termine an accurate molecular weight from vapor density data but a rough value of 600 was obtained as an upper limit. The volatility of this material is similar to that reported for $B_2[N(CH_3)_2]_4$,[20] but from the small amount of data available it would appear to have a lower heat of vaporization. The infrared absorption spectrum is fairly complex and different from that of $B_2[N(CH_3)_2]_4$ but consistent with the presence of B–N and C–N bonds. The most interesting feature of the spectrum is the disappearance or major shift in frequency of the band at 1010 cm.$^{-1}$ attributed to the B_4 cage in the spectrum of the parent B_4Cl_4.

Reaction of Tetraboron Tetrachloride with Diethyl Ether.—A sample of B_4Cl_4 weighing 0.0736 g. (0.398 mmole) was dissolved in 3.17 mmoles of anhydrous diethyl ether. When the solution was warmed from −79° to room temperature a reaction occurred, as indicated by the formation of a red solid precipitate. After 1 hr. at room temperature the volatile materials were removed from the reaction mixture and found to be a mixture of unchanged diethyl ether and 0.48 mmole of ethyl chloride. When the red solid remaining in the reaction vessel was again treated with diethyl ether more ethyl chloride was formed. The separation of ethyl chloride and diethyl ether is difficult and estimates of the amount of ethyl chloride formed did not indicate any favored stoichiometry.

Acknowledgment.—We gratefully extend our sincere appreciation to the Office of Naval Research for the generous financial support of that portion of the research, herein reported, carried out at the University of Chicago. The work accomplished at Purdue University enjoyed similar invaluable financial support from the National Cancer Institute of the Public Health Service under Grant Number CY-4382 and for this we are grateful.

Finally, in a more personal vein, G. U. cannot forego the opportunity, here afforded, to express his gratitude and indebtedness to his professor and the senior author of this paper, Dr. Hermann Irving Schlesinger, now deceased, for the patient understanding with which he displayed for this neophyte the elegance and power of chemistry as an experimental science.

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The Chemistry of the Boron Subhalides. II. Reactions of Diboron Tetrachloride with Compounds of Nitrogen and Phosphorus[1]

BY ALFRED G. GARRETT AND GRANT URRY[2]

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The results of the treatment of diboron tetrachloride with tetrafluorohydrazine, phosphorus trichloride, tetrachlorodiphosphine, and tetramethyldiphosphine are reported. With N_2F_4 a slow reaction occurs, forming nitrogen and a mixture of boron trichloride and boron trifluoride. With PCl_3 a complex, $B_2Cl_4 \cdot 2PCl_3$, is formed. No such complex is formed when diboron tetrachloride is treated with P_2Cl_4. With tetramethyldiphosphine B_2Cl_4 forms a complex, $B_2Cl_4 \cdot P_2(CH_3)_4$. Treatment of $B_2Cl_4 \cdot P_2(CH_3)_4$ with trimethylamine results in a new complex, $B_2Cl_4 \cdot P_2(CH_3)_4 \cdot N(CH_3)_3$. Pyrolysis of $B_2Cl_4 \cdot P_2(CH_3)_4$ produces a new substance which on the basis of its physical and chemical properties is tentatively identified as $[(CH_3)_2P \mathrel{\substack{-\\ \longrightarrow}} B \mathrel{\substack{-\\ \longleftarrow}} P(CH_3)_2]^+BCl_4^-$.

Introduction

Reactions of boron trichloride with various nitrogen compounds have been studied extensively. The formation of donor–acceptor addition compounds is the first result of most such reactions. In cases where protolytic hydrogens are present in the donor molecule, secondary reactions occur which lead either to substitution of amino moieties for chlorine or to more complex structures such as the borazenes.[3,4]

The extensive literature of boron nitrogen chemistry is already very well reviewed.[5-8]

Fewer reactions of boron trichloride with phosphorus compounds have been studied. Notable among these is the work of Gamble and Gilmont,[9] reporting the preparation of a boron trichloride–phosphine complex. A reported boron trichloride–phosphorus trichloride complex[10] was later shown to be a complex of boron trichloride with phosphorus oxychloride, $POCl_3$.[11]

Reactions of boron trichloride with alkylphosphines are reported to give stable adducts.[12] Another type of boron halide phosphorus compound results when the dimethylphosphinoborane trimer, $[(CH_3)_2PBH_2]_3$, is treated with methyl chloride–aluminum chloride mixtures to produce the analogous chlorinated trimer, $[(CH_3)_2PBCl_2]_3$.[13] A general review by Stone[14] of

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boron hydride chemistry includes references to most of the boron phosphorus chemistry so far explored. Wartik and Apple[15] report a complex between diboron tetrachloride and phosphine, $B_2Cl_4 \cdot 2PH_3$, which is apparently stable at room temperature *in vacuo* but reacts rapidly with air. In another reference[16] the same workers report a complex of diboron tetrachloride with cyanogen, $B_2Cl_4 \cdot 1.5(CN)_2$, stable *in vacuo* at ordinary temperatures but decomposing at 400°. A tetrameric complex of diboron tetrachloride with trimethylamine, $[B_2Cl_4 \cdot 2N(CH_3)_3]_4$, also has been reported.[17]

Results and Discussion

In the present work we have treated diboron tetrachloride with tetrafluorohydrazine, phosphorus trichloride, tetrachlorodiphosphine, and tetramethyldiphosphine.

With tetrafluorohydrazine, diboron tetrachloride undergoes a very slow reaction at room temperature which results in the formation of nitrogen gas along with a mixture of boron trichloride and boron trifluoride. Tetrafluorohydrazine is consumed in the slow reaction as described by the equation

$$3N_2F_4 + 6B_2Cl_4 \longrightarrow 8BCl_3 + 4BF_3 + 3N_2 \qquad (1)$$

The slow rate of this reaction compared to the very rapid reaction of nitric oxide with diboron tetrachloride[18] is difficult to understand in view of Colburn's suggestion that N_2F_4 is dissociated to an appreciable extent at room temperature into $\cdot NF_2$ radicals.[19] A modification of the same reaction presently is being studied in which a mixture of B_2Cl_4 and N_2F_4 vapors is subjected to prolonged ultraviolet radiation. In this case more extensive reaction occurs. The products of this reaction are being characterized and the results will be published later.

The treatment of diboron tetrachloride with phosphorus trichloride results in the formation of an interesting complex, $B_2Cl_4 \cdot 2PCl_3$, which melts from −16.3 to −15.8° and is completely dissociated in the vapor phase. The stoichiometry of the complex has been satisfactorily established by a liquid–solid phase study. This thus represents one of the rare examples of a complex where phosphorus trichloride acts as an electron pair donor outside the transition metal series. It is interesting to speculate upon the reasons for the stability of such a complex. First, diboron tetrachloride is one of the most avid electron acceptors among the boron halides. Second, there exists a possibility of additional stability arising from interactions of "non-bonding" electron pairs on the chlorines attached to boron with the vacant 3d orbitals of phosphorus.

The formation of the complex stabilizes diboron tetrachloride to the extent that no decomposition typical of B_2Cl_4 is observed even after 8 weeks in the dark at room temperature. Also, while diboron tetrachloride vapor is spontaneously inflammable in air,[17] the complex is not. It is difficult to understand this lack of inflammibility since the complex is largely dissociated in the vapor phase. It is possible that the air oxidation occurs readily but is moderated by the presence of PCl_3 to the extent that it occurs without inflaming.

Diboron tetrachloride does not react with tetrachlorodiphosphine within the limits of conditions wherein the phosphorus trichloride complex is formed. Under more vigorous conditions the complex $B_2Cl_4 \cdot 2PCl_3$ is formed along with orange solids which, with phosphorus trichloride, are typical products of the disproportionation of tetrachlorodiphosphine.

The stability of a 1:2 complex of diboron tetrachloride with phosphorus trichloride and the inability of tetrachlorodiphosphine to form such a complex is possibly an indication of the importance of enhanced bonding, previously discussed, involving the "nonbonding" electron pairs of the chlorines attached to boron and the vacant 3d orbitals of the phosphorus since the structure of the tetrachlorodiphosphine would limit or prohibit such interactions in a complex with diboron tetrachloride.

In contrast to the behavior of tetrachlorodiphosphine, tetramethyldiphosphine, being a much stronger base, reacts rapidly with diboron tetrachloride even at −79° to form an extremely stable complex, $B_2Cl_4 \cdot P_2(CH_3)_4$. There is no measurable dissociation pressure of this complex at temperatures below 150°. The nature of this complex is indicated by the fact that treatment with trimethylamine produces a new complex, $B_2Cl_4 \cdot P_2(CH_3)_4 \cdot N(CH_3)_3$, along with a small amount of $[B_2Cl_4 \cdot 2N(CH_3)_3]_4$ and $P_2(CH_3)_4$.

When the diboron tetrachloride–tetramethyldiphosphine complex is treated with ethanol, a slow reaction occurs. The complexity of this reaction is made evident by the diverse products, including hydrogen gas, hydrogen chloride, dimethylphosphonium chloride, and ethyl borate, as well as a solid residue containing phosphorus and boron.

When $B_2Cl_4 \cdot P_2(CH_3)_4$ is heated at 250° in an evacuated sealed tube for several hours, a melt is formed which, when cooled, solidifies at a temperature near 200°. Essentially all of the solid melt can be resublimed *in vacuo* at 185°. It is deposited in the cooler portions of the sublimation apparatus in the form of small, clear, needle-like crystals. These crystals are stable in moist air, do not react with liquid ethanol or with trimethylamine vapor at room temperature, and exhibit an infrared absorption different from the original complex. The most interesting difference is the appearance in the absorption spectrum of the pyrolysis product of a broad intense band from 670 to 790 cm.$^{-1}$ centering at 730 cm.$^{-1}$ similar in character to a band previously ascribed to the BCl_4^- ion.[20]

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A possible formula for the new solid is therefore $[(CH_3)_2PBP(CH_3)_2]^+BCl_4^-$. It also is possible that it is a polymer with the formula $[Cl_2B-P(CH_3)_2]_x$ but the infrared data would tend to support the first possibility.

While this new substance is stable in ethanol solution at room temperature and is not hydrolyzed by atmospheric moisture at room temperature, slow ethanolysis occurs at 70° in the ethanol solution. The products indicate a complex reaction.

Perhaps it should also be noted that attempts were made to prepare compounds such as dichloroboryldichlorophosphine, Cl_2BPCl_2, by the mercury arc reduction of a mixture of boron trichloride and phosphorus trichloride vapors as well as a similar reduction of the $B_2Cl_4 \cdot 2PCl_3$ complex. No new products resulted from either of these attempts.

Experimental

Apparatus and Experimental Methods.—All of the reactions reported in the present work were carried out in apparatus similar to that already described in the literature.[21] A special method for determining the melting points of mixtures was used for studying the diboron tetrachloride–phosphorus trichloride system and will be discussed in detail in a subsequent section.

Analytical Methods.—Measurements of gases such as nitrogen and the vapors of volatile liquids were made in calibrated volumes of the vacuum apparatus and are expressed in mmoles.

Reagents. Boron trichloride, obtained from the Matheson Company, Inc., Joliet, Illinois, was repeatedly distilled through a trap maintained at −79° into one maintained at −112° until its 0° vapor pressure was 477 mm. and its −79° vapor pressure was 4.0 mm.

Diboron tetrachloride was prepared by passing boron trichloride at 4 mm. pressure through four 2-cm. mercury arcs at about 1000 volts a.c. each, as previously described,[17] and stored at −79° in a tube connected to the vacuum line. Samples were purified just before use by repeated distillations through a trap maintained at −63° into one maintained at −79° until the fraction retained at −79° exhibited a 0° vapor pressure of 44 mm.

Trimethylamine, obtained from the Matheson Company, Joliet, Illinois, was purified by fractional condensation in traps maintained at −95, −112, and −196°. Trimethylamine, retained at −112°, had a vapor pressure of 75 mm. at −45.2°, (literature value, 73 mm).

Tetrafluorohydrazine.—Electrolysis of molten NH_4HF_2 produced NF_3 as reported by Ruff.[22] This was passed through a copper reactor packed with copper to produce N_2F_4 as described by Colburn and Kennedy,[23] from whose equation we calculate a vapor pressure of 42 mm. at −126°.

A mass spectrum analysis of our product after some purification indicated 99+% N_2F_4 with 0.2% NF_3, 0.4% air, and traces (less than 0.1%) of NO, N_2O, and CF_4. This product then was distilled in the vacuum line through a trap maintained at −126° into one at −160°. The fraction retained at −160° exhibited a vapor pressure at −126° of 25.6 mm. in a small volume and 25.4 mm. in a vapor volume 5.6 times as large.

Phosphorus trichloride, reagent grade, was obtained from the J. T. Baker Chemical Co., Phillipsburg, N. J., and fractionated in the vacuum line with traps maintained at −45 and −63°. PCl_3 passed the first trap slowly and was retained completely in the second, the −63° fraction exhibiting a vapor pressure of 36.2 mm. at 0°. Commercial PCl_3 usually reacts slowly with mercury, fouling it and creating some nuisance in a vacuum line. Stock, Brandt, and Fischer[24] suggested that most of this reactivity may be due to a small impurity of P_2Cl_4 which reacts readily with mercury, but may largely be removed by treatment of the sample with mercury or sodium. However, we found that the most carefully purified samples also gradually attacked mercury. According to Wolf,[25] red phosphorus and Hg_2Cl_2 are the products of this reaction.

For material to be used in the melting point and vapor pressure diagrams, a sample of the reagent grade PCl_3 was distilled under nitrogen in a spinning band column having an efficiency well over 100 theoretical plates. A constant-boiling fraction (approximately one-third of the contents of the pot, boiling point 75.0°, uncorrected) was introduced to the vacuum line and further purified as follows: The liquid was allowed to warm slowly and its vapor vacuum distilled through a trap maintained at −30° into one maintained at −196° until approximately one-tenth of the original material had evaporated, at which time a U-tube between the −30 and −196° traps was cooled to −45° and maintained at that temperature until one-half of the constant boiling fraction had evaporated. The −45° trap then contained perhaps one-third of the product from the spinning band column. This −45° fraction exhibited vapor pressures of 36.1 and 9.7 mm. at 0 and −22.8°, respectively, and was used for the melting point and vapor pressure diagrams.

Tetrachlorodiphosphine was prepared by a mercury arc reduction of PCl_3 and purified by distillation of the reaction mixture through traps maintained at −23, −45, and −196°. The −23 and −196° fractions were discarded and the −45° fraction again was distilled through the same set of traps. This process was repeated until the material in this fraction exhibited a vapor tension of 5 mm. at 0°.

Tetramethyldiphosphine.—Thiophosphoryl chloride, $PSCl_3$, was obtained from Fisher Scientific Co., New York, N. Y., and treated with CH_3MgI to produce tetramethyldiphosphine disulfide.[26] This then was treated with tri-*n*-butylphosphine[27] (Food Machinery and Chemical Corp., New York, N. Y.) by refluxing for 80 min. at 25° under N_2 to produce $P_2(CH_3)_4$. The sample used for reactions was volatile *in vacuo* at 0° and retained at −23°; the 0° vapor pressure was approximately 2.4 mm.

Treatment of Diboron Tetrachloride with N_2F_4.—A sample of pure diboron tetrachloride (0.818 mmole) was vacuum distilled into a reaction vessel maintained at −126°. Tetrafluorohydrazine vapor (0.668 mmole) then was allowed to distil into the reaction vessel. The mixture thus obtained was allowed to warm slowly. At a temperature only slightly above −126°, possibly the temperature at which the sample of B_2Cl_4 melted, a slight explosion accompanied by a purple flash was observed above the liquid reaction mixture. The reaction vessel immediately was cooled to −196° and a small amount of noncondensable material, presumably nitrogen, was observed to be present. The mixture again was allowed to warm slowly to room temperature and stand for 12 hr. at ambient temperatures. The volatile material then was removed from the reaction vessel. In addition to the low volatile subchlorides of boron which result from the usual disproportionation of B_2Cl_4[17] there was found 0.1 mmole of nitrogen, 0.572 mmole of unchanged N_2F_4, 0.140 mmole of BF_3, 0.762 mmole of BCl_3, and a small amount (less than 0.1 mmole) of unchanged B_2Cl_4. Thus, in the reaction 0.140 mmole of BF_3 was produced while 0.1 mmole of N_2F_4 was consumed. The amounts of boron trichloride produced and the diboron tetrachloride consumed are probably not significant in this case because extensive disproportionation into boron tri-

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chloride and lower boron chlorides occurred during the 12 hr. at room temperature.

Reaction of Diboron Tetrachloride with PCl_3.—Diboron tetrachloride reacts immediately with phosphorus trichloride at −79° to form a white solid. Since both of these reactants are liquids at −79° the presence of a solid at this temperature indicates the occurrence of some kind of reaction. It also proved impossible to separate the solid mixture into its components by the technique of fractional condensation. In order to determine the nature and composition of this solid, a liquid–solid phase diagram was obtained.

The most common method of determining the melting point of a substance in a vacuum system is the falling weight method. In this method a solid plug of the substance is vacuum distilled and frozen into a small tube. A small weight, usually a small glass rod, then is lowered onto this solid plug so the weight is supported by the solid. The solid then is allowed to warm to its melting point, at which point the weight falls. This method was unsuitable for determining the melting points of our diboron tetrachloride–phosphorus trichloride mixtures since the distillation of the mixture to form the solid plug resulted in varying composition throughout the solid. We also found that we could not freeze the mixtures in the bottom of a tube and determine the melting point by allowing the weight to fall into the mass of liquid and solid since we found that perceptible motion of the weight usually did not occur until the melting was well advanced. Reproducible results were obtained by the following procedure:

A Pyrex rod 2 mm. in diameter and approximately 100 mm. in length was fitted at the top with a small glass-enclosed iron slug. The bottom of the 2 mm. rod was shaped into a flanged foot 3 mm. in diameter. This rod was placed in a Pyrex tube 6 mm. in diameter with a small bulb 8 mm. in diameter blown on the bottom. This assembly then was sealed to the vacuum apparatus and evacuated. An a.c. solenoid was placed around the 6 mm. Pyrex tube in such a position that when activated it would raise the iron slug and Pyrex rod so that the flange foot was about 1 cm. above the bulb end of the outer 6 mm. Pyrex tube. When the solenoid was turned off the rod would fall to rest on the bottom of the 6 mm. Pyrex tube.

In a typical determination measured amounts of both diboron tetrachloride and phosphorus trichloride were distilled into the apparatus. The mixture then was allowed to melt and was thoroughly mixed and then frozen with the Pyrex rod encased in the solid mass. The solenoid then was activated.[28] The solid mixture then was allowed to warm slowly at a rate of temperature rise approximately 0.3°/min. The temperature at which the Pyrex rod began to move and the temperature at which it was raised to its highest point were noted by means of a vapor pressure thermometer.

A set of mixtures ranging from 100 to 24.86 mole % of B_2Cl_4 was prepared by placing pure B_2Cl_4 in the apparatus and, after determining its melting point, adding a small measured amount of pure PCl_3. After determining the melting point or melting range for this composition another increment of pure PCl_3 was added and a new determination was made. Compositions ranging from 24.84–0 mole % B_2Cl_4 were prepared in the same fashion starting with pure PCl_3. The results are shown in Table I.

The results are plotted in Fig. 1. The maximum at 33.3 mole % of B_2Cl_4 indicates a compound with a composition $B_2Cl_4 \cdot 2PCl_3$.

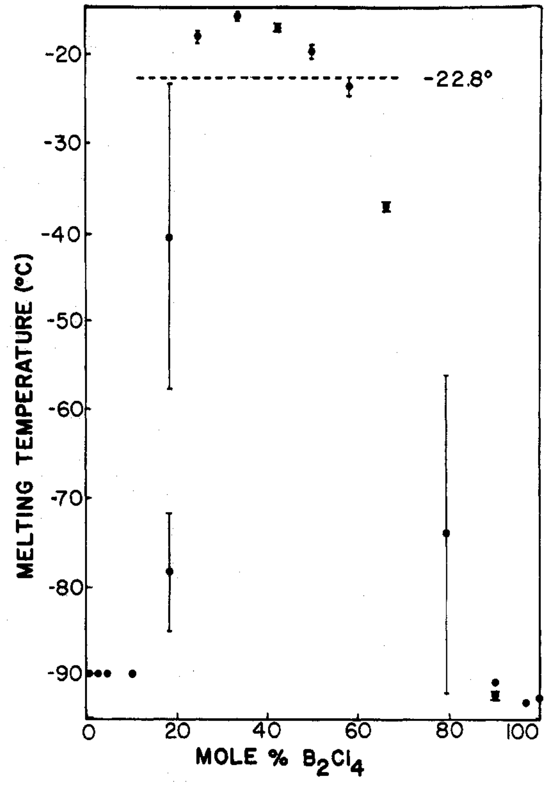

Fig. 1.—Melting temperatures for B_2Cl_4–PCl_3 mixtures.

TABLE I

MELTING TEMPERATURES OF B_2Cl_4–PCl_3 MIXTURES

Mole % B_2Cl_4	Melting temp.	Mole % B_2Cl_4	Melting temp.
100 (B_2Cl_4)	−92.8 + 0.1	33.47	−16.3 to −15.8
96.94	−93.3 ± 0.2	24.86	−18.7 to −17.0
90.31	−91 ± 1	24.84	−18.9 to −17.9
79.39	−92.0 to −56.4	18.24	−85.1 to −72
66.47	−37.9 to −37.2	10.06	−90.0
58.06	−24.8 to −23.2	4.396	−90.1
49.90	−20.6 to −19.4	2.093	−90.0 to −89.9
42.20	−17.7 to −17.1	0 (PCl_3)	−90.0 ± 0.1

The melting point of pure phosphorus trichloride is not well established in the literature. A value of −111.8° is listed in Lange's "Handbook of Chemistry," the "Handbook of Chemistry and Physics," and the "International Critical Tables." We were unable to find the original reference to this value. "Noveau Traite de Chimie Minerale" lists this value but erroneously credits it to Hückel, "Structural Chemistry of Inorganic Compounds," who lists a value of −91° in both the German (1948) and English (1950) editions. Zvoruikin[29] reports a value of −91° and Arii and Kawabata[30] a value of −93.6°. Fialkov and Kuzmenko[31] cite −112.5° "as given in the literature." After careful purification we determined a series of melting points at −90.0 ± 0.1° for phosphorus trichloride.

Properties of $B_2Cl_4 \cdot 2PCl_3$.—The diboron tetrachloride–phosphorus trichloride compound vacuum distils slowly through a trap maintained at −45° and is retained completely by a −63° trap. Diboron tetrachloride has a −63° vapor tension of 1.0 mm. and phosphorus trichloride has no measurable vapor tension at −45°. The solid retained at −63° is completely dissociated in the vapor phase at room temperature since the apparent molecular weight of the vapor is 145.5, in good agreement with the calculated average of 146.1 for one B_2Cl_4 and two PCl_3 molecules. The dissociation in the vapor state indicates that $B_2Cl_4 \cdot 2PCl_3$ is a reversible complex.

A sample of this material was stored in the dark at room temperature for 8 weeks without any apparent change. When stored in the light an orange precipitate slowly forms and boron

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[28] We found that the small flanged foot on the Pyrex rod was necessary since upon freezing the mixtures sometimes contracted away from the rod so that activating the solenoid would immediately lift an unflanged Pyrex rod out of the solid mass.

[29] A. Ya. Zvoruikin, *Chim. ind.* (Paris), **35**, 1034 (1936).

[30] K. Arii and M. Kawabata, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **17**, 299 (1938).

[31] J. A. Fialkov and A. A. Kuzmenko, *J. Gen. Chem. USSR*, **21**, 479 (1951).

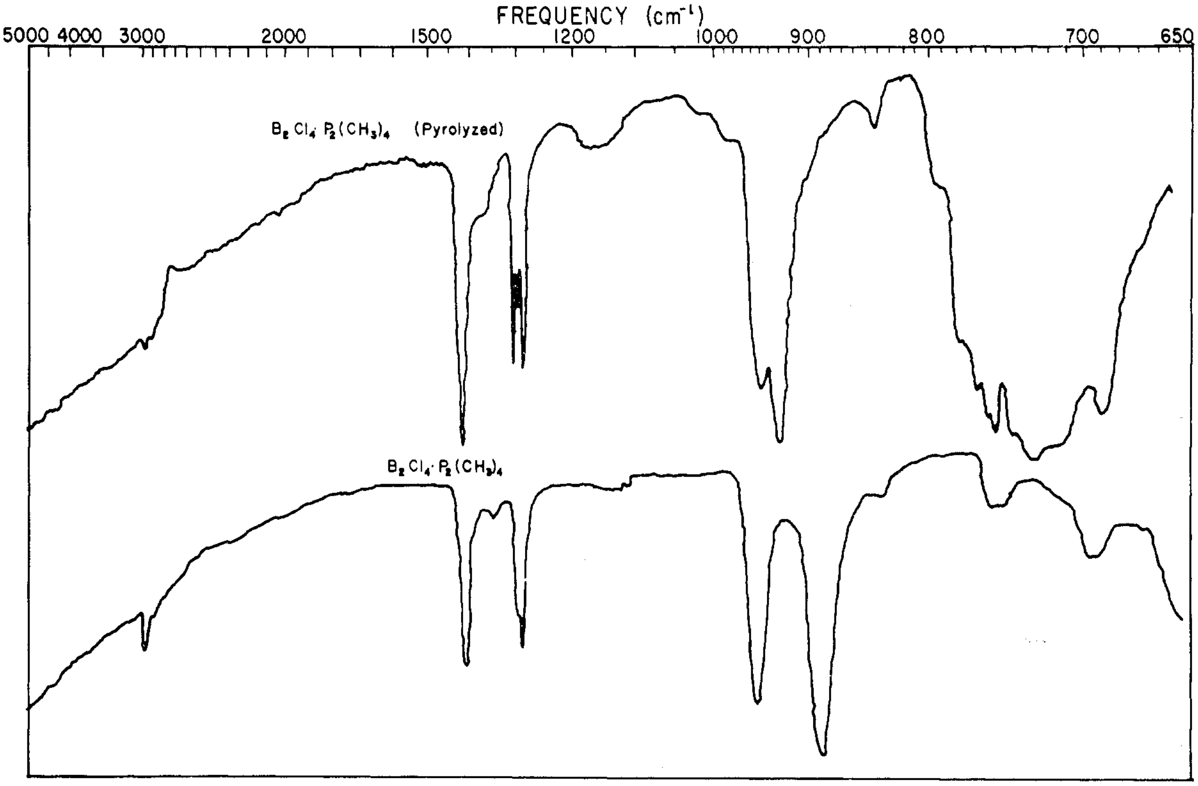

Fig. 2.—Comparison of infrared spectrum of $B_2Cl_4 \cdot P_2(CH_3)_4$ with that of its pyrolysis product.

trichloride is produced. The orange solid is different from the usual decomposition products of diboron tetrachloride since no part sublimes even at 200–300° *in vacuo*. In appearance this orange solid is similar to the product of the decomposition of tetrachlorodiphosphine.

Exposure of $B_2Cl_4 \cdot 2PCl_3$ to moist air results in copious white fumes but, unlike diboron tetrachloride, the complex is not spontaneously inflammable in air.

Treatment of Diboron Tetrachloride with P_2Cl_4.—In a qualitative experiment an unmeasured sample of tetrachlorodiphosphine containing a small amount of phosphorus trichloride was mixed with diboron tetrachloride at −23°. A small amount of $B_2Cl_4 \cdot 2PCl_3$ precipitated immediately. The mixture was separated into its components after being held at −23° for approximately 0.5 hr. Diboron tetrachloride and tetrachlorodiphosphine both were recovered unchanged. The reagents were returned to the reaction vessel and allowed to stand at 0° for 24 hr. During this period an orange solid similar to the typical product of the decomposition of P_2Cl_4 was formed. Fractionation of the volatile materials revealed more $B_2Cl_4 \cdot 2PCl_3$ along with some unchanged B_2Cl_4 and P_2Cl_4.

Reaction of Diboron Tetrachloride with $P_2(CH_3)_4$.—A sample of tetramethyldiphosphine (0.37 mmole) was distilled into a reaction vessel maintained at −196°. A slight excess of B_2Cl_4 (0.38 mmole) then was distilled into the reaction vessel so that it deposited upon the ring of solid $P_2(CH_3)_4$. The reaction system then was closed from the vacuum apparatus and placed in a bath maintained at −79°. As the reaction vessel warmed to −79° a reaction ensued so that a slight dusting of white solid was observed. The reaction mixture was allowed to stand at −79° overnight, then opened to the vacuum system and the material volatile at room temperature was removed. The volatile material was chiefly diboron tetrachloride containing a small amount of boron trichloride. The latter probably arises from slight decomposition of diboron tetrachloride caused by localized heating during complex formation. The vapor pressure of this mixture at −79° was 0.8 mm. and the total amount 0.01 mmole. Thus the complex contains 0.37 mmole of B_2Cl_4 and 0.37 mmole of $P_2(CH_3)_4$.

Ethanolysis of $B_2Cl_4 \cdot P_2(CH_3)_4$.—A total of 31.8 mmoles of absolute ethanol was added at −196° to a sample of the complex containing approximately 0.78 mmole of B_2Cl_4 and 0.78 mmole of tetramethyldiphosphine. The mixture thus obtained was allowed to warm to room temperature. A small amount of hydrogen was evolved immediately. After about 60 hr. at room temperature and an additional 36 hr. at temperatures ranging between room temperature and 70° a total of 0.67 mmole of hydrogen had been evolved. This amount corresponds to 86% of that expected from complete ethanolysis of the B–B bonds in the sample of $B_2Cl_4 \cdot P_2(CH_3)_4$ used. In addition to the hydrogen, hydrogen chloride, ethyl borate, ethyl chloride, and dimethylphosphonium chloride were identified among the volatile products of this ethanolysis.

Reaction of B_2Cl_4 $P_2(CH_3)_4$ with Trimethylamine.—A sample of the complex was prepared as previously described from 0.41 mmole of diboron tetrachloride and 0.41 mmole of tetramethyldiphosphine. A total of 3.69 mmoles of trimethylamine was added to the complex. In the reaction system used, this amount of amine was not sufficient for a liquid phase to be present. The mixture was allowed to stand at room temperature until no further decrease in trimethylamine pressure was noted. This occurred at the end of 12 days. The reaction vessel then was heated to 100° for a period of 12 hr. until no further decrease in trimethylamine pressure occurred at this temperature. At the end of this treatment a trace of tetramethyldiphosphine (0.04 mmole) and 3.28 mmoles of trimethylamine were recovered.

A white solid remained in the reaction vessel at this point. When this white solid was heated at 100° *in vacuo* for 10 hr., a small amount of $[B_2Cl_4\ 2N(CH_3)_3]_4$, identified by means of its 230° melting point[17] and infrared absorption spectrum, sublimed to cooler portions of the apparatus. There remained in the reaction vessel a white solid with a composition corresponding to $B_2Cl_4 \cdot P_2(CH_3)_4 \cdot N(CH_3)_3$ containing 0.37 mmole of amine, 0.37 mmole of tetramethyldiphosphine, and an amount of diboron tetrachloride estimated to be 0.37 mmole on the assumption that the amount of $[B_2Cl_4 \cdot 2N(CH_3)_3]_4$ which sublimed at 100° is equivalent in amount to the $P_2(CH_3)_4$ collected (0.04 mmole). The mixed complex melts at 180 ± 2° without noticeable decomposition and is alcoholyzed slowly at room temperature in the presence of ethanol.

Pyrolysis of $B_2Cl_4 \cdot P_2(CH_3)_4$.—A sample of the complex prepared from 0.37 mmole of diboron tetrachloride was heated in a sealed tube at 250° for a period of 10 hr. At this temperature a liquid was present in the tube. Upon cooling to 200° the mass solidified. The tube was cooled to room temperature and attached to the vacuum apparatus. No material volatile *in vacuo* at room temperature had been produced in the pyrolysis. The solid mass in the bottom of the pyrolysis tube then was heated to 185° *in vacuo*, at which temperature all of the solid sublimed and condensed as beautiful clear needle-like crystals on a cooler portion of the vacuum system. This crystalline solid dissolves readily in dry ethanol and can be recovered unchanged from this solution by removal of the alcohol *in vacuo*.[32] If the solution is heated to its boiling point a complex alcoholysis slowly occurs. Hydrogen, hydrogen chloride, ethyl borate, ethyl chloride, and dimethylphosphonium chloride were positively identified as the chief products of this alcoholysis.

The infrared absorption spectrum of this crystalline solid is compared with that of the initial complex in Fig. 2.

Treatment of the Pyrolysis Product with Trimethylamine.—A sample of $B_2Cl_4 \cdot P_2(CH_3)_4$ containing 0.20 mmole of B_2Cl_4 and 0.20 mmole of $P_2(CH_3)_4$ was heated in a sealed tube at 250° for several hours. The tube then was cooled and attached to the vacuum apparatus. The melt then was sublimed at 185° and deposited as small white needles. Trimethylamine vapor (5.1 mmoles) then was placed in contact with these white crystals. No change in pressure of trimethylamine was noted and after 8 hr. the entire amount of amine was recovered unchanged.

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[32] The ethanol solutions of the pyrolysis product were shown to conduct electric current in a qualitative experiment in which the conducting species were not identified.

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The Chemistry of the Boron Subhalides.
III. A Paramagnetic Boron Subchloride, $B_{12}Cl_{11}$[1]

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The main product of the spontaneous decomposition of diboron tetrachloride has been completely characterized as a free radical $B_{12}Cl_{11}$. Structural possibilities compatible with known properties are discussed. The reactions of $B_{12}Cl_{11}$ with water, ethanol, trimethylamine, and aluminum trimethyl are described. With alkaline water $B_{12}Cl_{11}$ hydrolyzes to form boron cage ions like $B_{10}Cl_8(OH)_2^{-2}$. In acidic hydrolysis more complete oxidation occurs. The main products of ethanolysis are hydrogen, hydrogen chloride, ethyl borate, ethyl chloride, and ethyl ether. Treatment of $B_{12}Cl_{11}$ in methylcyclohexane solution with trimethylamine produces a complex, $[B_{12}Cl_{11} \cdot 2N(CH_3)_3]_n$, which upon pyrolysis generates a small quantity of $BCl_3 \cdot N(CH_3)_3$, decomposing to a golden brown solid. Aluminum trimethyl reacts in a complex fashion with $B_{12}Cl_{11}$ producing, along with a non-volatile solid, trimethylborane, and a volatile red crystalline solid which contains aluminum, boron, chlorine, and methyl groups.

Introduction

The decomposition of diboron tetrachloride already has been described.[4] When the decomposition is carried out at temperatures in excess of 0°, boron trichloride is formed along with a small amount of tetraboron tetrachloride,[5,6] a moderate amount of a noncrystalline yellow solid slightly volatile *in vacuo* at room temperature, a small amount of a purple crystalline solid volatile at 45° *in vacuo*, a glassy red solid $(B_1Cl_{0.9})_x$,[4] volatile at 110° *in vacuo*, and a white non-volatile refractory solid, $(B_1Cl_{0.6})_x$.[4]

Atoji[7] recrystallized the glassy red $(B_1Cl_{0.9})_x$ from BCl_3 solution and obtained a product which was assumed to be the pure form of $(B_1Cl_{0.9})_x$. On the basis of an X-ray examination of this crystalline solid Jacobson and Lipscomb[8,9] reported the formula B_8Cl_8 and suggested a structure with boron atoms located at the apices of a distorted archimedian antiprism. To each boron a chlorine would be attached. The above model fails to account for the paramagnetism and intense color of the solid and suggests a formula which is well outside the experimental analytical values.

Qualitative experiments convinced us of the fact that the major constituent of the red subchloride $(B_1Cl_{0.9})_x$ was an odd electron molecule and we have expended considerable effort to obtain good quantitative data which would help us to characterize this free radical. This effort has consumed the major part of 5 years and was successful largely as a result of the development in this Laboratory of new techniques for handling reactive compounds volatile only at elevated temperatures. Impressive developments in other laboratories, namely the discovery of the very stable $B_{10}H_{10}^{-2}$

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