

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Electron Diffraction and Molecular Structure: Carbonyl Compounds¹

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This investigation was undertaken to determine the effect of the oxygen double bond on the valence angles of the carbon atom. Previous work³ has shown that the angle between the halogen atoms of disubstituted methanes is 125° and becomes 115° in the case of the trisubstituted methanes. It seems desirable, therefore, to study this effect in carbonyl compounds and to determine their molecular structures.

The angular intensity of electrons diffracted by gas molecules with random orientation may be calculated by the equation⁴

$$I = k \sum_i \sum_j \psi_i \psi_j \frac{\sin x_{ij}}{x_{ij}} \quad (1)$$

in which

$$x_{ij} = 4\pi l_{ij} \sin \theta / 2 / \lambda \quad (1a)$$

I is the relative intensity of electrons scattered at the angle θ , k is a constant under the experimental conditions, the ψ 's are the electron scattering coefficients of the atoms, l_{ij} is the distance between the i th and j th atoms of the molecule and λ is the wave length of the electrons. The double summation extends over all atoms of the molecule considered. The self-consistency of Wierl's results⁵ and their agreement with x-ray diffraction data have shown that Z , the atomic number of the atom, may be substituted for ψ in Eq. 1 rather than the expression derived by Mott.⁶ This simplified calculation of the theoretical intensity curves has been employed in the present work.

Experimental Procedure.—The procedure for electron diffraction is to allow a narrow beam of electrons to intersect a gas stream and to register the diffracted electrons on a photographic plate. The apparatus followed essentially the design by Wierl.⁷ A hydrogen discharge served as a source of electrons which were accelerated by constant potential D. C.⁸ The accelerating potential was measured by a calibrated electrostatic voltmeter. The electrons entered the diffraction chamber through a circular slit (0.1 mm.) in the electron nozzle which was at right angles to the gas nozzle. A trap immediately above the gas nozzle condensed the gas entering the diffraction chamber, which was evacuated by a high speed

(1) Presented at the Chicago Meeting of the American Chemical Society, September, 1933.

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(3) L. Bewilogua, *Physik. Z.*, **32**, 265 (1931); R. W. Dornté, *J. Chem. Phys.*, **1**, 630 (1933).

(4) P. Debye, *Ann. Physik*, **46**, 809 (1915); H. Mark and R. Wierl, *Fortschr. Chem., Physik physik. Chem.*, **B21**, 4 (1931).

(5) R. Wierl, *Ann. Physik*, [5] **13**, 453 (1932).

(6) N. F. Mott, *Proc. Roy. Soc. (London)*, **A127**, 658 (1930).

(7) R. Wierl, *Ann. Physik*, [5] **3**, 521 (1931).

(8) A. W. Hull, *Gen. Elec. Rev.*, **19**, 193 (1916).

diffusion pump.⁹ A mechanical shutter interrupting the electron beam controlled the time of exposure. The diffraction photographs were photometered with a Zeiss recording microphotometer; the diameters of the diffraction rings were measured on the enlarged photometer curves. This procedure avoided the physiological error inherent in measurements on the diffraction picture.

Preparation of Materials.—Carbonyl sulfide was obtained by dropping 50% sulfuric acid on potassium thiocyanate. The gas was purified by passage through a concentrated solution of potassium hydroxide, concentrated sulfuric acid, calcium chloride and charcoal. The product was condensed and fractionated.

The carbonyl chloride was a Kahlbaum product which was dried over phosphorus pentoxide and fractionated.

Carbonyl bromide was prepared by the action of concentrated sulfuric acid on carbon tetrabromide and purified by shaking with mercury and fractionation.

The acetyl chloride and bromide were obtained from the Eastman Kodak Company and were fractionated.

Results and Discussion

The photographs were obtained with electrons having a wave length corresponding to 45 kv. Figure 1 shows typical microphotometer curves of the diffraction pictures. The abscissas of these curves have been enlarged two-fold to emphasize the "bumps" indicating the diffraction maxima. In Table I are recorded, (1) the x values of the diffraction maxima, calculated for a definite molecular model, (2) the experimentally determined values of $\sin \theta/2\lambda$ for each maximum and (3) l , the corresponding carbon-oxygen interatomic distance in Å.

For carbonyl sulfide the relative intensity equation becomes

$$\frac{I}{k} = 2Z_C Z_O \frac{\sin x}{x} + 2Z_C Z_S \frac{\sin 1.40 x}{1.40 x} + 2Z_O Z_S \frac{\sin 2.40 x}{2.40 x} + Z_C^2 + Z_O^2 + Z_S^2 \quad (2)$$

(9) I. Estermann and H. T. Byck, *Rev. Sci. Inst.*, **3**, 482 (1932).

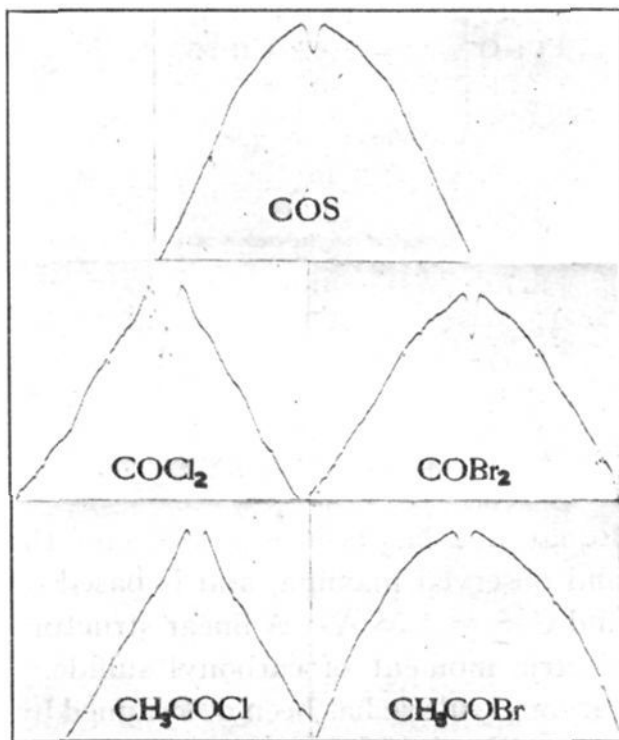


Fig. 1.—Microphotometer curves of electron diffraction photographs.

TABLE I

x	(Sin $\theta/2$)/ λ	l(C-O in Å.)	x	(Sin $\theta/2$)/ λ	l(C-O in Å.)
Carbonyl Sulfide			Acetyl Chloride		
5.85	0.412	1.13	3.30	0.232	1.13
8.60	.604	1.13	5.80	.400	1.15
10.75	.759	1.13	8.55	.597	1.14
	C-S = 1.58 \pm 0.08 Å.		11.50	.794	1.15
	C-O = 1.13 \pm 0.05		C-O	= 1.14 \pm 0.05 Å.	
Carbonyl Chloride			C-C	= 1.54 \pm 0.08	
3.10	0.221	1.11	C-Cl	= 1.82 \pm 0.10	
5.40	.385	1.12	<C-C-Cl = 110° \pm 10°		
8.05	.588	1.09	Acetyl Bromide		
12.40	.854	1.14	3.15	0.217	1.15
C-O	= 1.12 \pm 0.02 Å.		5.30	.376	1.12
C-Cl	= 1.80 \pm 0.04		7.75	.547	1.13
Cl-O	= 2.62 \pm 0.05		10.50	.742	1.12
<Cl-C-Cl = 110° \pm 5°			12.80	.903	1.13
Carbonyl Bromide			C-O	= 1.13 \pm 0.05 Å.	
2.70	0.191	1.12	C-C	= 1.54 \pm 0.08	
4.80	.341	1.12	C-Br	= 2.06 \pm 0.10	
7.15	.503	1.13	<C-C-Br = 110° \pm 10°		
8.70	.610	1.13			
11.05	.776	1.13			
C-O	= 1.13 \pm 0.02 Å.				
C-Br	= 2.05 \pm 0.04				
Br-O	= 2.85 \pm 0.06				
<Br-C-Br = 110° \pm 5°					

Equation 2 has been found to give the best correlation of the calculated and observed maxima, and is based on a linear model with C-O = 1.13 and C-S = 1.58 Å. A linear structure is consistent with the rather small electric moment of carbonyl sulfide.¹⁰ The crystal structure of solid carbonyl sulfide has been determined by Vegard,¹¹ who found a linear structure with C-O = 1.10 and C-S = 1.96 Å. Dadiou and Kohlrausch¹² determined the interatomic distances, C-O = 1.04 and C-S = 2.38 Å., from the Raman effect and previous results on the infra-red absorption spectrum.¹³ The nuclear separations obtained in this investigation are in good agreement with Wierl's results for carbon dioxide and carbon disulfide⁷ and with the values C=O = 1.13 and C=S = 1.63 Å. which are derived from the atomic radii formulated by Pauling.¹⁴ It seems probable that the discrepancy among the several values for the interatomic distances of carbonyl sulfide may arise from resonance between two or more Lewis

(10) C. P. Smyth, "Dielectric Constant and Molecular Structure," The Chemical Catalog Co., Inc., New York, Appendix 1.

(11) L. Vegard, *Z. Krist.*, **77**, 411 (1931).

(12) A. Dadiou and K. W. F. Kohlrausch, *Physik. Z.*, **33**, 165 (1932).

(13) C. R. Bailey and A. B. D. Cassie, *Proc. Roy. Soc. (London)*, **A135**, 375 (1932).

(14) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 293 (1932).

structures of the molecule as in the case of nitrous oxide.¹⁵ For phosgene Eq. 1 becomes

$$\frac{I}{k} = 2Z_C Z_O \frac{\sin x}{x} + 4Z_C Z_{Cl} \frac{\sin 1.61 x}{1.61 x} + 4Z_O Z_{Cl} \frac{\sin 2.34 x}{2.34 x} + 2Z_{Cl}^2 \left(1 + \frac{\sin 2.64 x}{2.64 x} \right) + Z_C^2 + Z_O^2 \quad (3)$$

This intensity equation is based on a plane "Y" model with a 110° angle between the carbon-chlorine bonds. Intensity curves were calculated with this angle taking values from 100 to 135°, but the best correlation of calculated and observed maxima was obtained at 110°. The intensity distribution for carbonyl bromide is

$$\frac{I}{k} = 2Z_C Z_O \frac{\sin x}{x} + 4Z_C Z_{Br} \frac{\sin 1.81 x}{1.81 x} + 4Z_O Z_{Br} \frac{\sin 2.52 x}{2.52 x} + 2Z_{Br}^2 \left(1 + \frac{\sin 1.97 x}{1.97 x} \right) + Z_C^2 + Z_O^2 \quad (4)$$

which is based on the same model as phosgene. The carbon-oxygen interatomic distance in carbonyl chloride and bromide (1.13 Å.) agrees well with the values obtained for formaldehyde (1.15 Å.) by electron diffraction,¹⁶ and 1.2 Å. from the absorption spectra.¹⁷ The absorption spectrum of phosgene¹⁸ indicates a plane "Y" structure similar to formaldehyde. An angle greater than 110° might be expected in carbonyl chloride and bromide since an angle of 125° was found in the methylene halides. This difference seems reasonable when the interaction of the dipoles is considered. The repulsion between the carbonyl group and the halogen atoms is probably equal to the mutual repulsion of the halogen atoms.

The effect of the hydrogen atoms was neglected in the intensity curves for acetyl chloride and bromide. The hydrogen-oxygen and hydrogen-halogen interatomic distances are variable if free rotation occurs around the carbon-carbon bond. Intensity curves were calculated for plane structures with 115, 125 and 135° angles between the carbon-oxygen and carbon-halogen bonds. A slightly better correlation of the maxima was

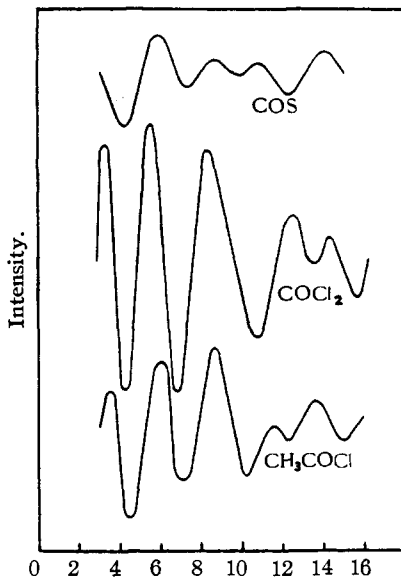


Fig. 2.—Theoretical intensity curves.

(15) L. Pauling, *Proc. Nat. Acad. Sci.*, **18**, 498 (1932).

(16) L. Bru, *Añales soc. españ. fis. quim.*, **30**, 483 (1932).

(17) V. Henri and S. A. Schou, *Z. Physik*, **49**, 774 (1928).

(18) V. Henri and O. R. Howell, *Proc. Roy. Soc. (London)*, **A128**, 178 (1930).

possible for the usual tetrahedral model. The intensity equation for acetyl chloride is

$$\frac{I}{k} = 2Z_C Z_O \left(\frac{\sin x}{x} + \frac{\sin 2.11 x}{2.11 x} \right) + 2Z_C^2 \left(1 + \frac{\sin 1.36 x}{1.36 x} \right) + 2Z_C Z_{Cl} \left(\frac{\sin 1.62 x}{1.62 x} + \frac{\sin 2.44 x}{2.44 x} \right) + 2Z_O Z_{Cl} \frac{\sin 2.34 x}{2.34 x} + Z_O^2 + Z_{Cl}^2 \quad (5)$$

and the equation for acetyl bromide is

$$\frac{I}{k} = 2Z_C Z_O \left(\frac{\sin x}{x} + \frac{\sin 2.11 x}{2.11 x} \right) + 2Z_C^2 \left(1 + \frac{\sin 1.36 x}{1.36 x} \right) + 2Z_C Z_{Br} \left(\frac{\sin 1.82 x}{1.82 x} + \frac{\sin 2.62 x}{2.62 x} \right) + 2Z_O Z_{Br} \frac{\sin 2.53 x}{2.53 x} + Z_O^2 + Z_{Br}^2 \quad (6)$$

For these molecules the angle between the carbon-carbon bond and the carbon-halogen bond is $110 \pm 10^\circ$ while the other angles are each $125 \pm 10^\circ$. The molecular structures of acetyl chloride and bromide are quite similar to the structure of acetone¹⁹ which has been determined by the same method. Interatomic distances common to the three structures are in agreement.

Summary

The molecular structures of carbonyl sulfide, chloride and bromide, acetyl chloride and bromide have been investigated by electron diffraction. The results are in agreement with other structural determinations. Carbonyl sulfide has been found to have a linear structure. The other molecules have been represented by plane "Y" models. An angle of 110° has been found between the halogen atoms of carbonyl chloride and bromide. The tetrahedral model has been found for acetyl chloride and bromide. The carbon-oxygen interatomic distance has been found constant in the carbonyl compounds.

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(19) J. Hengstenberg and L. Bru, *Annales soc. espagn. fis. quim.*, **30**, 341 (1932).