by Patrick and Hackerman[8] to explain their results on the boiling points of solutions of sulfur monochloride in various solvents. The first step recalls the slow reactions that have been postulated to explain the well-known equilibria between S_λ and S_μ in liquid sulfur.

Since the dependence of R on $[S_2Cl_2]$ in the second form of the rate equation is not known, it is not possible to give an unambiguous mechanism for the case that the monochloride is involved in the slow step of the exchange. A different kind of investigation will be required to settle this point, namely, one in which both the sulfur and the sulfur monochloride are present in small concentrations in a common solvent.

We wish to express our gratitude to Professor Edwin McMillan and Dr. Martin Kamen of the Radiation Laboratory of the University of California for furnishing us with radiosulfur, and to Dr. J. Norton Wilson for helpful suggestions.

Summary

In solutions of radiosulfur in liquid sulfur monochloride the rate of exchange of sulfur between solute and solvent is very slow at room temperature but is measurably rapid at 100°. From quantitative measurements it was found that the rate at which sulfur atoms pass from S_8 to S_2Cl_2 is directly proportional to the concentration of S_8. If the rate is not dependent on the concentration of sulfur monochloride, a satisfactory mechanism for the reaction consists in the slow dissociation $S_8 = S_6 + S_2$ followed by the rapid reversible reaction $S_2 + S_2Cl_4 = 2S_2Cl_2$.

PASADENA, CALIF. RECEIVED MAY 20, 1940

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[8] Patrick and Hackerman, *J. Phys. Chem.*, **40**, 679 (1930).

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 778]

The Structure of Thionyl Bromide

BY D. P. STEVENSON AND ROBERT A. COOLEY

In this communication we report the results of an electron diffraction investigation of the structure of thionyl bromide. The structure of this molecule is of particular interest since it is, as far as we are able to ascertain, the only molecule possessing a sulfur–bromine bond which is sufficiently stable to permit the preparation of electron diffraction photographs of the vapor.

Experimental

The electron diffraction apparatus used in this investigation has been described by Brockway.[1] The camera distance was 10.85 cm. and the wave length of the electrons, determined in the usual way[1] from transmission photographs of gold foil (a_0 = 4.070 Å.), was 0.0618 Å.

The thionyl bromide was prepared by the reaction of thionyl chloride with dry hydrogen bromide at 0° as described in "Inorganic Syntheses."[2] The product was twice distilled *in vacuo*, generous first and last portions being discarded. Analysis of the final material by the precipitation and weighing of silver bromide gave 76.88% bromine (theoretical 76.88%). After standing for thirteen weeks the sample showed 76.90% bromine, indicating that no appreciable decomposition had taken place.

The high temperature nozzle was used to form the gas jet in order to avoid the long gas path and resultant condensation difficulties which accompany the use of the low temperature nozzle. It was found that a temperature of from 40 to 60° sufficed to give the vapor pressure necessary for the preparation of the electron diffraction photographs.

The photographs showed eight measurable rings whose $s\left(s = \frac{4\pi}{\lambda}\sin\frac{\theta}{2}\right)$ values are given in Table I. The appearance of the photographs is very satisfactorily reproduced by curve C of Fig. 1.

TABLE I

Max.	Min.	C_n	s_0	s_c[a]	s_c/s_0
	1	−7	1.69	1.64	(0.970)[b]
1		6	2.54	2.63	(1.035)
	2	−5	3.23	3.25	1.006
2		13	4.16	4.10	0.986
	3	−17	5.10	5.11	1.002
3		20	6.20	6.18	0.997
	4	−15	7.53	7.38	0.980
4		18	9.10	9.08	0.998
	5	−22	10.28	10.48	1.019
5		19	11.57	11.61	1.003
	6	−12	12.89	12.77	0.991
6		14	14.58	14.92	1.023
	7	−15	15.86	16.10	1.015
7		12	17.33	17.24	0.995
	8	−10	18.52	18.32	0.989
8		8	19.95	19.30	(0.967)
		Average of 13 features			1.000 ± 0.009

[a] Model of curve C of Fig. 1. [b] Values in parentheses omitted from average because of unreliability of the measurements.

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[1] L. O. Brockway, *Rev. Mod. Phys.*, **8**, 231 (1936).

[2] H. S. Booth, "Inorganic Syntheses," McGraw-Hill Book Co., Inc., New York, N. Y., 1939, pp. 113 and 151.

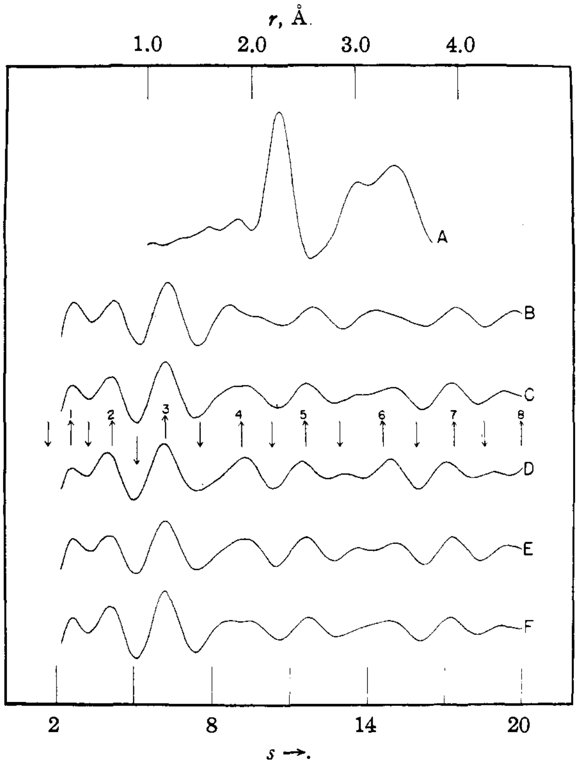

Fig. 1.—Curve A, radial distribution function. Curves B through F, theoretical intensity curves. S–Br = 2.27 Å., S–O = 1.45 Å.

Curve	Br–S–Br	Br–S–O
B	93°	108°
C	96°	108°
D	99°	108°
E	96°	105°
F	96°	111°

Interpretation

The radial distribution function[3a,b] shown as curve A of Fig. 1 was calculated with the coefficients C_n given in column 3 of the table. The three maxima at 2.27, 3.04 and 3.37 Å. correspond to the sulfur–bromine, bromine–oxygen and bromine–bromine distances, respectively. Using the first and last of these distances one obtains 96° for the bromine–sulfur–bromine angle, and if one assumes 1.45 Å. for the sulfur–oxygen distance (as found in thionyl chloride[4]) the bromine–oxygen distance of 3.04 Å. corresponds to 108° for the bromine–sulfur–oxygen angle.

Theoretical intensity curves were calculated for a number of molecular models closely related to the one suggested by the radial distribution function and the known structure of thionyl chloride.[4] The formula

$$I(s) = \sum_{i,j} \frac{(Z_i - f_i)(Z_j - f_j)}{(Z - f)^2_{\mathrm{Br}}} \frac{\sin l_{ij}s}{l_{ij}s}$$

was used for the theoretical intensity. The various symbols have their usual significance,[4] and the atomic scattering factors for x-rays, f, were taken from the table of Pauling and Sherman.[5] The curves for models with either of the bond angles more than two degrees different from those suggested by the radial distribution function do not satisfactorily reproduce the appearance of the fourth and sixth maxima while the curve for the model suggested by the radial distribution function reproduces the entire appearance of the photographs very well (see curve C of the figure).

Quantitative comparison of the photographs with curve C given in the table leads to the following values for the structural parameters.

S–Br = 2.27 ± 0.02 Å.
Br–O = 3.05 ± 0.03 Å.
Br–S–Br = 96 ± 2°

Due to the fact that the sulfur–oxygen term contributes but 5% to the total molecular scattering, it was not feasible to determine either the sulfur–oxygen distance or the ratio of the sulfur–bromine distance to the sulfur–oxygen distance.

Discussion

The sulfur–bromine distance found in thionyl bromide (2.27 ± 0.02 Å.) is considerably greater than the sum of the covalent radii of sulfur and bromine (2.18 Å.). The reason for this discrepancy is not known but it should be noted that the sulfur–chlorine distance in thionyl chloride[4] (2.06 ± 0.02 Å.) is also greater than the covalent radius sum (2.03 Å.) and the bond distance observed for sulfur dichloride[4] (2.00 Å.).

The bromine–sulfur–bromine angle (96 ± 2°) agrees well with the value found for the chlorine–sulfur–chlorine angle in thionyl chloride (97.5 ± 3°).[4b] The assumption of 1.45 Å. for the sulfur–oxygen distance seems quite safe since this distance has been found to be 1.45 ± 0.02 Å. in thionyl chloride and 1.46 ± 0.02 Å. in methyl sulfoxide.[6] The value of the bromine–sulfur–oxygen angle which results from this assumption (108 ± 3°) is in good agreement with the values found for the similar angle in thionyl chloride (107.5 ± 3°)[4b] and methyl sulfoxide (106 ± 3°).[6]

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(3) (a) L. Pauling and L. O. Brockway, This Journal, **57**, 2684 (1935); (b) V. Schomaker, American Chemical Society Meeting, Baltimore, Md., April, 1939.

(4) (a) K. J. Palmer, This Journal, **60**, 2361 (1938). (b) D. P. Stevenson and J. Y. Beach, unpublished observations.

(5) L. Pauling and J. Sherman, *Z. Krist.*, **81**, 1 (1932).

(6) R. E. Rundle and D. P. Stevenson, unpublished observation.

Summary

The interpretation of electron diffraction photographs of thionyl bromide yields the following values for the structural parameters in the gas phase.

$$\begin{aligned}\text{S–Br} &= 2.27 \pm 0.02\ \text{Å.}\\ \text{Br–S–Br} &= 96 \pm 2^\circ\\ \text{Br–O} &= 3.05 \pm 0.03\ \text{Å.}\\ \text{S–O} &= 1.45\ \text{Å. (assumed)}\end{aligned}$$

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, OREGON STATE COLLEGE]

Surface Tension in the System Hydrazine–Water at 25°[1]

BY NED B. BAKER AND E. C. GILBERT

No measurements of the surface tension of aqueous solutions of hydrazine are recorded in the literature, although the surface tension of pure hydrazine at 35° has been reported.[2]

Values for the surface tension of solutions over the entire concentration range at 25° have therefore been determined using the method of maximum bubble pressure.

Apparatus.—An all-glass apparatus similar in principle to that of Sugden[3] was placed in a constant temperature bath at 25.00 ± 0.02°. To determine the surface tension of a liquid by this method it is necessary to measure the difference in maximum pressure required to force bubbles alternately from two tubes of different diameter submerged to the same level in the liquid. Certain limitations as to dimensions have been established under which a considerable simplification of the calculations is made possible.[4]

According to Sugden, if the diameter of the large tube is not greater than 4 mm. and that of the small one not above 0.2 mm., surface tension is given by the formula

$$\gamma = AP[1 + (0.69rgD)/P]$$

where A is a constant determinable by measurements on a liquid of known surface tension; P is the difference in pressure (dynes) necessary to form bubbles from the large and small tube; r is radius of large tube in cm.; g is acceleration due to gravity; and D is density of liquid. Examination of the equation reveals that a high degree of exactness is not necessary in determining the radius r.

Because of the extremely reactive nature of hydrazine it was necessary to alter the arrangement of the apparatus so that no oxygen or air ever came in contact with the liquid. Inert gas (hydrogen) was forced through the two tubes from a reservoir in the constant temperature bath by allowing a fine stream of mercury to flow into the reservoir, whereas Sugden used a slight suction at the exit to draw air through the system.

The surface tensions thus obtained are therefore for the interface solution–hydrogen rather than solution–air. Examination of the data in the "International Critical Tables" reveals no significant difference between similar sets of data for liquids previously examined.

The manometer liquid was butyl phthalate and pressure differences were read to 0.01 mm. by means of a traveling microscope.

Procedure.—The apparatus was calibrated by the use of highly purified benzene, giving a constant A = 0.007530 cm. using a large tube of radius 0.180 cm. This in turn gave the surface tension for water at 25° as 71.96 dynes/cm. The calibration was repeated at times during the remainder of the work. When hydrazine was to be used, the system, including the manometer, was flushed out with dry hydrogen, and anhydrous hydrazine, prepared by Raschig's method,[5] was distilled directly into the apparatus in a stream of hydrogen. When the bubble pressure difference for this liquid had been read, a sample was withdrawn into a glass ampoule for analysis and the hydrazine estimated by Kolthoff's bromate method.[6]

De-aerated water which had been distilled in an all-glass still was then added to lower the concentration and another pressure reading taken.

The density of three hydrazine solutions taken at random was found to agree with the results of Semishin,[7] whose density data were therefore used in the remaining calculations.

Results

The results are shown in Table I and Fig. 1.

The values for the surface tension show a definite maximum at a concentration of 30–33 mole per cent. hydrazine. This was quite unexpected as other common physical properties of hydrazine such as density, viscosity, etc., show a maximum or minimum value in the region of 50 mole per cent. corresponding to the compound $N_2H_4 \cdot H_2O$ whose presence has been demonstrated by the phase diagram study of Semishin. A composition

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[1] Taken from a thesis submitted by Ned B. Baker toward the M.S. degree, Oregon State College, June, 1940. Published with the approval of the Monographs Publication Committee, Oregon State College, as Research paper No. 34, School of Science, Department of Chemistry.

[2] Barrick, Drake and Lochte, THIS JOURNAL, **58**, 160 (1936).

[3] Sugden, *J. Chem. Soc.*, **121**, 853 (1922).

[4] Sugden, *ibid.*, **125**, 27 (1924).

[5] Raschig, *Ber.*, **43**, 1927 (1910).

[6] Kolthoff, THIS JOURNAL, **51**, 2009 (1929).

[7] Semishin, *J. Gen. Chem. U. S. S. R.*, **8**, 654 (1938).