heated, then mix and oxidize as described before, which usually requires ten to fifteen minutes. Dilute to 100 ml. and acidify with 20 ml. of 5 *N* sulfuric acid in excess of that equivalent to the combined base in the bromide plus that in the standard periodate used. Heat and draw air through the solution until the bromine color disappears, then place the indicator solution in the U tube and repeat until no test for bromine is obtained. Cool, neutralize with 20 ml. of 5 *N* sodium carbonate, buffer the solution and titrate the excess of periodate.

TABLE III

DETERMINATION OF BROMIDE

No.	Bromine taken, g.	0.2 *M* KCl, ml.	Excess 0.1 *N* $K_2H_3IO_6$, ml.	5 *N* H_2SO_4, ml.	Time of heating, min.	Error bromine, mg.
1	0.3599		4.56	25	45	−0.1
2	.3600		4.54	20	55	.0
3	.3607		4.45	20	65	+ .1
4	.3401		7.48	10	90	− .6
5	.3038		11.86	10	95	+ .2
6	.2560		17.84	10	80	+ .3
7	.2001		24.84	10	55	+ .3
8[a]	.2211		22.25	18.5	150	.0
9	.3633	5	4.42	10	100	− .5
10	.3632	5	4.35	10	105	− .1
11	.3638	5	4.30	10	120	.0
12	.3621	10	4.33	10	120	+1.2
13	.3617	25	4.15	10	120	+3.1

[a] Reaction volume was 100 ml. except 300 ml. in No. 8.

Each milliliter of 0.1 *N* periodate is equivalent to 0.00792 g. of bromine.

Any considerable amount of chloride interferes but, as shown in the results of Table III, by using low acidity and a prolonged bubbling, separation from a millimole or less of chloride may be effected.

Summary

1. Potassium metaperiodate, KIO_4, can be purified readily so as to have the theoretical composition and may be used as a primary standard in iodimetry.

2. Dipotassium paraperiodate in a slightly alkaline solution, and sodium metaperiodate acidified with sulfuric acid are both stable volumetric solutions, the latter showing remarkable permanency. Metaperiodates in neutral solution decompose with noticeable rapidity.

3. Iodide may be determined in the presence of bromide, chloride, and other substances not oxidized by neutral periodate solution by oxidation to iodate with standard periodate, and titration of the excess of the latter with arsenious acid. Conditions required for a rapid reaction are shown.

4. Bromide may be determined in presence of small amounts of chloride by oxidation to bromine with standard periodate in slightly acid solution, expulsion of the bromine, and titration of the excess periodate.

ANN ARBOR, MICHIGAN RECEIVED SEPTEMBER 6, 1938

[CONTRIBUTION FROM FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Electron Diffraction Investigation of the Molecular Structures of Hydrogen Disulfide, Dimethyl Disulfide and Sulfur Dichloride

BY D. P. STEVENSON AND J. Y. BEACH[1]

We have investigated the structure of the gas molecules of hydrogen disulfide, dimethyl disulfide and sulfur dichloride by the electron diffraction method. The apparatus has been described elsewhere.[2] The electron wave length was 0.0590 Å., determined from transmission pictures of gold foil (*a* = 4.070 Å.). The distance from the gas nozzle to the photographic plate was 12.19 cm. The photographs were interpreted by the visual method.[3] The radial distribution method[4] and a modification[5] of the radial distribution method also were used.

Hydrogen Disulfide.—The hydrogen disulfide was prepared according to Vanino.[6] The compound was clear and colorless. The photographs were taken within an hour after the compound was made. After standing for several days at room temperature the hydrogen disulfide turned yellow. A few semiquantitative measurements of the vapor

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[1] National Research Council Fellow in Chemistry.

[2] Beach and Stevenson, *J. Chem. Phys.*, **6**, 75 (1938).

[3] Pauling and Brockway, *ibid.*, **2**, 867 (1934).

[4] Pauling and Brockway, THIS JOURNAL, **57**, 2684 (1935).

[5] Schomaker, to be published.

[6] Vanino, "Handbuch der präparative Chemie," Vol. 1, 1925, p. 80.

pressure agreed with the values reported by Butler and Maass.[7] This eliminated H_2S as a possible impurity. The only other possible impurity, hydrogen trisulfide, melts at $-52°$. As the melting point of our preparations was less than $-80°$ (the melting point of hydrogen disulfide is $-89°$),[6] not much hydrogen trisulfide could have been present. The photographs were taken with the sample at about 33°. Even if some hydrogen trisulfide had been present in our sample, because of its low vapor pressure the amount of it in the vapor phase would have been small as compared with the amount of hydrogen disulfide.

The photographs of hydrogen disulfide show six evenly spaced maxima and minima. The intensities of the maxima drop off uniformly from the first to the sixth. The observed values of s [$s_{\text{obsd.}} = (4\pi \sin \Theta/2)/\lambda$] for the maxima and minima and the visually estimated intensities of the maxima are tabulated in Table I.

TABLE I

HYDROGEN DISULFIDE

Max.	Min.	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	$s_{\text{calcd.}}/s_{\text{obsd.}}$
1		10	3.963	3.68	0.929
	2		5.730	5.17	.902
2		9	6.869	6.72	.978
	3		8.807	8.31	.944
3		8	9.932	9.81	.988
	4		11.822	11.39	.963
4		6	12.922	12.80	.991
	5		14.742	14.28	.969
5		4	15.898	15.76	.991
	6		17.631	17.37	.985
6		2	18.927	18.90	.999
Average (1st max., 2nd min. omitted)					0.979

Results: S–S = 2.04 Å.
H–S = 1.33 Å. (assumed)
H–S–S = 95° (assumed)

The radial distribution function obtained by treating these data by the ordinary distribution method[4] is shown in Fig. 1, curve A. The modified radial distribution function[5] is shown in Fig. 1, curve B. The ordinary radial distribution function shows a peak at 2.04 Å. representing the sulfur–sulfur distance. The modified radial distribution function shows a sulfur–sulfur peak at 2.06 Å. and a small peak at 1.36 Å., at about the expected hydrogen–sulfur distance. Knowing the sulfur–sulfur distance to be about 2.05 Å., we assume 1.33/2.08 for the ratio of the hydrogen–sulfur distance to the sulfur–sulfur distance in calculating the theoretical curve. 2.08 Å. is the radius table[8] value for the sulfur–sulfur single bond distance. The H–S–S angle was assumed to be 95°. The theoretical curve is shown in Fig. 2, curve A. The effect of the hydrogen–sulfur terms on the theoretical intensity curve is negligible. Accordingly no attempt was made to locate the hydrogen atoms. Quantitative comparison of the photographs with the theoretical intensity curve is made in Table I. The sulfur–sulfur distance is 2.04 Å. Averaging the three sulfur distances, 2.04, 2.06 and 2.04 Å., obtained from the radial distribution functions and the visual method gives a final value of 2.05 ± 0.02 Å. for the sulfur–sulfur distance in hydrogen disulfide.

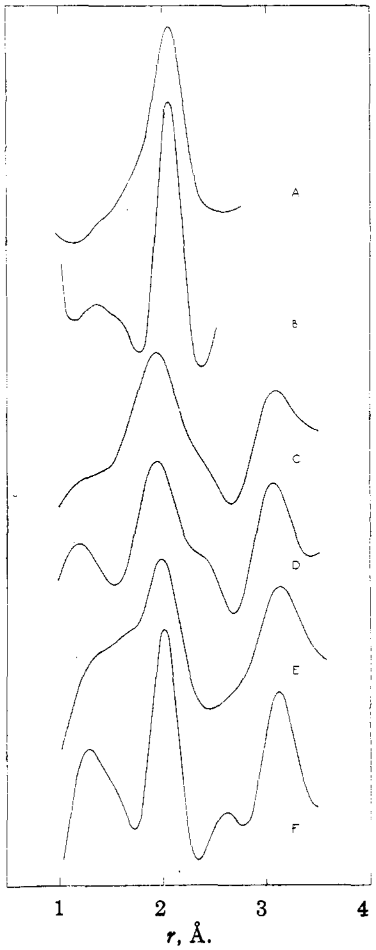

Fig. 1.—Radial distribution functions: Curve A, ordinary for H_2S_2; Curve B, modified for H_2S_2; Curve C, ordinary for $(CH_3)_2S_2$; Curve D, modified for $(CH_3)_2S_2$; Curve E, ordinary for SCl_2; Curve F, modified for SCl_2.

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[7] Butler and Maass, THIS JOURNAL, **52**, 2184 (1930).

[8] Pauling and Brockway, *ibid.*, **59**, 1223 (1937).

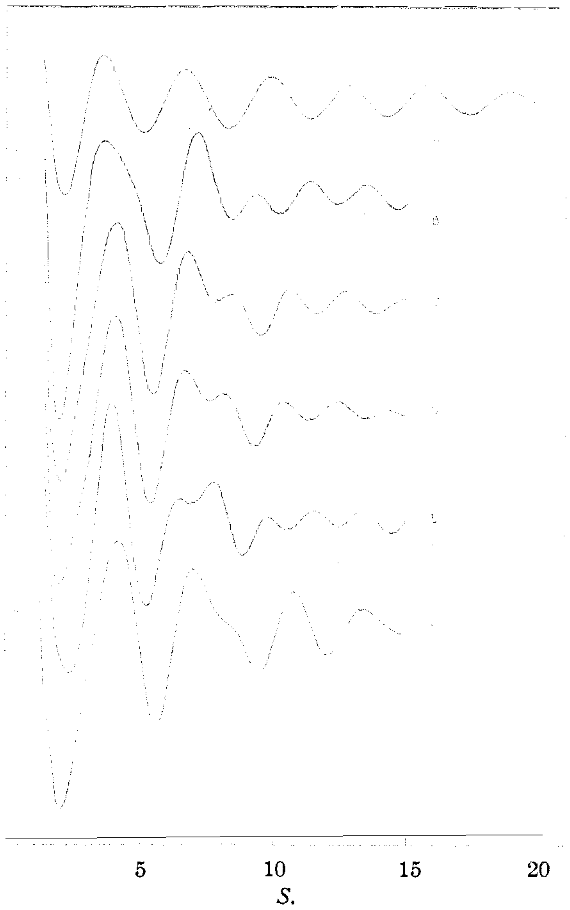

Fig. 2.—Theoretical intensity curves for H_2S_2 and $(CH_3)_2S_2$: Curve A, H_2S_2; Curve B, $[(CH_3)_2S_2]$, $\rho = 2.08/1.81$, $\alpha = 95°$; Curve C, $\rho = 2.08/1.81$, $\alpha = 105°$; Curve D, $\rho = 2.08/1.81$, $\alpha = 110°$; Curve E, $\rho = 2.08/1.81$, $\alpha = 120°$; Curve F, $\rho = 2.00/1.81$, $\alpha = 105°$.

Dimethyl Disulfide.—The method of Price and Twiss[9] for preparing disulfides was modified slightly according to the suggestions of Westlake.[10] In order to obtain the dimethyl disulfide one mole of methyl iodide and one mole of sodium thiosulfate were refluxed for an hour in an equal volume mixture of methyl alcohol and water. After cooling, potassium triiodide solution was added slowly with shaking until a faint iodine color remained for three minutes after addition. (Heat was applied near the end of the reaction in order to increase the rate.) Sodium sulfite was added to remove the excess iodine and the dimethyl disulfide was distilled out of the mixture along with water, methyl alcohol and some methyl sulfide. The dimethyl disulfide was salted out of the distillate, and distilled twice at atmospheric pressure. The boiling point (uncorr.) was 109°. Although the freshly distilled product was colorless, it developed a yellow color upon standing for a few hours, apparently losing dimethyl sulfide. The photographs were taken with the sample at 70° immediately after pumping off at room temperature any dimethyl sulfide which had formed after the distillation.

The photographs show five measurable maxima. The first two maxima are of roughly equal intensity. The third appears as a shelf on the second maximum. The fourth and fifth maxima are well defined but less intense than the first two maxima. The fourth is stronger than the fifth. The observed values of s are given in Table II, along with the intensities. The ordinary and modified radial distribution functions are shown in Fig. 1, curves C and D, respectively. Both radial distribution curves have maxima at 1.94 ± 0.01 Å. This is intermediate between a carbon–sulfur distance of 1.81 Å. and a sulfur–sulfur distance of about 2.06 Å. The two distances are not resolved. The peak at 3.08 Å. is due to the long carbon–sulfur distance. The sulfur–sulfur distance is more important in the scattering formula than the two equal carbon–sulfur distances so the peak at 1.94 Å. should be somewhat nearer the sulfur–sulfur distance than the carbon–sulfur distance. The carbon–sulfur single bond distance from the radius table[8] is 1.81 Å. The sulfur–sulfur distance then is about 2.05 Å. Later in the paper, in discussing hydrogen disulfide, we show that a sulfur–sulfur distance of about 2.05 Å. in a disulfide precludes the possibility that the molecule is pyramidal. We shall now proceed to determine more accurately the bond distances and angles of the chain molecule. The theo-

TABLE II

DIMETHYL DISULFIDE

Max.	Min.	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	$s_{\text{calcd.}}/s_{\text{obsd.}}$
1		18	4.185	4.14	0.989
	2		5.926	5.46	.921
2		16	6.795	6.75	.993
3 (shelf)		6	8.532	8.45	.990
	4		9.797	9.49	.969
4		10	10.770	10.65	.989
	5		12.197	11.62	.953
5		5	13.240	12.71	.960

Average (1st max. and 2nd min. omitted) 0.976

Results: S–S = 2.03 Å.
C–S = 1.77 Å.
H–C = 1.09 Å. (assumed)

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(9) Price and Twiss, *J. Chem. Soc.*, **95**, 1489 (1909).

(10) Westlake, private communication.

retical intensity curve for the *trans* configuration of the molecule is indistinguishable from the theoretical intensity curve for the same molecule with free internal rotation. No attempt was made, therefore, to determine the freedom of rotation by electron diffraction, and all theoretical intensity curves were calculated for *trans* molecules. Assuming a ratio $\rho = 2.08/1.81$ for the ratio of the sulfur–sulfur to the carbon–sulfur distance we have calculated intensity curves for values of the C–S–S angle, α, equal to 95, 100, 105, 110 and 120°. These curves are shown in Fig. 2. When α is less than 105° the calculated curves are unsatisfactory in that the third maximum is not high enough on the second maximum. When ρ is greater than 105° the third maximum is too high. When ρ is decreased to 2.00/1.81 the third maximum drops in intensity. The curve for $\rho = 2.00/1.81$, $\alpha = 105$ is shown in Fig. 2. Quantitative comparison of photographs with the curve calculated for $\rho = 2.08/1.81$, $\alpha = 105°$ is given in Table II. Because there are two parameters ρ and α as well as the internal rotation and absolute size of the molecule a slightly greater probable error than usual is placed on the results. The final results obtained from the visual method and the radial distribution method are: S–S = 2.04 ± 0.03 Å., C–S = 1.78 ± 0.03 Å., C–S–S = 107 ± 3°.

Sulfur Dichloride.—The sulfur dichloride was prepared by passing excess chlorine into sulfur monochloride in the presence of a small quantity of iodine. The resulting mixture was fractionally distilled through a 30-inch (76-cm.) column. The fraction boiling between 59 and 60° was collected and again distilled immediately before the pictures were taken. Pictures were taken of a sample which boiled between 59 and 59.5° (uncorr.). The pictures were taken with the sample at about 15° within half an hour after the final distillation. Any chlorine which might have been formed after distillation by the slow reaction

$$2SCl = Cl_2 + S_2Cl_2$$

was pumped off a few seconds before the exposures were made.

The photographs show six fairly evenly spaced maxima, the intensities of which decrease uniformly from the first to the sixth. The fourth maximum is rather broad. The s values of the maxima and minima and the visually estimated intensities of the maxima are tabulated in Table III. The ordinary radial distribution function has maxima at 1.98 and 3.13 Å. The modified radial distribution function has maxima at 2.01 and 3.12 Å. The first peak at 2.00 Å. represents the sulfur–chlorine distance. The second peak is the chlorine–chlorine distance. These distances lead to a Cl–S–Cl angle of 103°. The theoretical intensity curves are shown in Fig. 3. There is only one shape parameter, the Cl–S–Cl angle. When the angle is equal to 100° or less the fourth maximum is too sharp on the theoretically calculated curves. When the angle is 110° the third maximum on the calculated curve is too high. The 120° curve is unsatisfactory because the fourth maximum is too sharp. Quantitative comparison of the photographs with the 102° 30′ and the 105° calculated curves is made in Table III. The final results are: S–Cl = 2.00 ± 0.02 Å. and Cl–S–Cl = 103 ± 2°.

TABLE III

SULFUR DICHLORIDE

Max.	Min.	I	$s_{\text{obsd.}}$	$s_{\text{calcd.}}$	$s_{\text{calcd.}}/s_{\text{obsd.}}$	$s_{\text{calcd.}}$	s_c/s_o
1		10	4.368	4.06	0.929	4.04	0.925
	2		5.704	5.42	.950	5.36	.940
2		8	6.725	6.73	1.001	6.67	.992
	3		9.099	8.71	0.957	8.73	.959
3		6	10.295	10.18	.989	10.14	.985
	4		11.774	11.50	.977	11.48	.975
4		4	12.917	12.83	.993	13.05	1.010
	5		15.243	14.98	.983	14.86	0.975
5		2	16.382	16.29	.994	16.14	.985
	6		18.202	17.59	.966	17.57	.965
6		1	19.533	19.38	.992	19.54	1.000
Average (1st max. and 2nd min. omitted)					0.984		0.983

Results: S–Cl = 2.00 Å. Cl–S–Cl = 102° 30′. Cl–S–Cl = 105°.

Discussion.—The electron diffraction data on hydrogen disulfide do not show directly whether the two hydrogen atoms are on the same or different sulfur atoms. However, from the sulfur–sulfur distance it is possible to give the answer to this question. If the hydrogen atoms are on adjacent sulfur atoms the sulfur–sulfur bond is a single bond and would be expected to have the single-bond interatomic distance. The sulfur–sulfur single-bond distance has been observed in rhombic sulfur[11] to be 2.12 Å. Pauling and Huggins[12] from a study of interatomic distances decide that the most probable sulfur–sulfur single bond distance is 2.08 Å. If the two hydrogen atoms are on the same sulfur atom the sulfur–

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[11] Warren and Burwell, *J. Chem. Phys.*, **3**, 6 (1935).

[12] Pauling and Huggins, *Z. Krist.*, **87A**, 205 (1934).

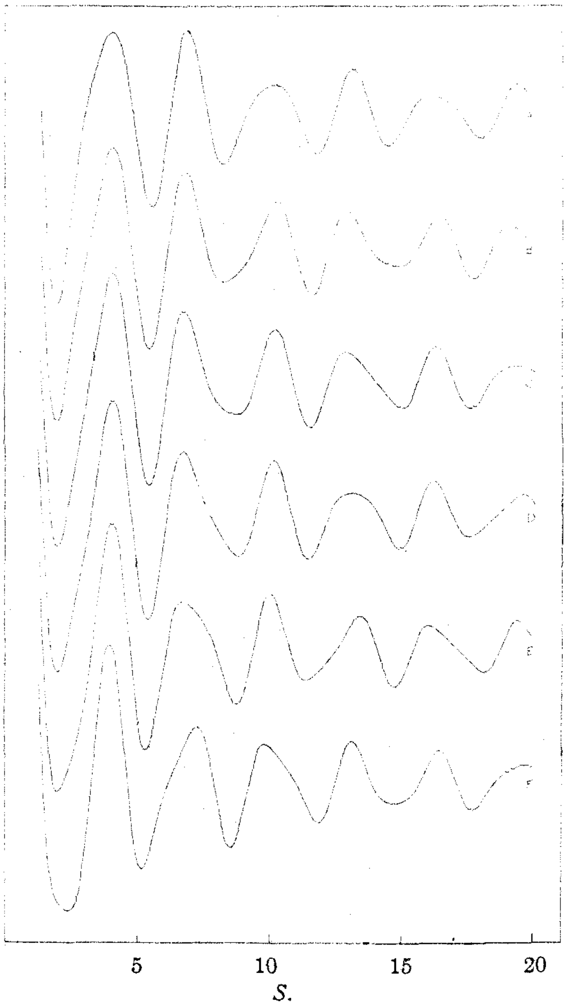

Fig. 3.—Theoretical intensity curves for SCl_2: Curve A, $\alpha = 95°$; Curve B, $\alpha = 100°$; Curve C, $\alpha = 102° 30'$; Curve D, $\alpha = 105°$; Curve E, $\alpha = 110°$; Curve F, $\alpha = 120°$.

sulfur bond will be a semipolar or dative bond. The interatomic distance for this type of bond has been observed in the case of several phosphates[13] and sulfates[14] to be about the double bond value. Electron diffraction work on $PSCl_3$,[2] $POCl_3$,[15] etc., has shown the interatomic distance for semipolar double bonds to be about the double bond value. The cause for this has been discussed.[2] The double bond sulfur–sulfur distance is 1.90 Å.[8] The observed distance in hydrogen disulfide is 2.05 ± 0.02 Å. This is practically identical with the single bond distance, 2.08 Å. We conclude, therefore, that the hydrogen disulfide molecule is a chain molecule, the two hydrogens being on adjacent sulfur atoms. Butler and Maass[7] from a study of the refractivity and parachor of hydrogen sulfide and hydrogen disulfide have reached the same conclusion.

In treating the electron diffraction data for dimethyl disulfide we did not calculate theoretical intensity curves for pyramidal models (both methyl groups on the same sulfur atom) because of the radial distribution function. If the molecule were pyramidal the first peak on the radial distribution function would have been at about 1.86 Å. instead of at 1.94 Å., because of the shorter sulfur–sulfur distance for the pyramidal model. Accordingly theoretical intensity curves were only calculated for chain models. The sulfur bond angle of 107° in dimethyl disulfide is about the same as the angle observed for sulfur[11] (105°). The carbon–sulfur distance (1.78 ± 0.03 Å.) is equal to the radius table value (1.81) for the carbon–sulfur single bond within the experimental error. Brockway and Jenkins[16] have found 1.82 ± 0.03 Å. for the carbon–sulfur distance in dimethyl sulfide. The sulfur–chlorine distance in sulfur dichloride (2.00 + 0.02 Å.) seems slightly less than the radius table value (2.03 Å.). This effect for similar compounds has been discussed.[16]

Summary

The molecular structures of hydrogen disulfide, dimethyl disulfide and sulfur dichloride have been investigated by the method of electron diffraction. Hydrogen disulfide and dimethyl disulfide are chain molecules. In hydrogen disulfide the S–S distance is 2.05 ± 0.02 Å. In dimethyl disulfide the S–S distance is 2.04 ± 0.03 Å., the C–S distance is 1.78 ± 0.03 Å. and the C–S–S angle is 107 ± 3°. Sulfur dichloride is a bent molecule. The S–Cl distance is 2.00 ± 0.02 Å., the Cl–S–Cl angle is 103 ± 3°.

PRINCETON, N. J. RECEIVED SEPTEMBER 13, 1938

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(13) West, *Z. Krist.*, **74**, 306 (1930).

(14) Zachariasen and Ziegler, *ibid.*, **81**, 92 (1932).

(15) Brockway and Beach, THIS JOURNAL, **60**, 1836 (1938).

(16) Brockway and Jenkins, *ibid.*, **58**, 2036 (1936).