able 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.

CONTRIBUTION FROM THE RICHARD BENBRIDGE WETHERILL LABORATORY,
PURDUE UNIVERSITY, LAFAYETTE, INDIANA

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

BY EUGENE P. SCHRAM[2] AND GRANT URRY[3]

Received August 18, 1962

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 non-crystalline 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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[1] The work herein reported was supported in part by the National Cancer Institute of the Public Health Service under Grant No. CY-4382 and constituted a part of the Ph.D. thesis of Eugene P. Schram, Purdue University, June, 1962.

[2] Union Carbide Chemicals Company Fellow, 1961–1962.

[3] To whom inquiries concerning this publication should be addressed.

[4] G. Urry, T. Wartik, R. E. Moore, and H. I. Schlesinger, *J. Am. Chem. Soc.*, **76**, 5293 (1954).

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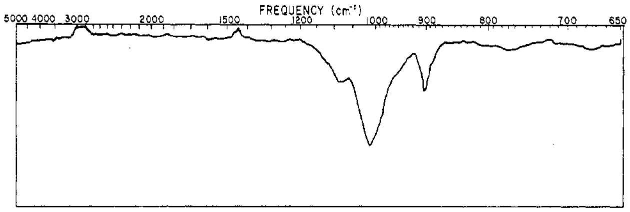

Fig. 1—Infrared spectrum of $B_{12}Cl_{11}$.

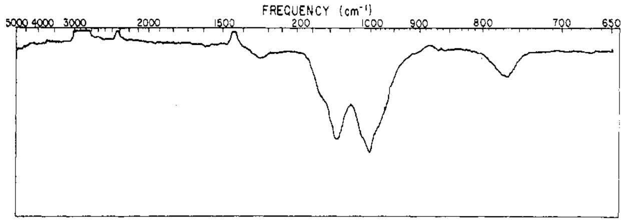

Fig. 2.—Infrared spectrum of purple subchloride.

and $B_{12}H_{12}^{-2}$ cage ions[10-12] and the chloro derivatives of these ions[12] equipped us to explain results obtained in chemical reactions of $(B_1Cl_{0.9})_x$, such as the alkaline hydrolysis, which previously had been very puzzling indeed.

Results and Discussion

In this study we found that the $(B_1Cl_{0.9})_x$ described in the original reference[4] consisted of a mixture containing about 95% of a paramagnetic red subchloride,[13] and about 5% of a purple paramagnetic subchloride[13] which so far has been obtained in quantities too small to allow a characterization. The relative amount of the purple subchloride formed is increased if the disproportionation of diboron tetrachloride is carrried out at temperatures near 70°. As yet, no real evidence for the B_8Cl_8 species reported by Lipscomb and co-workers has been detected. However, we have found that if a sample of the pure red subchloride is treated with boron trichloride a reaction occurs which apparently proceeds to an equilibrium. At equilibrium there is present, in addition to the starting materials, a brown solid insoluble in boron trichloride, a small amount of a yellow substance slightly volatile *in vacuo* at room temperature, and a small amount of the paramagnetic purple subchloride previously mentioned. It is possible that B_8Cl_8 may be found among the constituents of this equilibrium mixture which we have not yet examined.

The red subchloride was characterized by analysis and molecular weight determination, using the isopiestic method, as dodecaboron undecachloride, $B_{12}Cl_{11}$. Serious difficulties were encountered in the analysis, probably because of the formation of very stable boron cage ions.[10-12] While analyses gave boron to chlorine ratios very close to that of $B_{12}Cl_{11}$, material balances were defective by as much as 10–20%. After much work an analytical method was developed which gave good material balance and excellent reproducibility. This is described in detail in the Experimental part.

The new subchloride exhibits a broad intense paramagnetic resonance absorption centered at a *g*-value of 2.011 with a breadth of 25 gauss between points of extreme slope. Attempts to resolve the hyperfine structure of this resonance were unsuccessful. We have yet to perform a complete concentration study to determine the molar susceptibility but, to a first approximation, all of the dissolved material appears to be present as radicals.

The infrared absorption spectrum of $B_{12}Cl_{11}$ is simple in the NaCl region as shown in Fig. 1. The absorption at 1020 cm.$^{-1}$ is found in a similar position for most boron cage compounds.[10-12,14] The 910 cm.$^{-1}$ peak is similar to a strong absorption observed at 920 cm.$^{-1}$ in the case of diboron tetrachloride and has been ascribed to a B–Cl stretch.[15] There is no similar absorption in boron trichloride. There are some interesting differences between the infrared absorption spectrum of $B_{12}Cl_{11}$ and that of the paramagnetic purple subchloride previously mentioned. The latter spectrum is shown in Fig. 2. The $B_{12}Cl_{11}$ absorption at 910 cm.$^{-1}$ is not present in this spectrum and the weak $B_{12}Cl_{11}$ absorption at 765 cm.$^{-1}$ is considerably stronger here. This latter absorption probably is due to B–B stretch displaced somewhat from that observed at 746 cm.$^{-1}$ in the B_2Cl_4 spectrum.

We have studied a few chemical reactions of $B_{12}Cl_{11}$. The hydrolysis reaction has been in many ways the most difficult to understand. Diboron tetrachloride yields no hydrogen upon acid hydrolysis and is completely oxidized during hydrolysis. Acidic hydrolysis of tetraboron tetrachloride yields 3 moles of H_2 per mole of B_4Cl_4, while alkaline hydrolysis yields 4 moles of hydrogen. In contrast, the acidic hydrolysis of $B_{12}Cl_{11}$ proceeds more rapidly and produces more hydrogen than does the alkaline hydrolysis. In no case is the amount of hydrogen evolved upon hydrolysis that required by eq. 1 describing the complete oxidation of the boron subchloride.

$$2B_{12}Cl_{11} + 72H_2O \longrightarrow 22HCl + 24H_3BO_3 + 25H_2 \quad (1)$$

The most hydrogen evolved in any case was the amount obtained by acidic hydrolysis for a period of 27 days and was only 80% of that theoretically obtainable. The basic hydrolysis is more easily explained. The initial evolution of hydrogen is relatively rapid and the stoichiometry is that required by eq. 2.

$$2B_{12}Cl_{11} + 14OH^- = 2B_{10}Cl_8(OH)_2^{-2} + 4BO_2^- + 3H_2 + 6Cl^- + 2H_2O \quad (2)$$

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[11] W. N. Lipscomb, A. R. Pitochelli, and M. F. Hawthorne, *ibid.*, **81**, 5833 (1959).

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Addition of potassium or tetramethylammonium ion to the hydrolysis solution after the initial hydrogen evolution has ceased results in the precipitation of a potassium or tetramethylammonium salt. The infrared spectra of these salts are similar to those of the B_{10} cage ions already reported.[11-14]

It is possible that ions of a similar type also are formed in the acidic hydrolysis and are responsible for the incomplete evolution of hydrogen noted above

Upon treatment with trimethylamine at −79° the red color of a cyclopentane solution of $B_{12}Cl_{11}$ is discharged and a light tan solid, $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$, slowly precipitates. This complex when heated to 75° decomposes, forming $BCl_3\cdot N(CH_3)_3$ and a nonvolatile golden brown solid. Hydrolysis of $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$ proceeds at a much slower rate than the hydrolysis of the parent $B_{12}Cl_{11}$. The infrared absorption spectrum of this complex is shown in Fig. 3. It is of interest that the characteristic cage absorption is still present and that the absorption ascribed to B–Cl stretch in the BCl_2 group as well as that ascribed to the B–B bond have shifted to longer wave lengths, appearing at 850 and 720 cm.$^{-1}$, respectively. The intensity of the 720 cm.$^{-1}$ absorption also is increased over that of the corresponding peak in the spectrum of $B_{12}Cl_{11}$ itself.

It is possible that in the formation of the amine complex the free radical is no longer stabilized by delocalization and dimerization results. This would account for the discharge of the color as well as the increase in the infrared absorption ascribed to the B–B bond.

Ethanolysis of $B_{12}Cl_{11}$ produces, along with a small amount of ethyl borate, moderate amounts of hydrogen chloride, ethyl chloride, and diethyl ether. The major portion of the boron is retained in a residual golden brown solid. Treatment of the brown solid with aqueous potassium hydroxide resulted in a clear solution with very little evolution of hydrogen.

A similarly complex reaction occurs with aluminum trimethyl. Among the products of this reaction are methane, trimethylborane, a red solid volatile at room temperature, and a slightly yellow non-volatile solid. The volatile red solid was obtained in too small a quantity to characterize. The material hydrolyzes readily and a partial analysis thus was effected. The boron, chlorine, and methane produced upon hydrolysis were determined. On the basis of this partial analysis a rather interesting possibility is suggested. The B:Cl:CH_3 ratio in this compound is 3:4:8. Since the total of the Cl and methyl groups is 12 a suitable formula would be $AlB_3Cl_4(CH_3)_8$. If this material is a pure substance it thus would be one of the many possible methyl chloro analogs of aluminum borohydride. This possibility is being explored. Other interesting volatile materials are formed in the pyrolysis of the slightly yellow solid obtained as the principal product of the reaction of $B_{12}Cl_{11}$ with aluminum trimethyl. Some of the properties of the pyrolysis products are given in the Experimental portion of this paper. It is clear from even these fragmentary results that a study of the methylation of the boron cage chlorides such as $B_{12}Cl_{11}$ will be very fruitful.

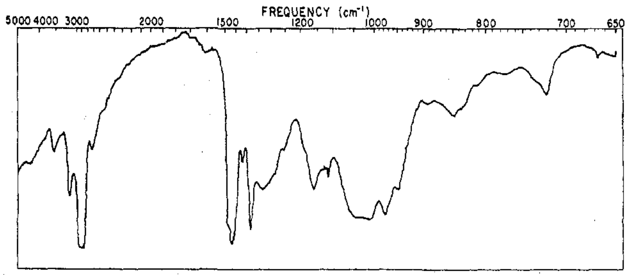

Fig. 3.—Infrared spectrum of $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$.

Pure dodecaboron undecachloride apparently does not react with nitric oxide nor with diboron tetrakisdimethylamide.

Concerning the paramagnetic purple subchloride[13] we have little to report. Most interesting to us is the paramagnetic resonance spectrum in which the hyperfine structure is resolvable. The *g*-value of 2.034 for this radical is very high and appears to indicate an even greater orbital contribution than in the case of $B_{12}Cl_{11}$.

On the basis of available evidence it is not possible to give an unequivocal structure for $B_{12}Cl_{11}$; however, several tentative models can be considered. A model based on a modification of the known icosahedral $B_{12}H_{12}^{-2}$ has been rejected on the basis that $B_{12}Cl_{11}$ would not be a closed shell structure[11,12] and that one terminal position would, of necessity, be occupied by an odd electron or an electron pair. The properties of $B_{12}Cl_{11}$ are not well described by such assumptions.

On the other hand, the results for the alkaline hydrolysis of $B_{12}Cl_{11}$ suggest that a structure based upon the known B_{10} cage of $B_{10}H_{10}^{-2}$ might be appropriate. In such a model 10 boron atoms would be arranged in the form of the known B_{10} cage and 8 chlorine atoms would be attached by σ-bonds to the non-apical positions. One BCl_2 group would be bonded by a σ-bond to one apical position and one BCl group double-bonded to the other apical position. The use of apical positions for the BCl and BCl_2 groups follows from symmetry arguments. Such a model would have a closed shell structure with one of the bonding orbitals occupied by the odd electron. Delocalization of electrons in the boron cage would contribute to the stability of this radical.

The reaction of $B_{12}Cl_{11}$ with trimethylamine to form $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$ can be rationalized on the basis of such a structure since only the borons external to the B_{10} cage could complex with the amine. Furthermore, the discharge of the intense color of $B_{12}Cl_{11}$ which accompanies the formation of the amine complex could be accounted for since the addition of a trimethylamine to the doubly bonded BCl group would serve to disrupt the double bond to cage resonance and would act to localize the odd electron at this boron. Under these conditions one would expect a radical dimer to result. We have yet to study the $[B_{12}Cl_{11}\cdot$

$2N(CH_3)_2]_n$ to determine whether it is paramagnetic as a test of this dimerization hypothesis. It also is interesting in this connection to note the changes which occur in the infrared absorption spectrum of $B_{12}Cl_{11}$ upon formation of the trimethylamine complex. The absorption at 910 cm.$^{-1}$ is a characteristic frequency of the BCl_2 group, and the absorption at 765 cm.$^{-1}$ is a characteristic frequency of a B–B stretch in diboron tetrachloride.[15] In the amine complex these two absorptions are observed at 850 and 720 cm.$^{-1}$, respectively. The relative intensity of the absorption due to the B–B bond also is greater in the amine complex than in the parent $B_{12}Cl_{11}$. The shift of these absorptions to longer wave lengths is similar to the changes which occur in the infrared spectrum of boron trichloride upon complex formation with trimethylamine.[16]

We are continuing our study of the products of the spontaneous decomposition of diboron tetrachloride, particularly the characterizations of the purple paramagnetic subchloride and the low volatile yellow solid.

Experimental

Apparatus and Experimental Methods.—All of the reactions reported in the present work were carried out in apparatus similar to that described in the literature.[17] Special methods developed for studying specific reactions will be discussed in detail in a subsequent section.

Analytical Methods.—**Boron analyses** were carried out volumetrically with a Fisher titrimeter, Model 36, fitted with a modified delivery tip such that the effective response of the titrimeter was increased, resulting in increment control of 0.01 ± 0.005 ml. of titrant. A sample containing 2 to 3 mmoles of boron was mixed with 0.5 g. of sodium carbonate in a platinum dish and the mixture heated at 450° for 4 hr. The resulting solid was treated with concentrated hydrochloric acid until a pH of 1 was obtained. The solution then was washed into a 200-ml. Berzelius beaker. Carbon dioxide was expelled from the solution by heating it at 80° for 5 hr. During this time, nitrogen was bubbled through the solution to aid the carbon dioxide expulsion. Next, the pH was adjusted to 3 with sodium hydroxide pellets and dilute hydrochloric acid. Carbon dioxide again was expelled from the solution for 3 hr. The sample was diluted to 80 ml. with distilled water, free from CO_2, and adjusted to a pH of 4.5. Boric acid was determined by a standard titration.

Chloride analyses were effected on solutions obtained by a treatment similar to that just described. In this case the sodium carbonate fusion mixture was dissolved in acetic acid instead of hydrochloric acid. Chloride ion was determined by a standard potentiometric titration.

Reagents.—**Aluminum trimethyl** obtained from the Ethyl Corp., New York, N. Y., was purified by distillation through U-tube traps maintained at 0, −23, and −196°. The procedure was repeated until the fraction retained at −23° exhibited a 0° vapor tension of 8.8 mm. **Azobenzene**, pure, obtained from Eastman Organic Chemicals, Rochester, N. Y., was used without further purification. **Boron trichloride** was purified by repeated vacuum distillation through a series of U-tube traps maintained at −79, −112, and −196° until the portion retained at −112° exhibited a −79° vapor tension of 4 mm. and a 0° vapor tension of 477 mm., a good indication of purity. **Cyclopentane**, obtained from Phillips Petroleum Company, Bartlesville, Okla., was dried over solid calcium hydride for several hours and purified by vacuum distillation through traps maintained at −63, −79, and −196°. The fraction retained at −79° was assumed to be pure since its 0° vapor tension of 107 mm. was in good agreement with previously reported values. **Diboron tetrachloride** was prepared by mercury arc reduction of boron trichloride vapor and purified as previously reported.[4] **Ethanol**, absolute, was distilled from solid calcium hydride through a −23° U-tube trap into one maintained at −45°. The fraction retained at −45° exhibited a 0° vapor tension of 12.0 mm. and was assumed to be pure. **Methylcyclohexane**, obtained from Phillips Petroleum Company, was dried by storage for several days over solid calcium hydride and further purified before use by vacuum distillation through traps maintained at 0, −45, and −196°. The fraction retained at −45° exhibited the proper 0° vapor tension for pure methylcyclohexane, namely, 12.0 mm. **Trimethylamine**, obtained from the Matheson Company, Joliet, Ill., was further purified by repeated vacuum distillation through a series of U-tube traps held at −95, −112, and −196°. The material retained at −112° was assumed to be pure trimethylamine when it exhibited a −79° vapor tension of 6.6 mm.

Preparation and Purification of $B_{12}Cl_{11}$.—In a typical preparation approximately 2 ml. of liquid diboron tetrachloride was sealed into an evacuated ampoule equipped with a standard break-off seal. The diboron tetrachloride then was heated at 60° for 24 hr. After this treatment the ampoule was attached to the vacuum system, opened, and the material volatile at room temperature *in vacuo* removed. Approximately 2 ml. of liquid cyclopentane then was distilled onto the solid brown residue in the ampoule. The resulting cyclopentane solution was filtered and the solvent removed from the filtrate. All of these procedures were managed *in vacuo* by means of apparatus assembled from O-ring sealed joints. The residue left by evaporation of cyclopentane from the filtrate then was heated at 45° *in vacuo* for 24 hr. During this treatment a small amount of the paramagnetic purple subchloride (estimated visually as less than 5% of the total) sublimed away, leaving a red solid which proved to be pure $B_{12}Cl_{11}$.

Physical Properties of $B_{12}Cl_{11}$.—The red solid $B_{12}Cl_{11}$ sublimes *in vacuo* at 110° with little decomposition. It is soluble in most alkanes and cycloalkanes, benzene, boron trichloride, and methylene chloride. Solutions in the last three solvents undergo chemical changes and so these are not satisfactorily inert toward $B_{12}Cl_{11}$ for use. The reaction with boron trichloride has been studied qualitatively and is described later. Dodecaboron undecachloride melts with slight decomposition at 115 ± 1°. A trace of boron trichloride is evolved during melting.

Molecular Weight and Analysis of $B_{12}Cl_{11}$.—A sample of $B_{12}Cl_{11}$ prepared in the manner described and contained in a bulb of known weight fitted with a break-off seal was weighed and then attached to an isopiestic molecular weight apparatus containing a weighed sample of pure azobenzene. The apparatus then was evacuated and a measured amount of cyclopentane was distilled in. The break-off seal confining the weighed sample of $B_{12}Cl_{11}$ then was opened and the cyclopentane allowed to equilibrate at room temperature between the azobenzene and the $B_{12}Cl_{11}$ for a period of 2 weeks. The two solutions thus obtained then were examined and the concentration of each determined by removal and measurement of the solvent. The solvent cyclopentane then was returned to each solution and the solutions were allowed to equilibrate again at room temperature for 3 days. The concentrations of the solutions again were determined and found to be identical with the concentrations determined earlier. The results of several such experiments using different concentrations of $B_{12}Cl_{11}$ are shown in Table I.

Analyses of samples weighing 0.0511 and 0.1440 g., respectively, gave these results. Found for the 0.0511-g. sample: B, 24.3; Cl, 73.9; Cl/B, 0.922. Found for the 0.1440-g. sample: B, 24.7; Cl, 74.4; Cl/B, 0.918. Calcd for $C_{12}Cl_{11}$: B, 24.9; Cl, 75.1; Cl/B, 0.916.

Paramagnetism of $B_{12}Cl_{11}$.—A cyclopentane solution of $B_{12}Cl_{11}$

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[16] W. Kynaston, B. E. Larcombe, and H. S. Turner, *J. Chem. Soc.*, 1772 (1960).

[17] R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley and Sons, New York, N. Y., 1949.

TABLE I

APPARENT MOLECULAR WEIGHT OF $B_{12}Cl_{11}$ IN CYCLOPENTANE SOLUTION

Mole % $B_{12}Cl_{11}$ at equil.	App. mol. wt.[a]
0.71	536
1.04	511
1.07	516
1.24	517

[a] Calculated for $B_{12}Cl_{11}$: 520.1.

was prepared in an ampoule arranged for volumetric distillation for obtaining different concentrations and fitted with a suitable tube for placement in the spectrometer probe. The instrument used was a 10,000 Mc. spectrometer designed and built by Dr. Jonathan Townsend of Washington University, St. Louis, Mo. The resonance spectrum was observed at various concentrations down to temperatures as low as −100° using several combinations of field modulation and sweep in an unsuccessful effort to resolve the hyperfine structures. At all concentrations these solutions exhibited a paramagnetic resonance absorption with a *g*-value of 2.011 and a breadth of approximately 25 gauss between points of extreme slope.

Infrared Absorption Spectrum of $B_{12}Cl_{11}$.—The absorption spectrum of a cyclopentane solution of $B_{12}Cl_{11}$ was obtained using matched 0.1-mm. cells in a Perkin–Elmer Model 221 spectrometer with NaCl optics. This spectrum is shown in Fig. 1.

Visible and Ultraviolet Absorption Spectrum of $B_{12}Cl_{11}$.—The spectrum of a cyclopentane solution of $B_{12}Cl_{11}$ in the region from 290 to 700 mμ was obtained using a Bausch and Lomb Spectronic 505 spectrometer. The spectrum consisted of a strong band at 420 mμ and a shoulder at 310 mμ. $B_{12}Cl_{11}$ apparently absorbs very strongly below 290 mμ.

Nuclear Magnetic Resonance Spectrum of $B_{12}Cl_{11}$.—An attempt was made to obtain the B^{11} spectrum of a saturated solution of $B_{12}Cl_{11}$ in cyclopentane. The B^{11} resonance was observed at a very low signal-to-noise ratio and valid conclusions concerning structure could not be reached on the basis of these spectra.

Reaction of $B_{12}Cl_{11}$ with Boron Trichloride.—A sample of pure $B_{12}Cl_{11}$ weighing 0.2000 g. (0.384 mmole) was dissolved in 16.69 mmoles of pure boron trichloride. The resulting solution was allowed to stand at 0° for a period of 9 days. At the end of this period it was noted that a brown solid had precipitated from the previously clear solution and a yellow solid coated all parts of the reaction system. The material readily volatile *in vacuo* at room temperature then was removed and found to be 16.58 mmoles of pure boron trichloride. The yellow material previously mentioned was found to be very slightly volatile at room temperature but the construction of the reaction system did not allow us to do anything further to characterize this material. The residue from the solution was heated to 45° and a small amount of a purple crystalline solid, presumably the paramagnetic substance already described, sublimed to the cooler portions of the apparatus. The residue at this point was heated to 110° and some $B_{12}Cl_{11}$ sublimed away, leaving a brown solid in the reaction tube.

Acidic Hydrolysis of $B_{12}Cl_{11}$.—Dodecaboron undecachloride weighing 0.1440 g. (0.277 mmole) was treated with approximately 2 ml. of degassed water. Because of immediate partial hydrolysis of the exposed B–Cl bonds the solution was acidic. Hydrogen evolved slowly during a long period of time was collected periodically.[18] The results of this hydrolysis are summarized in Table II.

TABLE II

ACID HYDROLYSIS OF $B_{12}Cl_{11}$

Hydrolysis temp., °C.	Total period of hydrolysis, days	Total H_2 collected, mmoles	moles H_2/mole $B_{12}Cl_{11}$
25	6	2.06	7.45
25	9	2.21	7.95
25	12	2.31	8.34
25	14	2.36	8.50
25	21	2.45	8.84
80	27	2.50	9.02
80	29	2.61	9.42
80	32	2.66	9.61
80	44	2.70	9.74

Alkaline Hydrolysis of $B_{12}Cl_{11}$.—A sample of the red subchloride weighing 0.1408 g. (0.271 mmole) was treated with a large excess of degassed aqueous potassium hydroxide solution. The hydrogen evolved at room temperature was collected periodically for 10 days, at which time the rate of evolution was very slow. The temperature of the hydrolysis system then was raised to 80°. For the next 18 days the rate of hydrogen evolution gradually decreased. The results of the hydrolysis are summarized in Table III.

TABLE III

ALKALINE HYDROLYSIS OF $B_{12}Cl_{11}$

Hydrolysis temp., °C.	Total period of hydrolysis, days	Total H_2 collected, mmoles	moles H_2/mole $B_{12}Cl_{11}$
25	0.3	0.137	0.508
25	1.0	.147	.544
25	2.0	.231	.855
25	4.0	.270	.997
25	10.0	.328	1.213
80	13.0	.392	1.450
80	16.0	.418	1.548
80	28.0	.597	2.210

In another such hydrolysis carried out only at room temperature there also appeared to be two definite changes in rate of hydrogen evolution. One occurred when approximately 0.5 mole of hydrogen per mole of initial $B_{12}Cl_{11}$ had been evolved and the other when approximately 1.5 moles of hydrogen had been evolved.

During the hydrolysis effected with potassium hydroxide a crystalline solid slowly precipitates. When sodium hydroxide was used no such precipitate was noted but addition of concentrated potassium chloride or tetramethylammonium chloride to the sodium hydroxide solutions resulted in the formation of the same kind of crystalline precipitates. The infrared absorption spectrum in Nujol and fluorolube mulls of these potassium and tetramethylammonium salts display the characteristic boron cage absorption at 1030 cm.$^{-1}$.

Reaction of $B_{12}Cl_{11}$ with Trimethylamine.—A solution containing 20.42 mmoles of methylcyclohexane and 0.2801 g. (0.539 mmole) of $B_{12}Cl_{11}$ was cooled to −79° and treated with 3.88 mmoles of trimethylamine vapor.

Over a period of several hours at this temperature the red color of the solution was discharged and a light tan solid precipitated. When there was no further evidence of reaction the solution was allowed to warm to room temperature. The material volatile at room temperature was removed at this point and found to be a mixture of 20.40 mmoles of methylcyclohexane and 2.67 mmoles of trimethylamine. Thus the ratio of moles of trimethylamine consumed in the reaction to moles of initial $B_{12}Cl_{11}$ is 2.24 to 1. This ratio probably is high due to entrapment of some trimethylamine in the tan solid. This particular sample of the amine adduct was treated with degassed water and allowed to hydrolyze for 41 days at room temperature followed by an additional 11 days at 80°. The rate of hydrogen evolution is summarized in Table IV.

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(18) In all experiments where evolved hydrogen was collected over extended periods of time the gas collected was converted to water by circulation over copper oxide at 300° in order to be sure that all of the noncondensable material was hydrogen. This procedure would detect any noncondensable material which resulted from leakage in the vacuum system.

TABLE IV

HYDROLYSIS OF $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$

Hydrolysis temp., °C.	Total period of hydrolysis, days	Total H_2 collected, mmoles	moles H_2/mole of initial $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]_n$
25	13	2.095	3.76
25	20	2.548	4.72
25	36	2.860	5.31
25	41	3.133	5.72
80	52	4.589	8.25

At the end of the hydrolysis period a small amount of a white precipitate was present. The amount of white solid was too small to allow us to examine the infrared absorption spectrum. However, if we assume that the complete hydrolysis proceeds according to eq. 3

$$2[B_{12}Cl_{11}\cdot 2N(CH_3)_3] + 72H_2O = 2N(CH_3)_3\cdot HCl + 20HCl + 24H_3BO_3 + 25H_2 \quad (3)$$

and that an incomplete hydrolysis also proceeds according to eq. 4

$$2[B_{12}Cl_{11}\cdot 2N(CH_3)_3] + 16H_2O = 2(N(CH_3)_3H)_2B_{10}Cl_8(OH)_2 + 4H_3BO_3 + 6HCl + 3H_2 \quad (4)$$

We can estimate from the total hydrogen evolved after 52 days that 64% of the amine adduct reacts according to eq. 3 and 36% reacts according to eq. 4. If such assumptions are correct we would expect to obtain in the hydrolysis of the 0.539-mmole sample of the amine adduct a total of 4.38 mmoles of free Cl^-, 3.80 mmoles coming from the complete hydrolysis of 64% of the sample and 0.58 mmole coming from the 36% which reacted according to eq. 4. A total of 4.65 ± 0.10 mmoles of free Cl^- was found in the hydrolysis solution. This can be seen to be in good agreement with the predictions of the above hypothesis considering the fact that the total evolved H_2, used in the estimation of the relative importance of reactions 3 and 4, was the sum of five volume measurements involving five separate combustions.[18]

Another sample of $[B_{12}Cl_{11}\cdot 2N(CH_3)_3]$ prepared as before from 0.2928 g. (0.563 mmole) of $B_{12}Cl_{11}$ was gradually heated to approximately 200°. Below 50° some trimethylamine was evolved with no apparent change in the tan solid, indicating the presence of a small amount of adsorbed amine. Between 50 and 75° the tan solid began to darken slowly and white crystals sublimed to cooler portions of the apparatus. The rate of formation of the volatile crystals increased as the temperature was raised and no further crystals sublimed when the temperature reached 200°. There remained in addition to the white crystals a dark golden brown solid. The white crystals were identified as $(CH_3)_3NBCl_3$ by melting point and chloride analysis. A total of 0.0290 g. (0.165 mmole) of $(CH_3)_3NBCl_3$ was formed in this pyrolysis. These pyrolysis results do not lend themselves to any simple stoichiometric rationalization.

Ethanolysis of $B_{12}Cl_{11}$.—Ethanol (4.74 mmoles) was distilled onto a 0.0533-g. (0.102-mmole) sample of $B_{12}Cl_{11}$ maintained at −79°. The resulting mixture then was allowed to warm slowly. At an undetermined temperature well below 0° an exothermic reaction ensued as indicated by a vigorous refluxing of the solution. After this reaction apparently had ceased the material volatile at room temperature was removed. The products were separated using standard vacuum techniques where possible and vapor phase chromatography for the remainder. The various fractions were identified by vapor pressure measurements and the infrared absorption spectra. The identified products and the amounts were: H_2, 0.51 mmole; HCl, 0.45 mmole; $B(OC_2H_5)_3$, 0.06 mmole; C_2H_5Cl, 0.2 mmole; $(C_2H_5)_2O$, 0.35 mmole.

A golden brown solid residue remained in the reaction vessel. Treatment of this residue with aqueous potassium hydroxide for a period of 8 hr. at room temperature yielded an additional 0.04 mmole of hydrogen. The hydrolysis solution was found to contain only 0.22 mmole of free Cl^- ion.

Treatment of $B_{12}Cl_{11}$ with Aluminum Trimethyl.—A cyclopentane solution of 0.4196 g. (0.807 mmole) of $B_{12}Cl_{11}$ was cooled to −79° and treated with approximately 1 g. of aluminum trimethyl. The mixture thus obtained was allowed to warm slowly. During the warming period a moderate reaction occurred accompanied by the formation of a yellow-white precipitate and a gentle refluxing of the cyclopentane. The reaction had ceased by the time the vessel had warmed to room temperature. The material volatile at room temperature was removed and separated into its constituents. In addition to the solvent cyclopentane 1.09 mmoles of trimethylborane was found along with a small quantity of a volatile red crystalline solid. Treatment of this red solid with water resulted in the evolution of 0.0896 mmole of methane. The remaining solution contained 0.038 mmole of boron and 0.048 mmole of Cl^- ion.

A yellow-white solid residue was left in the reaction vessel. When this material was pyrolyzed at about 75° a small amount of white solid tentatively identified as one of the methylaluminum chlorides sublimed along with a red crystalline solid. This red solid is volatile *in vacuo* at 35° and undergoes a reversible color change to a yellow microcrystalline solid at 80°. It is soluble in cyclopentane, giving a bright red solution from which it can be recovered unchanged. Treatment of this red solid with water resulted in the evolution of 0.017 mmole of hydrogen. The resulting hydrolysis solution reduced silver ion and was found to contain 0.036 mmole of boron and 0.046 mmole of Cl^- ion.