opposite direction. The difference between the two explanations is simply whether the potential as a function of the normal coördinate in question has a double minimum or not. Although the dipole moment data alone do not permit a choice between these alternatives, the high apparent moment of B-trichloroborazole, for which steric hindrance is presumed to be inappreciable, seems to favor a potential curve having a single minimum. In fact, Coursen and Hoard[16] have carried out X-ray crystal analysis on this compound and found that the molecules as they exist in the crystal are planar within experimental errors, no boron or nitrogen atom departing from the plane of the chlorine atoms by more than 0.01 Å. On the other hand, the high moment of hexamethylborazole suggests the importance of the steric effect which favors a non-planar polar structure. This effect is certainly great in a B-trimethyl-N-triphenylborazole. However, since from steric reasons phenyl groups presumably are oriented at right angles to the central ring and hold methyl groups between them, the bending of methyl groups out of the plane of the central ring does not lead to an appreciable gain in stability as in hexamethylborazole. Accordingly, the out-of-plane vibrations of B-trimethyl-N-triphenylborazole will be excited to a lesser extent than in a hexamethylborazole molecule and the moment of the former compound will be smaller than that of the latter compound, as was actually found in the present investigation. The discussion on the moments of ethyl-substituted borazoles is open to speculation owing to the axes of internal rotation involved but the values of the moments are of right order of magnitude.

It is of interest to compare the present results with those from a different physical method of attack. Bauer[17] studied borazole by means of an electron diffraction experiment using the visual method. He confirmed the benzene-like structure of this molecule but suggested that deviations from a planar model could amount to about 0.1 Å. to either side of the molecular plane before discrepancy between the theoretically calculated curve and the visual appearance of photographs became evident. B-Trichloroborazole and N-trimethylborazole were also studied,[18] but the analysis of diffraction data was made assuming D_{3h} symmetry. From the stand-point of the present investigation, it is very desirable to carry out similar experiments on hexasubstituted borazoles having substituted atoms or groups exerting greater steric effects than hydrogen atoms.

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(16) D. L. Coursen and J. L. Hoard, THIS JOURNAL, **74**, 1742 (1952).

(17) S. H. Bauer, *ibid.*, **60**, 524 (1938).

(18) K. P. Coffin and S. H. Bauer, *J. Phys. Chem.*, **59**, 193 (1955).

CHIKUSA, NAGOYA, JAPAN

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMICAL ENGINEERING (RESEARCH DIVISION) OF NEW YORK UNIVERSITY]

The Thermal Decomposition of Trialkylboranes[1]

BY PAUL F. WINTERNITZ AND ARRIGO A. CAROTTI

RECEIVED SEPTEMBER 25, 1959

The disproportionation of trialkylboranes containing C_2 and C_4 alkyl substituents by heating to give unsaturated hydrocarbons and diborane-6 derivatives has been substantiated. However, tri-*n*-amylborane-3 gave *trans*-2-pentene, hydrogen and a heterocyclic boron compound of formula $(\text{-}CH_2)_3CH(CH_3)\text{-}B\text{-}C_5H_{11}$, (1-*n*-amyl-2-methylboracyclopentane) in a 1:1:1 molar ratio. Heating tri-*n*-hexylborane-3 under reflux resulted in the formation of trans-3-hexene, hydrogen, a relatively small quantity of a heterocyclic boron compound of formula $(\text{-}CH_2)_4CH(CH_3)\text{-}B\text{-}C_6H_{13}$, (1-*n*-hexyl-2-methylboracyclohexane), a polymer of empirical formula $[B(C_6H_{13})]_x$ and tri-*n*-hexylborane-3. Trialkylboranes containing unsaturated alkyl substitutents are tentatively assumed to give diborane-4 type compounds.

According to Rosenblum,[2] Stock[3] and Meerwein[4] the thermal decompositions of tri-*n*-butyl-, tri-*n*-propyl-, triethyl- and trimethylborane-3 give mainly unsaturated hydrocarbons and alkylated boron hydrides. Rosenblum[5] described the disproportionation of tri-*n*-butylborane-3 as $2(C_4H_9)_3 \rightarrow (C_4H_9)_2B_2H_4 + 4\ C_4H_8$ and suggested a hydride bridge exchange mechanism for this reaction.

We have investigated the thermal decomposition of triethyl-, tri-*n*-propyl- and tri-*n*-butylborane-3[6] in a nitrogen atmosphere concurrently with Rosenblum and obtained the same general results reported by previous workers. The following general conclusions can be drawn: (1) Most trialkylboranes give, on pyrolysis in an inert atmosphere, substituted diboranes with the release of unsaturated hydrocarbons with the same number of carbon atoms as the original alkyl substituents. (2) The ease of decomposition increases with increasing molecular weight of the alkyl substituents. (3) The extent of decomposition increases with temperature; depending on the nature of the alkyl substituent, more than one may be lost at relatively higher temperatures. (4) Some of the resulting liquid and/or solid products contain boron to hydrogen bonding.

Anticipating that diborane-6 and diborane-6

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[1] (a) This investigation was carried out under subcontract to Olin–Mathieson Chemical Corporation, 4350-3, under United States Air Force prime contract AF 33(600)33920. (b) Presented at the Spring 1959 meeting of the Am. Chem. Soc. in Boston, Mass.

(2) L. Rosenblum, THIS JOURNAL, **77**, 5016 (1955).

(3) A. Stock and F. Zeidler, *Ber.*, **54**, 531 (1921).

(4) H. Meerwein, G. Hinz, H. Majert and H. Sonke, *J. prakt. Chem.*, **147**, 226 (1937).

(5) L. Rosenblum, NACA Research Memorandum, E56L18; February, 1957.

(6) Yearly Report covering work conducted from July 1, 1955 to June 30, 1956, under Olin–Matheson Chemical Corp. Subcontract N-3181 under Contract NOa(s)-52-1023.

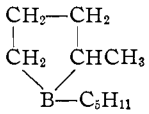
derivatives might be formed with greater ease from the pyrolysis of trialkylboranes with lengthy and bulky alkyl substituents, a study of the disproportionation of tri-*n*-amyl- and tri-*n*-hexylborane-3 was initiated.

Two main differences were at once noted. (1) No compounds embodying the diborane-6 structure resulted and (2) hydrogen was one of the products.

This disproportionation was thoroughly studied for both tri-*n*-amyl and tri-*n*-hexylborane-3.[7–9] In addition some preliminary studies on the thermal behavior of trialkylboranes with unsaturated alkyl substituents were made.

Results

A. Disproportionation of Tri-*n*-amylborane-3.—The compound thermally decomposed readily when heated at its boiling point under one atmosphere of nitrogen. The products were *trans*-2-pentene, hydrogen and the heterocyclic boron compound 1-*n*-amyl-2-methylboracyclopentane



(I). The mole ratio of pentene:hydrogen:cyclic compound was 1:1:1. The identity of (I) was established by its boron content, molecular weight and by destructive decomposition with 30% H_2O_2 in a strongly alkaline solution. From the latter reaction 2-methyltetrahydrofuran, amyl alcohol and sodium borate were isolated and identified. Bromination of (I), and then acid hydrolysis, yielded a mixture of products which gave small mass peaks corresponding to 1,4-pentanediol, among others. These results may be explained by the sequence of reactions

$$B(C_5H_{11})_3 \xrightarrow{\text{heat}} B(C_5H_{11})_2H + C_5H_{10}{}^{10} \qquad (1)$$

$$B(C_5H_{11})_2H \longrightarrow B(C_5H_{11})_2 + {}^1/{}_2H_2 \qquad (2)$$

$$B(C_5H_{11})_2 \longrightarrow B(C_5H_{11})(C_5H_{10}) + {}^1/{}_2H_2 \qquad (3)$$

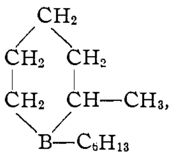
The over-all reaction then is given by

$$B(C_5H_{11})_3 \longrightarrow B(C_5H_{11})(C_5H_{10}) + H_2 + C_5H_{10} \quad (4)$$

The heterocyclic boron compound was thermally stable and fumed strongly in N_2 containing a small percentage of air (oxygen).

The five- and six-membered heterocyclic boron compounds 1-phenylboracyclohexane and 1-phenylboracyclopentane were prepared by Torssell[11] from phenyldifluoroborane-3 and dilithiumpentane, dilithiumbutane, respectively. Also Clark[12] and coworkers have reported the preparation of 1-*n*-butylboracyclopentane and 1-*n*-butylboracyclohexane.

B. Disproportionation of Tri-*n*-hexylborane-3.—The compound thermally decomposed readily when heated at its boiling point under one atmosphere of nitrogen. The products were *trans*-3-hexene and H_2 in a ratio slightly less than 2:1. The other products were the heterocyclic boron compound 1-*n*-hexyl-2-methylboracyclohexane



(II), a polymer $[B(C_6H_{13})]_x$ and tri-*n*-hexylborane-3. The identity of (II) was established not only by its boron content and molecular weight but also by boiling it with 33% H_2O_2 in a strongly alkaline solution. From the resulting acidified organic layer 1-hexanol, boric acid and 2-methyltetrahydropyran were isolated. Bromination of compound (II) in acetic anhydride yielded 1-bromohexane and a liquid boiling in the range of 1,5-dibromohexane. Boron acetate was a third product of this reaction.

From the experimental evidence the reaction scheme is postulated as

$$B(C_6H_{13})_3 \longrightarrow B(C_6H_{13})_2H + C_6H_{12}{}^{10} \qquad (5)$$

$$B(C_6H_{13})_2H \longrightarrow B(C_6H_{13})_2 + {}^1/{}_2H_2 \qquad (6)$$

$$2B(C_6H_{13})_2 \longrightarrow$$
$$B(C_6H_{13})_3 + B(C_6H_{13})\text{major reaction} \quad (7a)$$

$$xB(C_6H_{13}) \longrightarrow [B(C_6H_{13})]_x \text{ polymer formation}$$

$$B(C_6H_{13})_2 \longrightarrow$$
$$B(C_6H_{13})(C_6H_{12}) + {}^1/{}_2H_2 \text{ minor reaction } (6\text{–}10\%) \quad (7b)$$

This results in the over-all equations for the major reaction

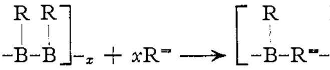
$$xB(C_6H_{13})_3 \longrightarrow \underset{\text{(III)}}{[B(C_6H_{13})]_x} + \underset{\text{(IV)}}{2xC_6H_{12}} + xH_2$$

and for the minor reaction

$$B(C_6H_{13})_3 \longrightarrow \underset{\text{(V)}}{B(C_6H_{13})(C_6H_{12})} + C_6H_{12} + H_2$$

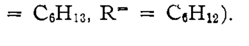
The reactions explain the formation of all of the products observed as well as the ratio of hexane to hydrogen being slightly less than 2:1 since as a whole the yield of the BR_2 species varied from 6–10%.

The polymer (III) undergoes further thermal decompositions. A sharp boiling, very viscous liquid containing 8.12% and a dark solid containing 20% boron were obtained by fractionating a portion of (III) which had been pyrolyzed for several hours. The dark solid product hydrolyzed in alcoholic KOH practically to completion and yielded approximately the stoichiometric quantity of H_2 corresponding to formula $[-B(C_6H_{13})-BH-]_x$. It is believed that the reactions which occurred are



$$\left[-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}\right]_{-x} \longrightarrow \left[-\overset{\mathrm{H}}{\overset{|}{\mathrm{B}}}-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}\right]_{-x} + x\mathrm{R}^{=} \qquad (8)$$

(VI) (VII)(20% boron)



$$\left[-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}\right]_{-x} + x\mathrm{R}^{=} \longrightarrow \left[-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}-\mathrm{R}^{=}-\overset{\mathrm{R}}{\overset{|}{\mathrm{B}}}\right]_{-x} \qquad (9)$$

(VIII) (8% boron)

where ($R = C_6H_{13}$, $R^{=} = C_6H_{12}$).

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[7] Quarterly Progress Reports, Aug. 20 to Nov. 20, 1957, New York University. Under Olin-Mathieson Chemical Corp. Subcontract 4350-3 under Contract AF 33(600)33920.

[8] Quarterly Progress Report, Nov. 20, 1957, to Feb. 20, 1958, New York University. Under Olin-Mathieson Chemical Corp. Subcontract 4350-3 under contract AF 33(600)33920.

[9] Quarterly Progress Report, Feb. 20, 1958, to May 20, 1958, New York University. Under Olin-Mathieson Chemical Corp. Subcontract 4350-3 under Contract AF 33(600)33920.

[10] Probably by Rosenblum's hydride exchange, ref. 5.

[11] K. Torssel, *Acta. Chem. Scand.*, **9**, 239, 1955.

[12] S. L. Clark, *et al.*, Reports at the Am. Chem. Soc. Meetings in San Francisco, Spring, 1958.

TABLE I

FRACTIONATION OF DISPROPORTIONATED TRI-*n*-HEXYLBORANE-3 (34 g., 0.25–0.30 mm.)

B.p., °C.	Weight. %	% B	Mol. wt.[a]	$R = C_6H_{13}$, $R^{=} = C_6H_{12}$ Assumed species	Theor. % B	Theor. mol. wt.	Remarks
34–36	6.5	5.81	180	$BRR^{=}$ (cyclic compound)	5.96	181	Stablzed. by cycliz.
38–40	9.7	5.41	147	?	...	..	....
40–50	6.4	6.61	163	Mixt. 0.6 BR + 0.4 BR_3	6.65	163	BR stablzd. as $(BR)_x$
60–70	4.1	4.82	212		...	..	....
90–100	18.0	4.60	238	BR_3 with impurities	4.06	266	....
100–120	9.3	4.74	262		...	..	....
120–126	20.4	5.03	297	Mixt. $BR_3$$^+$ polymer	...	..	BR as $(BR)_x$
126	26.4	10.3	400	Polymer $(BR)_x$ + impurities	11.2	..	Infrared anal.
	100.8						

[a] By freezing point depression in benzene.

According to this scheme compound (VIII) is formed by the addition of –BR– groups across the double bond of $R^{=}$ following the rupture of the B–B bonds in compound (VI). Similar type reactions between B_2F_4 and ethylene were reported by Schlesinger.[13] The two polymeric species (VII) and (VIII) have only been analyzed for boron and active hydrogen. No proof of structure was attempted. Therefore, the above reaction schemes are merely postulates.

Tri-*n*-hexylborane-3 and tri-*n*-amylborane-3 behave on pyrolysis similarly in the first two steps:

(1) Both trialkylboranes lose one alkyl substituent for form R_2BH and an unsaturated hydrocarbon.

(2) Both R_2BH species are unstable and lose one mole of hydrogen to form another unstable species BR_2. But they differ in the third step, the stabilization of the unstable BR_2 species.

(3a) In the case of tri-*n*-amylborane-3, the BR_2 species stabilizes itself completely through cyclization. b. In the case of tri-*n*-hexylborane-3, the BR_2 species stabilizes itself in two different ways. The first way leads to the formation of BR_3 and a $(BR)_x$ polymer, the second consists in cyclization.

C. Disproportionation of Trialkylboranes Having Unsaturated Alkyl Substituents.—Preliminary experiments with a trialkylborane containing unsaturated side chains consisted in heating triallylborane-3 under reflux in a nitrogen atmosphere. Diallyl and a compound corresponding to the formula of tetraallyldiborane-4 were obtained. The tentatively postulated reaction is

$$2(C_3H_5)_3B \longrightarrow \underset{\text{(IX)}}{(C_3H_5)_4B_2} + C_3H_5{\cdot}C_3H_5 \qquad (10)$$

Compound (IX) did not contain boron to hydrogen bridges. Also it showed in the infrared indication of conjugation and the analysis (%B) and molecular weight corresponded to the formula shown. Diallyl was identified beyond any doubt (b.p. and mol.wt.).

In a brief study of the pyrolysis of trihexanedienylborane-3, the products could not be identified because of excessive polymerization and copolymerization of products and reactants. No hydrogen was released.

General Conclusions

The disproportionation behavior of trialkylboranes is somewhat complex. Trialkylboranes with *n*-saturated alkyl substituents of C_1 to C_4 length will give in general unsaturated hydrocarbons and alkylated diboranes-6. There is some question as to the products obtained from those containing C_1 to C_4 unsaturated alkyl substituents; however in the case of triallylborane-3 no products with B—H were found. Trialkylboranes with saturated C_5 and C_6 substituents disproportionate to give unsaturated hydrocarbon, hydrogen and a BR_2 cyclic compound and in the case of C_6 substituents in addition a $(BR)_x$ polymer. Unsaturated C_6 alkyl substituted boranes disproportionate in a manner unlike their saturated counterparts as H_2 is not evolved in the process.

The stability of the BR_2H species seems, therefore, to be related to the electron density in the vicinity of the boron atom as well as to the chain length of the alkyl substituent.

Experimental

The disproportionations were carried out simply by refluxing the liquid under 1 atm. of N_2. The reflux condenser was kept at about 85–95°. Boron-containing liquid products remained in the pot while the hydrocarbon was condensed, using a cold finger cooled to about −80°. The hydrogen was measured in gas burets after being passed through a liquid N_2 trap. A drying tube was located between the gas burets and the latter.

The disproportionated liquid and solid products then were fractionated under high vacuum. The respective fractions were analyzed for boron using standard procedures.[14,15] The respective molecular weights then were determined by freezing point depression in benzene. Routine and standard laboratory methods were employed for chemical testing and for preparation of derivatives.

(a) **Thermal Decomposition of Tri-*n*-amylborane-3.**—55.6 g., about 0.25 mole. of tri-*n*-amylborane-3 was heated to its boiling point under 1 atm. of nitrogen for 1:26 hr. 0.053 mole of H_2 was evolved and 0.056 mole of *trans*-2-pentene was collected. 0.056 mole of BR_2 was obtained from the high vacuum fractionation of the liquid products. All but 13 g., 0.058 mole, of tri-*n*-amylborane-3 was recovered. On the basis of these results the reaction may be written as

$$\begin{array}{ccccccc} \text{(I)} & & \text{(II)} & & \text{(III)} & & \\ B(C_5H_{11})_3 & \longrightarrow & B(C_5H_{11})(C_5H_{10}) & + & C_5H_{10} & + & H_2 \\ \text{0.058 mole} & & \text{0.056 mole} & & \text{0.056 mole} & & \text{0.053 mole} \end{array}$$

The starting compound (I) boiled at 75–76° at 0.25 mm. and 88–89° at 0.6 mm. It was prepared from $BF_3{\cdot}Et_2O$ and

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[13] H. I. Schlesinger, "Hydrides and Borohydrides of Light Weight Elements and Related Compounds," Final Tech. Report, Aug. 1, 1956 to July 31, 1957. Contract Nonr-2121(02), Project NRO 52-255. Univ. of Chicago.

[14] C. E. Erickson, Ph.D. Thesis, Cornell University, 1953.

[15] Parr-Peroxide Bomb Method, Olin-Mathieson Chemical Corporation, private communications, 1955.

$C_5H_{11}MgBr$ 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.

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[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.

NEW YORK 53, NEW YORK

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

The Preparation and Crystal Structure of Molybdenum(III) Fluoride

BY D. E. LAVALLE, R. M. STEELE, M. K. WILKINSON AND H. L. YAKEL, JR.

RECEIVED SEPTEMBER 28, 1959

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).