

[CONTRIBUTION FROM THE U. S. BUREAU OF CHEMISTRY AND SOILS, WASHINGTON, D. C.]

THE DISSOCIATION OF OZONE AND THE MECHANISM OF ITS THERMAL DECOMPOSITION

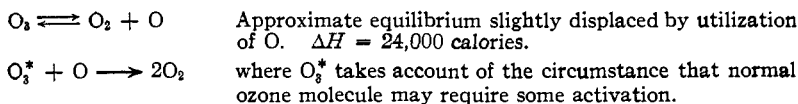
BY OLIVER R. WULF

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From the temperature coefficients of thermal ozone decomposition measured in their work, Wulf and Tolman¹ in 1927 computed the heat of dissociation of oxygen. To make this computation it was necessary to assume that the mechanism of the decomposition was of such a nature that the apparent heat of activation was the heat of dissociation of ozone into molecular and atomic oxygen. Completion of the decomposition was taken to be the reaction of oxygen atom with ozone molecule. This calculation involved, besides the apparent heat of activation, the thermochemically observed value for the heat of transformation of ozone into molecular oxygen. The heat of dissociation of oxygen thus computed was 128,000 calories, while the correct value has recently been shown² to be 117,000 calories. A combined uncertainty of about 6,000 calories in the determination of the heat of decomposition of ozone into molecular oxygen and of the heat of dissociation of ozone as determined from the temperature coefficient of this thermal decomposition, would bring these values into agreement, and it will be pointed out later that the assumed mechanism represents a sort of limiting case, the observed heat of activation being in general probably somewhat greater than the heat of dissociation of ozone if this mechanism does obtain.

The mechanism considered here is described in the equations



Much work has been done on this reaction with considerable disagreement in the results,³ and some differences of opinion have been held as to the

¹ Wulf and Tolman, *THIS JOURNAL*, **49**, 1650 (1927).

² Birge and Sporer, *Phys. Rev.*, **28**, 259 (1926). Birge, *Trans. Faraday Soc.*, **XXV**, 707 (1929). Frerichs, *Phys. Rev.*, **36**, 398 (1930).

³ Warburg, *Ann. Physik*, **9**, 1286 (1902); Clement, *ibid.*, **14**, 341 (1904); Jahn, *Z. anorg. Chem.*, **48**, 260 (1906); Clarke and Chapman, *J. Chem. Soc.*, **93**, 1638 (1908); Perman and Greaves, *Proc. Roy. Soc. (London)*, **80A**, 353 (1908); Chapman and Jones, *J. Chem. Soc.*, **97**, 2463 (1910); Griffith and McKeown, *ibid.*, **127**, 2086 (1925); Griffith and McKeown, *Z. physik. Chem.*, [A] **120**, 236 (1926); Belton, Griffith and McKeown, *ibid.*, **129**, 3153 (1926); Wulf and Tolman, *THIS JOURNAL*, **49**, 1183 (1927); **49**, 1202 (1927); **49**, 1650 (1927); Griffith and McKeown, *ibid.*, **49**, 2721 (1927); Riesenfeld and Bonholtzer, *Z. physik. Chem.*, [A] **130**, 241 (1927); Riesenfeld and Schumacher, *ibid.*, [A] **138**, 268 (1928); Riesenfeld and Wasmuth, *ibid.*, [A] **143**, 397 (1929); Schumacher and Sprenger, *ibid.*, [B] **6**, 446 (1930).

relative importance of the results. At this point, therefore, the author wishes to state explicitly the purpose of the present paper. It is not to give further review nor to discuss the merits of past work, but rather to give independent evidence which makes it seem probable that oxygen atoms are operative in thermal ozone decomposition for low concentration ozone in ozonized oxygen at one atmosphere pressure. These were the conditions under which Wulf and Tolman made their temperature coefficient measurements. Their work used the dynamic or flow method, a linear dependence of the logarithm of the specific second order rate on the reciprocal temperature was found, and the second order character of the reaction was also observed during the experiments.

The approximate agreement of the computed heat of dissociation of oxygen with the known value is suggestive. The authors continued in their 1927 work by investigating the kinetics of the second step in the mechanism, assuming that the concentration of oxygen atoms was practically the equilibrium concentration in the first step, to see whether or not the possible over-all rate of reaction was sufficiently large to account for the known rate of decomposition. To do this it was necessary to make detailed calculations of the thermodynamic quantities involved in the equilibrium represented in the first step. They found that there were not nearly sufficient collisions between oxygen atoms and ozone molecules to account for the observed rate. To make these calculations, Wulf and Tolman used the thermodynamic data available, even though some of these were not all that might be desired.

Somewhat later Professor W. F. Giaque very kindly pointed out that the value for the entropy of ozone, $S_{273}^{\circ}(\text{O}_3) = 86.5$, resulting from the calculations (see equation 23, Ref. 1) was probably wrong, being much too high, and, furthermore, that a fair estimate could be made of this quantity from entropies already known. The author is much indebted to Professor Giaque for these remarks, which formed the starting point of the present paper. The location of the chief source of difficulty was not hard to place. It probably lies in the value for $\Delta F_{273}^{\circ}(\text{O}_3 \rightarrow 3/2 \text{O}_2)$, a quantity the experimental determination of which is very difficult. The estimation of the entropy of ozone can, however, be made with fair assurance within a few entropy units. To do this the author has compared the entropies of four triatomic molecules which are quite similar in certain respects to ozone. Their entropies are either given or readily computed from data that are at hand, and in these four cases the material has been taken from Lewis and Randall.⁴ These molecules, their respective entropies so derived and their molecular weights are as follows

⁴ Lewis and Randall, "Thermodynamics," McGraw Hill Book Co., New York, 1923.

CO_2 (g), $S_{298}^\circ = 49.4$	M. w. = 44
NO_2 (g), $S_{298}^\circ = 53.7$	M. w. = 46
COS (g), $S_{298}^\circ = 52.4$	M. w. = 60
SO_2 (g), $S_{298}^\circ = 57.0$	M. w. = 64

From inspection of these values surely a fair estimate of the entropy of O_3 , M. w. = 48, can be made, reasonable limits being from 50 to 55 entropy units. In order to have some explicit basis for computing this quantity, however, the author has used an extension of the empirical formula suggested by Eastman⁵ for the entropy of diatomic molecules, taking the entropy of triatomic molecules to be given by the expression

$$S_{298}^\circ = 3/2 R \ln (A_1 A_2 A_3) + \text{constant}$$

and has determined the constant from the entropies of these four triatomic molecules as having the value 27.9. Computing the entropy of ozone from this formula one finds O_3 (g) $S_{298}^\circ = 52.6$. Without repeating in detail any of the calculations here, but following them through exactly as done in reference (1) except for this new value for the entropy of O_3 , one finds an equilibrium constant for the first step of the mechanism described above very nearly the value necessary to give a concentration of oxygen atoms just that required by this mechanism; that is, the number of collisions between O and O_3 is then approximately equal to the observed second order rate. In particular the value for ΔF_{373} in equation 25 of reference (1) is equal to 19,100 calories and (for the same conditions as in Ref. 1) the partial pressure of oxygen atoms 3.3×10^{-13} atm. This gives a number of collisions between O and O_3 of about 1.5×10^{15} per cc. per second, while the number of molecular reactions occurring under the same conditions was 1.2×10^{14} per cc. per second, thus reversing the conclusion from the calculations in Reference 1, there being ample collisions to account for the observed rate. It is evident, however, that if further activation were required in the over-all reaction, as for instance of O_3 in the second step in order that it might react with O, the correct value for the change in heat content ΔH in the first step to use in computing the equilibrium concentration of oxygen atoms, would not be that calculated from the heat of activation, since this, because of the additional activation, would yield a value greater than the heat of dissociation of ozone. Rather, the heat of dissociation of ozone itself should be used, and as has been pointed out above, this can be independently computed now from the heat of dissociation of oxygen, having the value of approximately 24,000 calories, a somewhat smaller value indeed than that computed from the temperature coefficient. With this we find a value for ΔF_{373} in equation (25) of 12,800 calories and the partial pressure of oxygen atoms equal to 1.6×10^{-9} atm. This gives approximately 7×10^{18} collisions per cc. per second between O and O_3 , while, as was

⁵ Lewis and Randall "Thermodynamics," p. 462.

mentioned above, the decomposition rate was 1.2×10^{14} reactions per cc. per second, thus over 10^4 more collisions than reactions. From a study of Kistiakowsky's results on the photochemical decomposition of ozone, Schumacher⁶ has recently concluded that normal oxygen atoms react with ozone molecules about once in every 2000 collisions. The present treatment found from a calculation of the concentration of oxygen atoms in equilibrium with ozone molecules and oxygen molecules over 10^4 more collisions between oxygen atoms and ozone molecules than were necessary to account for the thermal rate of decomposition. Thus, assuming that Schumacher's conclusion is justified, our calculation might be taken as indicating that the thermal decomposition actually does proceed through the interaction of oxygen atoms with ozone molecules.

A consideration of the general mechanism upon which these calculations have been based and which is illustrated in the above equations shows that at least two factors might, consistent with the principle of this mechanism, lead to a larger value for the heat of activation in reality than the heat of dissociation of ozone into O_2 and O . In the first place, the first of the two reactions represented in this equilibrium may require some activation. Whereas for true thermal equilibrium in the first step the apparent heat of activation of ozone decomposition would still appear, in spite of this consideration, to be exactly the heat of dissociation of ozone, nevertheless with reaction actually occurring and with conditions at some unknown distance from equilibrium in the first step, the apparent heat of activation for ozone would rise, tending toward the heat of dissociation of ozone plus the additional activation required in the forward reaction of the first step. However, while this may be important where the absolute rate is high, it does seem that at high total pressures and at the lowest ozone concentrations that have been studied, where the absolute rate is low, there is presumably sufficient time for the practical establishment of thermodynamic equilibrium in the first step, and hence this source of increase of the heat of activation over that of the heat of dissociation does not seem probable in the measurements of Wulf and Tolman. Secondly, however, the second step may require activation. In particular it would seem not improbable that the ozone molecule, normally possessing no unpaired electrons,⁷ would require activation before it would enter into reaction with an oxygen atom. As was shown above, this is quite in accord with the calculations, one interpretation of which would be that only one in about every 10^4 ozone molecules reacts with

⁶ Schumacher, *THIS JOURNAL*, **52**, 2377 (1930).

⁷ Lewis, "Valence and the Structure of Atoms and Molecules," Chemical Catalog Company, New York, 1923, pp. 130, 147, *et seq.*; *Chemical Reviews*, **1**, 234 (1924); Wulf, *Proc. Nat. Acad. Sci.*, **13**, 744 (1927); Vaidyanathan, *Indian J. Phys.*, **2**, 422 (1928).

an oxygen atom upon collision. The author believes that in the present state of our knowledge it is expedient to consider such a required activation as involving an alteration in the electronic structure of the molecule. Recent work on the absorption spectrum of ozone carried out in long paths by the author⁸ has shown that there is a low-lying electronic level in this molecule somewhere below 1.2 volts, which conceivably represents this reactive state required for the ozone molecule by the above considerations, although it is obvious that one cannot obtain a very close check upon this at present. But from energy considerations it remains that the observed rate of ozone decomposition can be described by the suggested mechanism, the concentration of oxygen atoms in equilibrium with ozone molecule and oxygen molecule being ample, the ozone molecule apparently requiring certain energy of activation before it can react with an oxygen atom.

Thus, summarizing the above considerations, the calculations of the heat of dissociation of oxygen made by Wulf and Tolman in 1927 from their data on the temperature coefficient of thermal ozone decomposition yielded a value in fair agreement (actually somewhat high) with the correct value now known from other sources. The mechanism of ozone decomposition assumed in these calculations, besides including a reasonable explanation of the somewhat high calculated value for the heat of dissociation of oxygen, is found to yield a rate of decomposition which is in good agreement with the observed rate, when a reasonable value for the entropy of ozone is used. This is shown to constitute evidence that a form of this mechanism is the chief process by which ozone decomposes at one atmosphere pressure and low ozone concentrations. Such a mechanism would represent a particularly simple case of thermal temperature coefficient. However, the sensitiveness of the strongly exothermic ozone decomposition to impurities makes it a difficult reaction to observe kinetically free of disturbances. In conclusion, it may lend emphasis to state the above in a somewhat different order. If normal oxygen atoms react with ozone molecules as frequently as once in every 10^4 collisions, then the use of our present knowledge of the heat of dissociation of oxygen leads to a concentration of oxygen atoms in equilibrium with ozone and oxygen which indicates that, for low rates and high total pressures, the reaction of oxygen atoms with ozone molecules is probably the principal cause of thermal ozone decomposition.

WASHINGTON, D. C.

⁸ Wulf, *Proc. Nat. Acad. Sci.*, **16**, 507 (1930).