[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 655]

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

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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, are 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 distilled carefully in an all-glass apparatus, and only a small fraction boiling at 59° 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 135–136°.

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

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

Sulfuryl 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 already has been described in the literature.[1] All radial distribution curves were calculated using C $(= s_0^2 Ie^{-as_0^2})$ 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_0 $[= 4\pi \sin /2/\lambda]$, I (the visually estimated intensities) and C $(=s_0^2 Ie^{-as_0^2})$ 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 reproduced 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

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

(2) V. Schomaker and C. Degard, to be published in THIS JOURNAL.

(3) L. O. Brockway and K. J. Palmer, THIS JOURNAL, **59**, 2181 (1937).

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.

TABLE I

SULFUR DICHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		10	3	4.545	4.15	(0.913)
	2			5.724	5.55	(.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 ± 0.03 Å.

Cl–Cl = (3.06)(1.006) = 3.08 ± 0.04 Å.

[a] Calculated for the model with S–Cl = 1.98 Å. and Cl–Cl = 3.06 Å.

On the other hand, curve A (101°10′ model) agrees very well with the photographs. The outside shelves 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

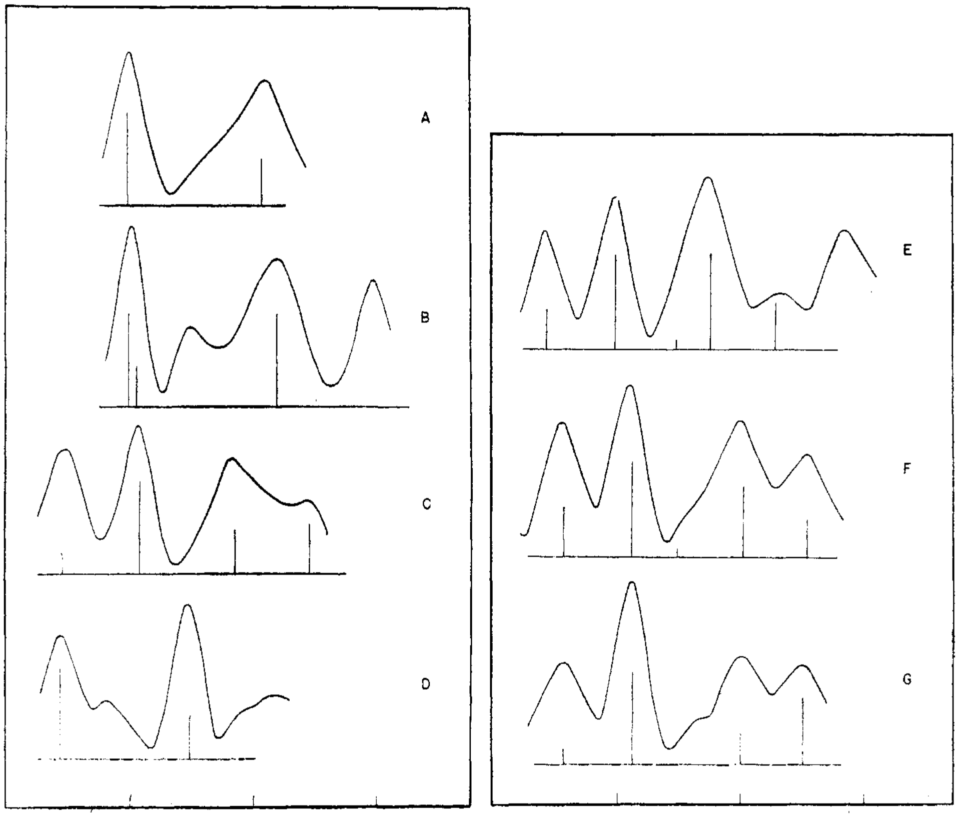

Fig. 1-A. Fig. 1-B.

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.

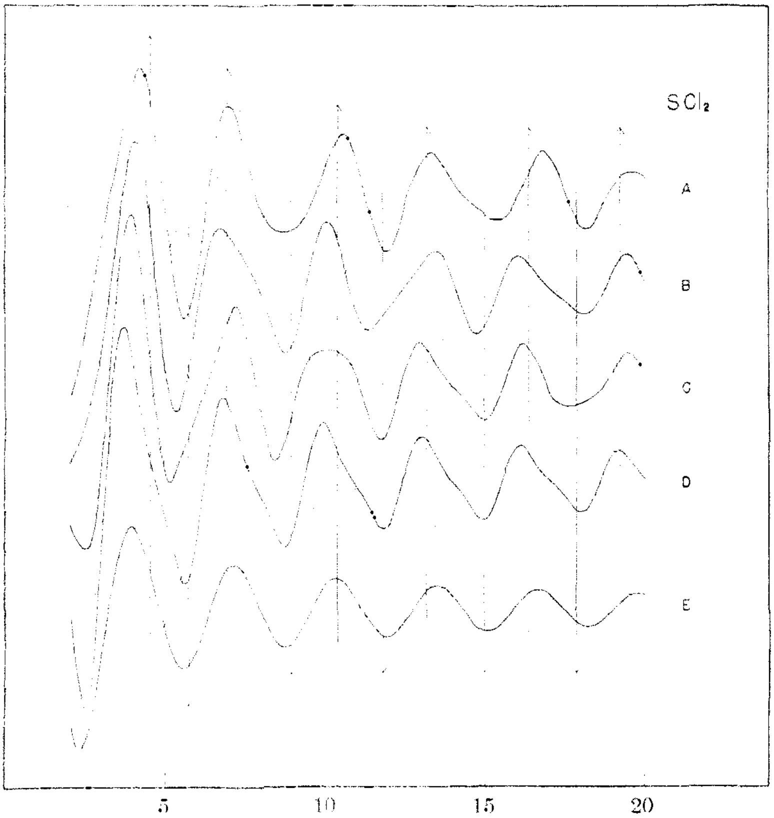

Fig. 2.—Theoretical intensity curves for sulfur dichloride.

of 1.995 Å. The final values are therefore taken as S–Cl = 1.99 ± 0.03 Å. and the angle Cl–S–Cl = 101 ± 4°.

Sulfur Monochloride.—The sample of sulfur monochloride was transferred to the high temperature nozzle inside a moisture-proof box. When the nozzle 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 measured accurately. 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_0, 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.[4] 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, however, compatible with the model in which one chlorine atom is attached to each sulfur atom. For this reason intensity curves were calculated only for models compatible with this latter configuration.

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

TABLE II

SULFUR MONOCHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		10	3	4.632	4.00	(0.864)
	2			5.603	5.48	(.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	0.990
	6			15.069	15.20	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 ± 0.03 Å.
S–S = 2.05 ± 0.03 Å.
Cl–S–S∠ = 103 ± 2°

[a] Calculated for the model with S–S = 2.05 Å., S–Cl = 1.99 Å. and Cl–Cl = 3.95 Å.

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(4) Refer to curve C, Fig. 1, for thionyl chloride.

S–S distance. The value found is 2.05 Å.[5] 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., 2.05 Å., and 103°35′, respectively. This is justifiable because the well resolved inner peaks on the radial distribution curve are probably reliable to within 1%. Curves A, B, and C for 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_0 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 curve which appears to be sensitive to the Cl–Cl separation, and it is consequently impossible at the present time 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,[6] whereas only three frequencies of the *trans* model are Raman active. It is evident therefore 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. The quantitative comparison of s to s_0 for curve A is given in Table II.

Y. Morino and S. Mizushima[6] recently have 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.

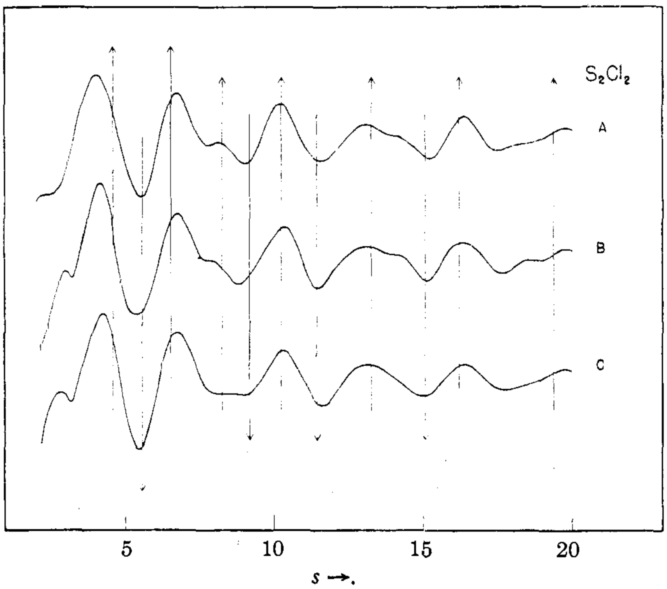

Fig. 3.—Theoretical intensity curves for sulfur monochloride.

Ackermann and Mayer[7] have investigated the molecular structure of sulfur monochloride by the diffraction of comparatively slow (about 6 kv.) 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 best agreement with their photographs. 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 com-

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(5) This value is in good agreement with that found in H_2S_2 by Beach and Stevenson (private communication).

(6) Y. Morino and S. Mizushima, *Sci. Papers I. P. C. R.*, **32**, 220 (1937).

(7) Ackermann and Mayer, *J. Chem. Phys.*, **4**, 377 (1936).

TABLE III

THIONYL CHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0	s^b	s/s_0
1		10	4	4.78	3.98	(0.833)	4.08	(0.854)
	2			5.79	5.18	(.894)	5.29	(.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	0.991
	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	0.993
5		2	3	16.07	16.08	1.001	15.75	.980
	6			17.43	17.33	0.994	17.38	.997
6		3	4	18.66	18.58	.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 = 1.44 Å., S–Cl = 2.07 Å., Cl–O = 2.84 Å., and Cl–Cl = 3.50 Å. [b] Calculated for the model with S–O = 1.44 Å., S–Cl = 2.07 Å., Cl–O = 2.84 Å., and Cl–Cl = 3.40 Å.

paratively 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_0, 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_0 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 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 minima. 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 ± 0.02 Å., S–Cl = 2.07 ± 0.03 Å., Cl–O = 2.84 ± 0.03 Å., and Cl–S–Cl angle = 114 ± 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 sulfuryl chloride.

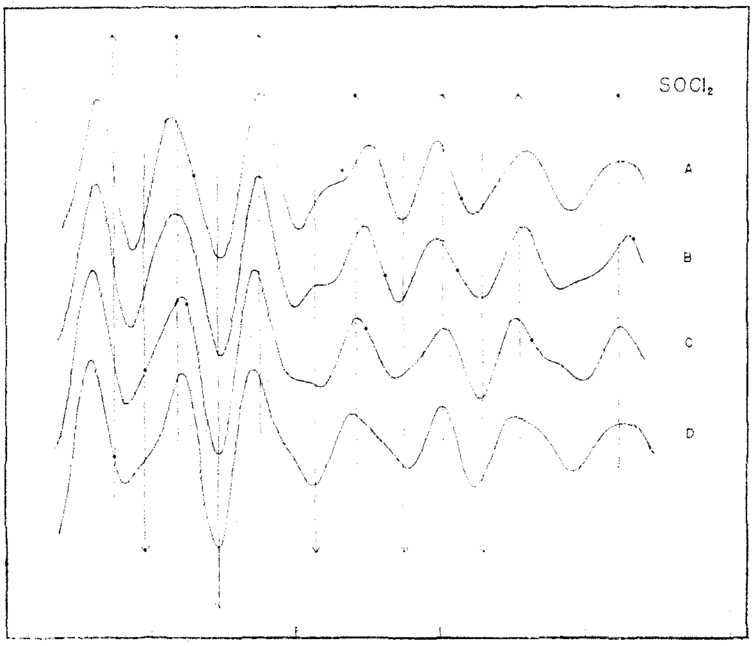

Fig. 4.—Theoretical intensity curves for thionyl chloride.

Sulfur Trioxide.—The sample of sulfur trioxide was distilled under vacuum into the sample holder, phosphorus pentoxide 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 shelf, the other rings being more or less regular in appearance. The average values 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 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. As no edge can be discerned on the photographs, model A is to be favored over model B.

The ratios s/s_0 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 recently has been measured[8] 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.

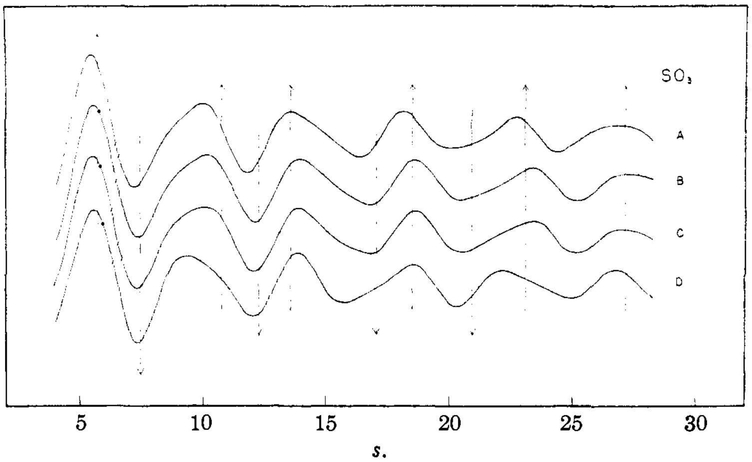

Fig. 5.—Theoretical intensity curves for sulfur trioxide.

TABLE IV

SULFUR TRIOXIDE

Max.	Min.	*I*	*C*	s_0	s^a	s/s_0	s^b	s/s_0
1		10	6	5.692	5.38	(0.945)	5.54	(0.973)
	2			7.422	7.13	(.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	0.983
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 ∠ = 120° ⩽ 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 ∠ = 117°50′.

Sulfuryl Chloride.—The photographs of sulfuryl chloride have eight measurable maxima. The values of s_0, *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

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[8] A. Smits, N. F. Moerman and J. C. Pathuis, *Z. physik. Chem.*, **B35**, 60 (1937).

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.

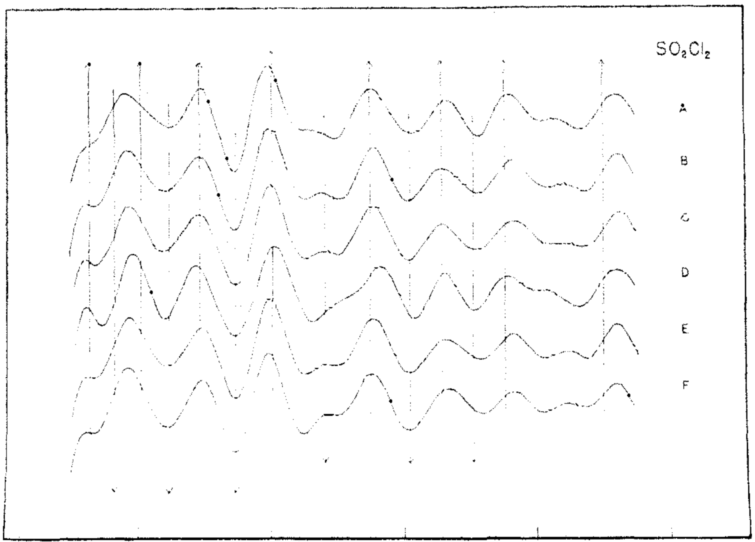

Fig. 6.—Theoretical intensity curves for sulfuryl chloride.

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 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 eliminated easily 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 cannot be observed on the photographs. Curve E is not satisfactory because the first maximum is not well resolved, and also the structures 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 unsatisfactory 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_0. The final values selected for the parameters are given in Table VI.

TABLE V

SULFURYL CHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		6	2	3.140	3.00	(0.956)
	2			4.085	3.29	(.805)
2		8	6	5.082	4.60	(.905)
	3			6.165	5.90	(.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			15.274	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 = 1.43 Å., O–S–O angle equal to 119°48', and Cl–S–Cl angle equal to 111°12'.

Chromyl Chloride.—The photographs of chromyl chloride show seven measurable maxima. The values of s_0, I, and C are listed in Table VII.

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 ± 0.02 Å.	Cr–O = 1.57 ± 0.03 Å.	V–O = 1.56 ± 0.04 Å.
S–Cl = 1.99 ± 0.02	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°

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_0, *I*, and *C* are given in Table VIII. 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_0 shown in Table VIII. The final values selected for the parameters are given in Table VI.

Discussion

The configurations found for the seven molecules studied in this investigation are all in agreement with expectation. The Cl–S–Cl angle of 101° found in sulfur dichloride lies between the limits 90° for pure p bonds and 109°28′ for sp^3 hybridization.

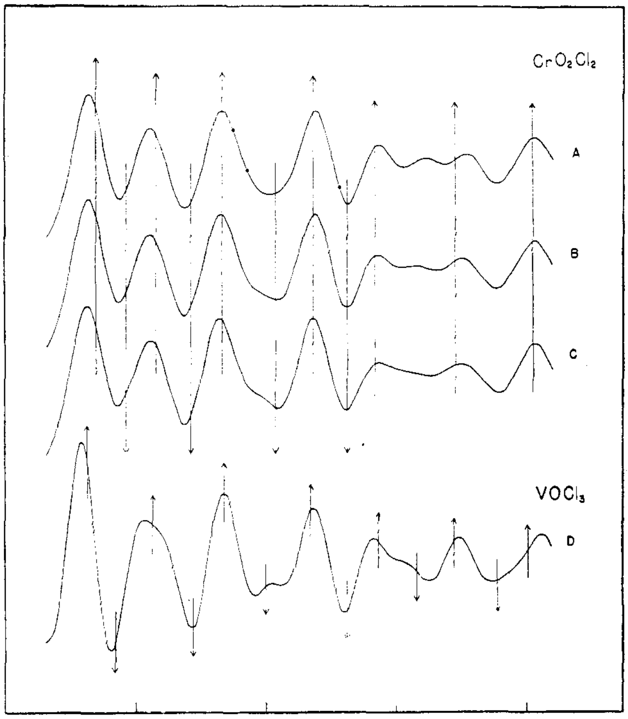

Fig. 7.—Theoretical intensity curves for chromyl chloride and vanadium oxytrichloride.

The generally accepted structure for sulfur monochloride, that in which there is one chlorine atom attached to each sulfur atom, has been confirmed. The Cl–S–S angle of 103° is in agreement with the angle to be expected from a con-

TABLE VII

CHROMYL CHLORIDE

Max.	Min.	I	C	s_0	s^a	s/s_0
1		10	6	4.438	4.13	(0.933)
	2			5.629	5.33	(.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_0	s^a	s/s_0
1		10	4	4.193	3.95	(0.943)
	2			5.310	5.11	(.964)
2		7	6	6.700	...	...
	3			8.261	8.22	0.995
3		7	10	9.427	9.42	.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	.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°.

sideration of the electronic formula for sulfur monochloride, since, as in sulfur dichloride, the sulfur atom is surrounded by an octet of electrons and both the S–S and S–Cl bonds are single bonds.

Thionyl chloride is pyramidal. The molecule would be planar if the S–O bond were a double bond, and the electronic structure were similar to that of phosgene. The unshared pair of electrons on the sulfur atom, however, causes the molecule to assume a pyramidal configuration.

The sulfur trioxide molecule is isoelectronic with the nitrate and carbonate ions and is expected to be planar for the same reasons that are advanced to explain the structure of these ions. The confirmation of the planarity of sulfur trioxide is also in agreement with the dielectric constant measurements which recently have been carried out.[8]

The electronic formula which usually is written for sulfuryl chloride shows the sulfur atom to be surrounded by eight electrons. This makes each S–O bond a single covalent bond (semipolar double bond), and leads one to anticipate that sulfuryl chloride will have a tetrahedral configuration. The actual configuration is considerably distorted from a regular tetrahedral arrangement, the O–S–O angle being increased from 109°28′ to about 120°. The Cl–S–Cl angle is only slightly larger than that expected, having the value 111°. It is interesting to note that the Cl–O distances in both thionyl and sulfuryl chlorides are nearly equal.

The increase in the O–S–O angle in sulfuryl chloride is probably due to a considerable amount of multiple bond character which is brought about by the swinging in of one or even two pairs of electrons from the oxygen atom. The excited structures no doubt disobey the octet rule which is, however, of little significance in a discussion of second row elements because of the comparative proximity in energy of orbitals such as the 3d or 4s orbitals in sulfur which can be used for bonding purposes.

In chromyl chloride the O–Cr–O angle has decreased to 105° as compared to the large increase in sulfuryl chloride. No explanation of this phenomenon can be given at present. The Cl–Cr–Cl angle shows an increase of a few degrees over the tetrahedral value.

The close analogy in both distances and angles in chromyl chloride and vanadium oxytrichloride is very striking. A similar phenomenon is observed in the case of the sequence of molecules $SiCl_4$, PCl_3, SCl_2, and Cl_2, where the observed interatomic distances are 2.00, 2.00, 1.99, and 1.98 Å., respectively,[9] as compared to the sum of the single bond radii 2.16, 2.09, 2.03, and 1.98 Å., respectively. The constancy of these observed interatomic distances is due to the fact that the double-bond character of each of the above bonds, which is a function of the difference in electronegativity of the bonded atoms, just compensates for the change in value of the sum of the single-bond radii. This same effect accounts for the observed similarities in distance in chromyl chloride and vanadium oxytrichloride.

This phenomenon is not observed for first row

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

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, Å.	1.99 ± 0.03	1.99 ± 0.03	2.07 ± 0.03	1.99 ± 0.02	......	2.12 ± 0.03	2.12 ± 0.02
A-O, Å.	......	......	1.45 ± 0.02	1.43 ± 0.02	1.43 ± 0.02	1.56 ± 0.04	1.57 ± 0.03
Cl-O, Å.	......	......	2.84 ± 0.03	2.76 ± 0.03	......	3.00 ± 0.04	3.03 ± 0.03
Cl-Cl, Å.	3.08 ± 0.04	......	3.47 ± 0.03	3.28 ± 0.10	......	3.50 ± 0.03	3.54 ± 0.05
O-O, Å.	......	......	......	2.48 ± 0.10	2.48 ± 0.03	......	2.49 ± 0.10
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 Å.	......	2.05 ± 0.03	......	......	......	......	......
Cl-S-S ∠	......	103 ± 2°	......	......	......	......	......

chlorides because in these cases double-bond formation can occur only when at least one other bond becomes ionic. This does occur in the case of some fluorides[10] where a very large difference in electronegativity between the bonded atoms exists.

The S-O distances observed in the four molecules sulfur dioxide,[11] sulfur trioxide, thionyl chloride, and sulfuryl chloride are from 0.06 to 0.09 Å. shorter than the sum of the normal double-bond radii which is 1.52 Å. This is particularly surprising when one considers the electronic formulas of these molecules. These formulas indicate that the S-O bond in sulfur dioxide possesses one-half, in sulfur trioxide one-third, and in thionyl and sulfuryl chlorides no double-bond character. Making a correction for the formal charges on the atoms, the values for the S-O distance predicted on the basis of structures of the octet type are 1.52 Å. for sulfur dioxide and sulfur trioxide, and 1.69 Å. for thionyl and sulfuryl chlorides. The fact that the observed distances are all nearly equal and much less than 1.52 Å. indicates that excited electronic structures in which double and triple S-O bonds are present must make a considerable contribution to the normal state of these molecules, being, however, more important for thionyl and sulfuryl chlorides than for sulfur dioxide and sulfur trioxide.

It is difficult to give a quantitative discussion of the observed interatomic distances in chromyl chloride and vanadium oxytrichloride because there is some uncertainty as to the values of the covalent radii of chromium and vanadium. If one assumes reasonable values of about 1.15 for chromium and 1.20 for vanadium, however, it is again evident that the Cr-O and V-O distances are considerably shorter than the sum of the single bond radii, indicating that also in these two molecules structures involving multiple Cr-O and V-O bonds make important contributions to the normal state.

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.

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 cannot be determined with certainty.

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(10) L. O. Brockway, *J. Phys. Chem.*, **41**, 185 (1937).

(11) P. C. Cross and L. O. Brockway, *J. Chem. Phys.*, **3**, 821 (1935).