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The Electron Diffraction Investigation of Propargyl Chloride, Bromide, and Iodide

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The surprising discovery that the carbon-carbon single-bond distance in methylacetylene² and some related substances^{2c} is less than the normal value suggested that the study of the propargyl halides would be of interest. We have carried out this study, and have found that the carbon-carbon triple-bond and single-bond distances are the same in these molecules as in methylacetylene, and that the carbon-halogen bond distances are somewhat larger than normal.

Experimental Methods

The propargyl halides were prepared in these Laboratories by Mr. Allan Grossberg from α -chloroallyl alcohol ($H_2C=CClCH_2OH$) kindly furnished by the Shell Development Company. This substance was converted into propargyl alcohol by the method described by Henry.³ Propargyl chloride and propargyl bromide were then prepared by treating the alcohol with phosphorus trichloride and phosphorus tribromide, respectively.⁴ Propargyl iodide was prepared from propargyl bromide and sodium iodide.⁵

The electron diffraction photographs were made in the usual way, with film distance 10.85 cm. and electron wave length 0.0613 Å. For each substance the ring diameters were measured separately by two observers on about ten photographs and the resultant values of $q_{obs} = 40 (\sin \theta/2)/\lambda$ were averaged. Estimates were made of the intensities of the apparent maxima and minima, and in addition curves were sketched reproducing the appearance of the photographs.

Radial distribution curves were calculated by the equation

$$ID(l) = \sum_k C_k \sin \frac{\pi}{10} q_k l$$

with use of coefficients C_k obtained from the estimated intensities by multiplication by the damping factor e^{-aq^2} .

(1) National Research Fellow in Physics.

(2) (a) G. Herzberg, F. Patat, and H. Verleger, *J. Phys. Chem.*, **41**, 123 (1937); (b) R. M. Badger and S. H. Bauer, *J. Chem. Phys.*, **5**, 599 (1937); (c) L. Pauling, H. D. Springall, and K. J. Palmer, *THIS JOURNAL*, **61**, 927 (1939).

(3) L. Henry, *Ber.*, **5**, 453, 569 (1872); **6**, 729 (1873).

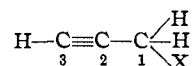
(4) L. Henry, *ibid.*, **7**, 761 (1874); **8**, 398 (1875); A. Kirsmann, *Bull. soc. chim. [iv]*, **39**, 698 (1926).

(5) L. Henry, *Ber.*, **17**, 1132 (1884).

The simplified theoretical intensity curves were calculated by the equation

$$I(q) = \sum_i \sum_j (\psi_i \psi_j / l_{ij}) \sin \frac{\pi}{10} q l_{ij}$$

The scattering powers ψ were taken proportional to the atomic numbers of the atoms. The values $C_3-H = 1.06$ Å. and $C_1-H = 1.09$ Å. were assumed, and as the bond angle C_2-C_1-X was varied the other five angles of C_1 were kept equal in value. The atoms $HC_3C_2C_1$ were assumed to be collinear, as indicated by the bonds in the model



All calculations were made with use of punched cards and International Business Machines.

Interpretation of the Data

Propargyl Chloride.—The photographs of propargyl chloride, showing about thirteen maxima and thirteen minima, have the appearance indicated by curve Chloride Obs. in Fig. 2. The radial distribution curve calculated from the data of Table I is given in Fig. 1. The peaks of this curve are at 1.18, 1.48, 1.81, 2.72, and 3.72 Å. The same values, to within 0.01 Å., were found for the three principal peaks for other curves calculated with somewhat changed values of the coefficients C . These distances correspond, respectively, to C_3-C_2 , C_2-C_1 , C_1-Cl , C_2-C_1 (plus C_3-C_1), and C_3-Cl .

We make the following assumptions: 1. The distance C_3-C_2 has the triple-bond value 1.20 Å. 2. The carbon chain is linear. 3. The three carbon-chlorine distances have approximately (to within about 0.02 Å.) the values 1.81, 2.72, and 3.72 Å. given by the three principal peaks of the radial distribution curve.

These assumptions determine the structure completely, except for the uncertainty resulting from the possible small deviations from the radial distribution values. The bond angle $\alpha = C_2-C_1-Cl$ is indicated to be near 112° . If the distance C_2-C_1 were equal to 1.47 or 1.48 Å., as indicated by the radial distribution curve and by the values for methylacetylene and related molecules, and the three carbon-chlorine distances were to

TABLE I
ELECTRON DIFFRACTION DATA FOR PROPARGYL CHLORIDE

Max.	Min.	<i>l</i>	<i>C</i>	<i>q</i> _{obs}	<i>q</i> _B	<i>q</i> _B / <i>q</i> _{obs}
	1	-2	-20	7.83	8.9	(1.14)
1		+0.5	+5	10.66	11.4	(1.07)
	2	-2.5	-23	13.81	13.9	1.007
2		+7	+63	16.97	17.1	1.007
	3	-6	-51	20.25	20.2	0.997
3		+7	+57	23.55	23.7	1.006
	4 ^a	0	0	28.53	29.9	...
4		+3	+20	32.42	33.6	(1.036)
	5	0	0	35.61	35.6	1.000
5		+6	+34	38.69	38.5	0.995
	6	-7	-35	42.38	42.0	0.991
6		+7	+32	45.43	45.6	1.003
	7	-2	-8	50.19	51.3	1.022
7		+5	+16	54.03	55.2	1.021
	8	0	0	57.33	57.5	1.003
8		+5	+12	60.09	59.9	0.997
	9	-7	-14	63.93	63.9	1.000
9		+7	+12	68.50	69.7	1.017
10		+4.5	+5	75.18	76.3	1.015
11		+6	+4	81.48	82.4	1.011
12		+6	+3	88.17	91.3	(1.023)
Average						1.006
Average deviation						0.008

^a A small apparent maximum could be seen between maxima 3 and 4.

show the minimum deviations from the above values, the bond angle would be 111° .

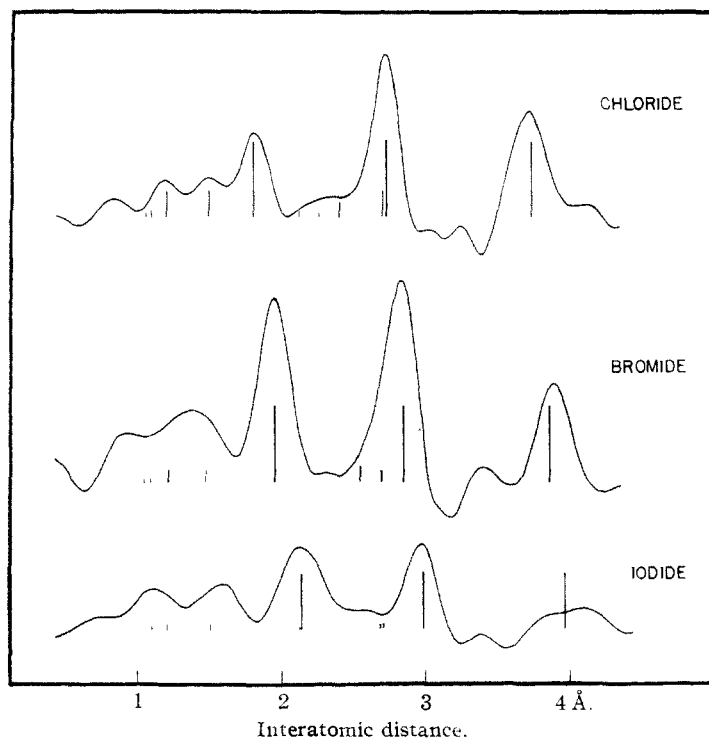


Fig. 1.—Radial distribution curves for the propargyl halides. The vertical lines correspond to the finally accepted structures.

In Fig. 2 calculated intensity curves are given for models with $\alpha = 109^\circ 30'$, 111° , and $112^\circ 30'$ and with the above assumptions satisfied (Table IV). These curves, A, B, and C, agree well with the appearance of the photographs; the agreement is best for the curve with $\alpha = 111^\circ$, in particular with respect to the relative intensities of maxima 7 and 8, and we accept the value of this angle as $\alpha = 111^\circ \pm 2^\circ$.

Curves for various other models for which interatomic distances differ from those for this model by as much as 0.03 \AA ., such as those for models D and E (Fig. 2, Table IV), were found to be less satisfactory, and those for models with larger deviations were unsatisfactory.

The quantitative comparison of values of q_{ob} and q_{calcd} for model B given in Table I leads to the average ratio $q_{\text{B}}/q_{\text{obs}} = 1.006$. Giving equal weight to this and the radial distribution values, we accept as the final values for propargyl chloride the following: $C_3-C_2 = 1.20 \text{ \AA}$. (not varied), $C_2-C_1 = 1.48 \pm 0.02 \text{ \AA}$, $C_1-Cl = 1.82 \pm 0.02 \text{ \AA}$., angle $C_2-C_1-Cl = 111 \pm 2^\circ$, $C_2-Cl = 2.72 \pm 0.03 \text{ \AA}$., $C_3-Cl = 3.73 \pm 0.03 \text{ \AA}$.

Propargyl Bromide.—The data for propargyl bromide given in Table II lead to a radial distribution curve (Fig. 1) with the two carbon-carbon peaks unresolved and with well-defined carbon-bromine peaks at 1.95 , 2.84 , and 3.85 \AA . The three intensity curves F, G, and H of Fig. 2 are calculated for the assumed values $C_3-C_2 = 1.20$ and $C_1-Br = 1.95 \text{ \AA}$., the angle α and C_2-C_1 distance being varied in such a way as to give the longer carbon-bromine distances approximately the radial distribution values. It is seen that all three curves are in good agreement with the appearance of the photographs as represented by the curve shown in Fig. 2; the C_1-C_2 distance and bond angle accordingly cannot be determined directly. We assume that the C_1-C_2 distance has the value 1.47 \AA ., the average of those found in methylacetylene (1.46 \AA .) and the chloride ($1.48 \pm 0.02 \text{ \AA}$.); the corresponding curve, G, is a little better than the other two, of which F makes the 8th maximum too weak and H makes the 5th too weak.

TABLE II

ELECTRON DIFFRACTION DATA FOR PROPARGYL BROMIDE

Max.	Min.	I	C	q_{obs}	q_{G}	$q_{\text{G}}/q_{\text{obs}}$
1		+ 1.3	+10	10.35	11.0	(1.06)
	2	- 3	-26	13.23	13.8	(1.04)
2		+ 8	+60	16.55	16.4	0.991
	3	-10	-68	19.45	19.1	0.982
3		+12	+75	22.45	22.8	1.015
	4	- 8	-48	27.20	28.0	(1.029)
4		+ 6	+30	30.85	32.3	(1.046)
	5	- 1.5	- 7	33.75	35.2	(1.043)
5		+ 4	+15	37.04	37.0	0.999
	6	- 6.5	-20	40.54	39.9	0.984
6		+10	+25	43.19	43.3	1.003
	7	- 6.5	-12	48.22	47.5	0.985
7		+ 5	+ 7	51.82	53.1	1.024
	8	- 2	- 2	54.1	55.7	1.029
8		+ 4	+ 4	57.1	57.7	1.011
	9	+ 7	+ 4	63.6	64.1	1.008
9		+ 7	+ 2	70.6	73.4	(1.039)
Average						1.003
Average deviation						0.003

Various other models were found to be unsatisfactory; for example, models I and J (Fig. 2), with C_1 -Br given the value 1.91 equal to the sum of the single bond radii and the C-C-Cl angle chosen so as to make the long C-Br distances close to the radial distribution values, fail to give the observed relative intensities of maxima 6, 7, and 8.

The quantitative comparison of q_{obs} and q_{calcd} for model G leads to the average ratio $q_{\text{G}}/q_{\text{obs}} = 1.003$ (omitting values which seem less reliable than the others). We accept the following parameter values: C_3 - $C_2 = 1.20 \text{ \AA}$., C_2 - $C_1 = 1.47 \pm$

TABLE III

ELECTRON DIFFRACTION DATA FOR PROPARGYL IODIDE

Max.	Min.	I	C	q_{obs}	q_{calcd}	$q_{\text{calcd}}/q_{\text{obs}}$
1		+ 3	+28	9.80	10.8	(1.10)
	2	- 4	-40	12.47	13.6	(1.09)
2		+ 2	+16	15.83	15.9	1.004
	3	- 6	-46	18.51	18.2	0.983
3		+11	+77	21.49	21.5	1.000
	4	- 8	-48	25.56	25.0	0.978
4		+ 7	+35	29.60	30.7	(1.037)
	5	- 6	-26	32.93	34.1	(1.035)
5		+ 2	+ 7	36.45	36.5	1.001
	6	- 3	-10	37.85	38.0	1.003
6 ^a		+ 9	+25	40.55	41.1	1.013
	7	- 9	-18	46.29	44.5	(0.962)
7		+ 9	+14	49.07	48.3	0.984
	8	+ 6	+ 6	54.8	56.0	1.022
8		+ 6	+ 3	62.4	61.4	0.984
Average						0.997
Average deviation						0.012

^a A shelf at $q = 44.7$ could be seen on the outer edge of this ring.

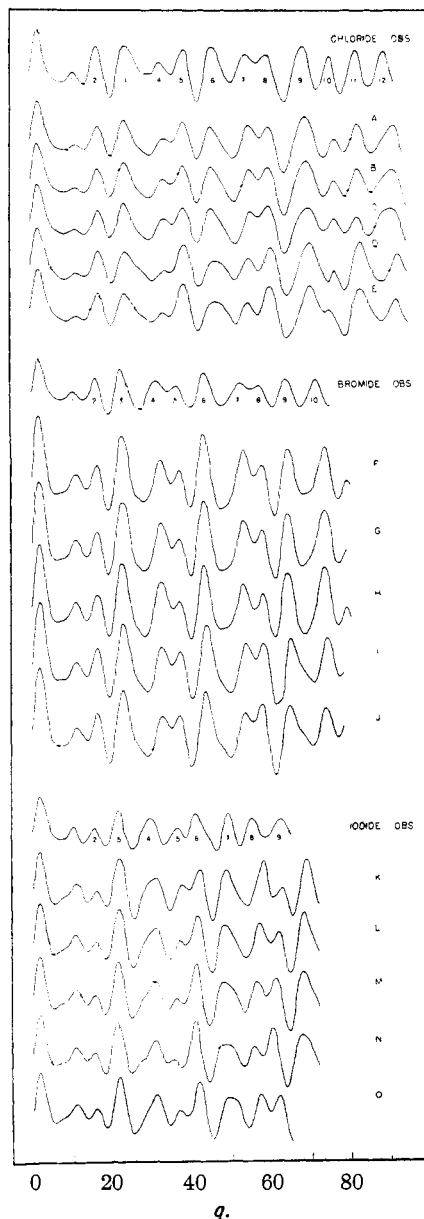


Fig. 2.—Curves (marked Chloride Obs., Bromide Obs., Iodide Obs.) drawn to represent the appearance of electron diffraction photographs, and calculated intensity curves for the propargyl halides.

0.02 \AA ., C_1 -Br = $1.95 \pm 0.02 \text{ \AA}$., angle C_2 - C_1 -Br = $112^\circ \pm 2^\circ$, C_2 -Br = $2.85 \pm 0.03 \text{ \AA}$., C_3 -Br = $3.85 \pm 0.03 \text{ \AA}$.

Propargyl Iodide.—The photographs of propargyl iodide were not so good as those of the bromide, which were themselves inferior to those of the chloride. The radial distribution curve of Fig. 1, corresponding to the data in Table III, has well-defined maxima at 2.13 and 2.96 \AA ., and poorer ones at 1.2, 1.5, and 4.1 \AA .

TABLE IV
DISTANCES AND BOND ANGLES FOR PROPARGYL HALIDE
MODELS

Model	C ₁ -X	C ₂ -C ₂	C ₂ -C ₁	Angle α	C ₂ -Cl	C ₂ -I
X = Cl						
A	1.81	1.20	1.50	109°30'	2.71	3.72
B	1.81	1.20	1.47	111°	2.71	3.72
C	1.81	1.20	1.44	112°30'	2.72	3.72
D	1.81	1.20	1.50	111°	2.69	3.72
E	1.76	1.20	1.47	113°40'	2.71	3.72
X = Br						
F	1.95	1.20	1.52	110°	2.85	3.85
G	1.95	1.20	1.47	112°	2.85	3.85
H	1.95	1.20	1.42	114°	2.84	3.85
I	1.91	1.20	1.47	112°	2.81	3.82
J	1.91	1.20	1.47	115°	2.86	3.88
X = I						
K	2.13	1.20	1.47	108°	2.95	3.90
L	2.13	1.20	1.47	110°	2.98	3.95
M	2.13	1.20	1.47	112°	3.01	4.00
N	2.13	1.20	1.47	114°	3.05	4.05
O	2.10	1.20	1.47	110°30'	2.95	3.94

There is no possibility of evaluating the carbon-carbon distances from the data. We assume the values $C_1-C_2 = 1.47 \text{ \AA.}$ and $C_2-C_3 = 1.20 \text{ \AA.}$ With these, the two C-I distances 2.13 and 2.96 \AA. lead to the value 109° for the C-C-I bond angle. Curves K, L, M, and N of Fig. 2 are calculated for models with C-I = 2.13 \AA. and with bond angle 108, 110, 112, and 114° , respectively (Table IV); of these K and N are unsatisfactory, especially with respect to the intensities of maxima 8 and 9. The best agreement is obtained for the curve interpolated between L and M; because of the poor quality of the photographs, however, this cannot be given much significance. Various other models also give unsatisfactory curves, such as that for model O (with $C_1-I = 2.10 \text{ \AA.}$, angle $110^\circ 30'$) shown in Fig. 2.

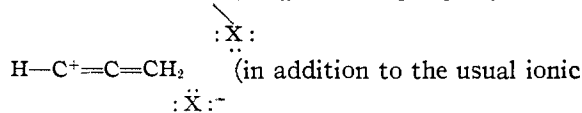
The quantitative comparison in Table III is for the model with angle 111° , intermediate between L and M. It leads to the ratio $q_{\text{calcd}}/q_{\text{obs}} = 0.997$. We accept for this molecule the values $C_3-C_2 = 1.20 \text{ \AA.}$, $C_2-C_1 = 1.47 \text{ \AA.}$, $C_1-I = 2.13 \pm 0.03 \text{ \AA.}$, angle $C_2-C_1-I = 111^\circ \pm 3^\circ$, $C_2-I = 3.00 \pm 0.05 \text{ \AA.}$, $C_3-I = 3.98 \pm 0.07 \text{ \AA.}$

Discussion of the Structures

There is only one surprising feature of the structures found for these molecules; this is that the

carbon-halogen bond distances are larger than those usually observed. Each of the values found, $C-Cl = 1.83 \text{ \AA.}$, $C-Br = 1.95 \text{ \AA.}$, and $C-I = 2.13 \text{ \AA.}$, exceeds the normal single-bond value (1.76, 1.91, and 2.10 \AA. , respectively) by a significant amount, the difference being largest (0.07 \AA.) for the chloride and smallest for the iodide.

A plausible *ad hoc* explanation for this is that there occurs resonance between the normal structure $H-C\equiv C-CH_2$ and an ionic structure



structure $H-C\equiv C-CH_2^+$ which confers ionic character on the C-Cl bond).

This explanation accounts for the decrease in magnitude of the deviation in the sequence chloride, bromide, iodide, for which the electronegativity of the halogen decreases.⁶

A much greater deviation, about 0.30 \AA. , of nitrogen-halogen interatomic distances from the single-bond values was observed for nitrosyl chloride and nitrosyl bromide by Ketelaar and Palmer,⁷ who offered a similar explanation, based on resonance with the ionic structure $:O^+\equiv N:$

We are indebted to Dr. V. Schomaker for valuable help in this work.

Summary

The electron diffraction investigation of the propargyl halides has been carried out, leading to the interatomic distances $C\equiv C = 1.20 \text{ \AA.}$ (assumed), $C-C = 1.47 \pm 0.02 \text{ \AA.}$, $C-Cl = 1.82 \pm 0.02 \text{ \AA.}$, $C-Br = 1.95 \pm 0.02 \text{ \AA.}$, and $C-I = 2.13 \pm 0.03 \text{ \AA.}$ and the angles $C-C-Cl = 111 \pm 2^\circ$, $C-C-Br = 112 \pm 2^\circ$, and $C-C-I = 111 \pm 3^\circ$.

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(6) It was suggested by Dr. S. Winstein [Dissertation, California Institute of Technology (1939)] that the large values of the mole refraction of the allyl halides could be explained as resulting from large polarizabilities of the molecules due to resonance of the type discussed in the text above. This would lead to large values of the mole refraction for the propargyl halides also.

(7) J. A. A. Ketelaar and K. J. Palmer, *THIS JOURNAL*, **59**, 2629 (1937).