(g) may be prepared in the same reaction by replacing H_2O by D_2O.

Discussion

The present observations on the chemical behavior of solid boroxine suggest that some of its reactions may be due to a BH_3 species which is formed in the initial stages of decomposition of the solid. When CO(g) is added to the reaction vessel, BH_3 may combine rapidly with CO to form an "adduct" $BH_3CO(g)$, according to the reaction scheme

$$H_3B_3O_3(s) = B_2O_3(s) + BH_3 \qquad (1)$$

$$BH_3 + CO(g) = BH_3CO(g) \qquad (2)$$

The formation of $B_2H_6(g)$ as a decomposition product of boroxine may be accounted for by the reaction

$$2BH_3 = B_2H_6(g) \qquad (3)$$

Reactions 2 and 3 could be either homogeneous or heterogeneous depending on whether BH_3 is produced as a gaseous species or a species chemically absorbed on the B_2O_3 surface. Furthermore, we cannot rule out the possibility that CO reacts directly with boroxine to form an intermediate donor–acceptor complex. Formation of BH_3CO from a reaction of B_2H_6 and CO cannot be important in our system since the kinetic data[3] indicate this reaction is slow at the temperatures and pressures employed in our experiments. It is reasonable to assume that the higher yield of BH_3CO in the reaction of CO with boroxine compared to that obtained in the reaction of CO with B_2H_6 is a result of more favorable kinetic processes followed by rapid quenching of the product at low temperatures. At temperatures below 0°, BH_3CO does not decompose rapidly to B_2H_6 and CO.[8] It was found that, when the reaction products were held at room temperature for several hours, some BH_3CO had decomposed to B_2H_6 and CO in nearly equilibrium concentrations (see last entry in Table I).

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Dimorphism in Thorium Tetrabromide

By D. E. Scaife

Received September 2, 1965

The crystal structure of thorium tetrabromide was reported by D'Eye.[1] From powder diffraction data, he showed that this compound was body-centered tetragonal, space group $I4_1/amd$, with the unit cell dimensions $a = 8.945$, $c = 7.930$ Å., and containing four molecules per unit cell. From this evidence he concluded that it was isomorphous with thorium tetrachloride.

During a differential thermal analysis study of the thorium–bromine system, we found that pure thorium tetrabromide showed a small endothermic peak at 420°, corresponding to a heat of reaction of about 1 kcal./mole, of the order expected for a solid state transition. X-Ray powder photographs confirmed the existence of two forms of thorium tetrabromide stable above and below this temperature.

Experimental Results

Thorium tetrabromide was prepared by reaction under vacuum of dry, vacuum-distilled bromine with thorium metal and was purified by vacuum sublimation. Samples were handled in the dry, oxygen-free argon atmosphere of an evacuable glove box. Ground samples were transferred to thin-walled silica or Lindemann glass capillaries of 0.3-mm. diameter for diffraction studies, and the techniques used in differential thermal analysis have been reported elsewhere.[2]

For powder photographs an 11.46-cm. Phillips camera was used with filtered Cu Kα radiation, and some photographs were internally calibrated with a small quantity of degassed thorium oxide with accurately known lattice parameters. A traveling microscope, accurate to better than ±0.02 mm., was used to measure line positions.

One sample was finely ground and heated in a silica capillary at 470° for several hours, then quenched by dropping into ice water. Its pattern, characteristic of the high-temperature form (hereafter designated β), is given in Table I. After this sample was heated at 330° for several hours, a quite different pattern resulted, and repeated cycling through the transition temperature showed that both forms were reproducible. The spacings of the low-temperature α form given in Table II are from the sharper patterns given by samples ground after annealing at 330°.

The β form reverts slowly to the α form at room temperature, the reversion being about half-complete in 10–12 weeks.

Both forms were examined microscopically in fluorocarbon oil. The β form consisted of well-formed uniaxial crystals with straight extinction, while the α form, observed in imperfect crystal habit, was probably biaxial, with straight extinction.

Attempts to grow single crystals of the α form were unsuccessful. Well-formed crystals of the β form were observed to shatter on cooling through the transition point, and the particle size of the resulting α form was very small. No appreciable growth of crystals of the α form was observed after 6 weeks at 375°.

The powder patterns of the β form were indexed in the usual manner, and the data were subjected to a linear least-squares fitting program. No extrapolation treatment was attempted, as absorption errors were cor-

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(1) R. W. M. D'Eye, *J. Chem. Soc.*, 2764 (1951).

(2) D. E. Scaife and A. W. Wylie, *ibid.*, 5450 (1964).

TABLE I

POWDER DIFFRACTION DATA FOR HIGH-TEMPERATURE (>420°) β-$ThBr_4$

Intensity	d (obsd.), Å.	$\sin^2\theta$ (obsd.)	$\sin^2\theta$ (calcd.)	hkl
s	5.91	0.0170	0.0168	101
s	4.453	0.0299	0.0297	200
vw	3.562	0.0468	0.0465	211
w	3.368	0.0523	0.0523	112
vvw	3.193	0.0582	0.0594	220
m+	2.972	0.0672	0.0668 0.0671	300 202
s	2.789	0.0763	0.0762	301
s	2.547	0.0914	0.0916	103
s	2.366	0.1060	0.1059	321
s	2.305	0.1117	0.1117	312
m	2.236	0.1187	0.1188	400
vw	2.161	0.1270	0.1263	410
vw	2.128	0.1310	0.1337	330
vw	2.091	0.1356	0.1356	411
vw	2.011	0.1467	0.1485	420
s	1.8273	0.1777	0.1794	204
w	1.8205	0.1790	0.1808	323
vw	1.7878	0.1856	0.1857 0.1860	430, 500 422
vvw	1.7659	0.1902	0.1931	510
s	1.7440	0.1950	0.1950	431, 501
m	1.6834	0.2093	0.2091	224
vw	1.6526	0.2172	0.2165 0.2179	304 333
w	1.6284	0.2238	0.2231 0.2240 0.2247	432, 502 314 521
vvw	1.6039	0.2306	0.2305	512
vvw	1.5803	0.2376	0.2377	440
m	1.4895	0.2674	0.2674	600
s	1.4809	0.2705	0.2699 0.2710	433, 503 215
vw	1.4439	0.2846	0.2841	611
w	1.4304	0.2900	0.2899	532
s	1.4116	0.2977	0.2971 0.2982	620 424

TABLE II

POWDER DIFFRACTION DATA FOR LOW-TEMPERATURE (<420°) α-$ThBr_4$

Intensity	d (obsd.), Å.	Intensity	d (obsd.), Å.	Intensity	d (obsd.), Å.
m	6.73	vw	2.054	vw	1.5570
s	6.03	w+	2.037	w	1.5438
m	3.910	m	2.016	w+	1.5212
vvw	3.776	vw	1.9560	vvw	1.4737
vvw	3.019	vw	1.8717	vw	1.3890
s	2.945	vw	1.8553	vw	1.3803
m+	2.776	vw	1.8104	vw	1.3627
s	2.520	vvw	1.6862	vw	1.3442
s	2.394	vw	1.6380	vw	1.3020
vvw	2.221	vw	1.6242		

rected for by the internal standard method. The results of this indexing showed that the high-temperature β form has a tetragonal unit cell with dimensions a = 8.939, c = 7.964 Å., containing four molecules per unit cell. The agreement between calculated and observed values of $\sin^2\theta$, shown in Table I, is fair, the standard deviation being 8.2×10^{-4}. The calculated density, 5.76 g./cc., is in good agreement with the measured value of 5.67 g./cc.[3]

Good numerical agreement was obtained by indexing the low-temperature α form on the basis of an orthorhombic unit cell with dimensions $a = 13.61$, $b = 12.05$, $c = 7.821$ Å., containing eight molecules per unit cell, corresponding to a calculated density of 5.72 g./cc. However, in the absence of single crystal data, this unit cell must be regarded as tentative.

The systematic absences found for the β form do not agree with the space group suggested by D'Eye, $I4_1/amd$, as three reflections are present which suggest a symmetry lower than body-centered. These reflections, although weak, persist in the same intensity in patterns of samples from different sources and are unlikely to be due to impurities.

Discussion

Several structures are found in the tetrachlorides, bromides, and iodides of the group IV-B and actinide elements. The tetrahalides of Ti, Zr, and Hf are generally of the cubic SnI_4 type. Several actinide tetrachlorides, including that of thorium,[4] have body-centered tetragonal structures. Uranium tetrabromide has a monoclinic structure[5] with lattice parameters a = 10.92, b = 8.69, c = 7.05 Å.; β = 93.9°, while thorium tetraiodide also has a monoclinic structure[6] with lattice parameters a = 13.216, b = 8.068, c = 7.766 Å.; β = 98.68°.

High-temperature β-$ThBr_4$ may have a structure related to that of $ThCl_4$. Low-temperature α-$ThBr_4$ appears to be of a new tetrahalide structure type, its pattern apparently being related neither to the patterns of the cubic nor to those of the monoclinic forms. This is the first X-ray evidence of dimorphism reported for group IV-B or actinide tetrahalides other than fluorides.

The data of D'Eye appear to relate to a mixture of α and β forms, with the β form predominating. In considering D'Eye's work, it is significant that some two-thirds of the lines of the α form can be indexed on the basis of a tetragonal unit cell with dimensions a = 8.982, c = 7.877 Å., almost identical with the unit cell of the β form. This accounts for the fact that the mixed phase data of D'Eye can be fitted well on the basis of a tetragonal unit cell very similar to that proposed here for the β form.

The evidence presented here throws considerable doubt on the previous structural work on thorium tetrabromide, and a full examination of this system is obviously necessary.

Acknowledgments.—The author thanks Mr. C. H. J. Johnson, Division of Physical Chemistry, C.S.I.R.O., for writing the least-squares program.

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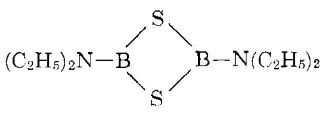
Boron-Sulfur Ring Compounds

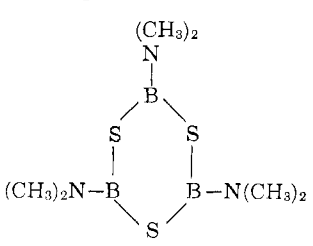
BY J. A. FORSTNER AND E. L. MUETTERTIES

Received September 27, 1965

We wish to report a simple, direct synthesis of boron-sulfur ring structures. Hydrogen sulfide attacks trialkylamine boranes at 200° to give hydrogen, alkane, and the cyclic boron sulfides. The type of ring structure obtained is dependent upon the trialkylamine borane employed. With triethylamine borane, the dithiaboretane **1** is formed exclusively, whereas with the methyl analog the six-membered ring **2** (borthiin) is obtained. Compound **2** has been previously described by Wiberg and Sturm.[1] The dithiaboretane structure has been known only with B-sulfhydro[2,3] and B-ethylmercapto substituents.[1] Surprisingly, the highly strained ring of **1** is stable to 200° and does not rearrange to a borthiin structure as does $(HSBS)_2$.[1]



1



2

Experimental Section

Materials.—Hydrogen sulfide (Matheson) was fractionated before use. Triethylamine borane was made in these laboratories and distilled, b.p. 65–68° (2 mm.). Trimethylamine borane (Callery) was used directly.

$(BN(C_2H_5)_2S)_2$.—Triethylamine borane (12.5 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated at 200° for 3 hr. in a 100-ml. stainless steel bomb. The gaseous products were vented and burned in a gas–oxygen flame. The viscous liquid product was heated under vacuum at 100°, yielding a white, solid sublimate. The latter was resublimed and crystallized from pentane to yield 4.2 g. of a white, very hygroscopic solid, soluble in chloroform and carbon tetrachloride, and melting at 70° under vacuum.

Anal. Calcd. for $B_2S_2N_2C_8H_{20}$: C, 41.8; H, 8.78; N, 12.2; B, 9.39; S, 27.9. Found: C, 42.4, 42.1; H, 8.80, 8.98; N (Kjeldahl), 12.0, 12.1; N (Dumas), 12.4, 12.5; B, 9.43, 9.44; S, 28.6, 28.5.

Molecular weight measurements confirm the proposed formulation: calcd. 230; found, cryoscopically in benzene (14 mg./100 g. of benzene), 234; ebullioscopically in carbon tetrachloride (0.11–0.49 mg./100 g. of CCl_4), 232. Mass spectral data, obtained by direct injection into the heated inlet of a spectrometer, confirmed these molecular weight data. The infrared spectrum (as a Nujol mull) included absorptions at 1715 (w), 1695 (w), 1635 (w), 1315 (m), 1265 (s), 1215 (m), 1190 (s), 1130 (s), 1095 (m), 1080 (m), 1065 (m), 995 (m), 980 (m), 945 (m), 885 (m), 830 (m), and 780 (m) cm.$^{-1}$.

The proton n.m.r. spectrum (carbon tetrachloride solution) consists of a distinct methylene quartet and methyl triplet at −3.3 and 1.2 p.p.m., respectively, referenced to external tetramethylsilane. The B^{11} resonance spectrum in the same solvent consists of a singlet at −18.5 p.p.m., referenced to external trimethyl borate.

$(BN(CH_3)_2S)_3$.—Trimethylamine borane (7.3 g., 0.1 mole) and hydrogen sulfide (6.5 g., 0.2 mole) were heated in a 100-ml. stainless steel bomb at 200° for 3 hr. The volatile products were vented and burned. The white, solid product was sublimed twice under vacuum at 200° to yield 4.7 g. of white solid, moderately soluble in acetone and chloroform and melting at 117° (lit.[1] 118°).

Anal. Calcd. for $B_3S_3N_3C_6H_{18}$: C, 27.6; H, 6.91; N, 16.1; B, 12.4; S, 36.9. Found: C, 28.4, 27.6; H, 6.79, 7.12; N, 15.9; B, 12.8; S, 38.6.

The infrared spectrum (as a Nujol mull) consisted of absorptions at 1300 (m), 1230 (w), 1190 (m), 1100 (s), 1080 (m), 1060 (m), 1000 (w), 975 (s), 930 (s), and 715 (w) cm.$^{-1}$.

The molecular weight found ebullioscopically in chloroform (0.20–1.00 mg./100 g. of $CHCl_3$) was 239 (calcd. for trimer, 261). The mass spectrum obtained by direct injection (system held at 70°) demonstrated the molecular weight to be 261. The peak at *m/e* 260 was 70% as intense as that at *m/e* 261, as would be predicted for three boron atoms in the molecule.

The H^1 resonance spectrum ($CDCl_3$ solution) consists of a singlet at −2.4 p.p.m. referenced to external tetramethylsilane. The B^{11} spectrum was a singlet at −20.1 p.p.m., referenced to external trimethyl borate.

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[1] E. Wiberg and W. Sturm, *Z. Naturforsch.*, **8b**, 689 (1953); **10b**, 108 (1955); *Angew. Chem.*, **67**, 483 (1955).

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Phosphorus-Fluorine Chemistry. XVII.[1] Nuclear Magnetic Resonance Studies of Pentafluorophosphates

BY G. S. REDDY AND R. SCHMUTZLER

Received August 20, 1965

In a previous communication[2] we have reported the unusual rearrangement of the covalent $C_6H_5PF_3N(CH_3)_2$ into the ionic $[C_6H_5PF[N(CH_3)_2]_2]^+[C_6H_5PF_5]^-$. The rearrangement was found to occur most rapidly for the product obtained by the dimethylaminolysis of $C_6H_5PF_4$ in ether at 0°[3]

$$2C_6H_5PF_4 + 2(CH_3)_2NH \longrightarrow C_6H_5PF_3N(CH_3)_2 + [(CH_3)_2NH_2]^+[C_6H_5PF_5]^-$$

We have now carried out the dimethylaminolysis with CH_3PF_4 and find that the $CH_3PF_3N(CH_3)_2$ formed undergoes the same type of rearrangement. While the F^{19} n.m.r. spectrum of $[CH_3PF_5]^-$ shows a simple first-order pattern, the F^{19} spectrum[2,3] of $[C_6H_5PF_5]^-$ is more complicated because of the closeness of the chemical shifts between the two different fluorine atom en-

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[2] R. Schmutzler, *J. Am. Chem. Soc.*, **86**, 4500 (1964).

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