

Electron Diffraction and Molecular Structure

Ralph W. Dornste

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Electron Diffraction and Molecular Structure

RALPH W. DORNT,¹ *Department of Chemistry, University of California*

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The molecular structures of *cis*- and *trans*- dibromoethylene, tribromoethylene, vinyl bromide, tetrachloroethylene and trichloroethylene have been determined by the method of electron diffraction in gases. It has been found that the diffraction pictures of these substances can

be satisfactorily represented by plane structures having the following interatomic distances: C=C 1.3, C-Br 2.0 and C-Cl 1.8Å. The diffraction in carbon tetrachloride has been investigated with several widely differing electron velocities.

INTRODUCTION

INVESTIGATIONS of electron diffraction in gases have led to the solution of many problems in the realm of molecular structure as the work of Wierl² has shown. The present investigation was undertaken to determine the structures of several chlorine and bromine derivatives of ethylene and particularly to study the variation of certain interatomic distances in closely related compounds.

Structure determinations by the method of electron diffraction in gases depend upon a comparison of the relative intensity distribution curve, calculated for a definite molecular model, with the observed angular intensity curve. The relative intensity I^3 as a function of the scattering angle θ , of electrons diffracted by a gas molecule is given by

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

where k is a constant under experimental conditions, the ψ 's are the electron scattering coefficients of the atoms and

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

Mott⁴ has derived the relation

$$\psi_i = (Z_i - f_i) / ((\sin \theta / 2) / \lambda)^2, \quad (1b)$$

in which Z_i is the atomic number and f_i is the x-ray scattering factor or the atomic form factor. In Eq. (1a) l_{ij} is the distance from the i th atom to the j th atom and λ is the de Broglie wave-length of the incident electron beam.

EXPERIMENTAL PROCEDURE

The method of studying electron diffraction in gases consists essentially in allowing a fine beam of electrons of uniform velocity to intersect the gas stream and recording the diffracted electrons on a photographic plate which is perpendicular to the incident electron path. The apparatus used follows in essentials the design of Wierl.² A hydrogen discharge served as a source of electrons which were accelerated by the high potential from a source of constant potential d.c.⁵ The primary of a Snook 10 kw 140 kv transformer was supplied with 500 cycle a.c. from Crocker-Wheeler motor-generator Type CB 23. Two kenotrons, General Electric Company Type KC-1, were connected to the secondary of the transformer to give full-wave rectification. Specially insulated transformers supplied the kenotron filaments. The ripple in the kenotron output was smoothed out by five 0.05 μ f glass condensers. An electrostatic voltmeter, consisting of two fixed 5 inch copper spheres and two 2.5 inch spheres on a bifilar suspension indicated the voltage across the hydrogen discharge tube. The voltmeter was calibrated by reference to a Taylor High Voltage Resistor of 50 megohms

¹ National Research Fellow in Chemistry.

² R. Wierl, Ann. d. Physik [5] 8, 521 (1931); *ibid.* [5] 13, 453 (1932).

³ H. Mark and R. Wierl, Fortschr. Chem. Physik physik. Chemie B21, 4 (1931).

⁴ N. F. Mott, Proc. Roy. Soc. (London) A127, 658 (1930).

⁵ A. W. Hull, Gen. Elec. Rev. 19, 193 (1916).

connected in series with a sensitive milliammeter.

The electrons entered the diffraction chamber through two holes 0.2 mm and 0.1 mm in diameter. The gas at a pressure of about 150 mm of mercury entered the diffraction chamber through a fine nozzle placed at right angles to the electron nozzle. Immediately above the gas nozzle (0.1 mm aperture) was a liquid air trap which condensed most of the gas. The electrons were recorded on an Eastman 33 plate which was 25.7 cm from the gas nozzle. The diffraction chamber was evacuated by a high speed diffusion pump⁶ which was backed by an oil pump. The

hydrogen discharge tube was evacuated independently of the diffraction chamber.

The diffraction pictures were taken at a pressure of 10^{-5} mm of mercury and the length of exposure varied from a fraction of a second to two seconds. A mechanical shutter which interrupted the electron beam controlled the time of exposure. The diffraction pictures were photometered on a Zeiss recording microphotometer and the photometer curves analyzed by enlarging. This procedure avoided the physiological error inherent in analyzing the diffraction photograph itself.

TABLE I. Carbon tetrachloride, λ , Å.

x	0.05805	0.05991	0.06195	0.06420	0.06670 ($\sin \theta/2$)/ λ	0.06951	0.07632	0.08055	Calc.
7.4	0.197	0.198	0.198	0.198	0.198	0.198	0.198	0.197	0.1975
13.6	.363	.364	.363	.363	.362	.363	.364	.362	.3630
20.3	.540	.542	.542	.541	.543	.542	.542		.5415
26.2	.698	.700	.700	.700	.700	.700			.6993
32.7	.874	.873							.8720

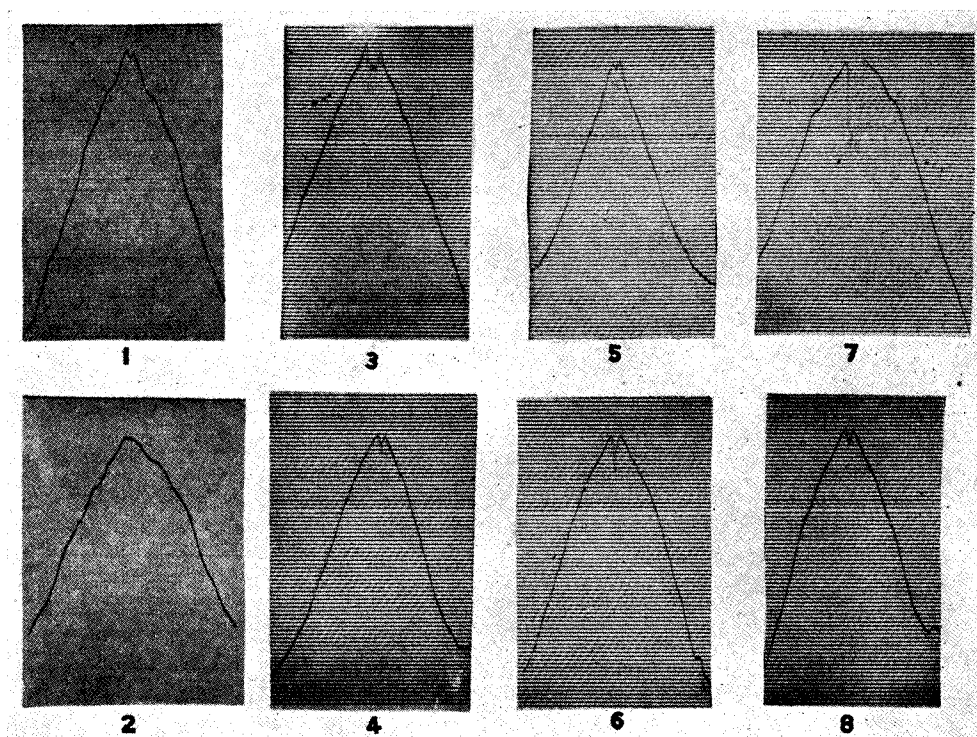


FIG. 1. Photometer curves of electron diffraction photographs. 1 and 2, carbon tetrachloride; 3, cis-dibromoethylene; 4, trans-dibromoethylene; 5, tribromoethylene; 6, vinyl bromide; 7, tetrachloroethylene; 8, trichloroethylene. Electron accelerating potential 45 kilovolts for all pictures except No. 2, 25 kilovolts.

⁶ I. Estermann and H. T. Byck, Rev. Sci. Inst. 3, 482 (1932).

RESULTS AND DISCUSSION

The preliminary work was an investigation of the diffraction of carbon tetrachloride and its dependence upon the electron accelerating potential. A series of pictures were taken at intervals of 2.5 kv from 20 to 45 kv. The first column of Table I gives the x values for the maxima calculated for a regular tetrahedron; the last column gives the $(\sin \theta/2)/\lambda$ values calculated for a carbon chlorine distance of 1.82Å. The other columns record the average values of $(\sin \theta/2)/\lambda$ obtained from several pictures at each wave-length. The agreement of

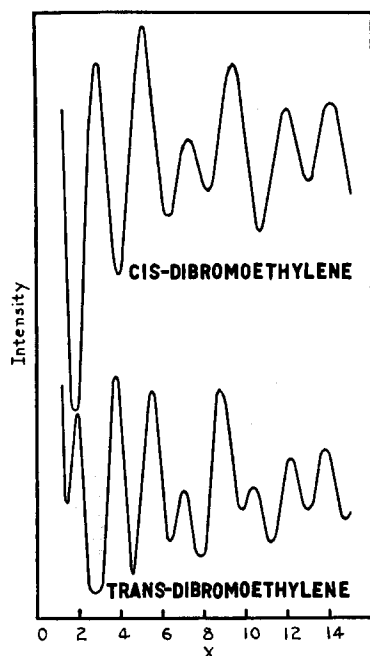


FIG. 2. Theoretical intensity curves.

the $(\sin \theta/2)/\lambda$ values for each maximum shows that true diffraction is obtained, and the agreement of the values with those calculated affords a check on the de Broglie relation. Curves 1 and 2 of Fig. 1 are photometer records for carbon tetrachloride at 45 and 25 kv, respectively.

The values of x recorded in Table II have been obtained by using the Mott expression for the electron scattering coefficient, ψ . The x values obtained by replacing ψ with Z are only slightly different for the first few maxima. The intensity curves shown in Figs. 2, 3 and 4 are calculated by the latter simpler method. The $(\sin \theta/2)/\lambda$ values

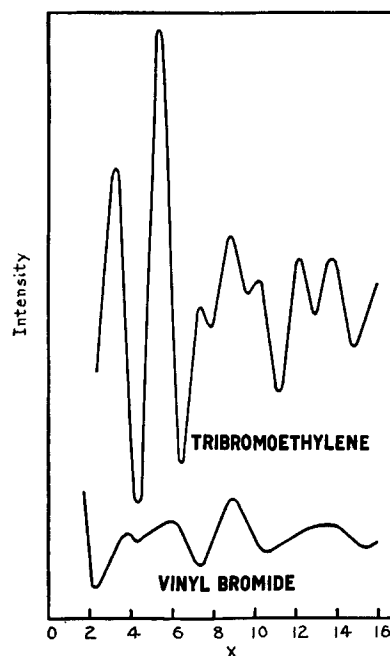


FIG. 3. Theoretical intensity curves.

of Table II are averages obtained from several pictures at each wave-length. The l values give the value of the C=C distance in Å. The error is estimated from the deviations of individual results from the mean.

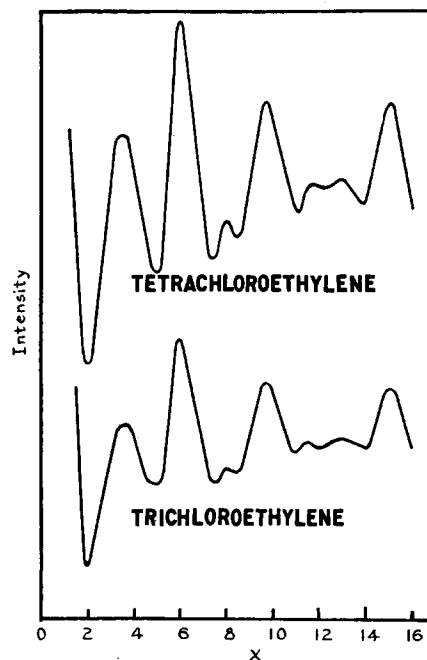


FIG. 4. Theoretical intensity curves.

TABLE II. λ , A.

x	0.05991		0.05805		0.05635		x	0.05991		0.05805		0.05635	
	$\frac{\sin \theta/2}{\lambda}$	IA	$\frac{\sin \theta/2}{\lambda}$	IA	$\frac{\sin \theta/2}{\lambda}$	IA		$\frac{\sin \theta/2}{\lambda}$	IA	$\frac{\sin \theta/2}{\lambda}$	IA	$\frac{\sin \theta/2}{\lambda}$	IA
<i>Cis-Dibromoethylene</i>							<i>Vinyl Bromide</i>						
2.90	0.174	1.33	0.174	1.33	0.174	1.33	3.90	0.235	1.32	0.230	1.35	0.226	1.37
4.90	.296	1.32	.297	1.31	.298	1.31	5.75	.349	1.31	.345	1.32	.349	1.31
7.30	.442	1.31	.439	1.32	.440	1.32	8.90	.534	1.32	.526	1.34	.537	1.32
9.35	.569	1.30	.563	1.32	.564	1.31	13.75	.820	1.33			.812	1.35
12.10	.782	1.23	.729	1.32	.731	1.32	$C=C=1.32\pm 0.08A$						
14.10					.847	1.32	$C-Br=2.05\pm 0.08A$						
$C=C=1.32\pm 0.08A$							$C-Br=2.05\pm 0.08A$						
$C-Br=2.05\pm 0.08A$													
$Br-Br=3.67\pm 0.08A$													
<i>Trans-Dibromoethylene</i>							<i>Tetrachloroethylene</i>						
1.85	0.112	1.31	0.109	1.35	0.114	1.29	3.35	0.204	1.31	0.203	1.31	0.202	1.32
3.75	.229	1.30	.226	1.32	.224	1.33	6.00	.364	1.31	.363	1.32	.363	1.32
5.50	.330	1.33	.339	1.29	.336	1.30	9.75	.590	1.31	.588	1.32	.586	1.32
6.95	.413	1.34	.417	1.33	.419	1.32	13.00	.783	1.32	.783	1.32	.783	1.32
8.75	.529	1.32	.528	1.32	.529	1.32	15.10			.905	1.33	.907	1.32
10.40	.625	1.32	.627	1.32	.630	1.31	$C=C=1.32\pm 0.08A$						
12.10					.733	1.31	$C-Cl=1.82\pm 0.08A$						
$C=C=1.32\pm 0.08A$							$C-Cl=1.82\pm 0.08A$						
$C-Br=2.05\pm 0.08A$							$Cl-Cl=3.41\pm 0.08A$						
$Br-Br=4.97\pm 0.08A$							$Cl-Cl=4.52\pm 0.08A$						
<i>Tri bromoethylene</i>							<i>Trichloroethylene</i>						
3.25	0.201	1.28	0.201	1.28	0.196	1.31	3.40	0.202	1.34	0.203	1.33	0.199	1.36
5.40	.325	1.34	.332	1.28	.329	1.30	6.10	.364	1.33	.373	1.30	.366	1.33
7.65	.458	1.32	.454	1.33	.461	1.31	9.75	.588	1.32	.609	1.27	.587	1.32
8.85	.534	1.28	.533	1.29	.542	1.26	13.05	.781	1.33	.806	1.29	.780	1.33
10.00	.604	1.31	.597	1.32	.606	1.30	$C=C=1.32\pm 0.08A$						
12.15			.736	1.30	.736	1.30	$C-Cl=1.82\pm 0.08A$						
$C=C=1.32\pm 0.08A$							$Cl-Cl=3.41\pm 0.08A$						
$C-Br=2.05\pm 0.08A$							$Cl-Cl=4.52\pm 0.08A$						
$Br-Br=3.67\pm 0.08A$													
$Br-Br=4.97\pm 0.08A$													

Eq. (1) for cis-dibromoethylene gives

$$\frac{I}{k} = 2\psi_C^2 \left(1 + \frac{\sin x}{x} \right) + 2\psi_{Br}^2 \left(1 + \frac{\sin 2.78x}{2.78x} \right) + 4\psi_C\psi_{Br} \left(\frac{\sin 1.55x}{1.55x} + \frac{\sin 2.28x}{2.28x} \right) + 4\psi_{Br}\psi_H \left(\frac{\sin 1.99x}{1.99x} + \frac{\sin 3.06x}{3.06x} \right) \quad (2)$$

which omits the scattering due to the C-H and H-H periods. The coefficients of x in the $\sin x/x$ terms were found to give satisfactory concordance with the measured maxima and corresponds to a plane model with a 110° angle between the single bonds of each carbon atom and the following interatomic distances: C=C 1.3, C-Br 2.0 and Br-Br 3.7A. The C-H distance was taken as 1.1A.

The intensity distribution for trans-dibromoethylene is:

$$\frac{I}{k} = 2\psi_C^2 \left(1 + \frac{\sin x}{x} \right) + 2\psi_{Br}^2 \left(1 + \frac{\sin 3.76x}{3.76x} \right) + 4\psi_C\psi_{Br} \left(\frac{\sin 1.55x}{1.55x} + \frac{\sin 2.28x}{2.28x} \right) + 4\psi_{Br}\psi_H \left(\frac{\sin 1.99x}{1.99x} + \frac{\sin 2.44x}{2.44x} \right) \quad (3)$$

when the same periods are neglected as in the cis compound. The structure of the trans compound differs from the cis only in the Br—Br distance 5.0Å. The marked differences in the calculated intensity curves for these stereoisomers (Fig. 2) is readily seen in the diffraction pictures.

For tribromoethylene Eq. (1) becomes

$$\begin{aligned} \frac{I}{k} = & 2\psi_C^2 \left(1 + \frac{\sin x}{x} \right) + 2\psi_{Br}^2 \left(\frac{\sin 2.54x}{2.54x} + \frac{\sin 2.78x}{2.78x} + \frac{\sin 3.76x}{3.76x} \right) \\ & + 6\psi_C\psi_{Br} \left(\frac{\sin 1.55x}{1.55x} + \frac{\sin 2.28x}{2.28x} \right) + 3\psi_{Br}^2, \end{aligned} \quad (4)$$

which neglects the hydrogen. Eq. (4) gives good representation of the observed maxima and is based on a plane model with the following distances: C=C 1.3, C—Br 2.0, Br—Br (attached to same carbon atom) 3.4, Br—Br (attached to different carbon atoms) 3.7 and 5.0Å. Wierl² has found that the distance between the bromine atoms in carbon tetrabromide was 3.35Å in good agreement with the value found in tribromoethylene. An appreciably larger distance might be expected for the latter compound because of the distortion of the tetrahedral angle. This effect could not be established in tribromoethylene as an increase in the distance between the bromine atoms attached to the same carbon is compensated by the decrease in the distance between bromine atoms on the adjacent carbon atoms.

For vinyl bromide Eq. (1) becomes

$$\begin{aligned} \frac{I}{k} = & 2\psi_C^2 \left(1 + \frac{\sin x}{x} \right) + 6\psi_C\psi_H \left(\frac{\sin 0.82x}{0.82x} + \frac{\sin 1.61x}{1.61x} \right) + 2\psi_{Br}\psi_C \left(\frac{\sin 1.55x}{1.55x} + \frac{\sin 2.88x}{2.88x} \right) \\ & + 2\psi_{Br}\psi_H \left(\frac{\sin 1.99x}{1.99x} + \frac{\sin 2.44x}{2.44x} + \frac{\sin 3.06x}{3.06x} \right) + \psi_{Br}^2 + 3\psi_H^2, \end{aligned} \quad (5)$$

which reproduced the observed maxima satisfactorily and is based on a plane model with 110° angle between atoms attached to the same carbon atom and having the following interatomic distances C=C 1.3, C—Br 2.0, C—H 1.1Å.

The intensity distribution for tetrachloroethylene is

$$\begin{aligned} \frac{I}{k} = & 2\psi_C^2 \left(1 + \frac{\sin x}{x} \right) + 8\psi_C\psi_{Cl} \left(\frac{\sin 1.38x}{1.38x} + \frac{\sin 2.11x}{2.11x} \right) \\ & + 4\psi_{Cl}^2 \left(1 + \frac{\sin 2.26x}{2.26x} + \frac{\sin 2.58x}{2.58x} + \frac{\sin 3.42x}{3.42x} \right), \end{aligned} \quad (6)$$

which corresponds to a plane structure with 110° angle between the chlorine atoms attached to the same carbon atom and having the following interatomic distances: C=C 1.3, C—Cl 1.8, cis Cl—Cl 3.4, trans Cl—Cl 4.5Å. Wierl² found 3.3Å for the chlorine-chlorine distance in cis-dichloroethylene and 4.3 for the trans isomer. Distortion of the tetrahedral angle in tetrachloroethylene cannot be established due to the compensation by the other periods, although such an increase of the tetrahedral angle has been found in methylene chloride.⁷

The scattering effect of the hydrogen in trichloroethylene is negligible and the intensity distribution is nearly identical with that of the tetrachloroethylene (Fig. 4). The intensity curve is

⁷ P. Debye, Zeits. f. Elektrochemie **36**, 614 (1930).

$$\begin{aligned} \frac{I}{k} = & 2\psi^2_{\text{C}} \left(1 + \frac{\sin x}{x} \right) + 6\psi_{\text{C}}\psi_{\text{Cl}} \left(\frac{\sin 1.38x}{1.38x} + \frac{\sin 2.11x}{2.11x} \right) \\ & + 2\psi^2_{\text{Cl}} \left(\frac{\sin 2.26x}{2.26x} + \frac{\sin 2.58x}{2.58x} + \frac{\sin 3.42x}{3.42x} \right) + 3\psi^2_{\text{Cl}}. \end{aligned} \quad (7)$$

The structure of trichloroethylene is the same as that of the tetrachloroethylene.

The diffraction photographs of the chlorine and bromine derivatives of ethylene led to plane structures with the following constant interatomic distances C=C 1.3, C—Br 2.0 and C—Cl 1.8A. These values are in good agreement with the atomic radii formulated by Pauling⁸ which give the following values respectively 1.38, 1.91 and 1.76A.

The writer is indebted to Professor G. N. Lewis for suggesting this field of research.

⁸ L. Pauling, Proc. Nat. Acad. Sci. **18**, 293 (1932).