

[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1108]

The Structure of Tellurium Dibromide

BY MAX T. ROGERS¹ AND ROBERT A. SPURR²

An electron diffraction investigation of tellurium dihalides was made by Grether,³ who reported the values Te-Cl = $2.36 \pm 0.03 \text{ \AA}$., Te-Br = $2.49 \pm 0.03 \text{ \AA}$., $\angle \text{Br-Te-Br}$ and $\angle \text{Cl-Te-Cl} \geq 150^\circ$. The extensive absorption bands of these compounds have been investigated by Larionov,⁴ and by Wehrli⁵; the former considered that the angles were similar to the angle ($115 \pm 4^\circ$) found⁶ for chlorine monoxide while the latter author reported that tellurium dichloride is nearly linear in the ground and first excited states. Neither spectroscopic investigation is conclusive, however, since it has not been possible to obtain a complete analysis of these complicated spectra.

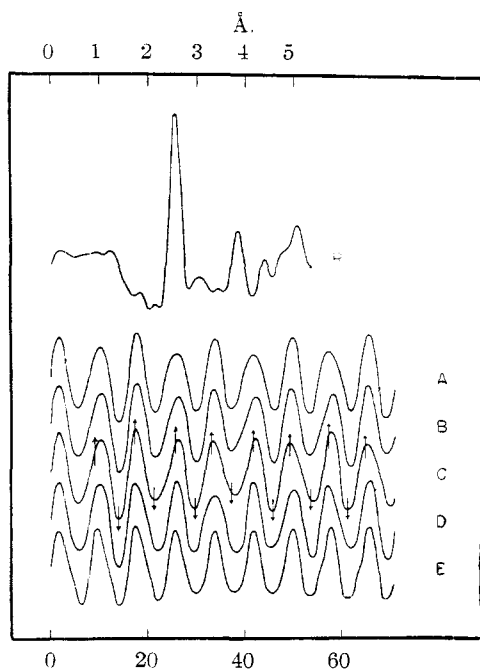


Fig. 1.—Electron diffraction curves for tellurium dibromide:

	$\langle \text{Br-Te-Br} \rangle$	Br-Br, \AA .
A	95°	3.70
B	97.5	3.77
C	100	3.85
D	105	3.98
E	155	4.90
R	Radial distribution curve	

(1) Present address: Kedzie Chemical Laboratory, Michigan State College, East Lansing, Michigan.

(2) Present address: University of Hawaii, Honolulu, Hawaii.

(3) W. Grether, *Ann. Physik*, **26**, 1 (1936).

(4) J. Larionov, *Acta Physicochimica, U. R. S. S.*, **2**, 67 (1935); **3**, 11 (1935).

(5) M. Wehrli, *Helv. Phys. Acta*, **9**, 208 (1936).

(6) L. Pauling and L. O. Brockway, *THIS JOURNAL*, **57**, 2684 (1935).

One would expect for these compounds bonds with some *s* character, giving angles between 90° and 110° , as observed for sulfur dichloride ($\angle \text{Cl-S-Cl} = 101^\circ$),⁷ and for elementary selenium and tellurium in the crystal ($\angle \text{Te-Te-Te} = 102^\circ$). Since the above experiments indicate a much wider angle (150° – 180°), it was considered desirable to reinvestigate one of the halides by the electron diffraction method. Tellurium dibromide was chosen because it is stable in the vapor state at the boiling point⁸ and offers the most favorable ratio of scattering factors for determining the angle.

Experimental

Tellurium dibromide was prepared by treating powdered C.P. tellurium metal with C.P. bromine in equivalent amount; the product was distilled *in vacuo* and purified by subliming *in vacuo*.

The wave length of the electrons was determined by calibration against gold foil ($a_0 = 4.070 \text{ \AA}$).

Photographs taken at temperatures up to the boiling point, using the high temperature nozzle,⁹ showed maxima out to $q = 66$.

Interpretation

The radial distribution curve (R of Fig. 1) was calculated using the formula

$$rD(r) = \sum_k C_k \sin(\pi r q_k / 10)$$

$$C_k = I_k(q_k) \exp(-a q_k^2)$$

where $I_k(q_k)$ is a visually estimated intensity as-

TABLE I

Min.	Max.	q obs.	$I_k(q_k)$	q calcd. (B)	q obs./ q calcd. (B)
	1	9.23	10	10.4	(1.127)
2		13.94	-10	14.2	1.019
	2	17.54	10	17.7	1.009
3		21.52	-5	21.5	0.999
	3	25.87	8	26.5	.986
4		30.08	-10	30.0	.997
	4	33.33	12	33.5	1.005
5		37.62	-6	37.1	0.986
	5	42.04	8	42.3	1.006
6		46.39	-10	46.0	.991
	6	49.92	10	49.6	.993
7		54.14	-7	53.5	.988
	7	57.92	8	58.2	1.005
8		62.02	-10	62.0	1.000
	8	65.62	10	65.5	0.998

Average .999

Average deviation .007

Final Te-Br 2.51 \AA .

(7) K. J. Palmer, *ibid.*, **60**, 2360 (1938).

(8) D. M. Yost and J. B. Hatcher, *ibid.*, **54**, 151 (1932).

(9) L. O. Brockway and K. J. Palmer, *ibid.*, **59**, 2181 (1937).

suming no falling off of intensity with q_k ,¹⁰ and a is chosen so that $\exp(-aq_k^2) = 0.1$ for the maximum value of q_k .

The prominent maximum at 2.52 Å. and the smaller one at 3.80 Å. may be taken as representing the Te-Br and Br-Br distances, respectively; $\angle \text{Br-Te-Br}$ is then 98° . The asymmetric peak at about 5 Å. is without significance; false peaks at abscissas about twice those of prominent features are common⁹ in radial distribution summations made with only one term for each feature of the diffraction pattern.

Theoretical curves (A to E of Fig. 1) for the correlation treatment were calculated with the use of the formula

$$I(g) = \frac{2}{2.51} \frac{(Z-f)r_0}{(Z-f)_{\text{Br}}} \sin(2.51 \pi q/10) + 1/r \sin(\pi r q/10)$$

where Z is the atomic number, f the atom form factor, r the Br-Br distance, and $q = 40/\lambda \sin \theta/2$; account was taken of the variation of f with θ . The Te-Br distance was taken as 2.51 Å. in all cases.

The third, fifth and seventh minima are observed to be shallow (decreasingly in the order named) in comparison with the second, fourth, sixth, and eighth minima. The sixth maximum

(10) The coefficients were chosen according to the recommendations of V. Schomaker. A. C. S. Meeting, Baltimore, April 1939.

is a little more prominent than the fifth and seventh maxima. These features are best represented by a curve intermediate between B and C but very close to B, and we have, therefore, chosen as most probable the angle 98° , which is also given by the radial distribution curve. To this value we assign a limit of error of $\pm 3^\circ$. Comparison with C gives the same value for the tellurium-bromine distance as comparison with B. This distance is the sum of the covalent radii.¹¹ Curve E, with $\angle \text{Br-Te-Br} = 155^\circ$, and curves for models with wider angles show regularly spaced strong maxima and do not correspond to the appearance of the photographs.

Summary

A redetermination of the structure of tellurium dibromide by the electron diffraction method has been carried out. The Te-Br distance 2.51 ± 0.02 Å. found agrees within experimental error with that found by Grether³ in an earlier electron diffraction investigation (2.49 ± 0.03 Å.), but the molecule has been shown to be triangular with $\angle \text{Br-Te-Br} = 98 \pm 3^\circ$, rather than nearly linear with $\angle \text{Br-Te-Br} \geq 150^\circ$ as reported by Grether.

(11) Linus Pauling, "The Nature of the Chemical Bond," 2nd ed., Cornell University Press, Ithaca, N. Y., 1940, p. 165.

PASADENA, CALIFORNIA

RECEIVED APRIL 4, 1947

CONTRIBUTION FROM THE PACIFIC EXPERIMENT STATION, BUREAU OF MINES, UNITED STATES DEPARTMENT OF THE INTERIOR]

Heats of Formation of $3\text{CaO}\cdot\text{B}_2\text{O}_3$, $2\text{CaO}\cdot\text{B}_2\text{O}_3$, $\text{CaO}\cdot\text{B}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{B}_2\text{O}_3$ ¹

BY D. R. TORGESON² AND C. H. SHOMATE³

The system calcium oxide-boron oxide was investigated by Carlson⁴ who established existence of four compounds: $3\text{CaO}\cdot\text{B}_2\text{O}_3$, $2\text{CaO}\cdot\text{B}_2\text{O}_3$, $\text{CaO}\cdot\text{B}_2\text{O}_3$ and $\text{CaO}\cdot 2\text{B}_2\text{O}_3$. Present interest in calcium borate slags enhances the desirability of having adequate thermal data for these substances. This paper presents measurements of heats of solution in hydrochloric acid from which heats of formation of the four borates are obtained.

Materials

The calcium borates were prepared⁵ by repeatedly heating, followed by grinding, stoichiometric mixtures of calcium and boric oxides. The heating periods were of two to three hours duration. The materials were analyzed between heatings and small additions of boric oxide were made to com-

pensate for boric oxide lost by volatilization. Table I lists the temperature of preparation and actual and theoretical analyses of the borates. The method of analysis for calcium and boric oxides was that described by Carlson.⁴

TABLE I
ANALYSES OF CALCIUM BORATES

Substance	t , °C.	Actual analyses		Theoretical analyses	
		CaO, %	B ₂ O ₃ , %	CaO, %	B ₂ O ₃ , %
$3\text{CaO}\cdot\text{B}_2\text{O}_3$	1200-1350	70.76	29.32	70.72	29.28
$2\text{CaO}\cdot\text{B}_2\text{O}_3$	1200	61.71	38.31	61.69	38.31
$\text{CaO}\cdot\text{B}_2\text{O}_3$	1200	44.67	55.36	44.61	55.39
$\text{CaO}\cdot 2\text{B}_2\text{O}_3$	950-970	28.58	71.12	28.71	71.29

The calcium diborate contained a measured 0.42% insoluble impurity, formed by superficial reaction with the nickel crucible in which it was prepared. This was not observed for the other borates.

X-Ray diffraction examination⁶ was made of the borates. Each gave a distinct diffraction

(6) The X-ray diffraction pictures were taken by A. E. Salo, formerly metallurgist, Pacific Experiment Station, Bureau of Mines.

(1) Published by permission of the Director, Bureau of Mines, U. S. Department of the Interior. Not copyrighted.

(2) Chemist, Pacific Experiment Station, Bureau of Mines.

(3) Formerly chemist, Pacific Experiment Station, Bureau of Mines.

(4) Carlson, *Bur. Standards J. Research*, **9**, 825 (1932).

(5) These compounds were prepared and their densities determined by R. J. O'Dea, formerly chemist, Pacific Experiment Station, Bureau of Mines.