pressures; certainly not unless they are sufficiently rapid to be observed at low pressures.

The technique employed in obtaining the results discussed here consists in dissociating a gas or mixture of gases in a bulb by means of an electrodeless discharge. The dissociation products are pumped rapidly through a series of traps cooled with dry ice or liquid air. If it is desired to prolong the time for reaction in the gaseous phase, a 5-liter flask is interposed between the discharge and traps. This does not greatly increase the surface area in contact with the gas, and does greatly increase the ratio of collisions in the gas phase to collisions with the walls. The pressure varies from 0.3 to 0.7 mm., and the time required for the gas to pass through the flask may be as much as thirty seconds.

The factors influencing dissociation are not well understood. It is known that the presence of water tends to reduce the catalytic activity of the walls in causing the recombination of hydrogen atoms, but this is not true for all atoms (8). Definite evidence has been obtained in this laboratory that impurities increase the amount of dissociation. It is well known that pure nitrogen does not give an afterglow, but if oxygen, water, or hydrogen is present in small amounts, an afterglow is obtained. A brilliant afterglow can be obtained with a small amount of hydrogen. Recent work by Rabinowitch and Wood (7) suggests the explanation of this phenomenon. When a molecule is excited by electron bombardment, it is likely to return to its normal state by radiating the acquired energy. Collision with another molecule may prevent this by transforming the molecule to a metastable or repulsive state. For reasons which may be surmised, foreign gas molecules may be more effective than molecules of the same kind. The whole subject requires further investigations.

## THE REACTION OF OXYGEN ATOMS WITH HYDROGEN

Oxygen atoms do not react with molecular hydrogen at low pressures. Exhaustive experiments fail to show any trace of reaction, either in the gas phase or on the walls of the liquid-air trap. What the experiments actually prove is that the recombination of oxygen atoms is a much more rapid reaction than any reaction with hydrogen. The recombination of oxgyen atoms does not involve any change in multiplicity, but it requires triple collisions and is not particularly rapid. There is no evidence of eatalytic activity by the walls under ordinary conditions.

The reaction

$$O + H_2 = H_2O$$

is not to be expected, both because of the large heat of activation and because of the change in multiplicity. The reaction

$$O + H_2 = OH + H$$

might, however, be expected to take place. It is slightly exothermic, and its failure to take place must be due to a fairly large heat of activation. If it did take place, regardless of what might happen to the hydroxyl, the hydrogen atoms so formed should react with oxygen molecules to form hyW. H. RODEBUSH

drogen peroxide and water, and no evidence for this reaction could be obtained. Oxygen atoms can undoubtedly be made to react with hydrogen at higher pressures, but it seems doubtful if a simple bimolecular mechanism will account for the results in the pressure region, where triple collisions are relatively frequent. The probability of reaction in a triple collision may, of course, be very different from that for a double collision.

Oxygen atoms will not react with hydrogen atoms in a double collision. The possibility of their reaction on the walls of a liquid-air trap will be discussed later.

# THE REACTION OF HYDROGEN ATOMS WITH OXYGEN MOLECULES

Hydrogen atoms react with oxygen molecules to form hydrogen peroxide and water, the relative amounts varying widely with the experimental conditions. That there is a primary gas-phase reaction here is almost certainly demonstrated by our experiments, in which the 5-liter flask is interposed in the system. There is evidence for the rapid disappearance of hydrogen atoms. Of course, there is possibility of reaction on the walls of the flask, especially if a triple collision reaction is involved. It is difficult to decide what the initial step may be, in view of the apparent rapidity of the reaction. The bimolecular mechanism

$$H + O_2 = OH + O$$

is doubtful for various reasons, but primarily because it is probably endothermic by 10 or more large calories. While the heat of formation of hydroxyl is not known with certainty, a number of observers believe it to be about 105 cal. Evidence will be presented later which indicates that hydroxyl is not a primary product in the reaction of hydrogen atoms with molecular oxygen.

The second possible mechanism is

$$\mathrm{H} + \mathrm{O}_2 = \mathrm{HO}_2$$

This mechanism should involve a triple collision. It is very difficult to prove by experimental methods that a mechanism involving triple collisions is taking place.

# THE FORMATION OF HYDROGEN PEROXIDE

Hydrogen peroxide is formed in large amounts in two ways,—when water vapor is passed through the discharge or when hydrogen atoms are mixed with molecular oxygen. In order to obtain hydrogen peroxide, it is necessary to use a liquid-air trap. A dry-ice trap will condense either water or hydrogen peroxide if either is present in the vapor, but in the experiments reported here no appreciable quantity of hydrogen peroxide

 $\mathbf{286}$ 

was ever obtained without the use of a liquid-air trap. We may, therefore, suppose that the final step in the formation of hydrogen peroxide takes place in the walls of the liquid-air trap. It is useless, therefore, to speculate as to the mechanism of these wall reactions. We can only inquire as to what the activated species may be that enter the trap.

When water vapor is passed through the electrodeless discharge, and immediately thereafter through the liquid-air trap, fairly consistent results are obtained. About 45 per cent of the water molecules are converted to hydrogen peroxide, 45 per cent are condensed as water, and the remainder escape as hydrogen and oxygen in the molecular state.

The first step in the dissociation of water is probably the formation of hydrogen atoms and hydroxyl radicals. There is reason to believe that the dissociation may be nearly complete, since, under some circumstances, very little of anything is condensed in a dry-ice trap. A corollary of this observation is that neither hydrogen atoms, oxygen atoms, nor hydroxyl radicals are condensed by a trap at  $-80^{\circ}$ C. We must, of course, believe that some of the hydroxyls are further dissociated into hydrogen and oxygen by the discharge, but we shall present evidence later that this dissociation does not take place to a very great extent, and is probably about equal to the amount of oxygen passing through the trap as molecular oxygen.

If the tube leading from the discharge bulb to the trap becomes warm, or a silver foil is introduced into the tube, no peroxide is obtained, and the yield of water is increased. But if a 5-liter flask is interposed, the yield of water remains unchanged, very little peroxide is obtained, and a large amount of hydrogen and oxygen escape from the trap in the molecular form. The first two results are explained by assuming that on the surface of the warm tube or the silver foil the reactions

$$H + OH = H_2O$$
$$OH + OH = H_2O + O$$
$$O + O = O_2$$
$$H + H = H_2$$

are taking place. The last phenomenon could be explained if the mechanism proposed by Bonhoeffer and Pearson (2) as a vapor-phase reaction

$$OH + OH = H_2O + O$$

occurs.

As we shall show later, there is no evidence for the presence of oxygen atoms in the flask. We shall, therefore, assume that the reaction above takes place only on the walls of the flask, and that the adsorbed atoms of oxygen recombine before desorption. This would account for the yield of water remaining substantially unchanged. We may summarize the results of the observations on water vapor by saying that there is no evidence for any gas-phase reactions. The principal products of the discharge appear to be hydrogen atoms and hydroxyl, and there is no reason to suppose that the direct condensation of these might not yield hydrogen peroxide and water. Geib (3) has suggested other possible mechanisms, and these may very well occur, but they presuppose, in most cases at least, rapid gas-phase reactions. The condensation of oxygen atoms and hydrogen atoms in the liquid-air trap may produce hydrogen peroxide, but when one allows for the considerable loss of molecular oxygen as such, it does not appear that this reaction can account for the major part of the peroxide formation.

The evidence in regard to hydroxyl still remains wholly negative. It is the most elusive radical in inorganic chemistry, and no one who has spent much time attempting to pin down any particular rôle on this radical would be dogmatic about his conclusions. Jackson (4) has shown that carbon monoxide is oxidized by something in water vapor from a discharge that is not removed by a platinum surface. It is known, of course, that atomic oxygen is not destroyed effectively by platinum. The reaction

$$O + CO = CO_2$$

is a forbidden reaction in the vapor phase, but might, of course, take place on the walls of the vessel. On the other hand, oxygen atoms were shown not to oxidize carbon monoxide, so that Jackson's evidence falls into the same class with the other evidence reviewed here. In the absence of evidence to the contrary or an alternative explanation, one must attribute an important rôle in these reactions to hydroxyl.

# THE DISCHARGE IN MIXED GASES

The primary products obtained on passing a mixture of hydrogen and oxygen through the discharge are certainly hydrogen atoms and oxygen atoms.

Since the oxygen atoms have been shown not to react with hydrogen (except possibly in the liquid-air trap), one might predict that a discharge in mixed gases would produce the same reactions as are produced by the introduction of hydrogen atoms into molecular oxygen. This prediction is, in the main, confirmed. Since hydrogen peroxide may be produced in considerable amounts in mixed gases, we have studied the reactions in this system carefully with the idea of contrasting the behavior with that of water vapor. In doing this, we reasoned that, whereas the water vapor from the discharge contained large amounts of hydroxyl and relatively few oxygen atoms, in a mixture of hydrogen and oxygen the active species must be chiefly hydrogen and oxygen with relatively small amounts of hydroxyl. The mechanism of the reactions to form hydrogen peroxide should be different in the two cases, and the behavior should, therefore, be different. The results obtained appear to substantiate this view.

Hydrogen and oxygen were mixed in the proportions in which they exist in water and passed through the discharge. The yield of peroxide is extremely variable,—in some cases very small. In these cases, however, there was evidence of catalytic activity on the walls of the vessel, as shown by a rise in temperature. A low yield of peroxide was not accompanied by a corresponding increase in water formed, but rather by an increased loss of hydrogen and oxygen in the molecular state. One may, therefore, disregard those runs in which low yields of peroxide were obtained. The runs in which relatively high yields of peroxide resulted on the other hand indicate that the catalytic activity of the walls was at a minimum, and these runs must, therefore, be taken at their face value.

The maximum conversion to peroxide obtained was about 37 per cent, calculated on the basis of the reaction

$$2H_2 + O_2 = H_2O_2 + H_2$$

in order to be comparable to the results on water vapor. This may be taken as the result when the catalytic activity was at a minimum. The loss of oxygen and hydrogen in molecular form was correspondingly larger than with water vapor running from 20 to 30 per cent. On the other hand, if a 5-liter flask is interposed in the system, the peroxide yield is not greatly reduced as in the case of water vapor, but falls to about 27 per cent, conversion being on the same basis as before. This behavior alone appears to establish a fundamental difference in the reaction mechanism in the two cases.

Another test which resulted in a markedly different behavior was made by introducing a piece of silver foil into the system. The peroxide yield dropped to zero in every case, but with water vapor, as has already been stated, the yield of water increased, while with the mixed gases, the result depended upon the location of the foil. If placed near the discharge, a large yield of water was obtained, which can probably be explained as resulting from the reactions of atoms of one or both elements on the surface of the foil. When the foil was placed at the exit of the 5-liter reaction chamber, loss of oxygen and nitrogen in the molecular form increased to 65 per cent of the total.

## THE PERCENTAGE OF OXYGEN ATOMS IN THE DISCHARGE

Recently Spealman and Rodebush (9) have investigated a very sensitive test for oxygen atoms. If nitric oxide is mixed with atomic oxygen, a brilliant greenish-white luminescence is obtained, which has apparently been called by some observers the "oxygen" afterglow, as distinguished from the nitrogen afterglow, which is an entirely different phenomenon. The mechanism of this reaction is the formation of a nitrogen dioxide molecule, presumably by a triple collision in an excited state. The radiation results from the return of the molecule to its normal state.

The nitric oxide was introduced into the exit end of the 5-liter reaction chamber and allowed to diffuse back against the gas flow. With the mixed gases, a quite intense glow was obtained which extended one-third to onehalf of the way across the flask. With water vapor, the glow was less intense, and did not extend very far into the reaction chamber. Since we know from previous work that not more than about 30 per cent of the oxygen is dissociated into atoms, it seems evident that not more than 10 to 15 per cent of the water is completely dissociated, and the oxygen atoms from this dissociation disappear very rapidly. The absence of oxygen atoms in the reaction chamber is evidence against the occurrence of the reaction

$$OH + OH = H_2O + O$$

in the gas phase.

# THE $HO_2$ MOLECULE

We shall finally consider the evidence for the existence of the HO<sub>2</sub> molecule, which has been proposed by Marshall, Bates (1), and others. The evidence is that in the mixed gases the mechanism for the formation of peroxide is different in some step, at least, from that in the water vapor discharge. When the 5-liter reaction chamber is in the system, about thirty seconds is required for the gases to pass from the discharge to the trap. All of the atoms must have certainly recombined in this time, and according to the evidence of Oldenberg (5) any hydroxyl present will have disappeared. No peroxide is present as such. However some active species is present, having a life period of thirty seconds or more, which will form peroxide in a liquid-air trap, but which is decomposed into the original elements by silver foil. The species which behaves in this way must have a much longer life period than a hydrogen or oxygen atom, but must still be very reactive. In the absence of any other possibility, one must consider the possibility of an HO<sub>2</sub> complex. The formation of this complex should require a triple collision, but our results indicate that the reaction is relatively rapid as compared with the recombination of hydrogen atoms. This result is in agreement with the observations of other investigators.

One concludes from the foregoing discussion that no special emphasis should be placed on the non-occurrence of reactions of oxygen with hydrogen, involving a change in multiplicity, since it has not been possible to prove that any homogeneous bimolecular mechanism, involving oxygen and hydrogen, takes place at low pressures. The reaction between hydrogen atoms and oxygen molecules, while relatively rapid, certainly requires further study.

The discussion in this paper has been restricted to results obtained in this laboratory. This is not because the author is not aware of a large amount of significant work that has been done elsewhere. He has hesitated to include a discussion of the results from other laboratories because of the uncertainty that must always exist as to the comparability of experimental conditions.

The conclusions expressed here are based upon a very large amount of data obtained in this laboratory, chiefly by Mr. C. W. J. Wende and Dr. R. W. Campbell. The detailed report of these experiments will be published elsewhere.

## REFERENCES

- (1) BATES, J. R.: J. Chem. Physics 1, 457 (1933).
- (2) BONHOEFFER, K. F., AND PEARSON, T. G.: Z. physik. Chem. 14B, 5 (1931)
- (3) GEIB, K. H.: J. Chem. Physics 4, 391 (1936).
- (4) JACKSON, W. F.: J. Am. Chem. Soc. 67, 82 (1935).
- (5) OLDENBERG, O.: J. Chem. Physics 3, 266 (1935).
- (6) PAULING, L., AND CORVELL, C. D.: Science 83, 489 (1936).
- (7) RABINOWITCH, E., AND WOOD, W. C.: J. Chem. Physics 4, 358 (1936).
- (8) RODEBUSH, W. H., AND KLINGELHOEFER, W. C.: J. Am. Chem. Soc. 55, 130 (1933).
- (9) SPEALMAN, M. L., AND RODEBUSH, W. H.: J. Am. Chem. Soc. 57, 1474 (1935).