The results seem to indicate that neither cerous nor ceric perchlorate reacts with the perchloric acid, that cerous perchlorate is not hydrolyzed in the presence of the perchloric acid, but that ceric perchlorate is hydrolyzed in stages with formation of two ions $CeOH^{+++}$ and $Ce(OH)_2^{++}$ in proportions to satisfy the equilibrium conditions of the reaction, $CeOH^{+++} + H_2O = Ce(OH)_2^{++} + H^+$. The equilibrium constant of this reaction was estimated to be 0.6, and the molal oxidation potentials of the electrode reactions $CeOH^{+++} + H^+ + E^- = Ce^{+++} + H_2O$ and $Ce(OH)_2^{++} + 2H^+ + E^- = Ce^{+++} + 2H_2O$ were found to be 1.7134 and 1.7265 volts, respectively.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 915]

The Molecular Structure of Ozone

BY W. SHAND, JR., AND R. A. SPURR

Ozone has interested many investigators, but, because of the difficulties of preparation of pure ozone, its great reactivity, and its explosive nature, no complete structure determination has yet been reported. Table I gives a summary of some of the structural parameters and oscillational frequency assignments which have been suggested for ozone. The present work was suggested by the idea that the purity of gas required for an electron diffraction determination is not so great as for spectroscopic work, and it seemed to us that a purity of 95% or better could readily be obtained in a suitable apparatus.

TABLE I

Author	Year	Angle	Distance	Fundamental frequencies[1]		
				ν_1	ν_2	ν_3
G. N. Lewis[2]	1923		Like SO_2			
S. L. Gerhard[3]	1933	*ca.* 60°		528	1033	1355
R. M. Badger and L. Bonner[4]	1933	*ca.* 120°		1050	440	1355
W. S. Benedict[5]	1933	*ca.* 122°	1.29 ± 0.1 Å.	1046	760	1355
Hettner, *et al.*[6]	1935	38°		2105	1037	710
Penney and Sutherland[7]	1936	127 ± 20°	1.23 Å.	1037	710	1740
Smyth and Lewis[8]	1939	140°	1.13 Å.			
Present Work	1942	127 ± 3°	1.26 ± 0.02 Å.			

Experimental.—The ozone was prepared by the method of Karrer and Wulf[9] using a silent electric discharge and an all-Pyrex glass apparatus attached directly to a glass nozzle in the electron diffraction apparatus described by Brockway.[10] A mixture of Apiezon M and graphite, which did not seem to be attacked by ozone, was used as a stopcock lubricant. Tank oxygen was passed through the ozonizer and a light blue mixture of oxygen and ozone was collected in a large trap cooled in liquid air. This mixture was fractionated into a smaller storage trap at hourly intervals until several ml. of blue-black ozone had accumulated for the final purification. This was fractionated into the large trap again and the system was pumped down until the pressure, indicated by a Pirani gage on the electron diffraction apparatus, was negligible. Enough ozone was usually made to fill a 300 ml. storage bulb at 1 atm. pressure.

It is important to establish the purity of the preparation. Oxygen (b. p. −183°), nitric oxide (b. p. −152°), and the other oxides of nitrogen (b. p. above 0°) boil at temperatures sufficiently removed from the boiling point of ozone (−112°) that they should be nearly completely removed by the fractionation and pumping off of the residual gases. After each set of pictures the

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(1) ν_1 is essentially the symmetrical stretching frequency, ν_2 the symmetrical bending frequency, and ν_3 the antisymmetrical stretching frequency.

(2) G. N. Lewis, "Valence and the Structure of Molecules," Chemical Catalog Co., New York, N. Y., 1923, p. 130.

(3) S. L. Gerhard, *Phys. Rev.*, **42**, 622 (1933).

(4) R. M. Badger and L. G. Bonner, *ibid.*, **43**, 305 (1933).

(5) W. S. Benedict, *ibid.*, **43**, 580 (1933).

(6) G. Hettner, R. Pohlman and H. J. Schumacher, *Z. Elektrochem.*, **41**, 524 (1933).

(7) W. G. Penney and G. B. B. M. Sutherland, *Proc. Roy. Soc.* (London), **A156**, 578, 654 (1936).

(8) C. P. Smyth and G. L. Lewis, THIS JOURNAL, **61**, 3063 (1939).

(9) S. Karrer and O. R. Wulf, *ibid.*, **44**, 2391 (1922).

(10) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

ozone was condensed in the traps and the pressure was always found to be of the order of a few mm., showing that little or no oxygen had been formed. (The v. p. of O_3 at $-180°$ is about 3 mm.) Deep blue ozone was observed in the traps of the electron diffraction apparatus after the exposures had been made, and the pictures obtained were uniform in appearance. Other investigators,[9,11] using the same method of preparation, have shown that pure ozone is obtained thereby.

The camera distance was 11.01 cm., and the wave length of the electrons was 0.0615 Å. Five of the best pictures, showing four rings, were selected for interpretation.

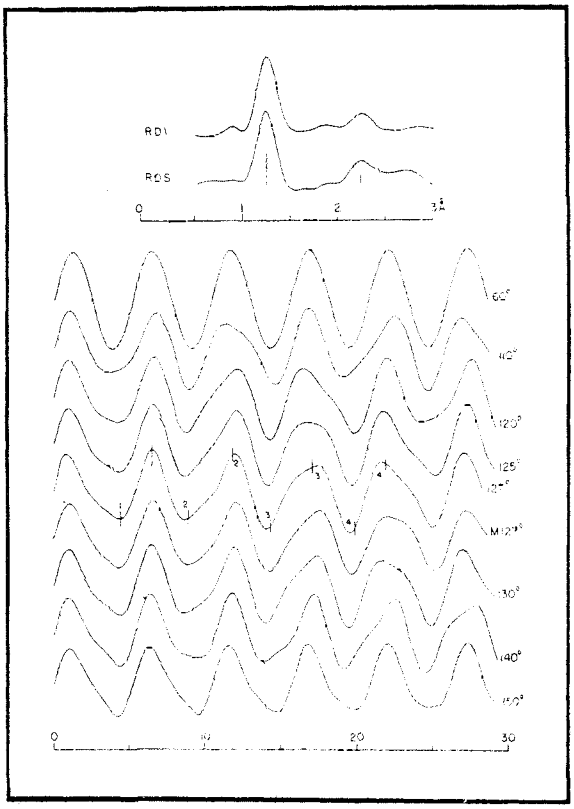

Fig. 1.

Interpretation.—Both the radial distribution method[12] and the correlation method[13] were used in interpreting the electron diffraction photographs. Radial distribution curves were calculated by two methods according to the formula

$$lD(l) = \sum_{k} C_k \sin s_k l; \quad C_k = I_k(s_k)e^{-as_k^2}$$

where $I_k(s_k)$ is a visually estimated intensity assuming no falling off of intensity with s_k, and a is chosen so that $e^{-as^2_{\max}} = 0.1$. The curve marked RDS of Fig. 1 was calculated using s_k values only at the maxima and minima of the observed curve; for the curve marked RDI, a plot of the visually estimated intensities was divided into about 40 segments, and the C_k's estimated at each end-point. The latter method is a good approximation to the integral inversion. Both methods give peaks corresponding to distances of 1.26 and 2.24 Å., indicating an angle of 127°. The lines under the peaks show the distances finally chosen and their relative expected intensities.

Theoretical intensity curves, calculated using the simplified theoretical scattering formula

$$I(s) = 2Z_0^2 \frac{\sin 1.26s}{1.26} + Z_0^2 \frac{\sin l_{13}s}{l_{13}}$$

for models having the form of an isosceles triangle with bond length 1.26 Å. and varying apical angle, are shown in Fig. 1. The characteristic features of the photographs, namely, the asymmetry of the second maximum, the depth of the third and fourth minima, and the complementary asymmetry of the third and fourth maxima, were best reproduced by the curve marked 127°. Table II gives the correlation of this curve with the measurements of the pictures.

Table II

Min.	Max.	$s_{\text{obs.}}$	$s_{\text{calcd.}}$	$s_{\text{obs.}}/s_{\text{calcd.}}$
1		4.14	4.20	1.014
	1	6.25	6.31	1.010
2		8.64	8.31	0.962
	2	11.35	11.51	1.014
3		13.72	13.48	0.983
	3	16.42	16.68	1.016
4		18.97	18.80	0.991
	4	21.22	20.79	.980
			Average	0.996 ± 0.016
			O-O	1.25_5 Å.

The curve marked M 127° was calculated for a mixture of 30 mole % O_2 (O—O = 1.21 Å.) and 70 mole % O_3 (O—O = 1.27 Å.) to show that even a relatively large impurity would not seriously falsify the results of this investigation. If the pictures had been taken of this mixture, the error would be an underestimation of the O—O distance by about 0.015 Å. and of the O—O—O angle by about 3°. As set forth above, however, there is ample reason for believing that the ozone was quite free of impurities.

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[11] P. Lamé, *Compt. rend.*, **198**, 918 (1934).

[12] L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935).

[13] L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

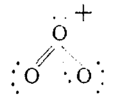
Using the moments of inertia of the structure given above the entropy of ozone was calculated, and the equilibrium constant of the reaction $O_3 = 3/2O_2$. The frequency assignments of Penney and Sutherland[7] were accepted in evaluating the vibrational entropy. The choice of any other recent frequency assignment would make a negligible change in the results. The value used by Stuart[14] of $E_0^0 = 34513$ cal./mole was used. The results are given in Table III.

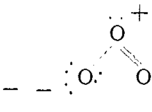
TABLE III

T, °K.	$\log K = \frac{3}{2} \log p_{O_2}/p_{O_3}$	$-\left(\frac{F - E_0^0}{T}\right)_{O_3}$	$-\left(\frac{F - E_0^0}{T}\right)_{O_2}$ [15]
298.16	28.461	48.617	42.058
500	18.373	53.454	45.662
1000	10.679	61.662	50.675
1500	8.093	67.594	53.779
2000	6.684	72.279	56.070
2500	5.376	76.061	57.901
3000	4.649	79.378	59.431

S_{t+r}	56.43
S_v	0.38
S_{tot}	56.81
	±0.1 cal./°/mole

Discussion.—The resonating structures of ozone which are probably most important are I–IV. Other singly bonded structures are neglected because they place a doubly positive formal charge on the central oxygen, and the structure involving two double bonds would put ten electrons on the central oxygen atom. The angle found for ozone, 127°, is slightly larger than would be expected from the structures I–IV. The van der Waals diameter of oxygen in non-hydrogen-bonded molecules is about 3.0 Å.; in ozone the non-bonded oxygen distance is only 2.24 Å., and hence the electron clouds, particularly in the double-bonded structures, would repel each other strongly, tending to increase the angle. The combination of structures III and IV contribute nothing to the dipole moment, which must be largely due to I and II. If one assumes the oxygen single bond radius 0.73 Å. found in hydrogen peroxide[16] and the double bond radius 0.55 Å.,[17] then, using the value 1.26 Å. found in this research for the O–O distance in ozone, the amount of double bond character is found to be approximately 30%.[18] The calculated dipole moment is then 1.62×10^{-18} e. s. u., compared with the observed value 0.49×10^{-18} e. s. u. measured in a solution of liquid oxygen and ozone.[8] Good agreement is generally not expected with this simple calculation for such molecules.


I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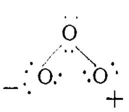
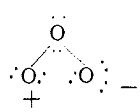

III


IV

Since this work was completed a paper[19] has appeared reviewing existing spectroscopic evidence on the structure of ozone, and favoring the structure of Hettner, Pohlman and Schumacher.[6] This structure consists of an acute isosceles triangle with apical angle 39° and O–O bond distances 1.12 and 1.68 A., being intermediate between $O_2^+O^-$ and $O_2^{++}O^{--}$. Such a molecule would certainly have a dipole moment in excess of 5 Debye units, and should exhibit the abnormal physical properties of a strongly polar substance. Ozone shows no such abnormalities, but possesses a normal boiling point and vapor density. Although the radial distribution curves already exclude this structure, theoretical scattering curves were calculated for the 39° model, and various mixtures of it with oxygen. Agreement could not be obtained, and the general appearance of the curves is definitely unlike that observed for ozone. (Added January 18, 1943.)

We wish to express our thanks to Dr. V. Schomaker and to Professor Linus Pauling for valuable advice and discussion during the course of this investigation.

Summary

The electron diffraction investigation of ozone shows that the molecule is of the form of an isosceles triangle with O–O bond distance 1.26 ± 0.02 Å. and O–O–O angle 127 ± 3°.

PASADENA, CALIF. RECEIVED OCTOBER 27, 1942

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(14) H. A. Stuart, "Molekülstruktur," J. Springer, Berlin, 1934.

(15) The values of this function for O_2 were calculated by Mr. D. R. V. Golding using the data of G. Herzberg, "Molecular Spectra and Molecular Structure," Prentice-Hall, N. Y., 1939. The physical constants are those of R. Birge, *Rev. Modern Phys.*, **13**, 235 (1941). For method of calculation and definition of terms see, for example, E. Bright Wilson, Jr., *Chem. Rev.*, **27**, 17 (1940).

(16) V. Schomaker and P. A. Giguère, unpublished investigation, and C. S. Lu, E. W. Hughes and P. A. Giguère, THIS JOURNAL, **63**, 1507 (1941).

(17) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, 1940, p. 164.

(18) L. Pauling, *ibid.*, p. 195.

(19) R. S. Mulliken, *Rev. Modern Phys.*, **14**, 204 (1942).