

lying between 90 and 120°. On the other hand, the dipole moment (2.5 *D*) of TeCl₄ in benzene solution may be attributed to the free molecule also, and interpreted as the sum of four Te-Cl bond moments each having the value 2.3 *D* estimated by Smyth, Grossman and Ginsburg. For an axial-axial bond angle of 170° in the trigonal bipyramidal structure this interpretation leads to an equatorial bond angle of 102°.

The structure for TeCl₄ discussed here is in agreement with the prediction made by Pauling.² Kimball¹¹ suggested that TeCl₄ should have an "irregular tetrahedral" configuration of symmetry *C*_{3v}. This configuration is certainly incompatible with the results of our electron diffraction investigation; moreover, it would probably lead to a dipole moment much smaller than that found by Smyth, Grossman and Ginsburg. Kimball

(11) G. E. Kimball, *J. Chem. Phys.*, **8**, 194 (1940).

apparently assumed that in TeCl₄ the unshared pair occupies a pure *s* orbital. This assumption apparently is incorrect.

The Te-Cl distance, 2.33 Å., is but slightly less than 2.36 Å., which is the sum of the covalent radii.

Summary

An electron diffraction study of gaseous TeCl₄ leads to the values 2.33 ± 0.02 Å. for the average Te-Cl distance, 3.37 ± 0.06 Å. for the only important Cl-Cl distance, and 93 ± 3° for the corresponding important bond angle. A distorted trigonal bipyramidal configuration with the unshared pair in one of the equatorial positions is compatible with these results and the known large dipole moment of the molecule. The equatorial bond angle is probably considerably less than 120°, but greater than 90°.

PASADENA, CALIFORNIA

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On the Molecular Structure of Sulfur Dioxide

BY VERNER SCHOMAKER AND D. P. STEVENSON

In the course of investigating the electron diffraction patterns of a number of simple molecules, we have obtained photographs of sulfur dioxide which are better than those previously obtained by Cross and Brockway,¹ in these Laboratories. Inasmuch as the interpretation of the new photographs leads to slightly different and probably more reliable values for the interatomic distances than those found by Cross and Brockway, we are reporting our results.

The apparatus and technique used in this investigation have been described by Brockway.² The camera distance was 10.85 cm. and the electron wave length 0.0611 Å. (*a*₀ = 4.070 Å. assumed for gold). The photographs were taken with the pressure of the sulfur dioxide in the sample bulb at about one atmosphere.

The photographs showed seven rings of which six could be measured easily. The resulting *s* values ($s = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) are given in Table I.

The radial distribution function,³ curve A of the figure, was calculated according to the modified

(1) P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, 821 (1935).

(2) L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

(3) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

TABLE I

Max.	Min.	<i>C_K</i>	<i>s</i> ₀ ^a	<i>s</i> ₀ ^b	<i>s</i> ₀ ^c	<i>s</i> ₀ / <i>s</i> ₀ ^a
	1	- 6	3.33	...	3.19	(0.958) ^d
1		10	5.54	5.63	5.48	(0.989) ^d
	2	-13	7.37	...	7.45	1.011
2		15	9.87	9.66	10.00	1.013
	3	-15	12.02	11.99	12.04	1.002
3		15	14.04	13.76	14.10	1.004
	4	-14	16.49	16.19	16.58	1.005
4		13	18.59	18.15	18.54	0.997
	5	-11	20.87		20.80	0.997
5		11	23.19		23.18	1.000
	6	- 7	25.33		25.13	0.992
6		6	27.50		27.58	1.003

Average 1.002 ± 0.005

S-O = 1.002 × 1.43 = 1.433 ± 0.01 Å.

^a This research.

^b Cross and Brockway, ref. 1, S-O = 1.46 Å.

^c From curve for model with ∠O-S-O = 120°.

^d Omitted from average because of unreliability of measurement.

procedure recommended by Schomaker,⁴ using the coefficients *C_K* given in Table I. The function has two peaks corresponding to an S-O distance of 1.435 Å., an O-O distance of 2.49 Å., and a bond angle of 121°.

(4) V. Schomaker, A. C. S. Meeting, Baltimore, Md., April, 1939.

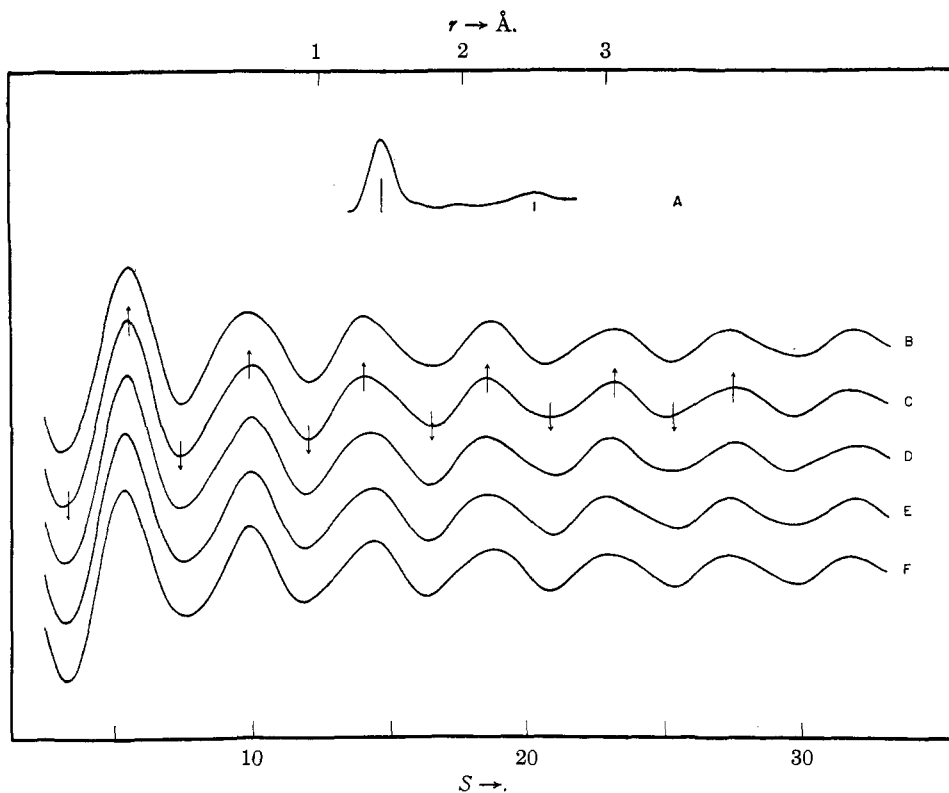


Fig. 1.—Theoretical intensity curves for sulfur dioxide: Curve A, radial distribution function; Curves B, C, D, E, F, simplified theoretical intensity curves with bond angles of 115, 120, 125, 130, 135°, respectively, and S-O = 1.43 Å. Observed s_0 values indicated by arrows.

Theoretical intensity curves, B-F of the figure, were calculated for five symmetrical models in which the bond angle was varied from 115 to 135°. It was found that the molecule could be regarded as rigid for the purposes of this investigation, and that the atomic numbers form satisfactory coefficients ($Z_i Z_j$) for the simplified intensity function. The curve for the 120° model (C) is the most satisfactory. Indeed, all of the other curves can be eliminated because of their appearance with respect to some or all of the following features: the width of the second maximum, the shape of the third maximum, the width and shape of the fourth maximum, and the width of the fifth maximum. Because the fifth, sixth and seventh rings of the photographs are quite faint, it is impossible to make any definite statements regarding the finer details of their appearance. The quantitative comparison of the observed and calculated s values is most consistent for the 120° model. This quantitative comparison for the 120° model is given in Table I and leads to the value 1.433 Å. for the S-O distance. The radial distribution function, and the qualitative and

quantitative comparisons of the correlation method are thus in excellent agreement, giving for the S-O distance and the bond angle the values 1.433 ± 0.01 Å., and $120 \pm 5^\circ$, respectively.

In previous electron diffraction investigations of sulfur dioxide Wierl,⁵ whose pictures showed only one ring, found 1.37 Å. for the S-O distance, Cross and Brockway¹ found 1.46 ± 0.02 Å., and Pauling and Brockway,³ interpreting the data of Cross and Brockway by the radial distribution method, found 1.43 Å.⁶ for the S-O distance and $124 \pm 15^\circ$ for the bond angle. The observed s values of Cross and Brockway also are given in Table I. We feel that our s values, each of which is based on 20 to 30 measurements of a ring diameter, are the more reliable because our photographs (commercial ortho film) are much "cleaner" and show six more measurable features

(5) R. Wierl, *Physik. Z.*, **31**, 1028 (1930).

(6) The s value reported by Cross and Brockway for the first maximum of the sulfur dioxide photographs is too large, leading to a too small value for the interatomic distance. The discrepancy between the values (1.46 and 1.43) obtained from the same data by the two methods of interpretation arises largely because the first maximum was excluded from the average in the correlation procedure (C and B) but was given (excessively) great weight in the radial distribution function (P and B).

than the older photographs (X-ray film). (These differences are only typical, however, of the more or less gradual improvement which has occurred since 1933 in the electron diffraction technique employed in these Laboratories.) Moreover, it so happened that this investigation was undertaken concurrently with a very satisfactory series of check measurements on diatomic molecules⁷ using the same technique and the same wave length calibrations.

There is some further information regarding the configuration of the sulfur dioxide molecule. Cross and Brockway¹ report the surprisingly consistent value $122 \pm 5^\circ$ as the bond angle obtained on fitting the three vibrational frequencies of the sulfur dioxide molecule to a two-constant, valence-force potential function. Much more important is the entropy determination of Giaque and Stephenson⁸ which leads to the value $(10.58 \pm 0.99) \times 10^{-116}$ g. cm.² for the product of the three principal moments of inertia of the molecule. This value and our S-O distance give 121° as a fairly precise value for the bond angle, substantiating our electron diffraction determination. A

(7) Schomaker and Stevenson, to be published.

(8) W. F. Giaque and C. C. Stephenson, *THIS JOURNAL*, **60**, 1389 (1938).

variation of 0.1 cal. mol.⁻¹ deg.⁻¹ in the entropy (corresponding to the uncertainty in the product of the moments of inertia given above), or of 0.02 Å. in the bond distance, would produce a change of 4° in the value calculated for the bond angle. In the calculations leading to the results reported in this paragraph the current values⁹ of N , h , and k were used. A correction of +0.2% was applied to our bond distance in order to compare it with the results of the entropy calculations based on the "new" constants. When the "old" values of the fundamental constants are used, the correlation of the entropy of sulfur dioxide with our bond distance leads to a bond angle value of 123° .

Summary

The structure of sulfur dioxide has been reinvestigated by the electron diffraction method, with the following results: S-O = 1.433 ± 0.01 Å., and \angle O-S-O = $120 \pm 5^\circ$. This value for the bond angle is in excellent agreement with the value, $121 \pm 5^\circ$, derived from the bond distance and the entropy.

(9) G. Herzberg, "Molecular Spectra. 1," Prentice-Hall, New York, N. Y., 1939, p. 3.

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Aldehyde Complexes of Copper Salts

BY TENNEY L. DAVIS AND WALTER P. GREEN, JR.

As part of an investigation of the ability of compounds containing the carbonyl group to enter into coördinative combination, we have found that acetaldehyde and butyraldehyde combine with certain copper salts, and have prepared the compounds listed below and have determined their dissociation pressures at 0° .

TABLE I
DISSOCIATION PRESSURES AT 0° (MM. AT 20°)

CuNCS·CH ₃ CHO.....	65.6
3CuNCS·2C ₃ H ₇ CHO.....	30.0
2CuI·CH ₃ CHO.....	6.3
3CuI·C ₃ H ₇ CHO.....	5.6
Cu(OCOCH ₃) ₂ ·CH ₃ CHO.....	89.9

For comparison with these dissociation pressures, we have determined the vapor pressure at 0° of pure acetaldehyde, 333.0 mm., and of pure butyraldehyde, 32.3 mm.

The formulas of the complexes show several interesting relationships. Cuprous thiocyanate combines (to form a complex which is fairly stable at 0°) with twice as many molecules of either aldehyde as cuprous iodide does. Two molecules of butyraldehyde are equivalent to three molecules of acetaldehyde in respect to the capacity of the aldehydes to combine with the cuprous salts.

When samples of the cuprous salts were exposed at 0° in closed vessels to atmospheres saturated with the vapors of the aldehydes, they absorbed the aldehydes rapidly in quantities much greater than correspond to the complexes listed above. Cuprous thiocyanate actually deliquesced in either aldehyde, and the crystals became covered with a layer of liquid. Cuprous iodide showed the same behavior with acetaldehyde, but