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The Determination of the Structures of Methane Derivatives by the Electron Diffraction Method

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The molecular structures of several bromine and iodine derivatives of methane have been determined by the electron diffraction method. For tertiary butyl bromide it has been found that the tertiary carbon atom has the tetrahedral angles between the valence bonds, and the interatomic distances are: tertiary $C-$ methyl C 1.55A and tertiary $C-$Br 2.06A. In methyl bromide and iodide the $C-X$ distances are 2.06 and 2.28A, respectively. In methylene bromide and iodide it has been found that the angle between the $C-X$ bonds is 125° and the interatomic distances are: $C-$Br 2.03, Br$-$Br 3.61, $C-$I 2.28 and I$-$I 4.06A. In bromoform the angles formed by the $C-$Br bonds are 115°, and the interatomic distances are: $C-$Br 2.05 and Br$-$Br 3.46A.

INTRODUCTION

THIS investigation was undertaken to determine the structures of several halogen derivatives of methane and to determine the effect of halogen substitution upon the angles between the bonds of the carbon atom. The theoretically predicted deviations from 109.5°[2] were in agreement with the x-ray diffraction data for methylene chloride and chloroform,[3] although the electron diffraction results for the same compounds[4] showed slightly smaller deviations from 109.5° than x-ray results. It seemed desirable, therefore, to determine the angle between the valence bonds of the carbon atom in bromine and iodine substituted methanes by the electron diffraction method. Tertiary butyl bromide was investigated to study the effect of methyl groups on the tetrahedral angles of a tertiary carbon atom. The tertiary butyl halides have much larger electric moments than the normal butyl and other aliphatic halides;[5] this difference has been explained as an induction effect on the three adjacent methyl groups.[6]

The angular intensity of electrons diffracted by gas molecules with random orientation may be calculated by the equation[7]

$$I = k \sum_i \sum_j \psi_i \psi_j (\sin X_{ij}/X_{ij}) \qquad (1)$$

in which

$$X_{ij} = 4\pi l_{ij}(\sin \theta/2)/\lambda. \qquad (1a)$$

I is the relative intensity of electrons scattered at the angle θ, k is a constant under experimental conditions, the ψ's are the electron scattering coefficients of the atoms, l_{ij} is the distance between the ith and jth atoms of the molecule and λ is the wave-length of the incident electrons. Previous work[8] has shown that Z, the atomic number of the atom, may be substituted for ψ in Eq. (1) rather than the expression derived by Mott.[9] This simplification has been employed in this work.

EXPERIMENTAL PROCEDURE AND RESULTS

The apparatus and procedure was that described in a previous paper.[10] The electron diffraction photographs were obtained with electrons having a velocity corresponding to 45 kv.

[1] National Research Fellow in Chemistry.

[2] J. H. Van Vleck, J. Chem. Phys. 1, 219 (1933).

[3] L. Bewilogua, Phys. Zeits. 32, 265 (1931); P. Debye, Zeits. f. Elektrochemie 36, 612 (1930).

[4] R. Wierl, Ann. d. Physik [5] 8, 521 (1931).

[5] C. P. Smyth, *Dielectric Constant and Molecular Structure, Appendix 1*, New York, The Chemical Catalog Co., Inc. (1931).

[6] C. P. Smyth and R. W. Dornte, J. Am. Chem. Soc. 53, 543 (1931).

[7] P. Debye, Ann. d. Physik 46, 809 (1915).

[8] R. Wierl, Ann. d. Physik [5] 13, 453 (1932); L. O. Brockway and L. Pauling, Proc. Nat. Acad. Sci. 19, 68 (1933).

[9] N. F. Mott, Proc. Roy. Soc. (London) A127, 658 (1930).

[10] R. W. Dornte, J. Chem. Phys. 1, 566 (1933).

The diffraction maxima were determined on the microphotometer records of the diffraction rings. Fig. 1 shows typical microphotometer curves of the electron diffraction photographs. The abscissae of these curves were enlarged twofold so that the "bumps" indicating the diffraction maxima were more pronounced in the small scale of the figure.

In Table I are recorded the X values of the diffraction maxima calculated for definite molecular models, the experimentally determined values of $(\sin \theta/2)/\lambda$ for each maxima and l the corresponding $C-X$ interatomic distance in A. The selection of a molecular model depends upon the concordance of the observed diffraction maxima with those calculated for different models. This correlation of calculated and observed maxima is measured by the constancy of the l values; the most probable structure of the molecule gives the smallest deviations in the values of l.
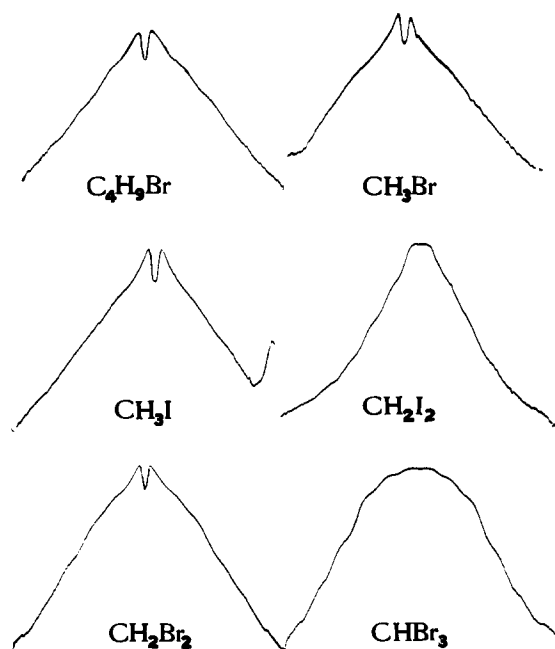

FIG. 1. Microphotometer curves of electron diffraction photographs.

TABLE I.

X	$(\sin \theta/2)/\lambda$	$l(C-X$ in A$)$
Tert. Butyl Bromide		
5.65	0.219	2.05
9.75	.376	2.06
14.15	.546	2.06
18.75	.714	2.09
22.50	.872	2.05
$C-C = 1.55 \pm 0.05$A		
$C-Br = 2.06 \pm 0.05$A		
Methyl Bromide		
7.15	0.276	2.06
14.70	.570	2.05
20.55	.791	2.07
$C-Br = 2.06 \pm 0.05$A		
Methyl Iodide		
7.25	0.252	2.29
14.50	.512	2.25
20.50	.707	2.31
$C-I = 2.28 \pm 0.05$A		

$\frac{\sin \theta/2}{\lambda}$	110°		125°		135°	
	X	l, (A)	X	l, (A)	X	l, (A)
Methylene Iodide						
0.150	4.75	2.52	4.30	2.28	4.15	2.20
.273	8.55	2.49	7.80	2.27	7.60	2.22
.400	12.75	2.55	11.50	2.29	11.00	2.19
.519	15.75	2.41	14.90	2.28	14.30	2.19
.649	19.75	2.42	18.70	2.29	17.80	2.18
$C-I = 2.28 \pm 0.05$A						
$I-I = 4.06 \pm 0.10$A						
$\angle I-C-I = 125 \pm 5°$						
Methylene Bromide						
0.166	4.75	2.28	4.25	2.04	4.15	1.99
.305	8.50	2.22	7.80	2.03	7.70	2.01
.452	12.75	2.24	11.55	2.03	11.05	1.94
.574	16.20	2.24	14.75	2.04	14.30	1.98
.738	20.25	2.18	18.75	2.02	17.90	1.93
$C-Br = 2.03 \pm 0.05$A						
$Br-Br = 3.61 \pm 0.10$A						
$\angle Br-C-Br = 125 \pm 5°$						

$\frac{\sin \theta/2}{\lambda}$	110°		115°		120°	
	X	l, (A)	X	l, (A)	X	l, (A)
Bromoform						
0.181	4.80	2.11	4.65	2.04	4.45	1.96
.324	8.50	2.09	8.35	2.05	8.10	1.99
.473	12.60	2.12	12.20	2.05	11.85	1.98
.612	16.25	2.11	15.75	2.05	15.35	2.00
.756	20.25	2.13	19.75	2.07	19.10	2.01
$C-Br = 2.05 \pm 0.05$A						
$Br-Br = 3.46 \pm 0.10$A						
$\angle Br-C-Br = 115 \pm 2°$						

DISCUSSION

In the interpretation of the electron diffraction pictures of tertiary butyl bromide the effect of the hydrogen atoms has been neglected so that Eq. (1) becomes

$$\frac{I}{k} = 2Z_C Z_{Br}\left(\frac{\sin X}{X} + 3\frac{\sin 1.43X}{1.43X}\right) + 6Z_C^2\left(\frac{\sin 0.75X}{0.75X} + \frac{\sin 1.23X}{1.23X}\right) + 4Z_C^2 + Z_{Br}^2. \qquad (2)$$

Eq. (2), shown in Fig. 2, gives a satisfactory correlation of the diffraction maxima and indicates a 110° angle between the bonds of the tertiary carbon atom. The distance between the tertiary carbon atom and the methyl carbon atoms is 1.55A; the separation of the methyl carbon atoms is 2.53A; the methyl carbon to bromine interatomic distance is 2.94A.

In the analysis of the diffraction pictures of methyl bromide and iodide the scattering of the hydrogen atoms has been considered although their effect causes only very slight deviations of the intensity curves from the simple $(\sin X)/X$ form, characteristic of a single interatomic distance. The inclusion of the effect of the hydrogen atoms gives a slightly better result for the carbon-halogen interatomic distance. Since the position of the hydrogen atoms cannot be determined by the diffraction experiments, the carbon-hydrogen distance was taken as 1.08A. The relative intensity expression for methyl bromide is

$$\frac{\overset{*}{I}}{k} = 2Z_C Z_{Br}\frac{\sin X}{X} + 6Z_H Z_{Br}\frac{\sin 1.28X}{1.28} + 6Z_H Z_C\frac{\sin 0.53X}{0.53X} + 3Z_H^2 + Z_C^2 + Z_{Br}^2. \qquad (3)$$

The carbon-bromide distance was found to be 2.06A. For methyl iodide the relative intensity equation is

$$\frac{I}{k} = 2Z_C Z_I\frac{\sin X}{X} + 6Z_H Z_I\frac{\sin 1.24X}{1.24X} + 6Z_H Z_C\frac{\sin 0.47X}{0.47X} + 3Z_H^2 + Z_C^2 + Z_I^2, \qquad (4)$$

which gives a carbon-iodine distance of 2.28A in agreement with the value found in ethyl iodide 2.32A.[11]
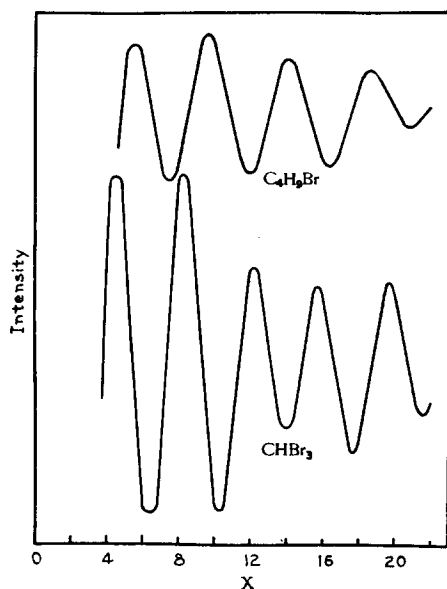

FIG. 2. Theoretical intensity curves for tert. butyl bromide and bromoform with 115° between the C—Br bonds.

The scattering effect of the hydrogen atoms in methylene iodide and bromide may be omitted without any appreciable error in the analysis of the diffraction pictures. On this basis the problem is simplified to a consideration of triatomic molecular structures. For methylene iodide Eq. (1) becomes

$$\frac{I}{k} = 4Z_C Z_I\frac{\sin X}{X} + 2Z_I^2\left(1 + \frac{\sin aX}{aX}\right) + Z_C^2, \qquad (5)$$

in which a is a parameter characteristic of the angle between the carbon-iodine bonds and has the values 1.63, 1.78 and 1.85 for the angle 110°, 125° and 135°, respectively. The data of Table I clearly show the best correlation of observed and calculated maxima for an angle of 125°. The distance between the carbon and iodine atoms is 2.28A and the separation of the iodine atoms is

[11] L. Bru, Anales soc. espan. fis. quim. **31**, 115 (1933).

4.06A. For methylene bromide the relative intensity equation is

$$\frac{I}{k} = 4Z_C Z_{Br} \frac{\sin X}{X} + 2Z_{Br}^2 \left(1 + \frac{\sin aX}{aX}\right) + Z_C^2, \quad (6)$$

in which a is now characteristic of the angle between the carbon-bromine bonds and has the same values as in Eq. (5). Fig. 3 shows the relative intensity curves of three cases considered for methylene bromide. Here, also, the correlation is best for an angle of 125° which corresponds to a bromine-bromine interatomic distance of 3.61A.
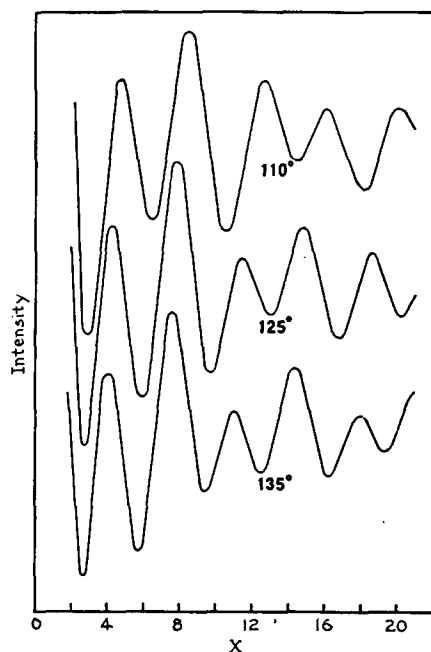

FIG. 3. Theoretical intensity curves for methylene bromide with 110°, 125° and 135° angle between the C — Br bonds.

The uncertainty in the determination of the angle is ±5°. In 1, 1 dibromo ethane the bromine separation was found to be 3.56A[12] in agreement with the value for methylene bromide.

For bromoform Eq. (1) becomes

$$\frac{I}{k} = 6Z_C Z_{Br} \frac{\sin X}{X} + 6Z_{Br}^2 \frac{\sin aX}{aX} + Z_C^2 + 3Z_{Br}^2 \quad (7)$$

where a is characteristic of the angle between the carbon-bromine bonds and has the values 1.63, 1.68 and 1.73 for the angles 110°, 115° and 120° respectively. Fig. 2 shows Eq. (7) for an angle of 115° which gives the best correlation of maxima. The distance between the bromine atoms of bromoform is 3.46A.

The present results on methylene bromide and iodide together with previous results on methylene chloride[3] indicate that the angle between the carbon-halogen bonds of methane derivatives containing two halogen atoms is practically a constant, 125°. In the tri-substituted methanes the angle between the carbon-halogen bonds is 115° for chloroform[3] and bromoform. An estimate of this angle in iodoform can be made from the x-ray analysis of crystalline iodoform by Huggins and Noble[13] who found 3.56A for the distance between iodine atoms of the same molecule and reported 3.80A as found by Brockway and Pauling for iodoform in benzene solutions. The latter value, which is preferable for comparison with results from experiments with gases, leads to a value around 115° in agreement with results for chloroform and bromoform.

[12] R. Wierl, Ann. d. Physik [5] 13, 453 (1932).
[13] M. L. Huggins and B. A. Noble, Am. Mineral 16, 519 (1931).