$C_5H_{11}MgBr$ and distilled from the mixture. It oxidized in air. Its refractive index was found to be $n^{20}_{WL} = 1.4340$, its density 0.765, 0.766 at 25°. The compound partly froze at −82°.

Anal. Calcd. for $B(C_5H_{11})_3$: B, 4.82; mol. wt., 224. Found: B, 4.82; mol. wt., 230.

The cyclic compound (II) was a clear colorless liquid which boiled at 29–30° at 0.30 mm. and 21–22° at 0.20 mm. It oxidized rapidly in an air deficient atmosphere.

Anal. Calcd. for $B(C_5H_{11})(C_5H_{10})$: B, 7.10; mol. wt., 152. Found: B, 7.10, 7.34 and 6.92; mol. wt., 160, 152.

Rigorous alkaline oxidation, using 30% H_2O_2, yielded 2-methyltetrahydrofuran, amyl alcohol and sodium borate. Bromination of compound (II) in glacial acetic acid and then acid hydrolysis yielded a mixture which gave small mass peaks corresponding to 1,4-pentanediol among others.

The hydrocarbon (III) was *trans*-2-pentene according to physical constants and infrared. The hydrogen was identified mass-spectrographically.

(b) **Thermal Decomposition of Tri-*n*-hexylborane-3.**—$B(C_6H_{13})_3$ boiled at 119–120° at 0.6 mm. and 106–108° at 0.25 to 0.3 mm. It was prepared from $BF_3 \cdot Et_2O$ and $C_6H_{13}MgBr$ and distilled from the mixture. It oxidized rapidly in air.

Anal. Calcd. for $B(C_6H_{13})_3$: B, 4.06; mol. wt., 266. Found: B, 4.24; mol. wt., 262.

250.5 g. of tri-*n*-hexylborane-3 was boiled under reflux for 5 hr. under 1 atm. of nitrogen. 119.5 g., 1.42 mole, of *trans*-3-hexene was collected together with about 0.80 mole of hydrogen. A portion of the liquid products was fractionated under high vacuum. Results are given in Table I.

The assumed cyclic compound $B(C_6H_{13})(C_6H_{12})$ was a clear colorless liquid which oxidized rapidly in an air deficient atmosphere.

Five g. was heated to boiling with 150 g. of NaOH pellets and 200 ml. of 30% H_2O_2 and 50 ml. of 50% H_2O_2. The resulting organic layer was acidified and yielded 1-hexanol, boric acid and 2-methyltetrahydropyran.

Anal. Calcd. for $(CH_2)_4CH(CH_3)$-O: b.p., 102–104°; mol. wt., 100. Found: b.p., 102–103°; mol. wt., 99.

Further evidence for the structure of $B(C_6H_{13})(C_6H_{12})$ was obtained by bromination in acetic anhydride. 1-Bromohexane and a high boiling liquid in the range of 1,5-dibromohexane were isolated. Boron acetate was a third product of this reaction.

The hydrocarbon was *trans*-3-hexene as analyzed by infrared. The hydrogen was identified by mass spectrography.

The polymer $[B(C_6H_{13})]_x$ reacted with alcoholic acid and base with an initial evolution of gas and the formation of an alcohol and an acid.

(c) **Thermal Decomposition of $[B(C_6H_{13})]_x$.**—Several grams of the polymer was heated to its boiling point under 1 atm. of N_2 for several hours. The products were fractionated. A sharp boiling very viscous liquid and a solid were isolated.

Anal. Calcd. for $[BHB(C_6H_{13})]_x$: B, 20.1. Found: B, 20 (solid). Calcd. for $[B_2(C_6H_{13})_2(C_6H_{12})]_x$: B, 7.84. Found: B, 8.12. (liquid); mol. wt., about 600.

The dark solid product hydrolyzed in alcoholic KOH practically to completion, at first rapidly and then slowly, and yielded over a period of 3–4 hr. approximately the stoichiometric quantity of H_2 corresponding to a formula BRBH.

(d) **Thermal Decomposition of Trialkylboranes Having Unsaturated Alkyl Substituents.**—Triallylborane-3[16] was prepared from $BF_3 \cdot Et_2O$ and C_3H_5MgBr in ether. The product, a clear colorless pyrophoric liquid of b.p. 116–117° was fractionated from the mixture.

The compound disproportionated when refluxed at its boiling point under 1 atm. of N_2. Two of the pertinent products were analyzed.

Anal. Calcd. for C_6H_{10}, hexadiene-1,5: mol. wt., 82; b.p. 60°. Found: mol. wt., 88; b.p., 58–59°. Infrared analysis verified compound.

Anal. Calcd. for $(C_3H_5)_4B_2$: mol. wt., 186; B, 11.8. Found: mol. wt., 177; B, 11.0, 11.5. Infrared showed no B—H and a conjugated system.

Acknowledgments.—We wish to thank both the Olin–Mathieson Chemical Corporation and the Air Force for encouragement and financial support as well as for permission to publish the results of our work.

[16] "Preparation and Properties of Triallylborane-3." P. F. Winternitz and A. A. Carotti, Technical Research Report MCC-1023-TR-126 under Contract NOa(s)52-1023c. (O.M.C.C.), 14 April 1955.

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[CONTRIBUTION FROM THE OAK RIDGE NATIONAL LABORATORY[1]]

The Preparation and Crystal Structure of Molybdenum(III) Fluoride

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MoF_3 has been prepared by the reduction of MoF_5 with molybdenum metal powder. X-Ray and neutron diffraction showed the crystal structure of this compound to be of the rhombohedral VF_3-type, rather than the cubic ReO_3-type structure previously reported.

Introduction

The anhydrous trifluorides of molybdenum, tantalum and niobium were reported to be isostructural with cubic rhenium trioxide by Gutmann and Jack[2] and Hepworth, Jack, Peacock and Westland.[3] The samples of MoF_3 and TaF_3 examined by Gutmann and Jack were prepared by Emeléus and Gutmann,[4,5] the former compound through heating $MoBr_3$ in a stream of HF at 500–600° for about 7 hours. MoF_3 was described as a non-hygroscopic, dark-pink powder. A possible transition to a "distorted structure" was noted for this compound when heated at 800° in the absence of air and moisture (unpublished observations with K. H. Jack, mentioned by Emeléus and Gutmann[4]). Subsequent attempts to duplicate or find alternatives to the preparation of MoF_3 by the method of Emeléus and Gutmann have been termed "unsuccessful" since they have failed to produce materials with anticipated properties.[6]

This paper describes a synthesis of anhydrous molybdenum trifluoride, together with the chemical and structural analysis of the compound. The cumulative data have been interpreted to show that a successful preparation of MoF_3 has been achieved despite variances with reported properties

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[1] Operated by the Union Carbide Corporation for the United States Atomic Energy Commission.

[2] V. Gutmann and K. H. Jack, *Acta Cryst.*, **4**, 244 (1951).

[3] M. A. Hepworth, K. H. Jack, R. D. Peacock and G. J. Westland, *ibid.*, **10**, 63 (1957).

[4] H. J. Emeléus and V. Gutmann, *J. Chem. Soc.*, 2979 (1949).

[5] H. J. Emeléus and V. Gutmann, *ibid.*, 2115 (1950).

[6] A. P. Brady, J. K. Clauss and O. E. Myers, WADC 56-4 (September 1957).

and that the crystal structure of the compound so prepared is rhombohedral, VF_3-type, rather than cubic.

Experimental

Preparation.—MoF_3 was prepared by the reaction of MoF_5 with molybdenum metal powder. The pentafluoride was produced by distillation in quartz from the residues obtained in the fluorination of molybdenum. MoF_5 is a yellow solid melting at 64°, as described by Peacock.[7] It fumes in air, forming a number of blue hydrolytic products but is unaffected by air dried with P_2O_5. No evidence has been found for the MoF_4 reported by Peacock, although it may be capable of existence below 200°. All attempted reductions of MoF_5 have yielded MoF_3.

A 50% excess of MoF_5 was ground with molybdenum powder in an inert-atmosphere glove box and this mixture transferred to a nickel tube and sealed under vacuum. The tube was heated at 180° for 2 hr., after which it was heated at 400° for 4 hr. When one end of the tube was opened in a glove box, the material was seen as a dull-green paste. The tube with its contents was placed in a quartz tube connected to a vacuum system and the excess MoF_5 was distilled, thereby leaving a yellowish-tan residue which was identified as MoF_3 through chemical and structural analyses.

Quantitative chemical analysis of the tan product for molybdenum gave 62.9 wt. % compared to the calculated value of 62.7 wt. % for MoF_3. The determination of fluorine in this compound has not given reproducible results because of the difficulty in dissolving the substance and the volatility of the oxyfluorides.

The density of tan MoF_3 was measured by a gas displacement technique which has intrinsic errors slightly biased toward a high result with a precision of ±3%. The average of four determinations was $\rho_{\text{obsd.}} = 4.64 \pm 0.07$ g./cm.^{3}.

Molybdenum trifluoride obtained from the reaction described above has been observed in colors ranging from ochre through light-green and gray, depending on the details of preparation. Tan MoF_3 heated in sealed evacuated nickel tubes at 800° yields a black MoF_3, but when it is heated at 900° for 16 hr., it yields a dark-red, sharply crystalline MoF_3. A black MoF_3 also has been prepared by the reaction of MoF_5 with excess SbF_3 in a stream of argon at 150–200°. In all conditions, the compound has the rhombohedral structure described below. When heated in a dynamic vacuum, MoF_3 is stable to 500° but begins to disproportionate into molybdenum metal and higher volatile fluorides at 600°.

Crystal Structure.—Debye–Scherrer X-ray diffraction patterns of the several products mentioned above were prepared in a 11.46 cm. diameter cylindrical camera using Cu Kα radiation (λ = 1.5418Å.). All observed reflections from samples designated MoF_3 could be indexed on the basis of a bimolecular rhombohedral unit cell with parameters: $a_0 = 5.666 \pm 0.001$ A.; $\alpha = 54° 43' \pm 10'$; $V = 112.79 \pm 0.10$ Å.^{3}; $\rho_{\text{x-rays}} = 4.50$ g./cm.^{3}, assuming 2 MoF_3 per cell; $\rho_{\text{obsd.}} = 4.64 \pm 0.07$ g./cm.^{3} Parameters of the corresponding hexamolecular hexagonal unit cell are: $a_0 = 5.208 \pm 0.001$ Å.; $c_0 = 14.40_9 \pm 0.01_0$ Å.; $c_0/a_0 = 2.767 \pm 0.002$. Only reflections *hkl* with $l = 2n$ were observed, which indicated the probable space group to be D^6_{3d}, $R\bar{3}c$.

From the measured lattice parameters, the probable space group and the general diffracted intensity distribution, it is apparent that the structure of this molybdenum trifluoride is of the VF_3-type described by Jack and Gutmann[8] and by Hepworth, *et al.*[3] In this structure, atoms are located in the special positions of the space group $R\bar{3}c$

2Mo in (b): $0,0,0;\ {}^1/_2,{}^1/_2,{}^1/_2$

6F in (e): $\pm(x,{}^1/_2-x,{}^1/_4);\ \pm({}^1/_2-x,{}^1/_4,x);\ \pm({}^1/_4,x,{}^1/_2-x)$

Neutron diffraction data from polycrystalline MoF_3 samples were used to fix the x(F) parameter since the intensities of X-ray scattering in "fluorine-only" reflections were relatively weak. The value so obtained is

$$x(\mathrm{F}) = -0.12 \pm 0.01$$

which gives excellent agreement between computed and observed neutron and X-ray diffraction intensities.

Discussion

Jack and his co-workers[8,9] have shown that the crystal structures of many transition metal trifluorides may be simply compared if they are described on the bases of bimolecular rhombohedral unit cells with atoms in the special positions of $R\bar{3}c$ given above. The value of the fluorine parameter then fixes the anion packing arrangement, which may vary continuously from hexagonal close-packed, as in RhF_3, PdF_3 and IrF_3 ($x = -{}^1/_{12}$), to cubic close-packed (with regularly located holes) if $x = -{}^1/_4$. The latter configuration corresponds to the cubic ReO_3 structure which was reported for MoF_3 by Gutmann and Jack.[2] The structure derived for MoF_3 prepared in the present investigation is intermediate in anion packing sequence and thus resembles the trifluorides of V, Cr,[9] Fe, Co, Ru and Ga.[10]

It is not impossible that molybdenum trifluoride may exist in more than one structural form or that its structure may be sensitive to slight changes in stoichiometry or impurity content. Any of these reasons could be responsible for the divergence of the results reported here and those of Gutmann and Jack. However, in the course of the preparation of MoF_3 for the present investigation, some materials suspected of contamination through reaction with quartz or water vapor were obtained. These substances gave X-ray diffraction patterns containing reflections from a cubic ReO_3-type phase in addition to those from rhombohedral MoF_3. The lattice parameter of this cubic phase was measured to be a_0 = 3.89Å., which is very close to the value of 3.90Å. reported by Gutmann and Jack for cubic MoF_3. It is also interesting to note that material with a cubic ReO_3-type structure has been formed by the treatment of MoF_5 with oxygen and water vapor at 100–180°. This substance, which has a lattice parameter a_0 = 3.83Å., is most likely to be an oxyfluoride of uncertain chemical composition. Analysis of the material for molybdenum and fluorine gave 72.5 and 11.5 wt. %, respectively.

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