

2. The solid solubility of zinc in antimony has been calculated.

3. The free energies and heats of formation and the entropies of ZnSb, Zn₃Sb₂ and Zn₄Sb₃

have been evaluated.

4. The heat of fusion of Zn₃Sb₂ has been calculated.

PITTSBURGH, PENNA.

RECEIVED SEPTEMBER 1, 1939

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORY OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 727]

The Electron Diffraction Investigation of the Molecular Structures of the *meso* and Racemic 2,3-Dibromobutanes¹

BY D. P. STEVENSON² AND VERNER SCHOMAKER

The recent electron diffraction investigations of the structures of some ethylene halides by Beach³ and co-workers have provided considerable information regarding the magnitude of the repulsive forces acting between halogen atoms attached to adjacent carbon atoms. In order to extend the work of Beach to the study of the interactions of the methyl group with other methyl groups and with bromine atoms attached to adjacent carbon atoms, *meso* and racemic 2,3-dibromobutane were selected for electron diffraction investigation. It was hoped that the quite different chemical properties of this pair of molecules⁴ might result from an appreciable difference in the relative orientations of the "isopropyl bromide" groups about the 2,3 carbon-carbon single bond, inasmuch as these molecules would be expected to show structural differences in only this respect.

Experimental.—The *meso* and racemic 2,3-bromobutanes used in this research were portions of samples prepared for another investigation.⁵ It was estimated by Dr. Winstein that neither compound contained more than 2% of the other and that both were otherwise very pure. Inasmuch as the racemic and *meso* compounds are structurally very similar, such a quantity of one in the other would have no effect on the electron diffraction photographs.

The electron diffraction apparatus used in this investigation has been described by Brockway.⁶ The wave length of the electrons, determined in

the usual way from transmission photographs of gold foil, was 0.0611 Å. Photographs were taken with two camera distances, 10.86 and 20.21 cm.

As the compounds are not very volatile (b. p. *ca.* 150°), it was necessary to use the high temperature nozzle⁷ in order to obtain sufficient gas pressure. Photographs were taken with the liquid in the boiler at 100 to 130°.

Interpretation.—The photographs of each molecule showed 13 rings, and were practically identical qualitatively. Only small quantitative differences of doubtful reality were found. Curve C of Fig. 2, to be discussed below, gives a good representation of the appearance of the photographs. The observed values of s ($s_0 = \frac{4\pi}{\lambda} \sin \frac{\theta}{2}$) for the maxima and minima as well as the visually estimated intensities, I , are given in Table I.

Radial distribution functions⁸ were calculated using the formulas

$$D(l) = \sum_n C_n \frac{\sin s_n l}{s_n l} \quad (1)$$

$$C_n = f(I_n, s_n) \quad (2)$$

The values of C_n were chosen in accordance with the recommendations of Schomaker⁹ and are given in column 4 of Table I.

The curves of Fig. 1 are plots of the radial distribution functions calculated from the measurements of the maxima and the minima for the *meso* and the racemic compounds. The two curves for each compound are in satisfactory agreement with respect to the two peaks at ~ 2.8 and ~ 4.6 Å., the precise location being for the *meso*-maxima curve, 2.83 and 4.61 Å., the *meso*-minima 2.85 and 4.62, the racemic-maxima 2.82 and 4.58 Å., and the racemic-minima 2.87 and

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

(8) L. Pauling and L. O. Brockway, *ibid.*, **57**, 2684 (1935).

(9) Verner Schomaker, A. C. S. meeting, Baltimore, Md., April, 1939.

(1) The results of this investigation were presented at the meeting of the A. A. A. S. in Stanford, June, 1939.

(2) National Research Fellow.

(3) (a) J. Y. Beach and J. K. Palmer, *J. Chem. Phys.*, **6**, 639 (1938);

(b) J. Y. Beach and A. Turkevich, *THIS JOURNAL*, **61**, 303 (1939).

(4) The rates with which the *meso* and the racemic dibromobutanes react with iodide ion are very different: *cf.* Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930), and Young, Pressman and Coryell, *ibid.*, **61**, 1640 (1939).

(5) S. Winstein, D. Pressman and W. G. Young, *ibid.*, **61**, 1645 (1939).

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

TABLE I
Values in parentheses have been omitted from the averages

Max.	Min.	l_0	C_n	$\frac{meso}{s_0}$	$\frac{dl}{s_0}$	s_c°	$\frac{meso}{s_c/s_0}$	$\frac{dl}{s_c/s_0}$
	1	-6	-1.4	1.86	1.71	2.01	(1.081)	(1.176)
1		7	2.5	2.93	2.99	2.93	(1.000)	(0.980)
	2	-10	-4.2	3.73	3.72	3.80	1.019	1.021
2		10	5.9	4.65	4.57	4.65	1.000	1.016
	3	-4	-2.2	5.07	5.15
3		3	2.2	5.68	5.84
	4	-10	-6.9	6.35	6.44	6.33	0.996	0.984
4		9	7.4	7.16	7.26	7.22	1.008	.995
	5	-65	-5.5	7.90	8.06	8.06	1.022	1.000
5		2	2	8.62	8.80	8.80	1.021	1.000
	6	-5.5	-5.2	9.24	9.26	9.28	1.005	1.002
6		8	8.4	9.79	9.82	9.93	1.014	1.011
	7	-7	-7	10.53	10.59	10.64	1.011	1.005
7		5	5.4	11.30	11.43	11.42	1.011	0.999
	8	-2.5	-2.6	11.91	12.14	12.15	1.019	1.001
8		4.5	5.1	12.60	12.83	12.80	1.017	0.992
	9	-3.5	-3.8	13.19	13.40	13.20	1.001	.985
9		4.75	5.5	13.89	13.87	14.04	1.011	1.013
	10	-5.5	-6.2	14.66	14.50	15.00	(1.023)	(1.034)
10		3	3.4	15.35	15.35
	11	-1	-1.1	15.94	15.97
11		3	3.3	16.53	16.44	16.80	1.016	1.021
	12	-4	-4.3	17.23	17.10	17.51	1.017	1.024
12		3	2.8	18.07	17.87	18.22	1.009	1.021
	13	-3	-3	18.88	18.71	19.06	1.010	1.018
13		2	2	20.07	19.40	20.02	0.998	(1.032)

Average 1.011 \pm 0.006 1.007 \pm 0.011

^a Calculated with C-Br = 1.91 Å., C-C = 1.54 Å., \angle C-C-C = 110.5°, \angle C-C-Br = 108.5° and "trans" configuration (Curve C).

4.60 Å. The pronounced peaks at lesser values of l are unreliable as is indicated by the disagree-

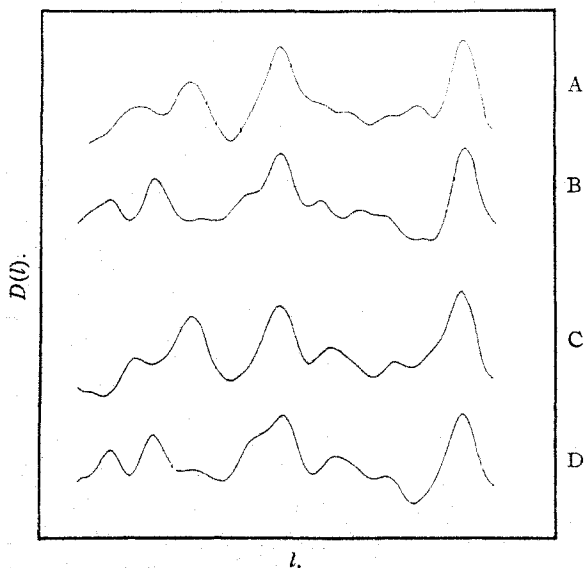


Fig. 1.—Radial distribution function $D(l)$ against l : Curve A, meso, maxima; Curve B, meso, minima; Curve C, racemic, maxima; Curve D, racemic, minima.

ment between the two distribution curves calculated for each compound. For a model with tetrahedral angles, C-C and C-Br bond distances of 1.54 and 1.91 Å. (the covalent values),¹⁰ respectively, and a "trans" configuration with respect to the bromines, the shorter non-bonded carbon-bromine distance is 2.82 Å., and the bromine-bromine distance is 4.57 Å. An increase of less than 1° in the carbon-carbon-bromine angle brings the calculated distances into agreement with those indicated by the radial distribution curves.

Three theoretical intensity curves were calculated using equation (3). The Z 's are the atomic

$$I(s) = \sum \sum \frac{(Z_i - f_i)(Z_j - f_j) \sin l_{ij} s}{(Z_c - f_c)^2 l_{ij} s} \quad (3)$$

numbers, the f 's the atomic scattering factors,¹¹ and the l_{ij} 's the interatomic distances involving the i^{th} and j^{th} atoms. It was assumed that the ends of the molecule are like isopropyl bromide¹²

(10) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **59**, 1234 (1937); H. A. Levy and L. O. Brockway, *ibid.*, **59**, 1662 (1937).

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

(12) J. Y. Beach and D. P. Stevenson, *THIS JOURNAL*, **61**, 2463 (1939).

with respect to angles and distances, and that the bromines are "trans" to each other, as is indicated by the radial distribution functions. Only one group of curves was calculated, since for the "trans" configuration there are, in $I(s)$, only unimportant terms which are different for the *meso* and racemic compounds. These terms, involving the methyl-methyl distances, have such small coefficients that they may be discarded without appreciably affecting $I(s)$. Furthermore, the terms involving hydrogen atoms, which are dependent on the orientation of the methyl groups with respect to their carbon-carbon bonds, were omitted because of their small coefficients and their undoubtedly severe temperature factors.

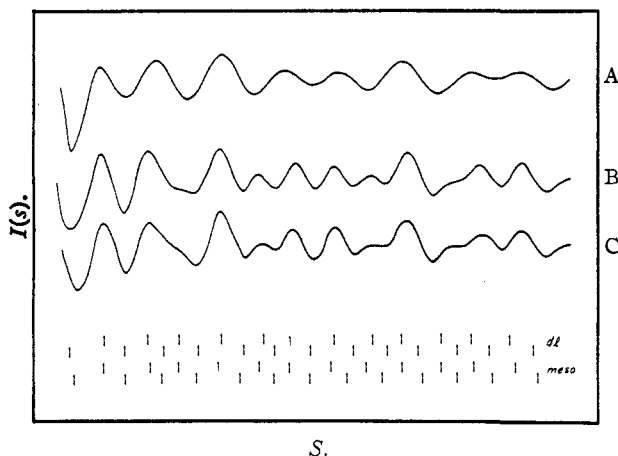


Fig. 2.—Theoretical intensity curves: Curve A, C-Br = 1.91 Å., C-C = 1.54 Å., C-C-C = 110.5°, C-C-Br = 108.7°. Terms dependent on rotational orientation omitted. Curve B, Curve A plus terms dependent on orientation, *trans* configuration. Curve C, Curve A plus bromine-bromine term, *trans* configuration.

In the calculation of curve A, Fig. 2, all of the terms which depend on the orientation about the 2,3-bond were omitted. Curve B includes these terms, with the exceptions indicated in the preceding paragraph. Curve C, which is in best agreement with the photographs, includes all the terms of B except that involving the bromine to methyl-carbon distance. The better agreement obtained when the methyl-carbon to bromine term is omitted indicates that the amplitude of libration is sufficiently large to make the temperature factor in the coefficient of this term severe, but that it is not large enough to cause an effective temperature factor in the coefficient of the bromine-bromine term. An average displacement of about 20 to 30° from the "trans"

configuration is consistent with these observations.

Dielectric constant measurements¹³ on liquid *meso* and racemic 2,3-dibromobutane show these molecules to have considerable dipole moments. This is possible only if the amplitude of libration is considerable, in agreement with the results of our investigation.

The quantitative comparison of the photographs with curve C is given in Table I. The agreement between the curve and the photographs of the racemic and *meso* compounds is quite satisfactory, indicating that the assumption of isopropyl bromide angles and distances is justified. Our final results are Br-Br = 4.60 ± 0.03 Å., C-Br = 2.83 ± 0.02 Å., ∠ C-C-Br = 109.5 ± 2°, C-Br = 1.91 Å. (assumed), C-C = 1.54 Å. (assumed), ∠ C-C-C = 110.5° (assumed).

Discussion.—The results of the studies of the deviations of the bond angles from the tetrahedral value in substituted methanes^{10b,12,14} may be summarized by the following set of inequalities, $R_{\text{CH}_3-\text{CH}_3} > R_{\text{CH}_3-\text{X}}$, $R_{\text{X-X}} > R_{\text{X-H}}$, $R_{\text{CH}_3-\text{H}}$, where R is the repulsion between the groups indicated by the subscripts and X represents a chlorine or bromine atom.

The data available at present are insufficient to set up a similar set of inequalities for substituted ethanes. On the basis of several fairly reasonable assumptions, however, it is possible to draw some conclusions regarding the interaction of nonbonded groups in substituted ethanes. We are interested in only that part of the total potential energy of an ethane-like molecule which depends on the internal rotation. This potential we regard as the sum of the interaction potentials of pairs of groups and a symmetrical three-fold potential similar to that of ethane. The three-fold potential drops out in any consideration of the relative energies of orientations differing by 120°. We designate the interaction potentials of the groups i and j in an ethane-like molecule for the two orientations of Fig. 3 by V_A and V_B and their differences $V_A - V_B$, by X_{ij} .

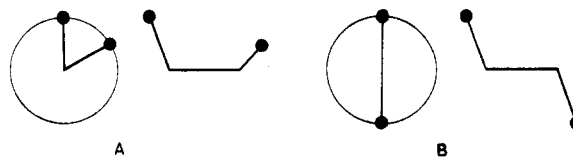


Fig. 3.

(13) S. Winstein and R. Wood, private communication.

(14) R. E. Sutton and L. O. Brockway, *THIS JOURNAL*, **57**, 413 (1935); J. Y. Beach and D. P. Stevenson, *ibid.*, **60**, 475 (1938).

The heat contents of *meso* and racemic 2,3-dibromobutane are practically the same¹⁵ and both molecules have the "trans" configuration; hence it follows that

$$X_{\text{CH}_3-\text{CH}_3} + X_{\text{H}-\text{H}} - 2X_{\text{CH}_3-\text{H}} = 0 \quad (\text{a})$$

and from the results of Beach and Turkevich^{3b} we have

$$X_{\text{Br}-\text{Br}} + X_{\text{H}-\text{H}} - 2X_{\text{Br}-\text{H}} > 2.5 \text{ kcal./mole} \quad (\text{b})$$

while from the "trans" configuration of racemic 2,3-dibromobutane

$$X_{\text{Br}-\text{Br}} + X_{\text{CH}_3-\text{CH}_3} - 2X_{\text{Br}-\text{CH}_3} > 0 \quad (\text{c})$$

It is interesting to note that while additivity obtains for the X 's involving methyl groups and hydrogen atoms, (a), it does not hold for the X 's involving bromine atoms in substituted ethanes.

From equation (a) it follows that the three staggered configurations of *n*-butane have ap-

(15) J. B. Conn, G. B. Kistiakowsky and E. A. Smith, *THIS JOURNAL*, **60**, 2770 (1938).

proximately the same energy, in agreement with the assumption of Pitzer.¹⁶

The authors would like to express their thanks to Dr. Saul Winstein of the Institute for the samples of the compounds used in this research, as well as for information regarding the properties and purity of the compounds.

Summary

From electron diffraction photographs it has been found that both racemic and *meso* 2,3-dibromobutane have "trans" configurations with respect to the bromine atoms, the bromine-bromine distance being $4.60 \pm 0.03 \text{ \AA}$. It has been shown further that a model for the structure of this pair of compounds, based on the known structure of isopropyl bromide, gives a theoretical scattering curve which is compatible with the photographs. Evidence for considerable torsional oscillation about the equilibrium "trans" configuration is presented.

(16) K. S. Pitzer, *J. Chem. Phys.*, **6**, 473 (1937).

PASADENA, CALIF.

RECEIVED SEPTEMBER 6, 1939

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

The Homogeneous Decomposition of Ethyl Chlorocarbonate

BY A. R. CHOPPIN, H. A. FREDIANI AND G. F. KIRBY, JR.

Though a number of homogeneous decomposition reactions in the gas phase are reported in current literature, the number of such reactions which are not complicated as to order or mechanism is comparatively small. From a series of compounds which have been investigated in this Laboratory, ethyl chlorocarbonate was chosen for more complete study since it appeared to have the characteristics of a member of this somewhat select group. Ethyl chlorocarbonate was found to undergo homogeneous, unimolecular decomposition to ethyl chloride and carbon dioxide between 150 and 200°.

Experimental

The ethyl chlorocarbonate used in this series of experiments was obtained from the Eastman Kodak Company. The commercial product was purified as follows: 250 ml. of the substance was placed in a round-bottomed flask, fitted with a 90-cm. fractionating column and distilled. The first and last 100 ml. were discarded, the intermediate 50 ml. retained. This intermediate portion was refractionated. The first 20 ml. was discarded and the next 10 ml., having a boiling range of 0.01°, was used for study.

The thermostat employed had a capacity of five gallons

(20 liters), was insulated with filter-cell set in a plaster of paris mold, and employed as a bath medium hydrogenated cottonseed oil circulated by means of a turbine stirrer. After a short period of use the oil darkened in color, cracking became less pronounced, and the bath was serviceable at temperatures as high as 250°.

Three specially wound resistance coils capable of a total heat input of 1200 watts constituted the permanent heater. In addition to this heating unit, two 250-watt hairpin type heaters were connected to the line through a 460-ohm rheostat to give a partial regulation of the heat input. These two sets of heaters were so adjusted as to maintain the bath within one degree of the desired temperature.

Exact temperature regulation was obtained by means of a 200-watt light bulb operated by the thermoregulator, which consisted of a Leeds and Northrup reflecting galvanometer connected to a platinum resistance thermometer through a Wheatstone bridge. The circuit was so arranged that light reflected from the galvanometer turned on the light heater at zero scale reading through a photoelectric cell. An unbalanced circuit through a resistance change in the platinum resistance thermometer caused the light to swing away from the cell a distance of 10 cm. for a change of less than 0.01°. The temperature of the bath was constant to 0.01°.

The reaction was followed by a static method in an all-glass system. Reaction vessels were constructed of