

The Structure of Ozone

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lar to that in water than to the free hydroxyl radical, as has been assumed by Pauling.²

Some empirical evidence is offered below which tends to support the lower value (1.51 ev) for the O—O bond in hydrogen peroxide. In connection with another problem, we have had occasion to calculate the O—O bond energies in several different molecules. We have made a comparison of the interatomic distances and bond energies as shown in Table I. These data are shown graphically in Fig. 2. It is seen that the O—O bond energy (2.37 ev) based on the assumption that the OH bond energy in H_2O_2 is more similar to the free hydroxyl radical does not fall on the curve obtained from the other structures containing O—O bonds. However, the O—O bond energy (1.51 ev) calculated on the basis that the OH bond in H_2O_2 is like the OH bond in water, fits very well into the curve, bond energy *vs.* interatomic distance. Hence the smaller value is to be preferred.

* A part of a thesis submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, in the Department of Chemistry and Chemical Engineering, in the Graduate College of the State University of Iowa.

¹ Skinner, *Trans. Faraday Soc.* **41**, 645 (1945).

² Pauling, *J. Am. Chem. Soc.* **54**, 3570 (1932).

The Structure of Ozone

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ADEL and Dennison¹ have recently re-examined the infra-red bands of ozone and have accepted the Hettner, Pohlman, and Schumacher assignment,² $\nu_1 = 2105$, $\nu_2 = 1043$, $\nu_3 = 710 \text{ cm}^{-1}$, which results in an acute angle

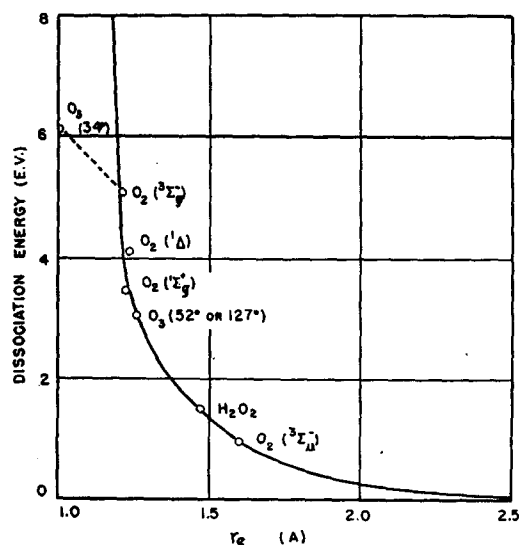


FIG. 1. Dissociation energy of oxygen-oxygen bonds *vs.* interatomic distance.

($\alpha = 34^\circ$) isosceles triangle model, with $c_2 = 3.4$ and $c_1 = 0.6$ megadyne/cm, when a simple central force field is used. c_2 is the central field force constant between the oxygen atoms at the base of the isosceles triangle, c_1 is the force constant between the oxygen atoms at the apex and the base. They also estimated that the base internuclear distance is about 1 Å. At the present time there is a good deal of conflict regarding the correct fundamental frequencies and the structure of ozone. In this connection we wish to make the following remarks.

It seems difficult to believe that the base distance in ozone should be less than the interatomic distance in the oxygen molecule (1.21 Å). It would mean that the bond energy in the base pair of oxygen atoms is greater than the bond energy in the free molecule (see Fig. 1). We have calculated other isosceles models on the assumption that the sum of the bond energies must be 6.12 electron volts, obtained from the usual thermochemical calculation



Assuming that the base line is 1.21 Å (as in the oxygen molecule), the bond energy of the base pair in ozone is 5.08 ev (heat of dissociation of O_2). The bond between the apical oxygen and one of the base line atoms is then $\frac{1}{2}(6.12 - 5.08) = 0.52 \text{ ev}$, corresponding to 1.84 Å (see Fig. 1). The apical angle would then be $38^\circ 24'$. Similarly, if 1.26 Å is taken to be the length of the base line, the energy curve yields 1.45 Å for the sides of the triangle and the apical angle is $51^\circ 30'$.

If the base bond were only one angstrom in length, it would mean that electrons from the third incoming oxygen

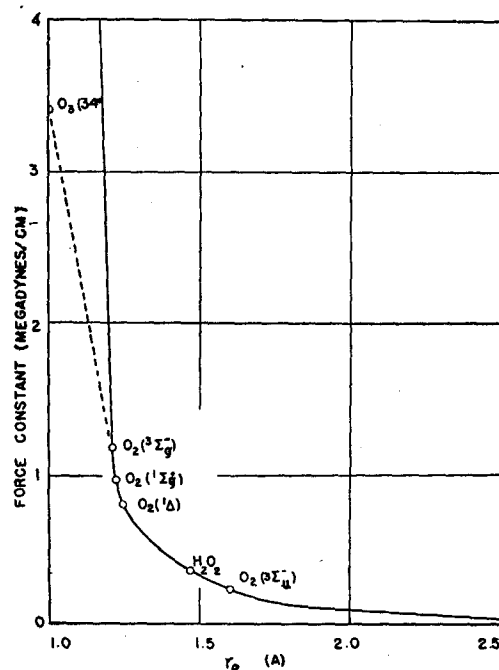


FIG. 2. Force constants of oxygen-oxygen bonds *vs.* interatomic distance.

atom attach themselves to the already existing oxygen bond, strengthening it, and decreasing its distance from 1.21Å to 1.0Å. It seems more reasonable to believe that the reverse happens. Even if it is assumed that all the binding energy (6.12 eV) resides in the 1Å base bond, it can be seen from Fig. 1 that this situation does not fit into the energy-distance relation. Hence it is believed that the base line must be greater than 1.21Å (oxygen molecule) and perhaps 1.26Å. Therefore, for the 52° model, it is estimated from Fig. 2, that the constant c_2 is about 0.7

megadyne/cm and c_1 is about 0.38 megadyne/cm. It is realized that these considerations are based on the assumption that the bond energies and force constants of all O—O bonds are given by the relations shown in Figs. 1 and 2. The 52° model gives moments of inertia $I_A = 51.1 \times 10^{-40}$ g cm², $I_B = 30.2 \times 10^{-40}$ g cm², and $I_C = 20.9 \times 10^{-40}$ g cm², so that the quantity $2I_AI_B/(I_A + I_B) = 38 \times 10^{-40}$ g cm². Adel and Dennison estimate $56 \times 10^{-40} \pm 20$ percent.

¹ A. Adel and D. M. Dennison, J. Chem. Phys. **14**, 379 (1946).

² G. Hettner, R. Pohlman, and H. J. Schumacher, Zeits. f. Physik **91**, 372 (1934).