Electron Diffraction Investigation of the Structure of Gas Molecules

Thesis by

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Contents

Propositions

1. An unusual temperature variation of ΔE_0° for the reaction $SO_2 + \frac{1}{2}O_2 = SO_3$ is found when values of $\Delta(F^\circ - E_0^\circ)$ calculated from Raman and electron diffraction data are combined with the best existing equilibrium data.

2. The considerations used to predict interatomic distances between atoms one of which is a member of the first row are not sufficient in general for a discussion of observed distances when a second row element is concerned. An additional assumption enables a reasonable correlation to be made.

3. A "right angled" structure for sulfur monochloride is compatible with all experimental evidence.

4. The relative reactivity of two organic halides can often be predicted from a consideration of their structures.

5. The entropy of sulfuryl chloride calculated from the most accurate chemical data is in error by approximately 10 E. U.

6. A relation connecting bond distance and bond character for bonds which resonate between single, double, and triple states can be derived from simple considerations.

7. The height of the Cl-Cl potential hump, restricting free rotation, in 1,2-dichloroethane is equal to or greater than 8kT.

8. The effect of formal charge on bond distances depends upon the character of the bond. The percent double bond character when calculated in the usual way is in error.

9. An error $\delta(Z_i Z_j)$ will cause a maximum error in the position of an intensity peak in the simplified theoretical intensity curve used in the electron diffraction method, proportional to the value s for that peak and inversely proportional to its intensity.

10. The formal charge effect and the d orbital effect can be separately determined for the Se-O bond from the results of the crystal structure determination of SeO_2.

11. It is time to give more consideration to the assignment of probable errors to interatomic distances.

12. The "serious discrepancies" found by G. B. B. M. Sutherland [Trans. Faraday Soc. 34, 325 (1938)] between the results of the electron diffraction and spectroscopic methods are more imaginary than real.

13. The present freshman and sophomore courses in chemistry should be replaced by one unified course extending over the two year period.

Respectfully submitted,

Kenneth J. Palmer.

Electron Diffraction Investigation of the Structure of Gas Molecules

Introduction

In the year 1931 Wierl[1] published a paper in which he gave the results of an investigation of the molecular structures of some twenty compounds in which high velocity electrons were diffracted by the respective compounds in the gaseous state. Since that time electron diffraction by gas molecules has come to be recognized as a powerful tool for the study of molecular structure, and today the structures of approximately two hundred compounds have been determined by this method.

Since the molecules of most compounds which have a fairly high vapor pressure at a temperature in the neighborhood of 300° C possess covalent bonds, the electron diffraction method is an excellent way of determining the covalent radii of atoms, and of studying the variations in interatomic distances due to differences in bond type and to differences in environment. The results of such studies have demonstrated the usefulness of assigning radii to atoms and have also led to empirical relations, for example that connecting bond distance and bond type, which enable one to predict with considerable accuracy the interatomic distances in many compounds. The reliability of these predictions has been adequately confirmed for compounds containing first row elements, in particular

(1) R. Wierl, Ann. d. Physik 8, 521 (1931)

organic compounds. This is due to the comparative simplicity of the carbon atom as compared with atoms lying outside the first row of the periodic table. However, further study will no doubt lead to the discovery of more embracing relations, which will enable one to predict, not only distances, but also angles for all simple molecules. It is hoped that the results of the investigation reported in the first part of this thesis will prove to be a step in this direction.

The second part gives the results of an investigation of the structures of the dimeric molecules aluminum chloride, bromide, and iodide. In the third part the structure of selenium dioxide is reported. The fourth part is concerned with the effect of the benzene ring on the C-Cl distance in seven of the chlorobenzenes, and in the fifth and last part of this thesis the structure of nitrosyl chloride and nitrosyl bromide are discussed.

The Structures of Sulfur Monochloride, Sulfur Dichloride, Sulfur Trioxide, Thionyl Chloride, Sulfuryl Chloride, Vanadium Oxytrichloride, and Chromyl Chloride

The Electron Diffraction Investigation of Sulfur Monochloride, Sulfur Dichloride, Sulfur Trioxide, Thionyl Chloride, Sulfuryl Chloride, Vanadium Oxytrichloride, and Chromyl Chloride.

Despite the rapid development of the electron diffraction method of studying the structure of molecules, comparatively few inorganic compounds have been investigated by this means. The stress which has been laid on organic molecules is due in part to the large number of organic compounds which have appreciable vapor pressures at, or near, room temperature, as compared with the number of inorganic compounds in this category, and in part to the fact that the organic chemist has in general been more interested in stereochemistry than the inorganic chemist, and has built up a large amount of purely chemical evidence supporting definite configurations.

From a purely structural point of view, inorganic molecules are nevertheless of great interest. Especially is it desirable to determine whether or not the empirical relations connecting bond distance with bond type, which have proved so useful in the discussion of interatomic distances in organic compounds, will be applicable to inorganic molecules as well. The investigations reported in this paper were carried out with these considerations in mind.

Preparation of Materials.

Sulfur Dichloride. The sulfur dichloride used was prepared by passing

dry chlorine into sulfur monochloride until the color of the liquid became deep red. This liquid was then carefully distilled in an all-glass apparatus, and only a small fraction boiling at 59° C at atmospheric pressure was retained. This product was redistilled twice, the middle fraction only, being retained. There was no evidence of decomposition during the distillation.

Sulfur Monochloride. Sulfur monochloride was prepared by passing chlorine over hot sulfur. The product was purified by distillation over activated bone charcoal and sulfur. The final product was light yellow and boiled at 135-6° C.

Thionyl Chloride. Eastman's thionyl chloride was purified by fractional distillation under reduced pressure.

Sulfur Trioxide. Kahlbaum's C. P. sulfur trioxide was used without further purification.

Sufuryl Chloride. Sulfuryl chloride was prepared by passing a mixture of sulfur dioxide and chlorine over camphor. The product was purified by distillation.

Chromyl Chloride. Chromyl chloride was prepared by heating potassium dichromate, potassium chloride, and concentrated sulfuric acid. The blood-red liquid was purified by distillation.

Vanadium Oxytrichloride. Vanadium oxytrichloride was prepared by passing hydrogen over heated V_2O_5 until it was completely reduced to V_2O_3. The

water which was generated by the reaction was carefully driven off, and chlorine was then introduced. The generated vanadium oxytrichloride was condensed in a trap cooled by a mixture of ice and salt. This product was purified by repeated distillation.

Experimental Method

The method of obtaining and interpreting the photographs has already been described in the literature[1]. All radial distribution curves were calculated using C (equal $\sum s^2 I e^{-as^2}$) in place of I as recently suggested[2]. Because the vapor pressure of some of the compounds investigated is very low at room temperature it was necessary to use a high temperature nozzle[3]. This design of nozzle was found to be particularly advantageous in these cases because of the hygroscopic nature of the compounds.

Sulfur Dichloride.- The photographs show six well defined rings. The second and fourth maxima appear to have shelves on the outer edge, the shelf on the fourth maximum being more pronounced than that on the second. The third and fifth minima (second and fourth on the reproduced curves) appear to be broad and less deep than the fourth.

Values of s_o ($= \frac{4\pi \sin \theta/2}{\lambda}$), I (the visually estimated intensities) and C ($= s_o^2 I e^{-as_o^2}$) are given in Table I. The radial distribution curve is reproduced as curve A in Fig. 1. The two well defined peaks at 1.98 and 3.06 Å correspond to the S-Cl and Cl-Cl distances, respectively. The Cl-S-Cl angle is 101°10'. Intensity curves calculated for S-Cl = 1.98 Å and Cl-S-Cl angle equal to 101°10', 109°28', 125° and 180° are repro-

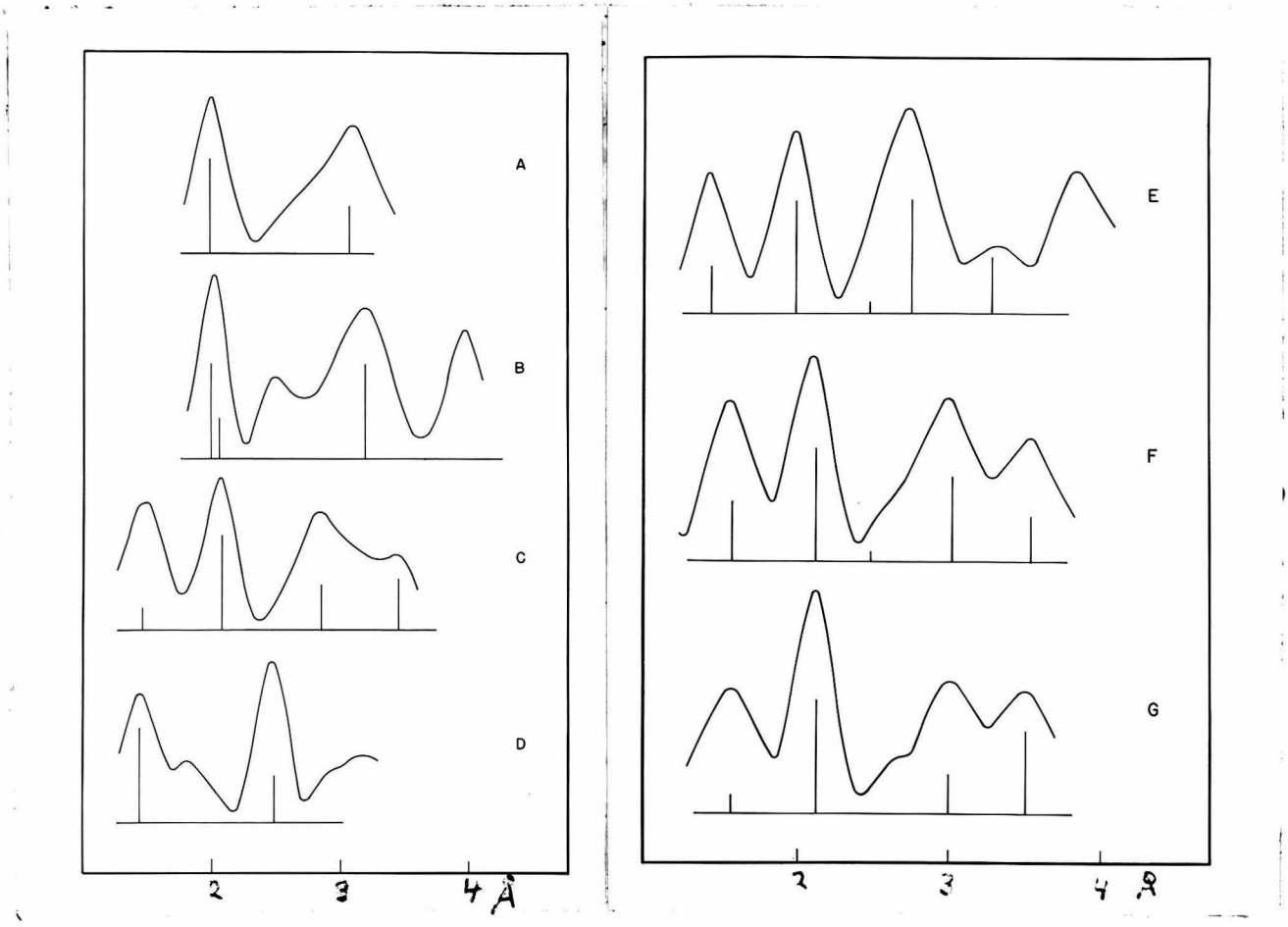


Fig. 1.- Radial distribution curves for (A) sulfur dichloride, (B) sulfur monochloride, (C) thionyl chloride, (D) sulfur trioxide, (E) sulfuryl chloride, (F) chromyl chloride, and (G) vanadium oxytrichloride.

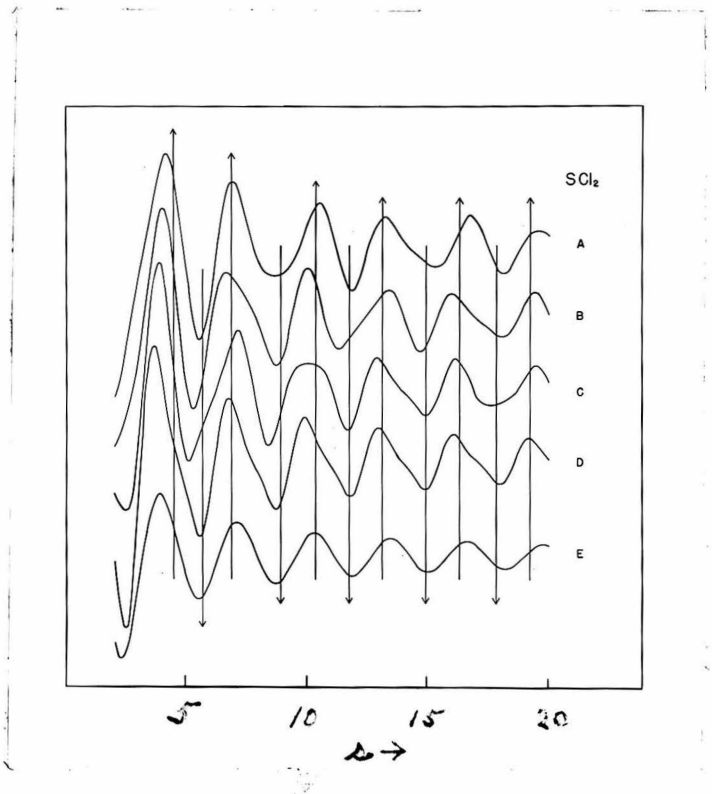


Fig. 2. - Theoretical intensity curves for sulfur dichloride. The arrows show the positions of the maxima and minima measured on the photographs.

TABLE I.

Sulfur Dichloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o
1		10	3	4.545	4.15	(0.913)
	2			5.724	5.55	(0.970)
2		8	5	6.910	6.92	1.001
	3			8.934	8.65	0.968
3		6	5	10.424	10.48	1.005
	4			11.790	11.87	1.007
4		3	2	13.178	13.24	1.005
	5			14.999	15.30	1.020
5		2	1	16.397	16.76	1.022
	6			17.851	18.12	1.015
6		1	1	19.227	19.52	1.015
					Average =	1.006
					Average deviation =	0.011

S-Cl = (1.98)(1.006) = 1.99 $\pm$ 0.03 Å

Cl-Cl = (3.06)(1.006) = 3.08 $\pm$ 0.04 Å

(a) Calculated for the model with S-Cl = 1.98 Å and Cl-Cl = 3.06 Å.

duced as curves A, B, C, and D respectively in Fig. 2. Curve E is the intensity curve for chlorine, which has been included because of the possibility of the sulfur dichloride decomposing to give sulfur monochloride and chlorine. This curve can be eliminated because the photographs do not appear to have the regular structure required. Curve D is also in disagreement with the photographs, in that all of the peaks have shelves on the outer edge, and the fourth minimum is not deeper than the third and fifth as is required by the photographs. In curve C the intensity relations of the minima are again wrong, and in addition the third maximum appears to be broad and flat, whereas the photographs show it to be quite sharp. Curve B can be eliminated because the shelf on the fourth maximum is on the inner edge instead of the outer edge, as required by the photographs, and also the third, fourth, and fifth minima have the wrong intensity relationship.

On the other hand, curve A (101°10' model) agrees very well with the photographs. The outside shelf on the second and fourth maxima are present, and the fourth minimum is deeper and narrower than either the third or fifth. Since this model agrees also with the results of the radial distribution curve it is accepted as correct. The quantitative comparison given in the last column of Table I leads to an S-Cl distance of 1.995 Å. The final values are therefore taken as S-Cl = 1.99 $\pm$ 0.03 Å and the angle Cl-S-Cl = 101° $\pm$ 4°.

Sulfur Monochloride. - The sample of sulfur monochloride was transferred to the high temperature nozzle inside a moisture proof box. When the nozzle

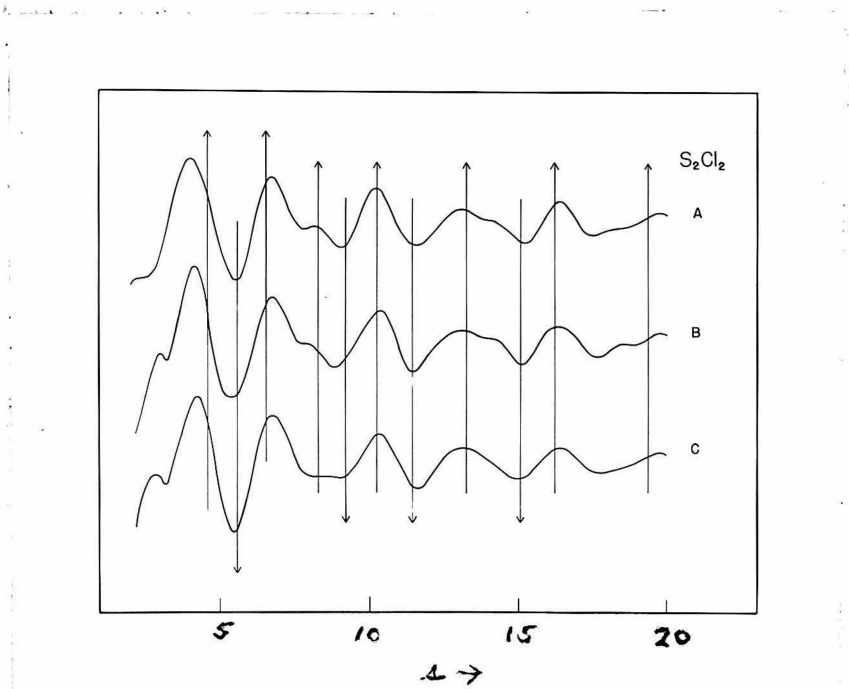


Fig. 3. - Theoretical intensity curves for sulfur monochloride. The arrows show the positions of the maxima and minima measured on the photographs.

was opened after the exposures were made there was no trace of sulfur and the remaining sample was still light yellow in color.

The photographs of sulfur monochloride show eight maxima, seven of which were accurately measured. The first maximum appears to be symmetrical, the second has a very decided outer shelf which is called the third maximum in the tables, the fourth is symmetrical, the fifth very broad, the sixth sharp, and the seventh is not very prominent. The values of s_o, I, and C are given in Table II. The radial distribution curve, calculated using the values of C, is reproduced as curve B in Fig. 1. The peaks at 2.01, 3.18, and 3.96 Å are interpreted as the sum of the S-Cl and S-S, the long S-Cl, and the Cl-Cl distances, respectively. The small peak at 2.47 Å is not given any significance.

The radial distribution curve immediately excludes the structure in which there are two chlorine atoms attached to one sulfur atom, because under these circumstances the radial distribution curve would exhibit only two peaks of about equal height, (the outer peak being due to the long S-Cl and Cl-Cl distances), or perhaps three peaks, the outer two lying very close together. Of these two outer peaks that representing the long S-Cl distance should be approximately twice as intense as that representing the Cl-Cl distance. Both the heights and the positions of the peaks are compatible with the model in which one chlorine atom is attached to each sulfur atom. For this reason intensity curves were calculated only for configurations compatible with this latter model.

Assuming the value 1.99 Å for the S-Cl distance (this value being

TABLE II.

Sulfur Monochloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o
1		10	3	4.632	4.00	(0.864)
	2			5.603	5.48	(0.978)
2		8	4	6.548	6.72	1.026
	3			-	-	-
3		3	2	8.239	8.10	0.983
	4			9.162	9.00	.982
4		7	6	10.216	10.18	.996
	5			11.456	11.52	1.005
5		5	5	13.237	13.10	.990
	6			15.069	15.10	1.009
6		5	4	16.201	16.32	1.007
	7			-	-	-
7		3	2	19.383	19.70	1.016

Average = 1.002

Average deviation = 0.012

Final values: S-Cl = 1.99 $\pm$ 0.03 Å

S-S = 2.05 $\pm$ 0.03 Å

Cl-S-S$\angle$ = 103° $\pm$ 2°

(a) Calculated for the model with S-S = 2.05 Å, S-Cl = 1.99 Å and Cl-Cl = 3.95 Å.

found in both SCl_2 and SO_2Cl_2), and considering the peak at 2.01 Å to be the weighted mean of the two S-Cl and the one S-S distance, it is then possible to calculate an S-S distance. The value found is 2.05 Å . Using the values 1.99 Å for the S-Cl distance, 2.05 Å for S-S, 3.18 Å for the long S-Cl and assuming the value 3.96 Å for the Cl-Cl distance, the S-S-Cl angle is calculated to be 103°35' and the angle between the Cl_1-S-S and Cl_2-S-S planes 97°7'.

In calculating intensity curves the S-Cl and S-S distances and the Cl-S-S angle were given the values 1.99 Å, 205 Å, and 103°35' respectively. This is justifiable because the well resolved inner peaks on the radial distribution curve are probably reliable to within one percent. Curves A, B, and C of Fig. 3 were calculated for models in which the angle between the two Cl-S-S planes is 97°7', 180° (trans), and 0° (cis), respectively. Model C can be eliminated because there is no shelf on the outside of the second maximum, this shelf being a very distinctive feature of the photographs. Curves A and B agree qualitatively with the photographs. The similarity of these two intensity curves, both as regards intensity and position of the maxima and minima, makes the reliability of the radial distribution peak at 3.96 Å very doubtful, since the distribution curve is calculated with the aid of just the s_o values and the visually estimated intensities.

No intensity curves were calculated for models in which there was either free or restricted rotation for the reason that there is no feature of the curves which appears to be sensitive to the Cl-Cl separation, and

it is consequently impossible to determine accurately the nature or height of the potential hump restricting free rotation.

The static trans model can be eliminated however from other considerations. Five Raman frequencies have been reported [4], whereas only three frequencies of the trans model are Raman active. It is therefore evident that the molecule can have only one static configuration, namely, the so-called "right angled" structure, or the chlorine atoms can be oscillating or rotating with respect to one another. It is unfortunate that more reliability cannot be placed upon the radial distribution peak at 3.96 Å because its position and sharpness would then immediately eliminate all but the static "right angled" structure.

Y. Morino and S. Mizushima [4] have recently measured the dipole moment of sulfur monochloride, reporting the value of 1 Debye unit. They have also measured the Raman spectrum in dilute hexane solution and have concluded from their results that the "right angled" static structure is the correct one. It can be said in support of this view that the electron diffraction results are compatible with this configuration.

Ackermann and Mayer [5] have investigated the molecular structure of sulfur monochloride by the diffraction of comparatively slow (about 6K.V.) electrons. They concluded that there is one chlorine atom attached to each sulfur atom and claimed to obtain best agreement when they assumed S-Cl = 1.98 Å, S-S = 2.04 Å, and Cl-S-S angle = 105°. They also state that the intensity curve calculated for free rotation gave the best fit. An

intensity curve calculated assuming free rotation is almost identical with curve A, Fig. 3, and consequently their results are in good agreement with those obtained in this investigation.

Thionyl Chloride. - The photographs of thionyl chloride show seven measurable rings, having the visually estimated intensities shown under I, Table III. The third minimum (second on curves) appears to be very deep, the fourth comparatively shallow and broad, the fifth fairly sharp but of even less depth than the fourth, the sixth deep and well defined, and the seventh broad and not as deep as the sixth. The fifth maximum appears to be less intense than either the fourth or sixth. The values of s_o, I, and C are given in Table III. The radial distribution curve calculated from these values is shown as curve C in Fig. 1. The peaks at 1.46, 2.07, 2.84, and 3.42 Å are interpreted as the S-O, S-Cl, Cl-O, and Cl-Cl distances respectively. The value 2.07 Å for the S-Cl distance seemed to be a little large, and to make sure that an impurity was not the cause of the apparent anomaly electron diffraction photographs were taken of a new sample of thionyl chloride. When these were measured, it was found that the s_o values from the two sets of photographs were in very good agreement, indicating that the large S-Cl distance is probably real.

Intensity curves were calculated for the following models: planar, with S-O = 1.44 Å, S-Cl = 2.07 Å, and a Cl-S-Cl angle of 110°, 113°, 116°, and 120°; pyramidal, with S-O = 1.44 Å, S-Cl = 2.07 Å, Cl-O = 2.84 Å and Cl-S-Cl angle equal to 106°, 110°, 115°, and 120°. These last four curves

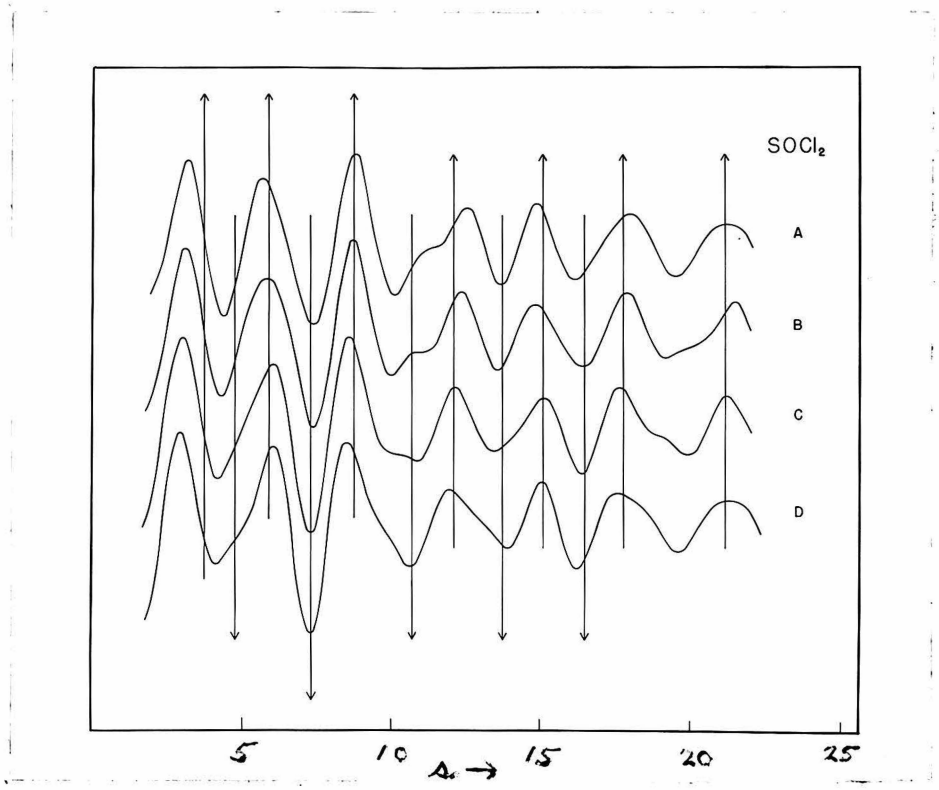


Fig. 4. - Theoretical intensity curves for thionyl chloride. The arrows show the positions of the maxima and minima measured on the photographs.

TABLE III.

Thionyl Chloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o	$s^{(b)}$	s/s_o
1		10	4	4.78	3.98	(0.833)	4.08	(0.854)
	2			5.79	5.18	(0.894)	5.29	(0.914)
2		8	6	6.91	7.05	1.020	6.80	.984
	3			8.30	8.32	1.002	8.38	1.010
3		9	11	9.78	9.79	1.001	9.69	.991
	4			11.67	11.60	0.994	-	-
4		4	6	13.07	13.12	1.004	13.32	1.019
	5			14.69	14.46	0.984	14.58	.993
5		2	3	16.08	16.08	1.001	15.75	.980
	6			17.43	17.33	0.994	17.38	.997
6		3	4	18.66	18.58	0.996	18.77	1.006
	7			-	-	-	-	-
7		1	1	22.10	22.17	1.003	22.45	1.016
				Average	=	0.999		1.000
				Average deviation	=	0.007		0.012

Final Values: S-O = 1.45 ± 0.02 Å O-S-Cl ∠ = 106° ± 1°

S-Cl = 2.07 ± 0.03 Å Cl-S-Cl ∠ = 114° ± 2°

Cl-O = 2.84 ± 0.03 Å

Cl-Cl = 3.47 ± 0.03 Å

(a) Calculated for the model with S-O = 1.44Å, S-Cl = 2.07Å, Cl-O = 2.84Å, and Cl-Cl=3.50

(b) " " " " " " " " " " " " " Cl-Cl=3.40

are shown as curves A, B, C, and D respectively in Fig. 4. None of the intensity curves for planar models has been reproduced because they are all in very definite disagreement with the photographs. Curve D can be eliminated because the intensity relationship between the first three maxima is wrong; also, the intensity of the fifth maximum should be less than that of either the fourth or sixth. Curve C is in good qualitative agreement with the appearance of the photographs. Curve B is also in good agreement except for the appearance of the shelf on the inside of the fourth maximum, and the equality in depth of the fifth and sixth minimum. The model finally selected is a weighted average of these two. Curve A is less satisfactory than B because the shelf on the fourth maximum has become too prominent and the intensity relationships of the fourth, fifth, and sixth maxima, which are about right in curves B and C, are unsatisfactory.

The quantitative comparison for models B and C is given in the last column of Table III. The final values selected, taking into account both the results of the radial distribution curve and the quantitative comparisons, are S-O = 1.45 Å $\pm$ 0.02 Å, S-Cl = 2.07 $\pm$ 0.03 Å, Cl-O = 2.84 $\pm$ 0.03 Å, and Cl-S-Cl angle = 114° $\pm$ 2°. This leads to an O-S-Cl angle of 106°17'. The same value for the O-S-Cl angle has been observed in sulphuryl chloride.

Sulfur Trioxide. - The sample of sulfur trioxide was distilled under vacuum into the sample holder, P_2O_5 being used as the lubricant on the stopcock. The best photographs showed six rings, the second of which appears to be quite broad, the intensity falling off gradually on the inside and somewhat more abruptly on the outside. The third ring has a distinct outer

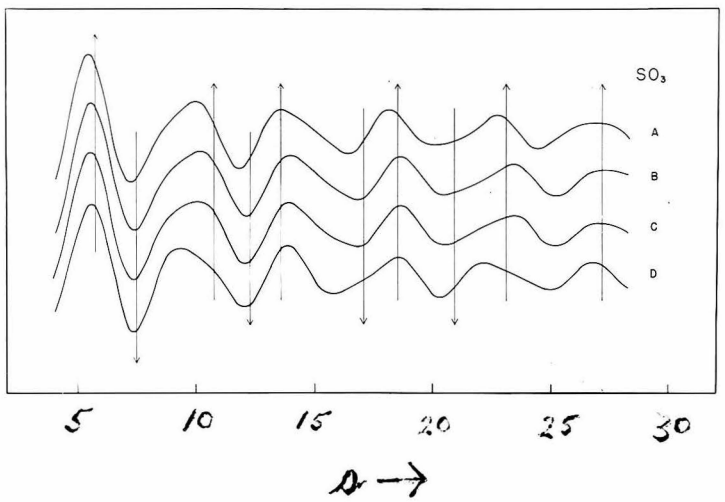


Fig. 5. - Theoretical intensity curves for sulfur trioxide. The arrows show the positions of the maxima and minima measured on the photographs.

shelf, the other rings being more or less regular in appearance. The average value of the visual measurements of the maxima and minima, as well as the estimated intensities I and the values of C are given in Table IV.

The radial distribution curve is reproduced in Fig. 1, curve D. The two well defined peaks at 1.43 and 2.45 Å are interpreted as the S-O and O-O distances respectively. These values lead to an O-S-O angle of 117°50'. Theoretical intensity curves calculated for models having an S-O distance equal to 1.43 Å and an O-S-O angle of 120°, 117°50', 116°, and 110° are shown as curves A, B, C, and D respectively in Fig. 5. Curve D is not acceptable because the shelf on the second maximum is on the outside, rather than the inside, and also because the third maximum does not possess a distinct enough outer shelf.

The rather flat top of the second peak with the subsequent steep slope on the inside exhibited by curve C, and the inner shelf on the fifth maximum are also in disagreement with the photographs. Curves A and B are very similar, except for the slight change in the nature of the inside shelf of the second maximum, and are both in good qualitative agreement with the photographs. The intensity of this peak reaches its maximum value at about the same point in both curves A and B, but falls off on the inside at approximately a constant rate in A, while for B the rate is at first less than for A and then becomes greater. This abrupt change in the rate of falling off of the intensity in curve B would, if exhibited by the photographs, probably give the impression of a definite edge to the shelf, whereas no such edge would be expected if the intensity followed curve A.

TABLE IV.

Sulfur Trioxide

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o	$s^{(b)}$	s/s_o
1		10	6	5.692	5.38	(0.945)	5.54	(0.973)
	2			7.422	7.13	(0.961)	7.35	.990
2		7	10	10.757	9.91	.921	10.20	.948
	3			12.251	11.72	.957	12.10	.988
3		5	8	13.576	13.50	.994	13.90	1.024
	4			17.038	16.30	.994	16.83	0.988
4		4	6	18.461	18.10	.980	18.60	1.007
	5			20.860	20.20	.969	20.50	.983
5		2	2	23.087	22.63	.981	23.32	1.011
	6			-	-	-	-	-
6		1	1	27.10	26.90	.992	27.20	1.003
				Average		= 0.974		0.994
				Average deviation		= 0.019		0.017

$(0.974)(1.47) = 1.43$ Å

$(0.994)(1.43) = 1.42$ Å

Final Values: S-O = 1.43 ± 0.02 Å

O-S-O $\angle$ = $120° \leq 2°$

(a) Calculated for the model with S-O = 1.47 Å ; O-S-O angle = 120°

(b) Calculated for the model with S-O = 1.43 Å ; O-S-O angle = 117°50'.

As no edge can be discerned on the photographs, model A is to be favored over model B.

The ratios s/s_o for curves A and B are given in Table IV. The final values selected for the parameters are S-O = 1.43 ± 0.02 Å and O-S-O angle 120° ± 2°. This leads to an O-O distance of 2.48 ± 0.03 Å.

The dielectric constant of sulfur trioxide vapor has recently been measured[6] over a considerable temperature range, and it was shown that the plot of the polarization against the reciprocal of the absolute temperature gives a horizontal straight line, indicating that the dipole moment is zero in agreement with the planar model.

Sulfuryl Chloride. - The photographs of sulfuryl chloride have eight measurable maxima. The values of s_o, I, and C are given in Table V. The radial distribution curve (curve E of Fig. 1) shows principal peaks at 1.43, 1.99, 2.76, and 3.85 Å. There is also a small peak at 3.32 Å. The first three values are interpreted as being due to the S-O, S-Cl, and Cl-O distances respectively. It is geometrically impossible for a model to have these values and at the same time a Cl-Cl distance of 3.85 Å. In agreement with past experience, it is considered that the radial distribution peak at 3.85 Å, which lies rather far out, is unreliable.

In calculating intensity curves it has been assumed that the S-Cl distance is 1.99 Å, and except in a few curves the Cl-O distance has been taken as 2.76 Å. The S-O distance has been varied from 1.57 to 1.43 Å, and the Cl-Cl distance from 3.55 to 3.06 Å (except for one planar model

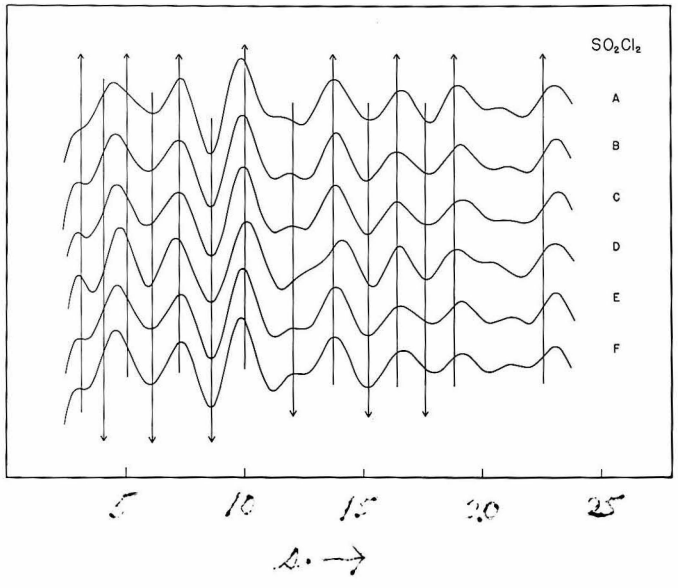


Fig. 6. - Theoretical intensity curves for sulfuryl chloride. The arrows show the positions of the maxima and minima measured on the photographs.

in which Cl-Cl = 4.06 Å). Of the twenty-five curves calculated, only six are reproduced in Fig. 6. Curves A, B, C, and D were calculated for models in which the S-O, S-Cl, and Cl-O distances were assumed equal to 1.43, 1.99, and 2.76 Å respectively, and the Cl-Cl distance was taken as 3.40, 3.32, 3.28, and 3.15 Å. Curves E and F were calculated for the following models: model E, S-O = 1.45 Å, S-Cl = 1.99 Å, Cl-O = 2.76 Å, and Cl-Cl = 3.32 Å; Model F, S-O = 1.48 Å, S-Cl = 1.99 Å, Cl-O = 2.76 Å, and Cl-Cl = 3.32 Å. All other models for which curves were calculated were easily eliminated as there was obvious disagreement between the intensity curves and the visual appearance of the photographs.

The qualitative appearance of the photographs is approximately the same as for curve C, Fig. 6,(which represents the finally selected model) except for the very small maximum at about s = 12 which is not observed on the photographs.

Curve A is not satisfactory because the first maximum is missing. Curves B, C, and D, which represent nearly identical models, are all approximately satisfactory. Curve C is, however, better than curve B because in the latter the first maximum is not sufficiently well defined, and is also superior to curve D because the shelves appearing on the inner edge of the fifth maximum and the outer edge of the seventh maximum of this latter curve can not be observed on the photographs. Curve E is not satisfactory because the first maximum is not well resolved, and also the structure of the two minima at s = 12 and 21 are not compatible with the broad, deep appearance of these minima on the photographs. Curve F is made un-

TABLE V.

Sulfuryl Chloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o
1		6	2	3.140	3.00	(0.956)
	2			4.085	3.29	(0.805)
2		8	6	5.082	4.60	(0.905)
	3			6.165	5.90	(0.957)
3		7	9	7.299	7.24	.992
	4			8.679	8.60	.991
4		10	13	10.036	9.93	.989
	5			12.068	-	-
5		4	8	13.725	13.85	1.009
	6			15.270	15.15	0.999
6		2	4	16.460	16.45	1.000
	7			17.660	17.70	1.002
7		2	3	18.840	19.15	1.016
8		1	1	22.580	23.18	1.026

Average = 1.003

Average deviation = 0.010

(a) Calculated for the model with S-Cl = 1.99, S-O = 1.43Å, O-S-O angle equal to 119°48', and Cl-S-Cl angle equal to 111°12'.

TABLE VI.

Final Values of Interatomic Distances for Sulfuryl Chloride, Chromyl Chloride, and Vanadyl Oxytrichloride.

SO_2Cl_2	CrO_2Cl_2	$VOCl_3$
S-O = 1.43 ± 0.02Å	Cr-O = 1.57 ± 0.03Å	V-O = 1.56 ± 0.04Å
S-Cl= 1.99 ± 0.02Å	Cr-Cl= 2.12 ± 0.02	V-Cl= 2.12 ± 0.03
Cl-O= 2.76 ± 0.03	Cl-O= 3.03 ± 0.03	Cl-O= 3.00 ± 0.04
Cl-Cl= 3.28 ± 0.10	Cl-Cl = 3.54 ± 0.05	Cl-Cl = 3.50 ± 0.03
O-O = 2.48 ± 0.10	O-O = 2.49 ± 0.10	-
O-S-O∠= 119°48' ± 5°	O-Cr-O ∠ = 105°6' ± 4°	-
Cl-S-Cl∠= 111°12' ± 2°	Cl-Cr-Cl∠= 113°16' ± 3°	Cl-V-Cl∠ = 111°17' ± 2°
Cl-S-O ∠ = 106°28' ± 2°	Cl-Cr-O ∠= 109°34' ± 3°	Cl-V-O ∠ = 108°12' ± 2°

satisfactory by the shelf on the inside of the fifth maximum.

The quantitative comparison for curve C is shown in Table V as the ratio of s to s_o. The final values selected for the parameters are given in Table VI.

Chromyl Chloride. - The photographs of chromyl chloride show seven measurable maxima. The values of s_o, I, and C are listed in Table VII. The radial distribution curve (curve F of Fig. 1) shows principal peaks at 1.57, 2.12, 3.03, and 3.54 Å. These are interpreted as the Cr-O, Cr-Cl, Cl-O, and Cl-Cl distances, respectively. The intensity curve calculated for this model agrees very well, both qualitatively and quantitatively with the photographs. This curve is reproduced as curve C, Fig. 7. Curves A and B were calculated for models in which Cr-O = 1.57, Cr-Cl = 2.12, Cl-O = 3.03, and the O-Cr-O angle was given the values 109°28' and 107° respectively. The value of the O-Cr-O angle in model C is 105°6'. Both curves A and B are less satisfactory than curve C because of the disappearance of the shelf on the outside of the third maximum and the appearance of a small maximum at approximately s = 17. Intensity curves were also calculated for a planar and a tetrahedral model, but the disagreement with the photographs was so marked that the curves have not been reproduced. The quantitative comparison for curve C is given in Table VII, and the finally selected values of the parameters are listed in Table VI.

Vanadium Oxytrichloride. - The photographs of vanadium oxytrichloride have seven measurable maxima. The values of s_o, I, and C being given in Table VIII.

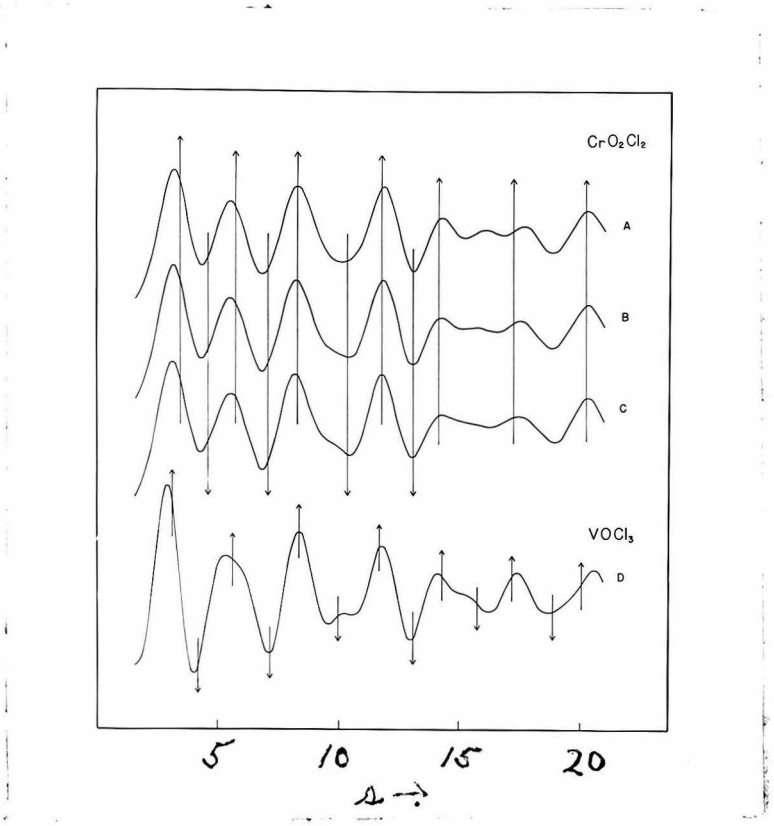


Fig. 7. - Theoretical intensity curves for chromyl chloride and vanadium oxytrichloride. The arrows show the positions of the maxima and minima measured on the photographs.

TABLE VII.

Chromyl Chloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o
1		10	6	4.438	4.13	(0.933)
	2			5.629	5.33	(0.946)
2		7	8	6.783	6.57	.969
	3			8.122	7.90	.973
3		8	15	9.304	9.22	.991
	4			11.310	11.48	1.012
4		8	19	12.788	12.82	1.002
	5			14.076	14.09	1.001
5		3	7	15.157	15.30	1.011
	6			-	-	-
6		1	2	18.210	18.48	1.013
	7			-	-	-
7		2	3	21.216	21.35	1.004

Average = 0.997

Average deviation = 0.013

(a) Calculated for the model with Cr-O = 1.57 Å, Cr-Cl = 2.12 Å, O-Cr-O angle equal to 105°, and Cl-Cr-Cl angle equal to 113°.

TABLE VIII.

Vanadium Oxytrichloride

Max.	Min.	I	C	s_o	$s^{(a)}$	s/s_o
1		10	4	4.193	3.95	(0.943)
	2			5.310	5.11	(0.964)
2		7	6	6.700	-	-
	3			8.261	8.22	0.995
3		7	10	9.427	9.42	0.999
	4			11.150	-	-
4		5	9	12.730	12.88	1.012
	5			14.170	14.07	0.993
5		4	7	15.36	15.20	0.990
	6			16.81	-	-
6		2	3	18.23	18.48	1.014
	7			19.91	19.90	0.999
7		1	1	21.10	21.66	1.026

Average = 1.004

Average deviation = 0.011

(a) Calculated for the model with V-O = 1.56 Å, V-Cl = 2.12 Å, O-V-Cl angle equal to 108°, and Cl-V-Cl angle equal to 111°.

The radial distribution curve, (curve G of Fig. 1) shows principal peaks at 1.56, 2.12, 3.01, and 3.50 Å. These values are interpreted as the V-O, V-Cl, Cl-O, and Cl-Cl distances, respectively.

The intensity curve calculated for the model with the above distances is given as curve D, Fig. 7. This curve gives excellent qualitative agreement with the photographs. All other curves which were calculated for models varying slightly from the above were less satisfactory and have not been reproduced. The quantitative agreement is also very good as is evident from the values of the ratio of s to s_o shown in Table VIII. The final values selected for the parameters are given in Table VI.

Discussion

It is interesting to inquire why the structure of sulfur monochloride is not similar to that of thionyl chloride in analogy to phosgene and thiophosgene. The electronic structures of these four molecules are shown in Fig. 8. In the case of phosgene and thiophosgene the C-O and C-S bonds are double bonds and consequently the stability of these structures is apparent. In thionyl chloride, however, the S-O bond can only be a single bond (semi-polar double bond) if the octet rule is rigorously applied, because the sulfur atom possesses an unshared pair of electrons. A semi-polar double bond is nearly equivalent in energy to a double bond when it is formed between atoms which have a large difference in electronegativity (as for example sulfur and oxygen) and therefore thionyl chloride can be

considered to have nearly four bonds. If it assumed the sulfur monochloride structure, it could,on the other hand, form only three bonds, and it consequently prefers the "thionyl chloride" structure.

When the oxygen in thionyl chloride is replaced by sulfur, there will be a strong tendency on the part of the sulfur atom with the negative formal charge to share its electrons with the other sulfur atom which possesses a positive formal charge, because in this case both atoms have the same electronegativity. This excess of negative charge on the central sulfur atom weakens the S-Cl bonds to such an extent that the total bond energy would be less than the sum of the three single bond energies,and consequently the configuration in which there is only one chlorine atom bonded to each sulfur atom is more stable.

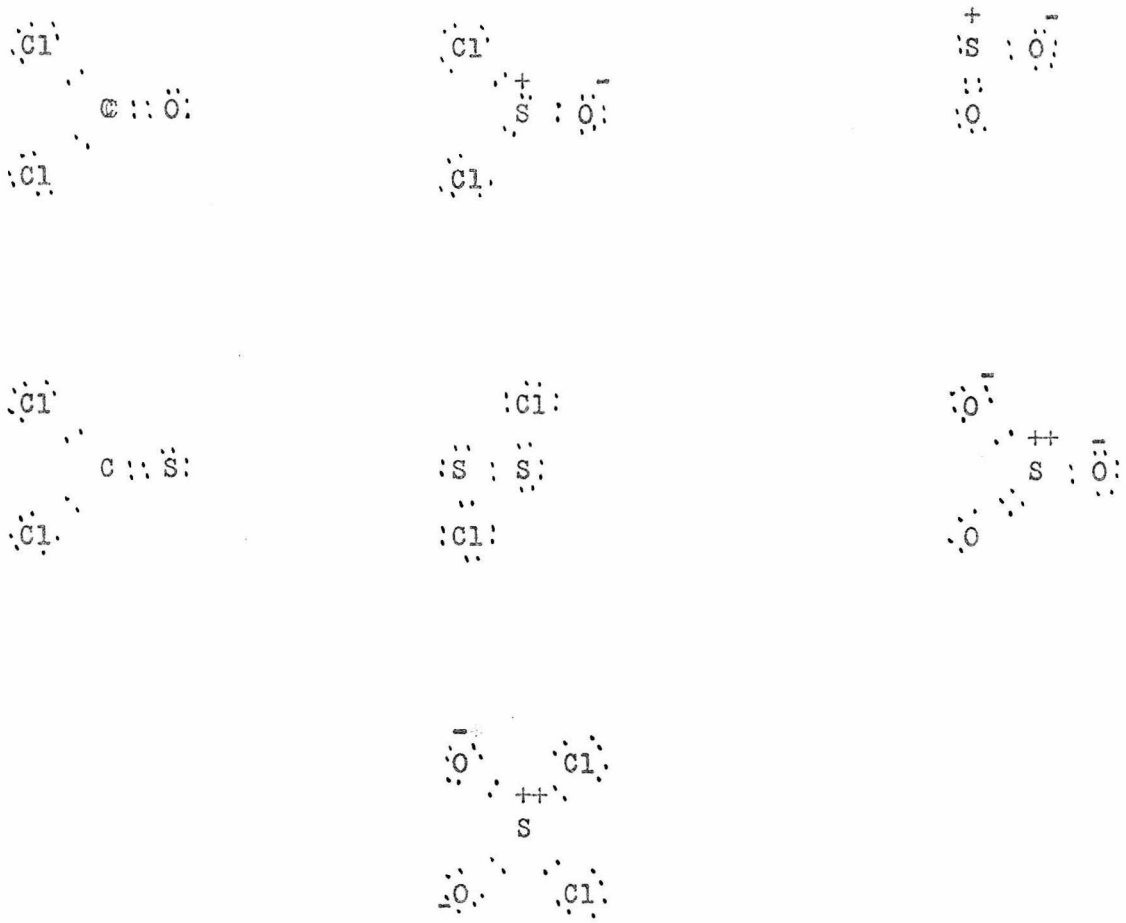
The values of the S-O distance found in this investigation are approximately 0.08 Å shorter than the sum of the double bond radii.[7] The observed distance in sulfur dioxide[8] is 1.45 Å. Short P-O and P-S distances have also been found in P_4O_{10}[9] and $PSCl_3$.[10] These short distances are without much doubt due to unstable structures in which the oxygen atom swings in one and sometimes two pairs of electrons, forming double and triple bonds respectively with the central atom. These unstable structures make use of either 3d or 4s orbitals on the sulfur atom, and consequently this effect is not present when a first row element occupies the same position as the central sulfur atom.

If one considers only electronic structures in which the sulfur atom

is complying with the octet rule, then it is apparent from Fig. 8 that the S-O bond possesses $\frac{1}{2}$ double bond character in sulfur dioxide, 1/3 double bond character in sulfur trioxide, and no double bond character in either thionyl or sulfuryl chloride. The predicted S-O distances for these four molecules, taking into consideration the formal charge effect,[11] are 1.53, 1.51, 1.69, and 1.69 Å, respectively. The predicted distance in sulfur trioxide is actually 0.02 Å less than that for sulfur dioxide because in the former the sulfur atom has a double positive formal charge while in sulfur dioxide the sulfur atom has only a single positive formal charge, and this more than compensates for the difference in double bond character. It is therefore obvious that a consideration of these electronic structures alone is not sufficient to account for the observed distances.

In order to obtain an insight into the importance of the unstable structures in which the octet rule is not obeyed, let us consider the results found for $SiCl_4$, PCl_3, SCl_2, and Cl_2. The discrepencies between the observed A-Cl (A = Si, P, S, and Cl) distances and the sums of the radii are 0.16, 0.09, 0.04, and 0.00 for the above four molecules. These values, when plotted against the atomic number of A fall on a straight line. Now, it is interesting to observe that the 3p-3d separation for Si, P, S, and Cl is also a linear function of the atomic number,[12] the separation being least for the silicon atom and most for the chlorine atom. In accord with the usual conditions for resonance, it is to be expected that there will be more resonance when two energy levels lie close together, and for this reason the excited structures will be most important in $SiCl_4$ and least

Fig. 8



The electronic structures of phosgene, thiophosgene, thionyl chloride, sulfur dioxide, sulfur trioxide, sulfur monochloride, and sulfuryl chloride.

important in Cl_2, which is in accord with the observed shortenings.

The observed S-O distances in sulfur dioxide, sulfur trioxide, thionyl chloride, and sulfuryl chloride can be qualitatively accounted for in the same way. It is necessary to compare the differences in energy of the S-O bonds in the normal and excited states for each of the above compounds. The energy of a bond has been shown to vary with distance in roughly the same sort of way as the bond character[13]; and therefore, the energy of the S-O bonds resulting from the unexcited structures alone will be about equal in sulfur dioxide and sulfur trioxide (1.52 Å) and considerably larger than this in thionyl or sulfuryl chloride (1.69 Å). Let us now make the assumption that the energies of the S-O bonds in the excited structures are nearly equal in all four molecules(the energy being less than for the normal state of thionyl or sulfuryl chloride). It immediately follows that resonance between the normal and excited states will be much more important in the cases of thionyl chloride and sulfuryl chloride than in the cases of sulfur dioxide and sulfur trioxide. This is due to the fact that the energy of the normal and excited states lie close together in the first two molecules and far apart in the latter two.

In consequence of this resonance relationship it is to be expected that the S-O distance in thionyl and sulfuryl chloride will be decreased below the value expected from a consideration of the unexcited structures to a greater extent than the corresponding distances in sulfur dioxide and sulfur trioxide.

Although it is to be expected from the above considerations that the

S-O distance in the four molecules will be of the same order of magnitude, it is regarded as fortuitous that they turn out to be nearly equal.

It is also of interest to note that whereas the O-S-O angle in sulfuryl chloride is nearly 120°, the O-Cr-O angle in chromyl chloride is only 105°. The reason for this difference is not apparent.

A comparison of the results found for vanadium oxytrichloride and chromyl chloride shows a striking similarity. Not only are the distances practically identical but even the angles are nearly equal. This result is not surprising, however, in view of the arguments given above concerning the observed interatomic distances for second row elements; also the factors affecting spatial orientation are probably nearly the same in both of these molecules since vanadium and chromium are adjacent in the periodic table.

I wish to express my sincere thanks to Mr. Ray Clinton who prepared the samples of sulfur monochloride, sulfur dichloride, sulfuryl chloride, and chromyl chloride, and especially to Professor Linus Pauling for his many helpful suggestions and for his encouragement during the course of this investigation.

Summary

The molecular structures of sulfur monochloride, sulfur dichloride, thionyl chloride, sulfuryl chloride, sulfur trioxide, vanadium oxytrichloride, and chromyl chloride have been investigated by the electron diffraction method. The final values of the interatomic distances and angles are given in Table IX.

TABLE IX.

Final Values of Interatomic Distances and Angles

	SCl_2	S_2Cl_2	$SOCl_2$	SO_2Cl_2	SO_3	$VOCl_3$	CrO_2Cl_2
A-Cl	1.99 ± 0.03Å	1.99 ± 0.03Å	2.07 ± 0.03Å	1.99 ± 0.02Å	-	2.12 ± 0.03Å	2.12 ± 0.02Å
A-O	-	-	1.45 ± 0.02Å	1.43 ± 0.02Å	1.43 ± 0.02Å	1.56 ± 0.04Å	1.57 ± 0.03Å
Cl-O	-	-	2.84 ± 0.03Å	2.76 ± 0.03Å	-	3.00 ± 0.04Å	3.03 ± 0.03Å
Cl-Cl	-	-	3.47 ± 0.03Å	3.28 ± 0.10Å	-	3.50 ± 0.03Å	3.54 ± 0.05Å
O-O	-	-	-	2.48 ± 0.10Å	2.48 ± 0.03Å	-	2.49 ± 0.10Å
Cl-A-Cl∠	101° ± 4°	-	114° ± 2°	111°12' ± 2°	-	111° ± 2°	113° ± 3°
O-A-O ∠	-	-	-	119°48' ± 5°	120° ± 2°	-	105° ± 4°
Cl-A-O ∠	-	-	106° ± 1°	106°28' ± 2°	-	108° ± 2°	109° ± 3°
S-S	-	2.05 ± 0.03Å	-	-	-	-	-
Cl-S-S ∠	-	103° ± 2°					

It has been shown that sulfuryl chloride, vanadium oxytrichloride, and chromyl chloride have tetrahedral configurations which are however considerably distorted. Thionyl chloride is pyramidal, and sulfur trioxide planar. Sulfur monochloride has been shown to have one chlorine atom attached to each sulfur atom. The positions of the chlorine atoms can not be determined with certainty.

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(2) V. Schomaker and C. Degard, to be published in the J. A. C. S.

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The Structures of Aluminum Chloride, Bromide, and Iodide

The Electron Diffraction Investigation of Aluminum Chloride, Bromide, and Iodide.

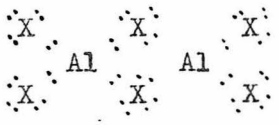
By K. J. Palmer and Norman Elliott.

The unusual physical and chemical properties of aluminum chloride, bromide, and iodide lend considerable interest to the electron diffraction investigation of these compounds in the gas phase. Vapor density measurements have shown that in the gaseous state below approximately 400°C the substances exist as the dimeric molecules Al_2Cl_6, Al_2Br_6, and Al_2F_6.

The same configuration is suggested for these molecules by considerations based on the extreme ionic and the extreme covalent point of view. The radius ratio of the ions Al^{3+} and Cl^- is 0.40 (ratio of univalent radii[1]), which

(1) Linus Pauling, J. A. C. S. 49, 765 (1927).

corresponds to tetrahedral coordination. This can be achieved for a molecule Al_2X_6 by the sharing of an edge between two tetrahedra, as shown in Fig. 1. From the covalent point of view this configuration would be expected as the result of the tendency of the aluminum atoms to complete their octet valence shells, the electronic structure of the molecule being



The suggestion of this as a possible structure for the aluminum halides was made by Fajans[2].

(2) K. Fajans, Zeit. f. Electrochemie 34, 502 (1928).

We have carried out the study of these substances by the electron diffraction method, and have verified the double-tetrahedral configuration of Fig. 1,

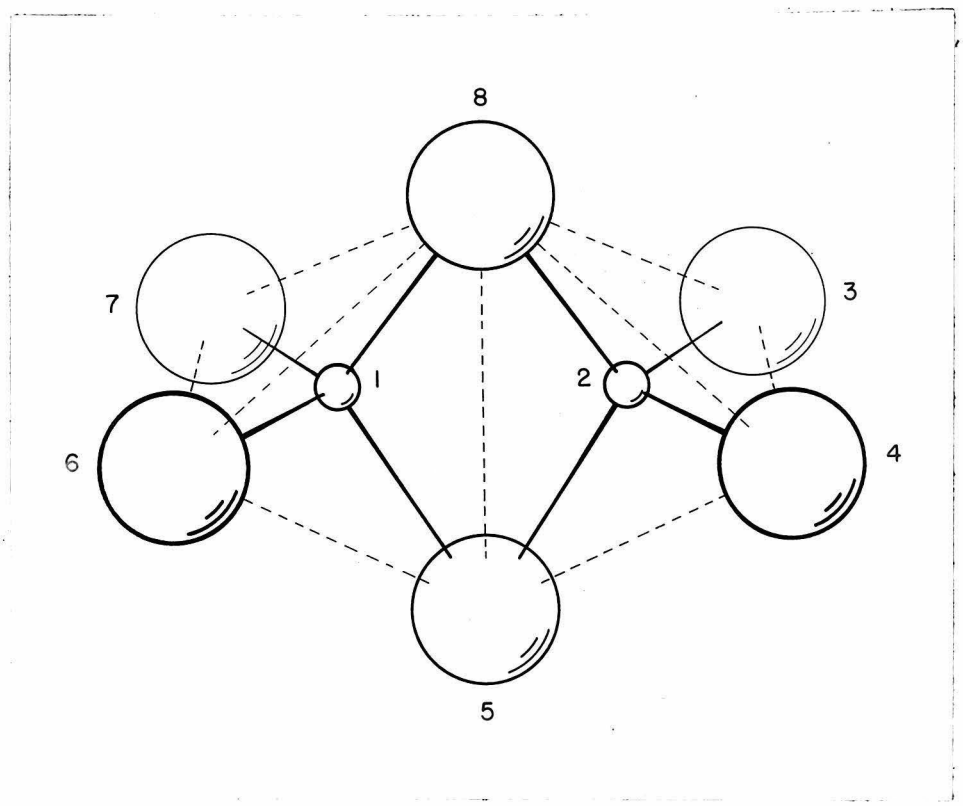


Fig. 1. - The spatial configuration of the dimeric molecule Al_2X_6. Positions 1 and 2 correspond to the aluminum atoms; the remaining positions are occupied by chlorine atoms.

with some deformation of the tetrahedra, as described below.

Experimental

The electron diffraction photographs were obtained and interpreted in the usual way.[3] The wave length of the electrons was 0.0613 Å and the camera

(3) L. O. Brockway, Rev. Modern Phys. 8, 231 (1936).

distance 10.85 cm. for the chloride and bromide and 20.16 cm. for the iodide.

The strong tendency of the aluminum halides to hydrolyze made it necessary to transfer the samples to the high temperature nozzle inside a moisture proof box. The nozzle[4] could then be sealed and inserted into the

(4) L. O. Brockway and K. J. Palmer, This Journal 59, 2181 (1937). J.A.C.S.

electron diffraction apparatus, the sample not being allowed to come into contact with moist air. This procedure proved to be satisfactory, as was verified by inspection of the nozzle after the exposures were made. In no case was there any sign of decomposition.

Merck's C. P. aluminum chloride was used without further purification. The aluminum bromide was made by the method of Richards and Krepelka[5]. The

(5) W. Richards and H. Krepelka, This Journal 42, 2221 (1920). J.A.C.S.

aluminum iodide was prepared by heating iodine with excess aluminum in an evacuated glass tube held in a vertical position. The temperature was maintained at 300°C for six hours, in which time the color due to the iodine vapor had completely disappeared. The aluminum iodide which collected in the lower part of the tube along with the excess aluminum was separated from the latter by distilling it to the upper part of the tube and then sealing the tube off at the center. The product appeared in the form of colorless highly refractive crystals. There was no evidence of any iodine vapor being present either during or after the distillation. These crystals were used without further purification.

Aluminum Chloride.-- The photographs of aluminum chloride show nine maxima. The averaged values of s_o, I (the visually estimated intensities), and C (equal to $Is_o^2e^{-as_o^2}$) are given in Table I. The qualitative appearance of the photographs is well represented by curve F of Fig. 3 which was calculated for the finally accepted model. The radial distribution curve[6], curve A of

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(6) L. Pauling and L. O. Brockway. This Journal 57, 2684 (1935). The use of the values of C in place of $I_{\not}$ has been suggested by V. Schomaker and C. Degard. They will publish an account of their investigation soon in This Journal. (J.A.C.S.).

Fig. 2, calculated using the values of C (Table I) in place of I, shows principal peaks at 3.56 and 2.11 Å. These values are interpreted as the Cl-Cl and the short Al-Cl distances respectively. The ratio of these, 1.69, is close to that (1.633) for a regular tetrahedral arrangement of chlorine atoms about the aluminum atoms. Strong support for this structure is provided by the simplified theoretical intensity curve calculated for the regular tetrahedral model (Curve A of Fig. 3), which shows good, although not complete, agreement with the characteristics of the photographs.

In order to find a model in which the ratio of Cl-Cl to Al-Cl is 1.69, all of the edges of the two tetrahedra except the shared edge were assumed to have the value 3.56 Å, and the eight smallest Al-Cl distances the value 2.11 Å. The shared edge would then have the value 2.58 Å. Although this distance is much less than the distance of closest approach (2.86 Å) observed for two non-bonded chlorine atoms, a theoretical intensity curve was calculated for this model (curve B, Fig. 3), which again is in good but not complete agreement with the photographs. Curves C and D, Fig. 3, were calculated for models in which the shared edge has the value 2.75 Å and 2.85 Å respectively. The other ten edges have the values 3.56 Å in model C and 3.54 Å in model D and the smallest Al-Cl distances the values 2.12 and 2.11 Å respectively. These curves do not agree with the photogaaphs quite so well

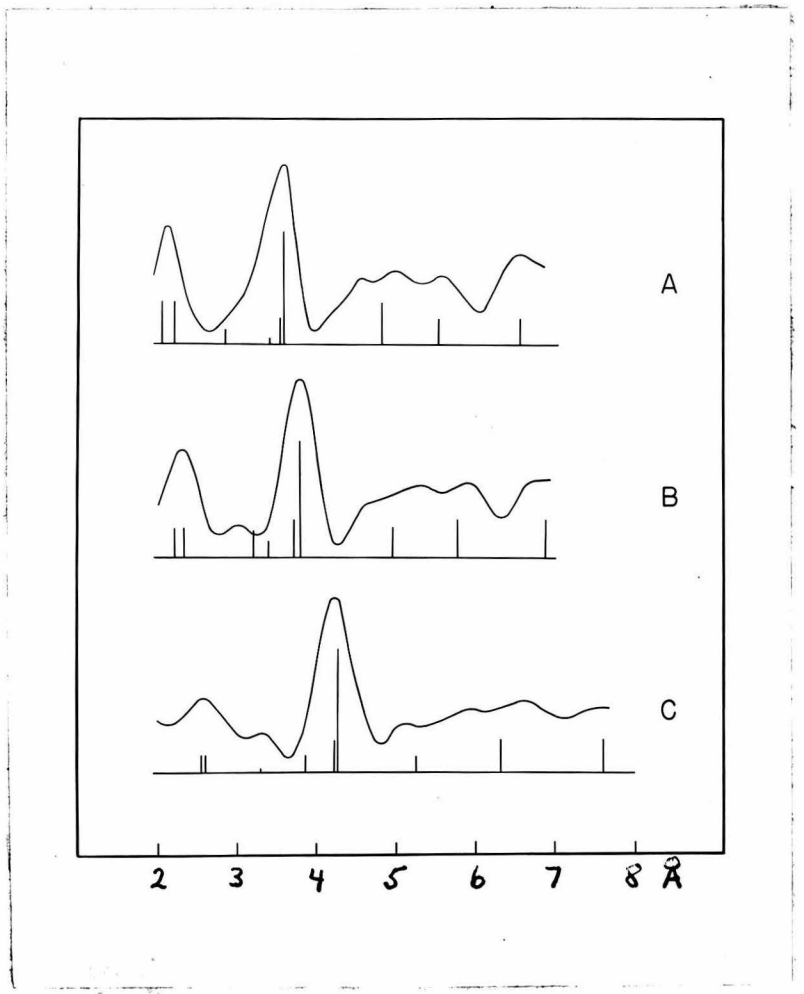

Fig. 2. - Radial distribution curves for (A) aluminum chloride, (B) aluminum bromide, and (C) aluminum iodide.

as does curve B.

A very large decrease in the value of the shared edge is necessary in order to obtain the ratio 1.69 when at the same time one keeps the other edges of the tetrahedron about equal to 3.56 Å and the short Al-Cl distances all equal to 2.11 Å. Thus it is evident that the models so far assumed have been over-simplified and that the stable configuration, although approximating two regular tetrahedra sharing an edge, is in reality considerably distorted. In order to obtain an insight into the type of distortion to be expected the following calculation was made.

The molecule is assumed to be completely ionic, and to be represented by the potential function

$$V = - \sum_{ij} \frac{e_i e_j}{r_{ij}} + \sum_{ij} \frac{B_{ij} e_i e_j}{r_{ij}^{n}}$$

in which r_{ij} is the distance between the ith and jth atoms, B_{ij} is the Born coefficient, n is a constant, taken to have the value 9 for this calculation, and e_i, e_j are the charges on the ith and jth atoms, taken equal to -1 and +3 for chlorine and aluminum respectively. It was further assumed that the ratio of the B's is given by the expression

$$\frac{B_{Al-Cl}}{B_{Cl-Cl}} = \frac{(R_{Al} + R_{Cl})^8}{(2R_{Cl})^8}$$

where R_{Al} and R_{Cl} are the ionic radii of aluminum and chlorine respectively. The absolute magnitudes of the B's were obtained by setting $\frac{\partial V}{\partial r} = 0$ and using r_{ij}'s corresponding to two regular tetrahedra with all short Al-Cl distances equal to 2.11 Å. The values so obtained are $B_{Al-Cl} = 48.15$ and $B_{Cl-Cl} = 1755$. These values were retained throughout the calculation.

A method of successive approximations was used to carry out the calculation. Each of the four independent parameters necessary to specify the structure was successively varied, the process being repeated once. The

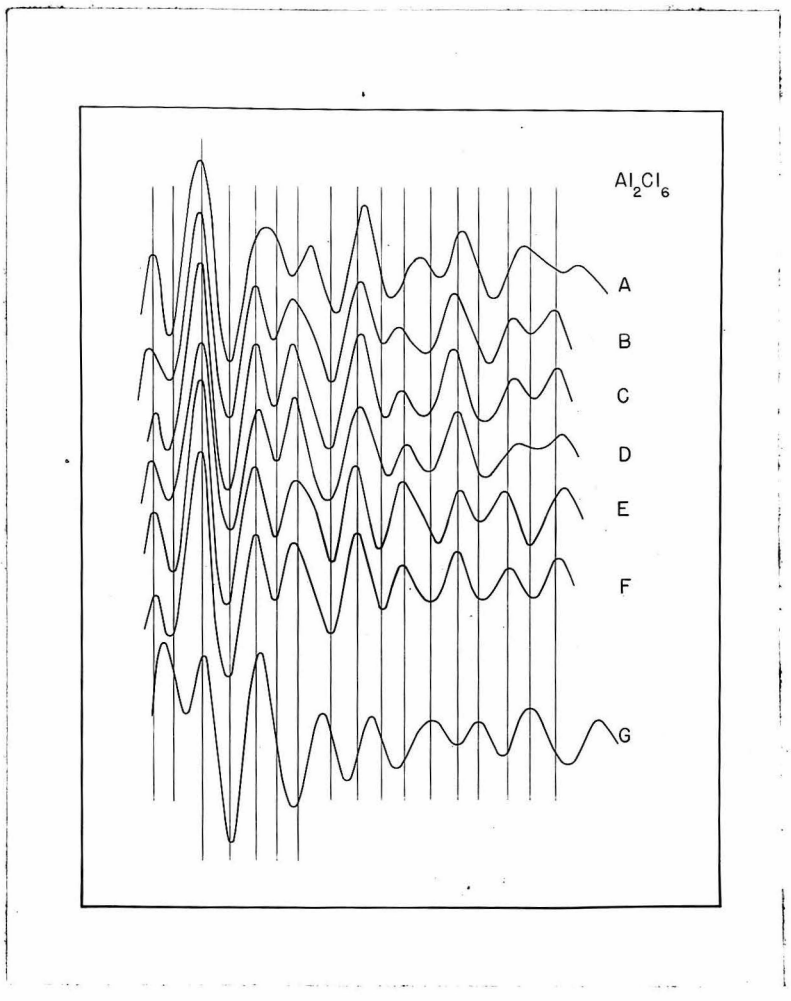

Fig. 3. - Theoretical intensity curves for aluminum chloride. The vertical lines show the position of the maxima and minima measured on the photographs.

final values of the parameters so obtained indicate the type of distortion to be expected in such a structure. With a charge of +3 assumed to reside on each of the two aluminum atoms, the repulsion between them is very strong, and the most notable changes in going from two regular tetrahedra to the final equilibrium configuration are the decrease in the length of the shared edge and the increase in the Al-Al distance. This latter effect changes the values of the short Al-Cl distances by a large amount. The final values of the interatomic distances calculated in this way are Al_1-Al_2 = 3.60, Al_2-Cl_5 = 1.99, Al_2-Cl_8 = 2.31, Al_2-Cl_6 = 4.89, Cl_3-Cl_4 = 3.49, Cl_3-Cl_8 = 3.57, Cl_5-Cl_8 = 2.90, Cl_3-Cl_7 = 5.52, Cl_3-Cl_6 = 6.52 Å. The subscripts on the atomic symbols refer to the position of the atoms as given in Fig. 1. The average of the four Al_2-Cl_3 distances equal to 1.99 Å and the four Al_2-Cl_8 distances equal to 2.31 Å (refer to Fig. 1) is 2.15 Å, in fair agreement with the radial distribution peak at 2.11 Å. However, if this were the correct model, the two shortest Al_2-Cl distances would probably appear as separate peaks in the radial distribution curve. Moreover, the intensity curve calculated for this model, (Curve E, Fig. 3) does not agree qualitatively with the photographs; the sixth maximum is too high and the eighth and ninth minima are not of equal depth.

Seven additional intensity curves were calculated for models in which the four parameters were varied. The model finally selected gives an intensity curve (Curve F, Fig. 3) which reproduces the qualitative features of the photographs in every respect. The values of the interatomic distances for this model are listed in Table II. Table I gives the values of s and s_o and their ratio, s/s_o, for model F.

Table I

Electron Diffraction Data for Aluminum Chloride

Max.	Min.	$I_{\mathscr{A}}$	C	s_o	s*	s/s_o
1		5	2	2.24	2.35	(1.049)
	2			3.08	2.91	(0.946)
2		10	14	4.08	3.93	(.963)
	3			4.96	4.91	(.989)
3		5	12	5.86	5.86	1.000
	4			6.61	6.51	0.985
4		3	10	7.43	7.18	.967
	5			8.33	8.40	1.008
5		4	16	9.23	9.32	1.009
	6			10.11	10.20	1.009
6		1	4	10.98	10.90	0.993
	7			11.90	11.91	1.000
7		3	12	12.71	12.77	1.005
	8			13.42	13.71	1.022
8		1	3	14.47	14.60	1.009
	9			15.22	15.41	1.013
9		2	5	16.07	16.30	1.014
				Average		1.003
				Average deviation		0.010

* Calculated for model F.

Table II

Interatomic Distances in Aluminum Chloride

	Distance	Number of times distance occurs in molecule.
Al_2-Cl_3	2.06 ± 0.04 Å	4
Al_2-Cl_8	2.21 ± 0.04	4
Cl_5-Cl_8	2.83 ± 0.1	1
Cl_3-Cl_4	3.53 ± 0.04	2
Cl_3-Cl_8	3.56 ± 0.02	8
Al_1-Al_2	3.41 ± 0.20	1
Cl_3-Cl_7	5.49 ± 0.05	2
Cl_3-Cl_6	6.52 ± 0.05	2
Al_2-Cl_6	4.77 ± 0.15	4

Aluminum Bromide.-- The photographs of aluminum bromide show seven well defined rings and have the same qualitative features as those for aluminum chloride. The radial distribution curve has two well defined peaks at 2.28 and 3.77 Å. The ratio of 3.77 to 2.28 is 1.65, indicating that the tetrahedra in this molecule are probably not distorted to so great an extent as for the chloride. Curve A of Fig. 4 was calculated for two regular tetrahedra sharing an edge. The curve is in good but not complete qualitative agreement with the photographs. Curves B and C of Fig. 4 were calculated for models having the same type of distortion as that found for the chloride, but smaller in magnitude. The two models are essentially the same except for the length of the shared edge. In model B this edge was assumed to be 3.36 Å and in model C 3.20 Å. The Al_2-Br_3 and Al_2-Br_8 distances were taken equal to 2.21 and 2.33 Å respectively in model C, and 2.21 and 2.35 Å in model B.

The qualitative agreement of curve C with the photographs is better than that of curve B in that the fifth maximum in the former is slightly more intense than the fourth, ~~in the former~~, in agreement with the appearance of the photographs. The differences in these two curves are, however, very slight in spite of the fact that the Br_5-Br_8 distance has been changed by 0.16 Å. The insensitiveness of the intensity curves to variations in this parameter makes it necessary to assign to it a large probable error. In Table III there are listed the values of I, C, s_o, s(for model C), and the ratio of s/s_o, and in Table IV there are given the values of the interatomic distances for the molecule and their estimated probable errors.

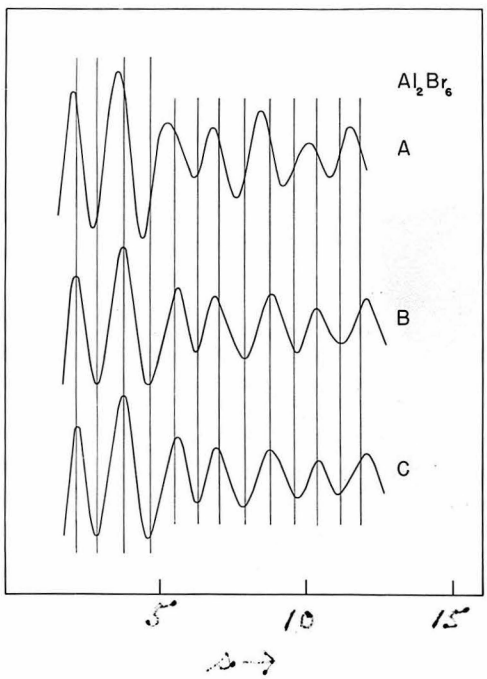

Fig. 4. - Theoretical intensity curves for aluminum bromide. The vertical lines show the position of the maxima and minima measured on the photographs.

Table III

Electron Diffraction Data for Aluminum Bromide

Max.	Min.	I	C	s_o	s*	s/s_o
1		5	2	2.11	2.11	1.000
	2			2.85	2.87	1.007
2		10	11	3.78	3.72	0.998
	3			4.68	4.61	0.999
3		6	11	5.48	5.60	1.022
	4			6.28	6.22	0.990
4		4	9	7.02	6.88	0.980
	5			7.85	7.88	1.004
5		5	13	8.73	8.78	1.006
	6			9.59	9.68	1.009
6		1	2	10.38	10.35	0.997
	7			11.19	11.17	0.998
7		2	3	11.84	12.08	1.023
			Average			1.003
			Average deviation			0.009

* Calculated for model C.

Table IV

Interatomic Distances in Aluminum Bromide

	Distance	Number
Al_2-Br_3	2.21 ± 0.04 Å	4
Al_2-Br_8	2.33 ± 0.04	4
Br_5-Br_8	3.20 ± 0.10	1
Br_3-Br_4	3.72 ± 0.03	2
Br_3-Br_8	3.78 ± 0.03	8
Al_1-Al_2	3.39 ± 0.10	1
Br_5-Br_7	5.76 ± 0.10	2
Br_3-Br_6	6.86 ± 0.10	2
Al_2-Br_6	4.93 ± 0.10	4

Aluminum Iodide.-- The photographs of aluminum iodide, taken with a camera distance of 20.16 cm, show seven well defined maxima, the general appearance of the photographs being closely similar to that for the chloride and bromide. This similarity is strong evidence for the assumption that the structures of the three molecules are similar in configuration.

The radial distribution curve (curve C, Fig. 2), shows principal peaks at 2.58 and 4.23 Å. The ratio of the latter to the former distance is 1.64, indicating that the structure is very nearly that of two regular iodine tetrahedra sharing an edge.

The ratio of the scattering due to the iodine atoms to that due to the aluminum atoms is very large in aluminum iodide; this makes the determination of the positions of the aluminum atoms with any degree of accuracy impossible. The intensity curves shown in Fig. 5 were calculated for models approximating those described for aluminum bromide. Curve A is for undistorted tetrahedra, and curves B and C for tetrahedra whose shared edge has the value 4.00 and 3.85 Å respectively, and for which the Al_2-I_3 and Al_2-I_8 distances have the values 2.58 and 2.54 Å respectively. Curve A does not agree with the photographs in that the relative intensities of the maxima are unsatisfactory. Curve C gives a somewhat better representation of the appearance of the photographs than curve B, but the differences in these two curves, namely, the variation of the intensities of the third, fourth, and fifth maxima, are so small that, as in the case of the bromide, it is impossible to determine the length of the shared edge with much accuracy. The values of the interatomic distances with their estimated probable errors are given in Table VI. The quantitative comparison of the s values obtained from curve C with the observed s_o values is given in Table V.

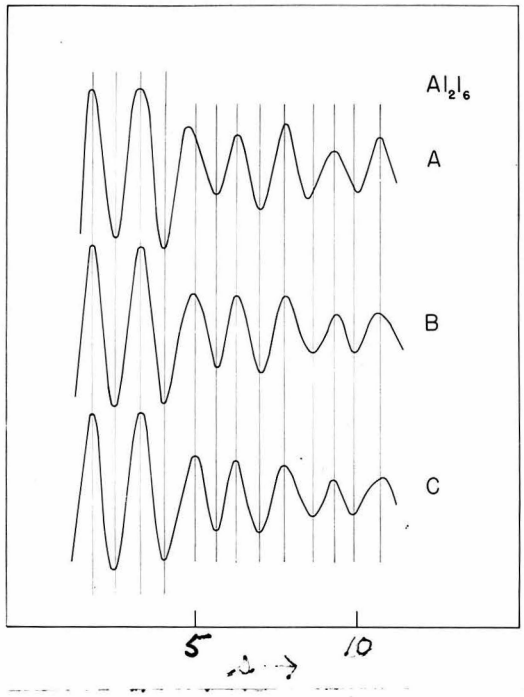

Fig. 5. - Theoretical intensity curves for aluminum iodide. The vertical lines show the position of the maxima and minima measured on the photographs.

Table V

Electron Diffraction Data for Aluminum Iodide

Max.	Min.	I	C	s_o	s*	s/s_o
1		9	3	1.88	1.87	0.995
	2			2.51	2.52	1.004
2		10	9	3.32	3.33	1.003
	3			4.14	4.08	0.986
3		7	10	4.85	4.99	1.029
	4			5.56	5.65	1.016
4		6	9	6.29	6.26	0.995
	5			7.03	7.00	.996
5		5	10	7.80	7.75	.994
	6			8.62	8.67	1.006
6		2	3	9.27	9.29	1.002
	7			9.95	9.89	0.994
7		1	1	10.67	10.70	1.003
			Average			1.002
			Average deviation			0.008

* Calculated for model C.

Table VI

Interatomic Distances in Aluminum Iodide

	Distance	Number
Al_2-I_3	2.58 ± 0.04 Å	4
Al_2-I_8	2.58 ± 0.04	4
I_5-I_8	2.90 ± 0.15	1
I_3-I_4	4.20 ± 0.03	2
I_3-I_8	4.24 ± 0.02	8
Al_1-Al_2	3.24 ± 0.15	1
I_3-I_7	6.24 ± 0.15	2
I_3-I_6	7.54 ± 0.10	2
Al_2-I_6	5.22 ± 0.15	4

Discussion: The only report on the structures of aluminum chloride, bromide, or iodide previous to the present one is that of Ketelaar[7] on the structure of

(7) J. A. A. Ketelaar, Z. Krist. 90, 237 (1935).

aluminum chloride crystals. He found that the chlorine atoms are in hexagonal closest packing, this arrangement being compatible with that found for the gas molecule in this investigation. However, he chose to place two aluminum atoms inside an octahedron of chlorine atoms, and only 0.56 Å apart, rather than one each inside of two tetrahedra sharing an edge, both of these possibilities being provided by the hexagonal closest packed arrangement. The extent to which the x-ray data can be accounted for by this latter configuration is being investigated by one of us.

Curve G, Fig. 2, is the simplified theoretical intensity curve calculated for the "octahedral" model of Ketelaar; it is apparent from a comparison with curve F that this model cannot represent the structure of the gas molecule.

The large difference in electronegativity between aluminum and the halogen atoms leads one to expect that the Al-X bond will be largely ionic, and this is confirmed by the observed contraction of the shared edge. The percentage decrease in length of the shared edge is found to be largest in the chloride and least in the iodide which is in accordance with expectation.

The sums of the tetrahedral radius of aluminum and the normal radii for the halogen atoms are 2.24, 2.40, and 2.59 Å for the chloride, bromide, and iodide respectively. These values are to be compared with the observed values, 2.06, 2.21, and 2.53 Å, which are the Al_2-X_3 distances, and 2.21, 2.33, and 2.58 Å, which are the Al_2-X_8 distances, for the chloride, bromide, and iodide respectively. The observed shortening in the case of the Al_2-X_3 distances is probably due to the excited structures in which an X_3 halogen

atom swings in a pair of electrons and forms a double bond with the aluminum atom. This type of resonance is not expected to occur to the same degree for halogen atoms forming two bonds, which accounts for the fact that the observed Al_2-X_8 distances are nearly equal to the sum of the appropriate radii.

It is interesting to note that the observed values of the Al_2-X_3 distances show a greater tendency for the chlorine and bromine atoms to form double bonds than of iodine atoms; this is compatible with the results of other investigations.

We wish to express our thanks to Professor Linus Pauling for his aid and helpful criticism during the course of this investigation.

Summary: It is shown that in the gaseous state the dimeric molecules of aluminum chloride, bromide, and iodide consist of two tetrahedra sharing an edge with six halogen atoms at the corners, each tetrahedron containing one aluminum atom. The final values of the interatomic distances are as follows:

	Al_2Cl_6	Al_2Br_6	Al_2I_6
Al_1-Al_2	3.41 ± 0.20 Å	3.39 ± 0.10 Å	3.24 ± 0.15 Å
Al_2-X_3	2.06 ± 0.04	2.21 ± 0.04	2.53 ± 0.04
Al_2-X_8	2.21 ± 0.04	2.33 ± 0.04	2.58 ± 0.04
Al_2-X_6	4.77 ± 0.15	4.93 ± 0.10	5.22 ± 0.15
X_3-X_4	3.53 ± 0.04	3.72 ± 0.03	4.20 ± 0.03
X_3-X_8	3.56 ± 0.02	3.78 ± 0.03	4.24 ± 0.02
X_5-X_8	2.83 ± 0.10	3.20 ± 0.10	2.90 ± 0.15
X_3-X_7	5.49 ± 0.05	5.76 ± 0.10	6.24 ± 0.15
X_5-X_6	6.52 ± 0.05	6.86 ± 0.10	7.54 ± 0.10

The subscripts on the atoms refer to their positions in the molecule as given in Fig. 1.

The Structure of Selenium Dioxide

The Molecular Structure of Selenium Dioxide Vapor

By K. J. Palmer and Norman Elliott.

Electron diffraction photographs of selenium dioxide vapor were taken and interpreted in the way already described in the literature.[1] The photographs showed five well-defined but rather broad maxima, whose relative positions and intensities were approximately those to be expected for a diatomic molecule. This is due to the relative unimportance of the oxygen-oxygen scattering as compared to the selenium-oxygen scattering. The values of s_o ($= \frac{4\pi \sin \theta/2}{\lambda}$), the visually measured intensities (I), and C ($= Is_o^2 e^{-as_o^2}$) are given in Table I. The values of C and s_o were used in calculating a radial distribution curve as recently suggested[2], and the resulting curve is reproduced in Fig. 1. The well-defined peak at 1.61 Å corresponds to the selenium-oxygen distance; the other peaks lying farther out are too unreliable to be of any importance in determining the oxygen-oxygen distance.

Two simplified intensity curves were calculated, one for a linear model and the other for a model having an O-Se-O angle of 120°. The latter is reproduced in Fig. 2. The two curves are so nearly identical, both with regard to shape and position of the maxima, that it is impossible from a qualitative comparison with the photograph to make a choice between them. The quantitative comparison of s_c/s_o given in Table I leads to the selenium-oxygen distance 1.61 ± 0.03 Å, in exact agreement with the radial distribution curve. In analogy with sulfur

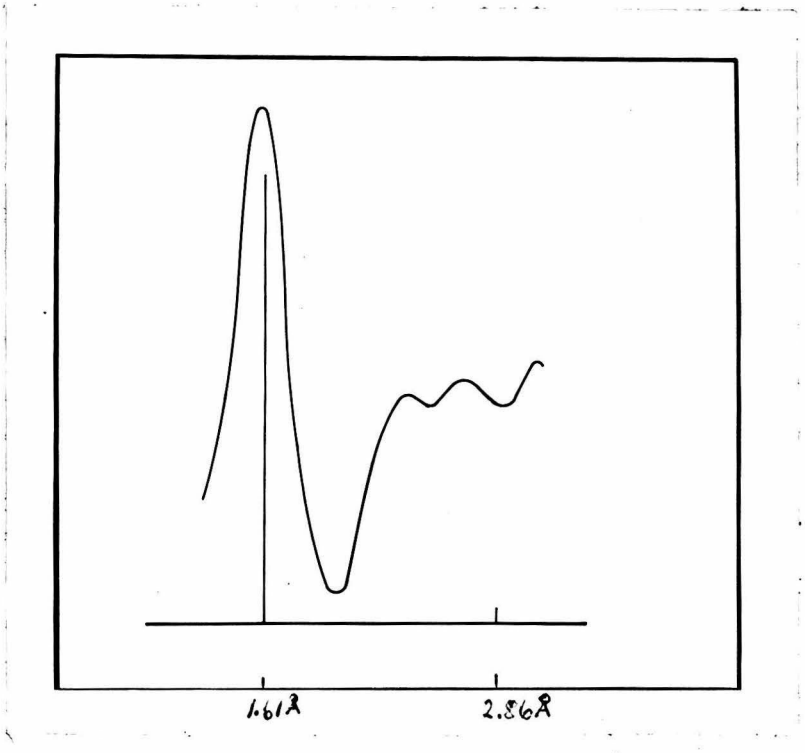

Fig. 1. - Radial distribution curve for selenium dioxide.

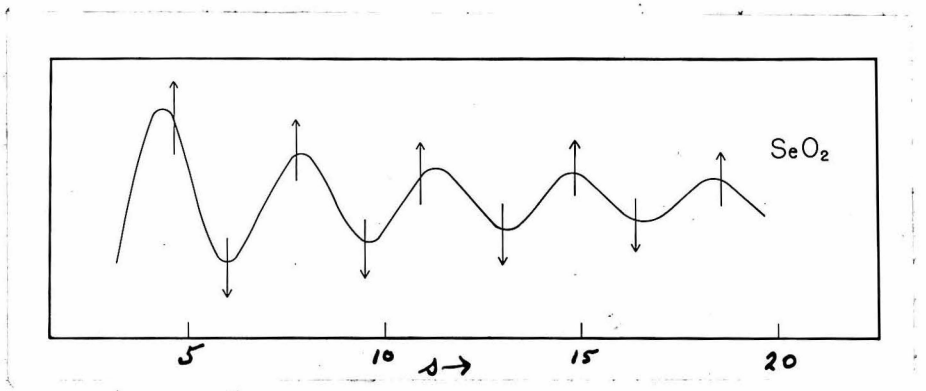

Fig. 2. - Intensity curve for selenium dioxide, calculated for Se-O = 1.80Å and O-Se-O angle = 120°. The positions of the arrows, indicating measured maxima and minima, have been decreased by 8.9 percent to indicate the quantitative agreement with the final model with Se-O = 1.61Å.

TABLE I

Max.	Min.	I	C	s_o	s_c [a]	s_c / s_o
1		10	33	5.185	4.32	(0.833)
	2			6.800	6.00	.882
2		7	50	8.771	7.88	.898
	3			10.700	9.55	.893
3		4	38	12.404	11.28	.909
	4			14.690	13.15	.895
4		2	17	16.652	14.75	.886
	5			18.458	16.50	.894
5		1	6	20.391	18.37	.901
					Average	0.894
					Average deviation	0.006

$$\text{Se-O} = (1.80)(0.894) = 1.61 \pm 0.03 \text{ Å}$$

[a] Calculated for the model with Se-O = 1.80 Å and the angle O-Se-O = 120°.

dioxide, the O-Se-O angle is probably close to 125°. Using this value for the angle the oxygen-oxygen distance is 2.86 Å.

Discussion:

The value 1.61 Å is considerably lower than the sum of the double bond radii of selenium and oxygen. The double bond factor for third row elements is 0.93. This gives 1.66 Å for the selenium-oxygen double bond distance. On correction for the formal charge effect as suggested by Elliott [3], this is reduced to the value 1.64 Å. If one considers only the electronic structures representing resonance between a selenium-oxygen double bond and a single bond, then each bond would posses 50 % double bond character. The interatomic distance, found by application of the usual resonance curve, is 1.69 Å. The discrepancy between this value and that observed is probably due to the importance of electronic structures in which the oxygen is bonded to the selenium atom by a triple bond. A bond of this type is possible because selenium is not restricted rigorously by the octet rule.

The observed sulfur-oxygen distance is sulfur dioxide bears about the same relation to the radii as that found for selenium dioxide, and the two molecules are probably closely similar in electronic structure.

The selenium dioxide crystal [4] does not contain discrete SeO_2 molecules, but instead consists of infinite chains. The observed Se-O distances in the crystal, 1.78 Å and 1.73 Å, have been discussed by McCullough.

We are indebted to Dr. James D. McCullough for furnishing us with

the sample of selenium dioxide, and to Professor Linus Pauling for his aid and criticism during the course of this investigation.

Summary

Electron diffraction photographs of selenium dioxide vapor have been interpreted to lead to the value 1.61 ± 0.03 Å for the Se-O distance. The value of the angle O-Se-O could not be determined.

References

(1) L. O. Brockway, Rev. Modern Phys. 8, 231 (1936).

(2) V. Schomaker and C. Degard, To be published soon.

(3) Norman Elliott, J. A. C. S. 59, 1380 (1937).

(4) James D. McCullough, J. A. C. S. 59, 789 (1937).

The Structure of Seven Chlorobenzenes

[Reprint from the Journal of the American Chemical Society, 59, 2181 (1937).]

[Contribution from the Gates and Crellin Laboratories of Chemistry, California Institute of Technology No. 619]

The Electron Diffraction Investigation of Seven Chlorobenzenes

By L. O. Brockway and K. J. Palmer

Introduction

The effect of conjugation on bond length was demonstrated a few years ago in the case of diacetylene and cyanogen,[1] in which the single carbon bond lying between two triple bonds, as the structures are ordinarily written, is 0.11 Å. shorter than a single bond in an unconjugated system. This bond shortening was explained as the effect of some double bond character introduced by the resonance of the molecules among several electronic structures including some having a double bond in the position of the single bond in the ordinary structure. This effect is well illustrated by the benzene molecule in which resonance chiefly between the two Kekulé structures shortens the single bonds in the individual structures by 0.15 Å.

More recently in an investigation of the chloroethylenes[2] a conjugated system of a similar type was found to exist when a single bond lies between two atoms, one of which has an unshared pair of electrons and the other is connected by a double bond to a third atom. In this case similar resonance possibilities arise; and the carbon–chlorine bonds in the chloroethylenes were found to be from 0.03 to 0.09 Å. shorter than they are in the chloromethanes. At that time it was suggested that in the halogen substituted benzenes also the carbon–halogen bonds would probably be affected; and the present investigation was begun to measure the effect and to test the possible influence of the number and position of the substituent atoms. We are now reporting the results of the electron diffraction investigation of the vapors of hexachlorobenzene, 1,2,4,5-tetrachlorobenzene, 1,3,5-trichlorobenzene, *o*-, *m*-, and *p*-dichlorobenzenes, and monochlorobenzene.

(1) L. O. Brockway, *Proc. Nat. Acad. Sci.*, **19**, 868 (1933).

(2) L. O. Brockway, J. Y. Beach and L. Pauling, This Journal, **57**, 2693, 2705 (1935).

Experimental

The materials used were obtained from the Eastman Kodak Co. Because of their relatively low vapor pressures at room temperature it was necessary to use a sample holder and gas nozzle which could be heated to about 300°. This consisted of a cylinder of monel metal about an inch (2.5 cm.) long and one-half inch (1.27 cm.) in diameter. The upper end was fitted with a removable cap which gave access for charging the holder with the sample. In the cap was a copper plug containing a 0.016″ (0.41-mm.) hole through which the vapor passed to meet the electron beam just above the top surface of the cap. The flow of vapor was controlled by a needle-pointed rod seated into the hole in the copper plug. The lower end of the monel cylinder was closed by a plate through which a sleeve passed for supporting the valve needle. The movement of this needle was controlled from the outside through a siphon connection. A resistance wire wound on the monel cylinder with mica insulation heated the

whole arrangement to temperatures which were followed by a thermocouple on the top of the removable cap. This style of high temperature nozzle has the advantage that vapor flows into the apparatus only at the time the exposure is being made.

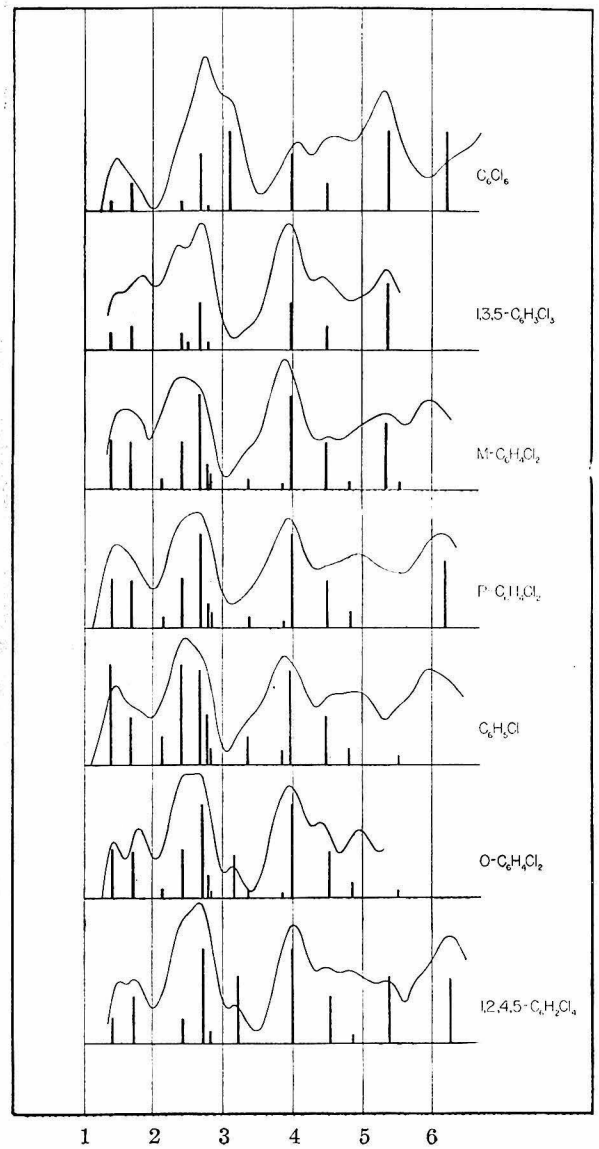

Fig. 1.—Curves showing the observed radial distributions of scattering matter in the chlorobenzenes. The heavy vertical lines indicate the values of the interatomic distances determined with the aid of theoretical scattering curves; the relative heights of the lines for each substance are proportional to the scattering power associated with the respective atomic separations.

Photographs were obtained of the seven substances mentioned above by the usual technique[3] using a camera distance of 10.87 cm. and an electron wave length of 0.0611 Å. From seven to ten maxima were measured for each compound and the corresponding values of s_0 (equal to 4π (sin $\theta/2)/\lambda$) are listed in Tables I–VII. These were combined with visually estimated intensities to give the observed radial distributions of scattering matter[4] shown in Fig. 1. The positions of the stronger peaks in these curves were taken into account in determining the interatomic distances in the respective molecules.

For the calculation of theoretical scattering curves models were used in which the benzene ring was taken as a regular hexagon with an edge of 1.39 Å., the distance found in benzene[5] and in mesitylene and hexamethylbenzene.[6] The carbon–chlorine bonds in all of the compounds except *o*-dichlorobenzene and 1,2,4,5-tetrachlorobenzene were assumed to make 120° angles with the sides of the carbon hexagon, and the different carbon–chlorine bonds in a single molecule were assumed to be equal in length. Wherever carbon–hydrogen bonds occurred, the distance 1.06 Å. was used. All interference terms except those of hydrogen–hydrogen were included in the calculations. Various carbon–chlorine distances were assumed, but on account of the greater scattering power of chlorine compared with carbon it was found that the curves for the molecules containing several chlorine atoms were not affected by small changes in the relative size of the benzene ring. Only in the case of chlorobenzene could the carbon–carbon distance be determined directly. A value for the sum of the carbon–carbon and carbon–chlorine bond distances was obtained in each case, and the latter distance was fixed with the aid of assumed values for the C–C separation. For reasons discussed in the final section of this paper the carbon–carbon distance in some of the compounds (as indicated in the following paragraphs) was assumed to be 0.01 Å. larger than in benzene.

Hexachlorobenzene.—Three curves calculated for hexachlorobenzene, with carbon–chlorine distances of 1.68, 1.70, and 1.76 Å., respectively, show excellent qualitative agreement with the observed ten-maximum diffraction pattern. The second of these is reproduced in Fig. 2 with the

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

(4) For the procedure used in obtaining these curves see L. Pauling and L. O. Brockway, THIS JOURNAL, **57**, 2684 (1935); also W. Schomaker and C. Degard, to be published in THIS JOURNAL.

(5) L. Pauling and L. O. Brockway, *J. Chem. Phys.*, **2**, 867 (1934).

(6) L. Pauling and L. O. Brockway, THIS JOURNAL, **59**, 1223 (1937).

positions of the measured maxima and minima marked. From the data in Table I the ortho chlorine–chlorine distance is fixed at 3.11 ± 0.03 Å., the same value being obtained from the other two models. This is equal to the sum of the carbon–carbon and carbon–chlorine bond distances; and with the former assumed to be 1.41 Å., the latter is given as 1.70 ± 0.03 Å.

TABLE I

HEXACHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		8	2.82	2.57	(0.912)
	2		4.00	3.85	(.963)
2		10	4.98	4.96	.996
	3		5.67	5.77	1.017
3		2	6.30	6.33	1.005
	4		6.77	6.77	1.000
4		3	7.33	7.31	0.998
	5		7.85	7.78	0.991
5		6	8.44	8.45	1.001
	6		9.08	9.18	1.011
6		4	9.83	(10.00)	
7		2	12.21		
	8		13.61	13.78	1.012
8		5	14.35	14.56	1.014
9		1	16.49	16.66	1.011
10		2	18.87	19.15	1.014
				Average	1.006
				Cl–Cl (ortho)	3.11 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

1,3,5-Trichlorobenzene.—Carbon–chlorine distances of 1.70, 1.72, and 1.76 Å., respectively, were used in calculating theoretical intensity curves for 1,3,5-trichlorobenzene. Because they lead to the same result the first one only is reproduced in Fig. 2. The qualitative agreement with the photographs is again very good. A small change in the scale of this curve is required by the quantitative comparison in Table II, which leads to the value Cl–Cl (meta) = 5.38 ± 0.05 Å. The sum of the C–C and C–Cl distances is then 3.10 ± 0.03 Å.; and with C–C = 1.41 Å., we obtain the final value C–Cl = 1.69 ± 0.03 Å.

TABLE II

1,3,5-TRICHLOROBENZENE

Max.	Min.	I	s_0	s^a	s/s_0
1		8	3.41		
2		10	5.22	5.05	(0.968)
3		4	7.29	7.40	1.015
	4		7.84	7.88	1.005
4		4	8.48	8.42	0.993
	5		9.09	9.12	1.004
5		6	9.86	9.83	0.997
6		5	11.72	11.87	1.013
	7		12.39	12.60	1.017
7		2	13.03	13.08	1.004
	8		13.68	13.72	1.003
8		5	14.34	14.50	1.011
9		1	16.55	16.58	1.002
10		2	19.04	19.18	1.007
				Average	1.006
				Cl–Cl (meta)	= 5.38 Å.

[a] Calculated for C–C = 1.39 Å., C–Cl = 1.70 Å., and C–H = 1.06 Å.

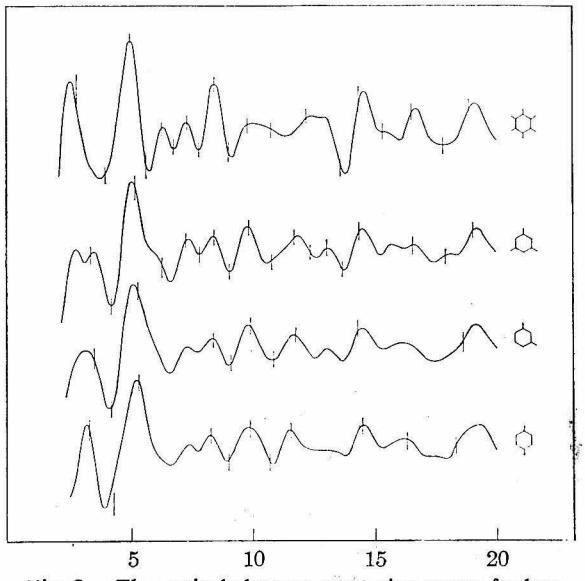

Fig. 2.—Theoretical electron scattering curves for hexachlorobenzene, 1,3,5-trichlorobenzene, *m*-dichlorobenzene, and *p*-dichlorobenzene. The positions of the maxima and mimima measured on the photographs are shown for each substance.

***m*-Dichlorobenzene.**—Ten maxima were observed on the photographs of *m*-dichlorobenzene, but the last two were too faint for reliable measurements of their diameters to be made. In choosing molecular models to be considered those involving a distortion of the C–Cl bond angles were neglected because the interaction of two chlorine atoms separated by more than 5 Å. is scarcely great enough to bend the bonds. The undistorted models give curves which reproduce the observed pattern satisfactorily. The three theoretical curves, calculated for C–Cl distances of 1.68, 1.70, and 1.76 Å., respectively, show slight qualitative differences; but in the quantitative comparisons with the s_0 values from the photographs the same value for the meta chlorine–chlorine separation is obtained, namely, 5.35 ± 0.05 Å. (Table III). Accordingly, it is impossible also in this case to make a direct determination of the size of the benzene ring. With the sum of the C–C and C–Cl distances equal to 3.09 ± 0.03 Å. the

separate distances are given the values C–C = 1.40 Å. and C–Cl = 1.69 ± 0.03 Å.

TABLE III

m-DICHLOROBENZENE

Max.	Min.	*I*	s_0	s^a	s/s_0
1		8	3.46	3.28	(0.948)
2		10	5.34	5.13	(.961)
3			(7.02)	7.39	
4		4	8.28	8.34	1.007
	5		9.07	9.07	1.000
5		5	9.91	9.86	0.995
	6		10.86	10.79	.993
6		4	11.77	11.73	.996
7			13.07	13.06	.999
8		2	14.33	14.50	1.012
9			(16.47)	16.10	
10		1	(18.64)	19.15	
				Average	1.000

Cl–Cl (meta) = 5.35 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

p-Dichlorobenzene.—The three theoretical curves for *p*-dichlorobenzene with C–Cl equal to 1.68, 1.70, and 1.76 Å., respectively, do not show significant differences, and on comparison with the photographs each of them gives a value for the para chlorine–chlorine separation of 6.18 ± 0.06 Å. (Table IV). The sum of C–C and C–Cl, accordingly, is 3.09 Å., so that with a C–C distance of 1.40 Å., the C–Cl distance is 1.69 ± 0.03 Å.

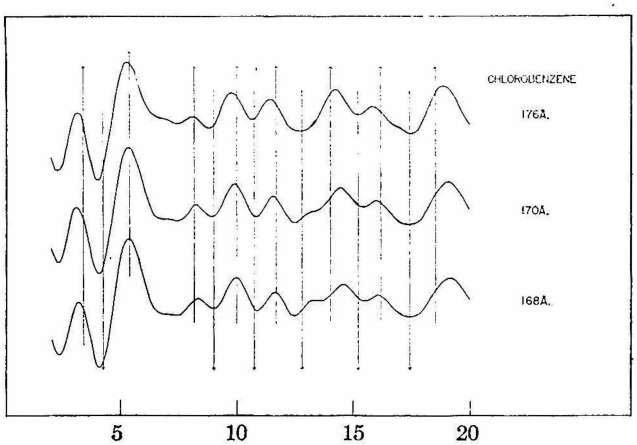

Fig. 3.—Theoretical scattering curves for three molecular models of chlorobenzene.

Chlorobenzene.—The three theoretical curves calculated for chlorobenzene are shown in Fig. 3. Of these the first (C–Cl = 1.76 Å.) is less satisfactory than the other two because it fails to show the shelf observed in the photographs on the inner side of the sixth maximum (near s = 14.4). In Table V it is seen that the "1.76" model leads

TABLE IV

p-DICHLOROBENZENE

Max.	Min.	*I*	s_0	s^a	s/s_0
1		5	3.38	3.25	(0.961)
2		10	5.33	5.27	0.989
3		2	8.27	8.30	1.004
	4		9.05	8.98	0.993
4		3	9.89	9.90	1.001
	5		10.77	10.86	1.008
5		3	11.57	11.58	1.001
6		2	14.38	14.53	1.011
7		1	16.30	16.24	0.996
				Average	1.000

Cl–Cl (para) = 6.18 Å.

[a] Calculated for C–C = 1.39 Å. and C–Cl = 1.70 Å.

to a carbon–carbon distance of 1.37 Å., which is 0.02 Å. less than that in benzene. For these two reasons the "1.76" model is rejected. The other models are equally good, and the average results given by them are C–Cl = 1.69 ± 0.03 Å. and C–C = 1.39 ± 0.02 Å.

o-Dichlorobenzene.—Theoretical intensity curves were calculated for three undistorted models of *o*-dichlorobenzene; model A, C–Cl = 1.76 Å.; model B, C–Cl = 1.70 Å.; and model C, C–Cl = 1.68 Å. Model C is in definite disagreement with the photographs, since it shows two equal maxima at s = 11.6 and 13.0, respectively, where a strong maximum and a weak shelf are observed (Fig. 4). Model B is unsatisfactory for the same reason. Model A, on the other hand, shows good qualitative agreement with the photographs with respect to the relative intensities of successive maxima. From the data of Table VI model A gives an ortho Cl–Cl separation of 3.11 Å., a C–Cl distance of 1.74 Å., and a C–C distance of 1.37 Å. This value for the C–C distance smaller than in benzene is probably not correct, however, and the possibility of distortion of the carbon–chlorine bonds was considered.

The satisfactory qualitative appearance of curve A required that only very small changes be made in the relative lengths of the more important interatomic separations. The group of carbon–chlorine terms is responsible for more than half of the total scattering, and their relative contributions were held practically constant by choosing new models having the value for the sum of the carbon–carbon and carbon–chlorine distances required by model A, that is, 3.11 Å. With this restriction three additional models were considered in which the chlorine–

Table V

Chlorobenzene

Max.	Min.	I	s_0	s_A	s_A/s_0	s_B	s_B/s_0	s_C	s_C/s_0
1		6	3.41	3.18	(0.932)	3.08	(0.903)	3.14	(0.921)
2		10	5.42	5.37	.991	5.34	.985	5.29	.976
3		3	8.17	8.33	1.020	8.24	1.008	8.10	.991
	4		9.01	8.97	0.996	8.95	0.994	8.83	.980
4		4	10.00	9.95	.995	9.91	.991	9.78	.978
	5		10.75	10.88	1.012	10.85	1.010	10.67	.993
5		3	11.67	11.63	0.997	11.58	0.993	11.44	.980
	6		12.81	12.49	(.975)	12.50	(.976)	12.65	.987
6		3	14.06	14.60	(1.038)	14.50	(1.031)	14.28	1.015
	7		15.28	15.50	1.015	15.46	1.012	15.25	0.998
7		1	16.24	16.10	0.991	16.05	0.989	15.87	.978
				Average	1.002		0.998		0.988
				C–Cl, Å.	1.684		1.696		1.739
				C–C	1.393		1.387		1.374

s_A: calculated for C–C = 1.39 and C–Cl = 1.68.
s_B: calculated for C–C = 1.39 and C–Cl = 1.70.
s_C: calculated for C–C = 1.39 and C–Cl = 1.76.

Table VI

o-Dichlorobenzene

Max.	Min.	I	s_0	s_A	s_A/s_0	s_D	s_D/s_0
1		8	3.35	3.05	(0.911)	3.05	(0.911)
2		10	5.24	5.03	(.960)	5.12	(.977)
3		2	(7.00)	6.78		6.79	
4		4	8.31	8.18	0.984	8.29	.998
	5		9.18	8.98	.978	9.10	.991
5		6	10.03	9.88	.985	10.01	.998
	6		10.86	10.70	.985	10.88	1.002
6		4	11.74	11.45	.976	11.67	0.994
	7		13.37	13.36	.999	13.50	1.010
7		6	14.39	14.35	.997	14.50	1.008
	8		15.43	15.31	.993	15.44	1.000
8		1	16.35	16.03	.980	16.20	0.991
	9		17.57	17.55	.999	17.53	0.998
9		3	18.80	18.84	1.002	19.00	1.011
		Average			0.989		1.000
		Cl–Cl (ortho) Å.			3.115		3.150
		Sum of C–C and C–Cl			3.115		3.110

s_A: calculated for C–C = 1.39 Å., C–Cl = 1.76 Å., Cl–Cl = 3.15 Å.—undistorted. s_D: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., Cl–Cl = 3.15 Å.—C–Cl angles bent through 0°48′.

chlorine distance is increased above that in the undistorted molecule but with the chlorine atoms still in the plane of the benzene ring: model D, Cl–Cl = 3.15 Å.; model E, Cl–Cl = 3.30 Å.; and model F, Cl–Cl = 3.30 Å. In the curve for model F (Fig. 4) the third maximum observed on the photographs is entirely missing, and the shelf observed on the outside of the sixth maximum (at s = 11.6) does not appear. In curve E these features are a little better, and in curve D the representation is entirely satisfactory. The quantitative comparison from curve D is the most consistent, and it is shown in Table VI. In the final result the ortho chlorine–chlorine separation is 3.15 ± 0.03 Å. and the sum of the carbon–carbon and carbon–chlorine distances is 3.11 ± 0.03 Å. This latter distance is divided between C–C = 1.40 Å. and C–Cl = 1.71 ± 0.03 Å.

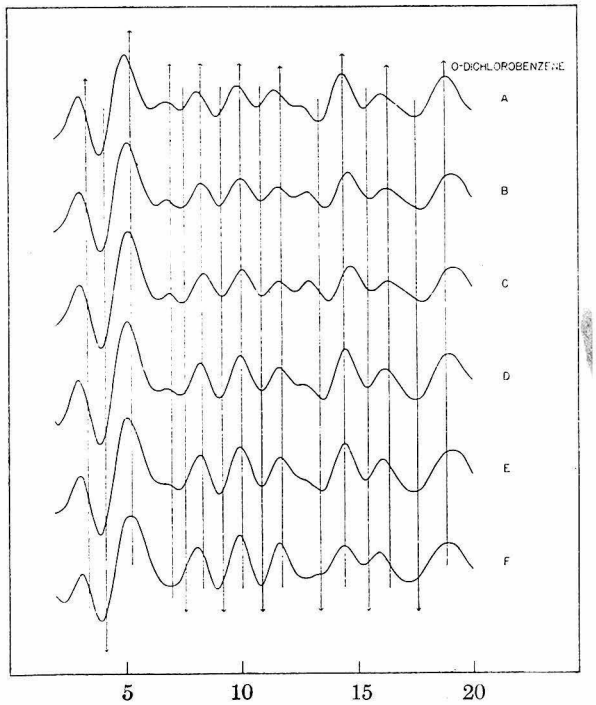

Fig. 4.—Theoretical scattering curves for various models of *o*-dichlorobenzene.

1,2,4,5-Tetrachlorobenzene.—Five molecular models of 1,2,4,5-tetrachlorobenzene were used in calculating theoretical intensity curves. The first two were undistorted, *i. e.*, with all C–Cl bonds directed toward the center of the benzene ring and with C–Cl = 1.70 and 1.76 Å., respectively.

Both curves failed to reproduce the diffraction pattern in the region between $s = 5$ and 8, and the maximum near $s = 10$ is too small relative to the maxima on either side. The second of these curves is shown as A in Fig. 5. The following

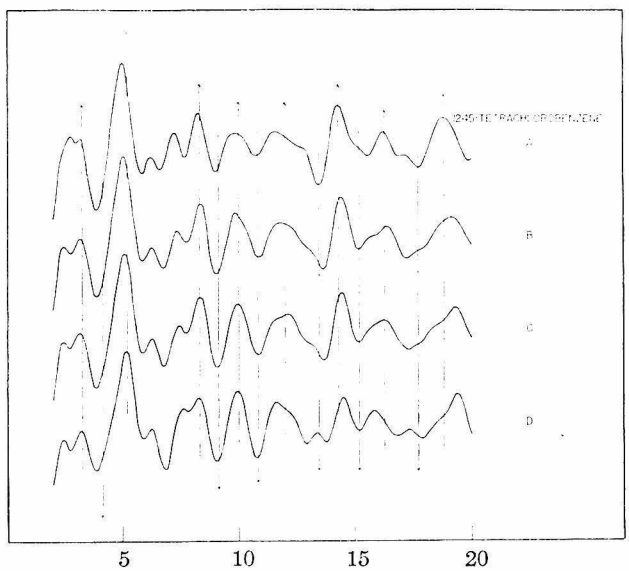

Fig. 5.—Theoretical scattering curves for various models of 1,2,4,5-tetrachlorobenzene.

distorted models similar to those of *o*-dichlorobenzene were calculated: model B, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.18 Å.; model C, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.20 Å.; and model D, C–Cl = 1.72 Å., Cl–Cl (ortho) = 3.30 Å. It may be noted that the ratios of the meta and ortho chlorine–chlorine separations in the four models have the respective values: 1.732, 1.685, 1.662, 1.593. Model D is eliminated because the fourth measured maximum (at $s = 10.0$) is too strong relative to the third and fifth; moreover, no suggestion of the small maximum at $s = 13.4$ appears on the photographs. Models B and C give better qualitative representations of the photographs, and the quantitative consistency of the data in Table VII is better than for model D. The final values taken as intermediate between the results from models B and C are known with a little less certainty than in the foregoing substances: Cl–Cl (ortho) = 3.20 ± 0.04 Å., Cl–Cl (meta) = 5.37 ± 0.06 Å., Cl–Cl (para) = 6.25 ± 0.07 Å. The sum of C–C and C–Cl is accordingly 3.12 ± 0.04 Å., which is divided between C–C = 1.40 Å. and C–Cl = 1.72 ± 0.04 Å.

The foregoing results may be compared with the results of previous investigations. The only other electron diffraction investigation is that of de Laszlo[7] on hexachlorobenzene, for which he reports an ortho Cl–Cl distance of 3.10 Å., a value supported by our result of 3.11 ± 0.03 Å.

R. Schoppe[8] obtained X-ray diffraction photographs of the vapors of chlorobenzene, *o*-, *m*-, and *p*-dichlorobenzenes, and 1,2,4-trichlorobenzene. He reports the distances C–Cl = 1.65 ± 0.03 Å., Cl–Cl (ortho) = 3.30 ± 0.05 Å., Cl–Cl (meta) = 5.35 ± 0.08 Å., and Cl–Cl (para) = 6.10 ± 0.09 Å. with an assumed C–C distance of 1.42 Å. The procedure used in fixing on the reported distances is not entirely clear, but it seems probable that the observed agreement between theory and experiment would not be affected if values outside of the ranges given by the investigator were used. In particular, the chlorine–chlorine distance in *o*-dichlorobenzene cannot be greater than 3.20 Å. because of the definite disagreement (pointed out in the above discussion of this compound) between our electron-diffraction photographs and theoretical diffraction patterns based on models having distances greater than 3.20 Å. This disagreement is not marked in the region out to $s = 8$ observed by Schoppe but is unmistakable in our photographs extending to $s = 19$. His value for the meta chlorine–chlorine distance, 5.35 Å., is supported by our results; but the para distance of 6.10 Å. is about 0.10 Å. too small. The distance 1.42 Å. which he used for the carbon–

TABLE VII

1,2,4,5-TETRACHLOROBENZENE

Max.	Min.	I	s_0	s_B	s_B/s_0	s_C	s_C/s_0
1		8	3.26	3.18	(0.976)	3.15	(0.966)
2		10	5.20	5.07	(.975)	5.07	(.975)
3		6	8.31	8.33	1.002	8.33	1.002
	4		9.11	9.07	0.996	9.05	0.993
4		5	9.95	9.85	.990	9.92	.997
	5		10.82	10.87	1.005	10.85	1.003
5		3	11.86	11.80	0.994	12.11	1.021
	6		13.44	13.62	1.014	13.65	1.016
6		5	14.29	14.47	1.014	14.43	1.010
	7		15.18	15.22	1.003	15.20	1.002
7		1	16.27	16.35	1.005	16.25	0.999
8		2	18.82	19.12	1.016	19.30	1.026
		Average			1.004		1.007
		Cl–Cl (ortho) Å.			3.193		3.222
		Cl–Cl (meta)			5.380		5.357
		Cl–Cl (para)			6.26		6.25
		Sum of C–C and C–Cl			3.12		3.125

s_B: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., and Cl–Cl (ortho) = 3.18 Å.

s_C: calculated for C–C = 1.39 Å., C–Cl = 1.72 Å., and C–Cl (ortho) = 3.20 Å.

(7) H. de Laszlo, *Proc. Roy. Soc.* (London), **A146**, 662 (1934).

(8) R. Schoppe, *Z. physik. Chem.*, **B34**, 461 (1936).

carbon distance was originally observed in graphite and is 0.02 or 0.03 Å. larger than the distance in benzene and its derivatives. With this correction Schoppe's carbon–chlorine distance becomes 1.67 or 1.68 Å., as compared with our values of 1.69 to 1.71 Å.

An X-ray investigation of hexachlorobenzene was made by Kaiser,[9] who obtained an ortho chlorine–chlorine separation of 3.35 ± 0.05 Å. Pierce[10] investigated chlorobenzene and *o*- and *p*-dichlorobenzenes and reported ortho Cl–Cl = 3.0 Å. and para Cl–Cl = 6.25 Å.

Hendricks[11] obtained a para chlorine–chlorine separation of 6.2 Å. (our result—6.18 Å.) in an X-ray investigation of crystalline *p*-dichlorobenzene. Mrs. Lonsdale[12] studied crystalline hexachlorobenzene; and while she did not obtain a complete set of parameter values for the atomic positions, the average of the minimum values suggested by her for the carbon–chlorine bond distances is 1.71 Å., in good agreement with the result of the present investigation.

Discussion

Carbon–Chlorine Distances.—The carbon–chlorine bond distances in the seven chlorobenzenes investigated all lie in the range from 1.69 to 1.71 Å., inclusive (with the exception of the value 1.72 Å. observed with less certainty in tetrachlorobenzene). As was remarked by de Laszlo[7] this is 0.06 Å. less than the carbon–chlorine distances observed in saturated aliphatic chlorine compounds. That such a difference might be expected on the basis of a characteristic difference in the radii of aliphatic and aromatic carbon atoms was suggested by Mrs. Lonsdale[13] in her investigation of hexamethylbenzene. A recent more complete analysis[6] of hexamethylbenzene, however, leads to the same value for the length of the bond C_{ar}–C_{al} which is observed for the bond C_{al}–C_{al} in many aliphatic compounds.

We suggest that the situation which gives rise to the shortening is entirely analogous to the situation in the chloroethylenes.[2] If we consider the various Lewis electronic structures which make appreciable contributions to the normal state of *o*-dichlorobenzene, for example, the first two (Fig. 6) are the Kekulé structures of the benzene ring. In addition we can write a set of three others in which one of the chlorine atoms is connected to the ring by a double bond, and an unshared pair of electrons appears on one of the three carbon atoms ortho or para to the first. A second set of three structures exists in which the other chlorine atom is double bonded. If each of these sets of three makes a 10% contribution to the normal state of the molecule, the observed shortening of 0.05 Å. below the value 1.76 Å. found in the chloromethanes is just accounted for on the basis of the empirical relation which has been developed between bond length and double bond character.[2,6] A contribution of this magnitude is not unreasonably large, and similar formulations can be made for the other chlorobenzenes. Variations in the degree of double bond character might be expected with variations in the number and positions of the chlorine atoms attached to the ring, but the effect on the bond distances is evidently less than the experimental error. The small variations which are observed in the distances bear no definite relation to the number or positions of the chlorine atoms, although the shortest distances are obtained in the four compounds not containing chlorine atoms attached to adjacent carbon atoms.

The effect observed in the chlorobenzenes amounts to 16% double bond character for a C–Cl distance of 1.69 Å., decreasing to 10% for a distance of 1.71 Å. This is comparable in magnitude to the effect in the chloroethylenes, in which the C–Cl distances range from 1.69 to 1.73 Å. In these latter substances there is more certain evidence for an increase in the distance with increase in the number of chlorine atoms. This may be due to the fact that the number of chlorine atoms adjacent to the double bond ranges from one to four, whereas the corresponding number in the chlorobenzenes is either one or two. The range of the carbon–chlorine distances in the chlorobenzenes accordingly is less than in the chloroethylenes.

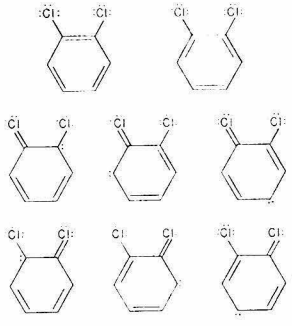

Fig. 6.—Figures representing the electronic structures of *o*-dichlorobenzene which make appreciable contributions to the ground state of the molecule. The C–H bonds are not shown; unshared electron pairs are indicated by pairs of dots.

(9) R. Kaiser, *Physik. Z.*, **36**, 92 (1935).
(10) W. C. Pierce, *J. Chem. Phys.*, **2**, 1 (1934).
(11) S. B. Hendricks, *Z. Krist.*, **84**, 85 (1933).
(12) K. Lonsdale, *Proc. Roy. Soc.* (London), **A133**, 536 (1931).
(13) K. Lonsdale, *ibid.*, **A123**, 494 (1929).

A similar shortening of bond distance is expected for any other substituent atom having an unshared electron pair. This has been observed by de Laszlo[7] for bromobenzenes and iodobenzenes. Dibromoacetylene[14] also shows such an effect.

Distortion of the Benzene Ring.—The resonance situation described above changes the character of the bonds in the benzene ring. When only the two Kekulé structures are to be considered, each of the six carbon–carbon bonds has 50% double bond character and the distance 1.390 Å. observed in benzene itself. With the consideration of other structures required by the observations made on the carbon–chlorine distances the fraction of double bond character is changed and in different amounts for the several carbon–carbon bonds. For example, in the case of *o*-dichlorobenzene formulated in Fig. 6 the observed C–Cl distance corresponds to a 79% contribution of the two Kekulé structures with 10.5% for each of the two sets of structures with double-bonded chlorine atoms. Considering the carbon–carbon bond between the two atoms to which the chlorines are attached we see that of the eight structures in the figure only the first has a double bond in this position. Accordingly, the contribution of this single structure represents the degree of double bond character in the bond, namely, 39.5%, instead of the 50% which it has in benzene. This change affects the bond distance in accordance with the relation referred to above, and we expect 1.408 Å. in place of 1.390 Å. Consideration of the other five bonds in the same fashion leads to anticipated distances of 1.396, 1.390, 1.396, 1.390, and 1.396 Å., respectively. While the accuracy of the absolute values is affected by the uncertainty in the determination of the carbon–chlorine distance (from which the relative contributions of the resonating structures were determined), the directions and orders of magnitude of the changes are correct, and we believe that the benzene ring actually is distorted in this way. The average of the above distances is 1.40 Å., and this value was used in interpreting the photographs in preference to 1.39 Å.

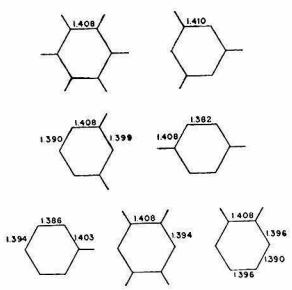

Fig. 7.—Expected values for the C–C bond distances in the chlorobenzenes based on the observed shortenings in the C–Cl bonds. The numbers represent the C–C bond lengths in Ångström units; the unmarked bonds are fixed by the symmetry of the molecule. The lines extending out from the ring show the positions of the attached chlorine atoms.

Changes are expected in the carbon–carbon distances in the other chlorobenzenes, too; and the observed carbon–chlorine distances have been used to obtain the anticipated values shown in Fig. 7. The extended bonds mark the positions of the chlorine atoms. The numerals represent bond lengths in Ångström units; where a numeral is not shown the bond length is fixed by the symmetry of the molecule. In each case the average carbon–carbon distance for the ring was used in the structure determination, since the deviations from the average are too small to be detected in a diffraction experiment.

Distortion of the Ortho Chlorine Atoms.—In the two unsymmetrical compounds having chlorine atoms attached to adjacent carbon atoms, the chlorine–chlorine separation is larger than it would be if their bonds made a 60° angle. In *o*-dichlorobenzene the observed separation is 3.15 Å., while the "undistorted" separation would be 3.11 Å., an increase of 0.04 Å. In 1,2,4,5-tetrachlorobenzene the observed separation is 3.20 Å. and the "undistorted" 3.12 Å.; the greater experimental error in the investigation of this substance makes it uncertain that the increase is actually twice as great as in the former compound.

Such increases in the separation of ortho-substituted atoms have been ascribed to the bending of the carbon–chlorine bonds due to the mutual repulsion of the chlorine atoms. A comparison may be made with dichloromethane, in which the 2.5° increase in bond angle above the value in the symmetrical tetrachloro derivative corresponds to an increase in the chlorine–chlorine separation from 2.87 to 2.92 Å. Since the repulsive potential is approximately proportional to the inverse ninth power of the separation, the increase in the "undistorted" chlorine–chlorine distance to 3.11 Å. in the chlorobenzene is accompanied by a decrease to less than half in the force acting between the chlorine atoms. Although the decrease in force is partly compensated by the more favorable direction in which it is applied to the atoms (due to the smaller angle between the bonds in chlorobenzene), we would expect an increase in the chlorine–chlorine separation in *o*-chlorobenzenes of

(14) Unpublished work by Mr. Henri Lévy in these Laboratories.

about 0.02 or 0.03 Å. The increase observed is from 0.04 to 0.08 Å. Accordingly, an explanation in addition to the mutual repulsion of the atoms is necessary. The distortion of the benzene ring discussed above occurs in these unsymmetrical compounds in a manner which would increase the ortho chlorine atom separations from 0.02 to 0.04 Å. according to the deviations from 120° of the various ring angles. Although still other effects may be involved it seems probable that some of the increase is to be ascribed to distortions of the benzene ring.

It should be noted that even if a regular benzene ring is assumed the bending of the carbon–chlorine bonds is not large. In *o*-dichlorobenzene the bending calculated with a regular ring is less than 1°; in 1,2,4,5-tetrachlorobenzene it is 1.5°. The distortion of the bond angles is much less than has been estimated on the basis of dipole measurements, in the interpretation of which insufficient allowance was made for the interaction of the moments in the adjacent carbon–halogen bonds.

We are grateful to Professor Linus Pauling for his encouragement and advice during the course of this investigation.

Summary

The molecular structures of some of the chlorobenzenes have been investigated with the following results

Substance	Sum of C–C and C–Cl, Å.	C–C (assumed), Å.	C–Cl, Å.	Cl–Cl (ortho), Å.	Cl–Cl (meta), Å.	Cl–Cl (para), Å.
C_6Cl_6	3.11	1.41	1.70	3.11	5.39	6.22
1,3,5-$C_6H_3Cl_3$	3.10	1.41	1.69		5.38	
m-$C_6H_4Cl_2$	3.09	1.40	1.69		5.35	
p-$C_6H_4Cl_2$	3.09	1.40	1.69			6.18
C_6H_5Cl	3.08	1.39	1.69			
o-$C_6H_4Cl_2$	3.11	1.40	1.71	3.15		
1,2,4,5-$C_6H_2Cl_4$	3.12	1.40	1.72	3.20	5.37	6.25

The decrease of the carbon–chlorine distances below the value 1.76 Å. observed in the chloromethanes is due to the contribution of electronic structures which introduce a degree of double bond character in the carbon–chlorine bonds. The resonating structures involved produce distortions in the benzene ring amounting in some cases to an increase of 0.02 Å. in the carbon–carbon distances. The benzene ring distortion is responsible in part for the increased chlorine–chlorine separation observed in the unsymmetrical ortho substituted compounds. The distortion of the bond angles in the ortho positions is not as great as has been supposed previously; even with the assumption of a regular benzene ring the ortho bonds are bent to the order of 1°.

PASADENA, CALIF. RECEIVED AUGUST 17, 1937

The Structure of Nitrosyl Chloride and Nitrosyl Bromide

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY NO. 626 AND FROM THE LABORATORY OF INORGANIC AND PHYSICAL CHEMISTRY OF THE UNIVERSITY OF LEYDEN]

The Electron Diffraction Investigation of Nitrosyl Chloride and Nitrosyl Bromide

BY J. A. A. KETELAAR AND K. J. PALMER

An investigation of the molecular structure of nitrosyl chloride and bromide seemed to be of interest especially with regard to the conclusions which Klinkenberg[1] has drawn from the determination of the crystal structures of some complex compounds formed by nitrosyl chloride and nitrosyl fluoride. He found that the nitrosyl group in many compounds is present in the state of the univalent ON^+ ion. In this respect there may be specially mentioned the case of the compound $2ONCl{\cdot}SnCl_4$, which is isomorphous with $(NH_4)_2SnCl_6$ and so really has the constitution $(ON)_2SnCl_6$.[2] In the same way he found the compounds $(ON)ClO_4$ and $(ON)BF_4$ to be isomorphous with the corresponding ammonium compounds.

Electron diffraction photographs were prepared in the usual way[3] with a film distance of about 11 cm., the electron wave length being 0.0613 Å. Some ten to fifteen photographs were taken of each compound and several of the best were inter-

(1) L. J. Klinkenberg, *Rec. trav. chim.*, **56**, 749 (1937).

(2) In course of publication.

(3) L. O. Brockway, *Rev. Modern Phys.*, **8**, 231 (1936).

preted both by the radial distribution method and by the visual method involving the comparison of calculated curves with the visually estimated intensity curves. Tables I and II contain the values of $s = (4\pi \sin \vartheta/2)/\lambda$ for the apparent maxima and minima together with the estimated intensity values as used in the calculation of the radial distribution curves given in Fig. 1.

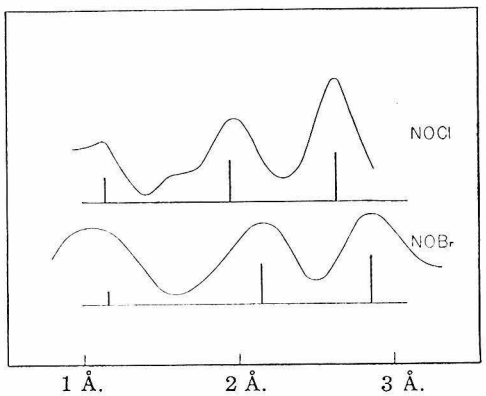

Fig. 1.—Radial distribution curves for nitrosyl chloride and nitrosyl bromide.

In applying the visual method we calculated intensity curves for different models. Some of these are reproduced in Figs. 2 and 3, whereas the data for the models used are found in Tables I and II.

TABLE I

NITROSYL CHLORIDE, ONCl

Max.	Min.	I	$s_{obsd.}$	s_{calcd} [a]	$s_{calcd.}/s_{obsd.}$
1		10	3.19	3.18	0.997
	2		4.28	4.25	.999
2		3	5.23	5.27	1.008
	3		6.32	6.02	(0.953)
3		7	7.58	7.45	.983
	4		8.99	8.95	.996
4		5	10.24	10.33	1.009
	5		11.48	11.47	0.999
5		4	12.66	12.84	1.014
	6		13.71		
6		1	14.67	Shelf	...
	7		15.92	15.77	0.991
7		3	17.06	17.20	1.008
	8		18.45	18.53	1.004
8		2	19.61	19.69	1.004

Average 1.001
Average deviation 0.007

[a] Averaged for models B and C.

Model A: Cl–O = 2.63 Å., Cl–N = 1.97 Å., N–O = 1.14 Å.
B: Cl–O = 2.64 Å., Cl–N = 1.95 Å., N–O = 1.12 Å.
C: Cl–O = 2.65 Å., Cl–N = 1.94 Å., N–O = 1.16 Å.
D: Cl–O = 2.65 Å., Cl–N = 1.92 Å., N–O = 1.16 Å.
E: Cl–O = 2.64 Å., Cl–N = 1.95 Å., N–O = 1.18 Å.

Results: Cl–O = 2.65 ± 0.02 Å. N–O = 1.14 ± 0.04 Å.
Cl–N = 1.95 ± 0.02 Å. Angle Cl–N–O = 116 ± 2°

TABLE II

NITROSYL BROMIDE, ONBr

Max.	Min.	I	$s_{obsd.}$	$s_{calcd.}$ (Model B)	$s_{calcd.}/s_{obsd.}$
1		8	2.98	2.94	0.997
	2			4.04	
2		1	4.90	4.90	1.000
	3			5.63	
3		10	6.90	6.87	0.997
	4		8.32	8.20	.986
4		6	9.40	9.37	.997
	5		10.67	10.59	.993
5		4	11.71	11.83	1.010

Average 0.997
Average deviation .004

Model A: Br–O = 2.82 Å., Br–N = 2.15 Å., N–O = 1.16 Å.
B: Br–O = 2.86 Å., Br–N = 2.15 Å., N–O = 1.16 Å.
C: Br–O = 2.86 Å., Br–N = 2.10 Å., N–O = 1.16 Å.

Results: Br–O = 2.85 ± 0.02 Å.
Br–N = 2.14 ± .02 Å.
[N–O = 1.15 ± .04 Å.]
Angle Br–N–O = 117 ± 3°

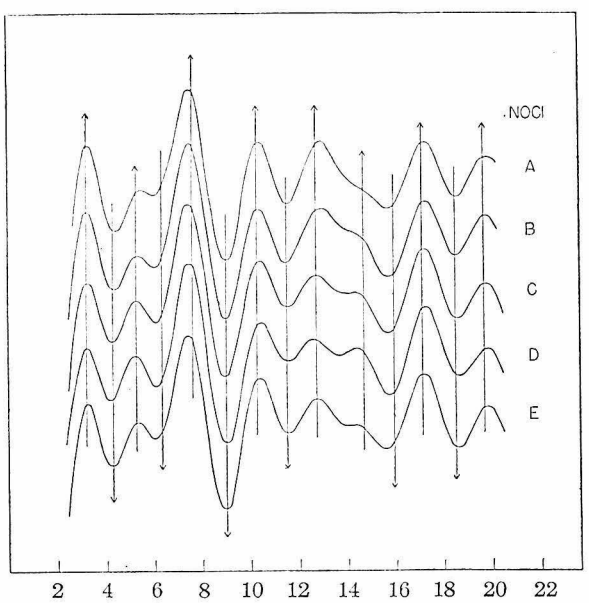

Fig. 2.—Intensity curves for nitrosyl chloride. Models described in Table I.

Curves B and C of Fig. 2 both give a good representation of the appearance of the photographs

of nitrosyl chloride. Curve B gives probably a better representation of the intensity ratio of the fourth and fifth maxima, whereas the faint but distinctly visible sixth maximum is perhaps somewhat better represented by curve C. The final distances chosen were assumed to be between those for these two very closely related models, taking into account also the values from the radial distribution curve, *i. e.*, Cl–O = 2.65 Å., Cl–N = 1.94 Å., and N–O = 1.14 Å. The values found are: Cl–O = 2.65 ± 0.01 Å., Cl–N = 1.95 ± 0.01 Å., and N–O = 1.14 ± 0.02 Å. The bond angle Cl–N–O calculated from these distances is found to be 116 ± 2°. The correspondence between calculated curves and the observed intensities is decidedly less satisfactory for the other models especially with regard to the second maximum with the adjacent second and third minima, thus proving the accuracy of the results obtained.

In the case of the calculation of the intensity curves for different models of nitrosyl bromide, the N–O distance, which contributes in this case only very little to the total intensity, was assumed to be about the same as in nitrosyl chloride and taken as 1.16 Å. In this case model B leads to the curve corresponding most satisfactorily with the estimated intensities both with regard to the second maximum and to the part of the curve outside the fifth maximum. The distances for the different models are listed in Table II. The results on nitrosyl bromide are thus: Br–O = 2.85 ± 0.02 Å., Br–N = 2.14 ± 0.02 Å., N–O = 1.15 ± 0.01 Å., and the bond angle Br–N–O = 117 ± 3°.

The interatomic distances and bond angles are provided with estimated probable errors, indicating the extent to which they can be considered as reliable.

The sample of nitrosyl chloride used in this investigation, provided by Professor Don M. Yost of these Laboratories, was considered to be of high purity. A sample of nitrosyl bromide was especially prepared for us by Mr. Carroll Beeson of these Laboratories. In the case of nitrosyl chloride no decomposition of the compound was to be feared, as the values of the dissociation constant determined by Dixon[4] indicate that at room temperature the dissociation is still practically zero. In the case of the less stable nitrosyl bromide a possible decomposition has to be discussed more extensively. The determinations of Blair, Brass, and Yost[5] lead to a decomposition of about 4% at −15° and 200–300 mm. pressure. The sample was prepared by combining bromine with almost four times the necessary amount of nitrous oxide. The extra amount of nitrous oxide was removed later by pumping it off at a temperature of −70°. The sample was kept constantly at low temperature except for about twenty minutes during the exposures when it was at −30 to −15°. From the measurements of Krauss[6] on the velocity of the reaction by which ONBr is formed, combined with the values for the equilibrium, the reaction velocity for the decomposition reaction can be calculated. It is found that even at +15° and a pressure of 200 mm. only 10^{-6} part is decomposed in one second. From these data the conclusion can be drawn that the decomposition of the sample itself at the temperature at which it is kept is negligibly small and also that no decomposition occurs at room temperature during the exposure time of about one-fifth second.

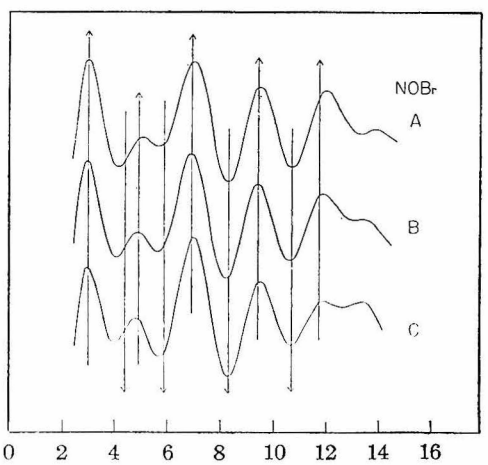

Fig. 3.—Intensity curves for nitrosyl bromide. Models described in Table II.

In the paragraphs above the assumption has been made that the halogen atom in the nitrosyl halides is closer to the nitrogen atom than to the oxygen atom. Because of the small difference in scattering powers of nitrogen and oxygen, the electron-diffraction data do not distinguish between the structures described above and those obtained from them by interchanging the nitrogen and oxygen atoms. We feel, however, that the arrangement ONX is more reasonable from

(4) J. K. Dixon, *Z. physik. Chem. Bodenstein Festband*, 679 (1931).

(5) C. M. Blair, P. D. Brass and D. M. Yost, THIS JOURNAL, **56**, 1916 (1934).

(6) W. Krauss, *Z. physik. Chem.*, **A175**, 295 (1936).

the standpoint of valence theory than NOX, and so have based our discussion on it, and we have correspondingly used the formulas ONCl and ONBr rather than the conventional NOCl and NOBr in referring to nitrosyl chloride and bromide.

Discussion

As a result of the electron diffraction investigation[7] of ONCl and ONBr it is found that these molecules are non-linear with a bond angle in both cases of 116 ± 3°. The distances between nitrogen and chlorine and bromine are 1.95 and 2.14 Å., respectively, which are much larger than those expected from the sums of single bond radii, these latter being 1.69 and 1.84 Å., respectively. In many cases interatomic distances smaller than the sum of the covalent radii have been observed arising from contributions of structures with double bonds instead of single bonds. Distances appreciably larger than those expected from single bond radii have, however, only been observed in very few cases, *e. g.*, in B_2H_6[8] where the B–B and B–H distances were found to be 5 and 7%, respectively, larger than those calculated for single bond distances.

A possible explanation of this surprising discrepancy is gained from a discussion of the possible structures for the ONCl and ONBr molecules besides the normal structure described by the electronic formula $:\ddot{\underset{\cdot\cdot}{X}}:N::\ddot{O}:$. A large contribution of a structure with a double bond between chlorine and nitrogen atoms is excluded as this would result in an even shorter distance than that calculated for a pure single bond. It will be shown, however, that resonance between the normal structure and an ionic structure in which the molecule is built up from a chlorine (or bromine) ion and a nitrosyl ion results in a larger distance between nitrogen and halogen nuclei. An estimate of the distances to be expected for a pure ionic structure can be gained from the following considerations. Klinkenberg has found that the volume of the nitrosyl ion is somewhat less than that of the ammonium ion and about the same as that of the hydronium ion. If we assume a spherical form for the NO^+ ion, this leads to a radius of 1.40 Å. The assumption of spherical symmetry, suggested by the observed isomorphism between K, NH_4, and NO compounds, can be explained easily by the possibility that this high symmetry is caused by the rotation of the group just as, *e. g.*, in the case of the cyanide ion.[9] Taking the radius 1.40 Å. for the nitrosyl ion and setting the nitrogen and oxygen nuclei at equal distances from the center of the ion and at the mutual distance observed in ONCl, *i. e.*, 1.14 Å., we find for the distance from the nitrogen nucleus to the surface 1.40–0.57 = 0.83 Å. With the radius of 1.81 Å. for the chlorine ion we subsequently find 1.81 + 0.83 Å. = 2.64 Å. as the Cl–N distance in a pure ionic structure. We see that the assumption of an appreciable contribution of the ionic structure, as suggested by the above-mentioned results of Klinkenberg on the crystal structure of nitrosyl compounds, indeed leads to the high observed halogen–nitrogen distances. The electronic constitution of the ionic structure could only be $:\ddot{\underset{\cdot\cdot}{Cl}}:^- \ :N::\overset{+}{\ddot{O}}:$,[10] having a triple bond between nitrogen and oxygen. The distance calculated from covalent radii with the revised value[11] of the double bond factor is 1.18 Å.; similarly the triple bond distance is 1.06 Å. So we see that the observed nitrogen–oxygen distance is somewhat smaller than that calculated for the sum of double bond radii, pointing to some triple bond character just as demanded by a structure resonating between the normal and the ionic structures.

The dependence of the distance on the bond character is not known for the N–Cl bond. Assuming, however, this dependence to be of the same form as that for the C–C bond, we calculate about 50% ionic character for nitrosyl chloride and bromide. This percentage would result in an N–O distance of 1.11 Å., fairly close to the observed value of 1.14 Å. The data obtained from the electron diffraction investigation thus lead to the conclusion that ONCl and ONBr have an appreciable amount of ionic character. Data on their dipole moments are not found in the literature, and one of us (J. A. A. K.) proposes to determine the values of these quantities. The low boiling points suggest, however, that they will be small.

We are indebted to Professor Don M. Yost and

(7) About two years ago some electron diffraction photographs of ONCl were taken by L. O. Brockway, L. Pauling, and J. Y. Beach in these Laboratories. They arrived at about the same results, especially regarding the large Cl–N distance, as we did from very much better photographs. These results were not published, as the purity of the sample used was doubtful.

(8) S. H. Bauer, THIS JOURNAL, **59**, 1096 (1937).

(9) J. M. Bijvoet and H. J. Verweel, *Rec. trav. chim.*, **54**, 631 (1935).

(10) L. Pauling, THIS JOURNAL, **53**, 3230 (1931).

(11) L. Pauling and L. O. Brockway, *ibid.*, **59**, 1223 (1937).

Mr. C. Beeson for samples used in this investigation, and to Professor Linus Pauling for his constant interest and his criticism. One of us (J. A. A. K.) is indebted to the Netherland-America Foundation for a gift enabling him to stay at the California Institute of Technology while carrying out this investigation.

Summary

The arrangements of atoms in the molecules of nitrosyl chloride and nitrosyl bromide have been determined by electron diffraction, the interpretation being made both by the radial distribution method and by the usual visual method. The following results were obtained—nitrosyl chloride: Cl–O = 2.65 ± 0.01 Å., Cl–N = 1.95 ± 0.01 Å., N–O = 1.14 ± 0.02 Å., angle Cl–N–O = 116 ± 2°; nitrosyl bromide: Br–O = 2.85 ± 0.02 Å., Br–N = 2.14 ± 0.02 Å., N–O = 1.15 ± 0.04 Å., angle Br–N–O = 117 ± 3°.

The surprisingly large halogen–nitrogen distances found are explained as caused by resonance between the normal covalent structure and the ionic structure.

LEYDEN, THE NETHERLANDS
PASADENA, CALIF. RECEIVED SEPTEMBER 28, 1937

Summary

The structure of sulfur dichloride, sulfur monochloride, thionyl chloride, sulfur trioxide, sulfuryl chloride, chromyl chloride, vanadium oxytrichloride, aluminum chloride, aluminum bromide, aluminum iodide, selenium dioxide, nitrosyl chloride, nitrosyl bromide, and seven chlorobenzenes have been investigated by the electron diffraction method. The results are reported in this thesis.

An explanation of the short S-O distance which occurs in sulfur dioxide, sulfur trioxide, thionyl chloride, and sulfuryl chloride is given.

The effect of the benzene ring on the C-Cl distance, and the distortion produced in the benzene ring itself by the C-Cl bond is discussed.

The values of the interatomic distances and angles are summarized on the following pages:

Page 42. - Sulfur dichloride, sulfur monochloride, thionyl chloride, sulfur trioxide, sulfuryl chloride, chromyl chloride, and vanadium oxytrichloride.

Page 66. - Aluminum chloride, aluminum bromide, and aluminum iodide.

Page 73. - Selenium dioxide.

Page 83. - Monochlorobenzene, O-m-p-dichlorobenzene, 1,3,5,trichlorobenzene, 1,2,4,5, tetrachlorobenzene, and hexachlorobenzene.

Page 89. - Nitrosyl chloride and nitrosyl bromide.