

neither of the two species in question was present in the solid in appreciable amounts.

The assignments in Table I are taken from the paper on the infrared spectrum of the solid.² In view of the fact that the crystal structure of solid perchloric acid is not known, there appears to be no point in making a detailed discussion and comparison of the Raman and infrared results. One interesting difference, however, is that the strong Raman band at 740 cm^{-1} was observed² only as a partly resolved shoulder on a more intense infrared band at 760 cm^{-1} . No indication of the latter band was observed in the Raman spectrum. The molecular motion involved presumably corresponds to the breathing frequency of the ClO_4^- ion so that only one fundamental of the molecule is to be expected in this region. It is possible that the overtone of the infrared band at 371 cm^{-1} is involved and is causing two bands to appear. However, the intensity ratio of the two infrared peaks is reversed from what one would expect if the Raman band is the fundamental and the full explanation is not immediately apparent. The bands in the neighborhood of 550 cm^{-1} in the infrared spectrum presumably derive from the triply degenerate deformation modes of the ClO_4^- ion. Although individual lines were not resolved in this region of the Raman spectrum, the band listed at 585 cm^{-1} was rather broad, suggesting the presence of unresolved components.

The failure to detect spectroscopically the presence of either Cl_2O_7 or H_3OClO_4 , together with the excellent agreement between the Raman lines of the solid and liquid perchloric acid, serves as excellent evidence that the interpretation of the phase diagram proposed by Zinov'ev and Rosolovskii is in error. In seeking reasons for their apparent misinterpretation, it can be noted that these workers analyzed their samples titrimetrically. In this region of the phase diagram, the composition in terms of mole per cent is quite sensitive to small errors in the weight per cent. This fact, together with the observation that the data points near the 1:1 composition were not numerous, makes it probable that the true nature of the diagram in this region was not delineated. A more detailed investigation appears desirable to clarify the situation.

Acknowledgment.—The authors wish to express their gratitude to the National Science Foundation for financial support of this investigation.

CONTRIBUTION FROM THE RESEARCH LABORATORIES
OF THE STAUFFER-AERCJET CHEMICAL CO.,
RICHMOND 4, CALIFORNIA

On the Properties of Monochlorodiborane

By HULON W. MYERS AND ROY F. PUTNAM

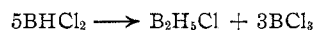
Received December 17, 1962

Preparation of diborane by the hydrogen reduction of

boron trichloride proceeds through the formation of chloroboranes.¹⁻³ Separation of these reactive intermediates from synthesis mixtures, however, is extremely difficult by conventional vacuum-line fractionation. As a result, the successful isolation of chloroboranes has been reported only twice,^{4,5} and little knowledge exists relative to properties of the pure compounds.

By using low temperature gas chromatography techniques, we recently have resolved two major intermediates in the diborane synthesis, BHCl_2 and $\text{B}_2\text{H}_5\text{Cl}$.⁶ In the present investigation, preparative gas chromatography methods were employed to obtain sufficient quantities of monochlorodiborane for physical measurements and chemical reactivity studies. Contrary to all previous indications, we have found the pure compound to be comparatively stable. No detectable decomposition occurred at 25° in a 1-hr. period for samples maintained at pressures less than 300 mm. Samples stored at 0° were unchanged after 8 hr.

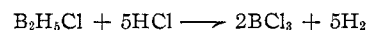
With quantities of purified $\text{B}_2\text{H}_5\text{Cl}$ available, it has been possible to establish the sequence in dichloroborane disproportionation at 30° to proceed from BHCl_2 through $\text{B}_2\text{H}_5\text{Cl}$ to B_2H_6 . The initial step



has not been reported previously. This reaction is easily reversible and can be made to go completely to the left when a large excess of liquid BCl_3 is present. Although no unidentified peaks appeared in the gas chromatograms or infrared spectra, it is unlikely that the reaction could proceed without the formation of other, short-lived, intermediates.

During disproportionation of $\text{B}_2\text{H}_5\text{Cl}$ (to B_2H_6 and BCl_3) at 35° under 1 atm. of nitrogen, the secondary reaction of BCl_3 with unreacted $\text{B}_2\text{H}_5\text{Cl}$ leads to the presence of BHCl_2 in the final mixture. The reaction is extremely slow, reaching equilibrium only after 70 hr. In the presence of finely divided B_2O_3 , however, the rate of $\text{B}_2\text{H}_5\text{Cl}$ disproportionation is greatly increased. The products of this reaction are B_2H_6 and a substance sorbed on the B_2O_3 [probably of the general formula $(\text{BOCl})_x$]⁷ that gives off BCl_3 when heated under vacuum.

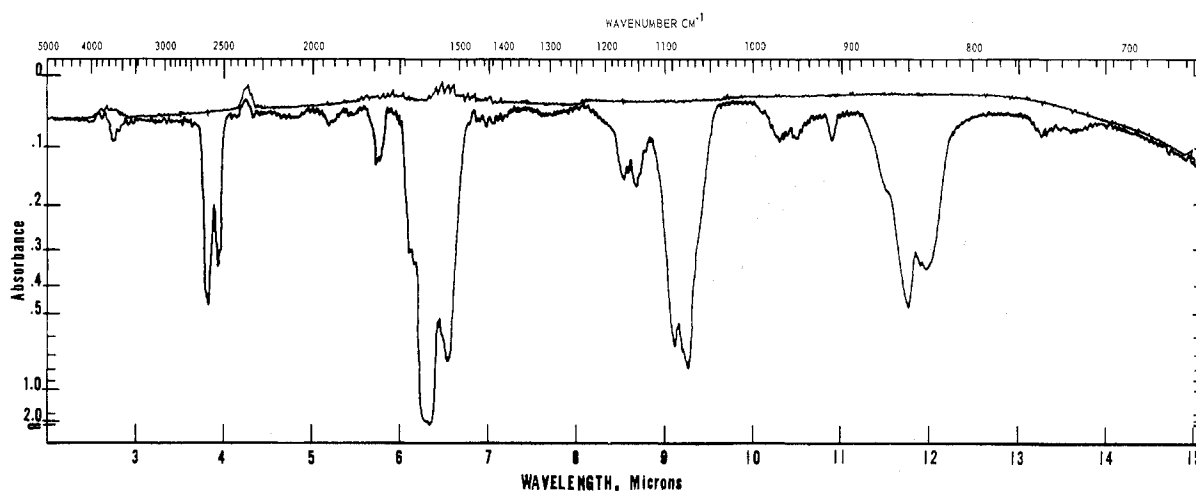
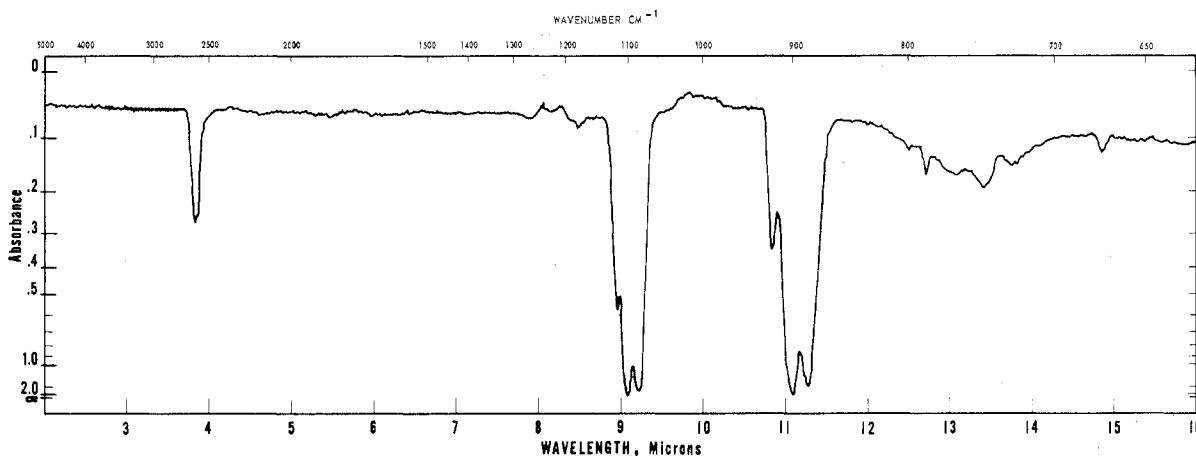
Monochlorodiborane reacts rapidly with HCl in the vapor phase at 25° . With a relatively large mole ratio of $\text{HCl}/\text{B}_2\text{H}_5\text{Cl}$, the reaction is quantitative



When HCl was added to $\text{B}_2\text{H}_5\text{Cl}$ in small increments, conversion to BHCl_2 was observed to be an intermediate step in the reaction.

Vapor pressure measurements of $\text{B}_2\text{H}_5\text{Cl}$ are recorded in Table I. The calculated values were obtained from

- (1) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).
- (2) D. T. Hurd, *ibid.*, **71**, 20 (1948).
- (3) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933, p. 51.
- (4) A. B. Burg, *J. Am. Chem. Soc.*, **56**, 499 (1934).
- (5) L. Lynds and D. R. Stern, *ibid.*, **81**, 5006 (1959).
- (6) H. W. Myers and R. F. Putnam, *Anal. Chem.*, **34**, 664 (1962).
- (7) J. Goubeau and H. Keller, *Z. anorg. allgem. Chem.*, **265**, 73 (1951).

Fig. 1.—Infrared spectrum of B_2H_5Cl .Fig. 2.—Infrared spectrum of $BHCl_2$.

the equation $\log p = 7.412 - (1188/T)$. Extrapolation of these data gave the normal boiling point to be -11.0° .

Melting point determinations for two different samples gave average readings of $-143.1^\circ \pm 0.8$ and $-143.7^\circ \pm 0.6$, compared to Burg's⁴ value of -142.0° .

Monochlorodiborane exhibits the infrared absorption spectrum shown in Fig. 1.

Experimental

The relatively standard high-vacuum system was constructed entirely of borosilicate glass, mercury, and stainless steel. The system included a Toepler pump for circulating samples over fractionation traps or for collecting gases in known volumes. A section was provided for quantitative aqueous hydrolysis and measurement of the resulting products: H_2 , $B(OH)_3$, and HCl . Direct connections were made from the vacuum system and reaction chambers to gas cells positioned on the infrared spectrophotometer and to the inlet and exit of a low-temperature gas chromatographic unit. By employing standard vacuum techniques,⁸ all transfer operations were made with strict exclusion of

oxygen and moisture. The analytical gas partition columns used in this study were described previously.⁶

To prevent errors from pressure effects in the infrared studies, calibration mixtures and unknown gases were analyzed at the same total pressure.

Vapor pressure measurements were made in a relatively standard 5-ml. isoteniscope and the melting point was determined by Stock's magnetic method. Temperatures were controlled with appropriate slush baths and measured with conventional vapor pressure thermometers.

Materials.—Electrolytic grade hydrogen (Matheson) was used without further purification. The other gases were twice distilled under reduced pressure: **diborane** (Olin Mathieson), v.p. 228 mm. at -111.4° ; **boron trichloride** (Stauffer), v.p. 471 mm. at 0° ; **hydrogen chloride** (Matheson), v.p. 126 mm. at -111.0° . The **boric oxide** (Baker) was ground and sieved within a drybox. The 100 mesh fraction was collected and heated at 100° for 3 hr. under high vacuum.

Preparation of B_2H_5Cl .—An equimolar mixture of B_2H_6 and HCl (0.461 mole at a total pressure of 11,800 mm.) was stored at 35° within a stainless steel chamber. After 17 hr., 1.46% (mole) B_2H_5Cl and 2.27% H_2 were present in the mixture. After 35 hr., no HCl was detectable: $B_2H_5Cl = 6.7\%$, $BHCl_2 = 3.6\%$, $BCl_3 = 9.4\%$, $B_2H_6 = 32.1\%$, and $H_2 = 47.8\%$. The H_2 was removed by evacuation at -195° . The gas chromatography column used to resolve the resulting mixture consisted of

TABLE I

t , $^\circ C$.	-97.7	-78.2	-58.0	-22.3
p (obsd.), mm.	4.9	20.3	79.4	475.2
p (calcd.), mm.	4.4	20.9	78.0	475.3

(8) R. T. Sanderson, "Vacuum Manipulation of Volatile Compounds," John Wiley & Sons, Inc., New York, N. Y., 1948.

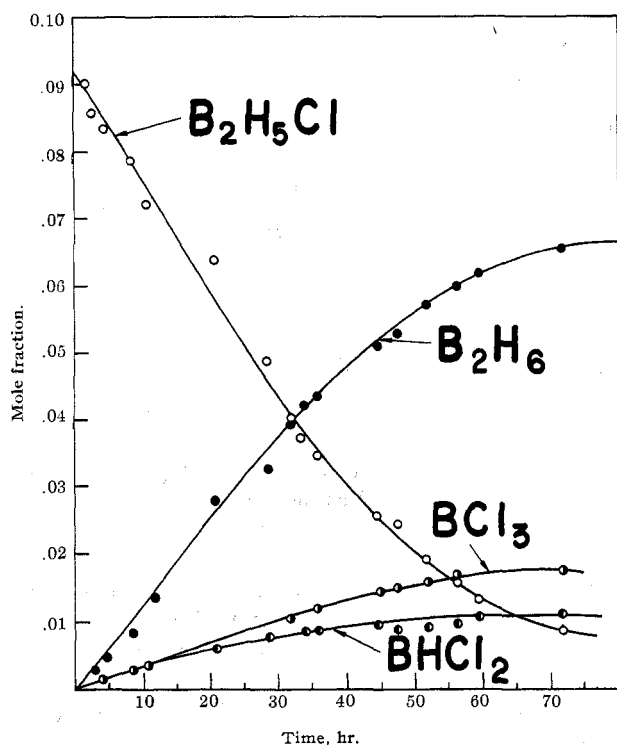


Fig. 3.—Decomposition of monochlorodiborane in nitrogen at 35°.

a 33 ft. $\times$ 0.25 in. stainless steel tube, containing 60–80 mesh firebrick coated with 20% (wt.) silicone oil (Dow Corning No. 703). With the column maintained at 0° and a 100 ml./min. He flow, B_2H_5Cl emerged as a pure fraction at 22.5 min. By using numerous samples of the mixture, quantities were selectively trapped in a section of the vacuum line at liquid nitrogen temperature. By infrared analysis, no traces of B_2H_6 , BCl_3 , or $BHCl_2$ were detected in the collected fractions.

Anal. Calcd. for B_2H_5Cl : B, 34.8; H, 8.1; Cl, 57.1. Found: B, 34.0; H, 8.4; Cl, 56.7.

Based on PVT measurements at 25°, a molecular weight corresponding to 60.5 was found (calculated = 62.1).

The infrared spectrum for monochlorodiborane at 8.8 mm. is given in Fig. 1. The cell path length was 10 cm. and the temperature was 25°.

Preparation of $BHCl_2$.—Preheated streams of H_2 and BCl_3 (in a 1:1 mole ratio) were passed through a quartz tube maintained at 900°. With a retention time of 1.7 sec., a 17% conversion of BCl_3 occurred to give a $BHCl_2$ yield of 97.3%. No traces of B_2H_5Cl , B_2H_6 , or B_2Cl_4 were present in the gaseous product mixture. By condensing the $BHCl_2$ and BCl_3 at -111° , excess H_2 and HCl were removed from the mixture. Dichloroborane samples then were separated from BCl_3 by employing a preparative, low-temperature, gas chromatography column.⁸

Anal. Calcd. for $BHCl_2$: B, 13.1; H, 1.2; Cl, 85.7. Found: B, 12.6; H, 1.0; Cl, 87.1.

An infrared spectrum of the compound is shown in Fig. 2. The tracing was obtained at a total gas pressure of 16 mm. in a 5.0-cm. path length at -10° . By placing 0.6 mm. of BCl_3 in an identical 5.0-cm. reference cell at 30°, absorption due to this impurity was “blanked” from the spectrum. The resulting spectrum agrees well with the absorption peaks reported by other investigators.^{5,9,10}

Conversion of $BHCl_2$ to B_2H_5Cl .—A solution (300 ml.) containing 3.93% (mole) $BHCl_2$ in liquid BCl_3 reached an equilibrium vapor pressure of 599.6 mm. at 0.5° in a 2-l. vacuum-

jacketed, glass chamber. Samples of the vapor phase, which contained 21.20% (mole) $BHCl_2$, were raised slowly to 40° under autogenous pressure while gas chromatograms and infrared spectra were recorded. The first analysis, at 10°, showed that 0.91% B_2H_5Cl (but no B_2H_6) was present in the mixture. A concentration of 2.54% B_2H_5Cl was reached before traces of B_2H_6 appeared.

Reaction of B_2H_5Cl with Excess BCl_3 .—A 0.214-mmole sample of B_2H_5Cl was condensed in a vacuum-line trap with 50.23 mmoles of BCl_3 and allowed to stand at 30° for 4 hr. (liquid BCl_3 was present). The mixture was vaporized completely into a large known volume and analyzed by infrared, gas chromatography, and gasometry. The B_2H_5Cl had diminished to 0.132 mmole while 0.391 mmole of $BHCl_2$ had formed in the mixture. No quantities of B_2H_6 , HCl , or H_2 were detected. After 1 week at 20°, an identical mixture showed that all the B_2H_5Cl had reacted to form $BHCl_2$.

Disproportionation of B_2H_5Cl .—Under a pressure of 760 mm., a gas mixture containing 9.1% B_2H_5Cl in nitrogen was maintained at 35° in a 2-l. glass chamber. Over a 70-hr. period, small samples were removed for analyses by gas chromatography, gasometry, and infrared spectrometry. The results are shown in Fig. 3.

Reaction of B_2H_5Cl with B_2O_3 .—A 1.0-g. (14.36 mmoles) sample of -100 mesh B_2O_3 was placed in the U section of a cold trap attached to the side of an infrared gas cell. A 0.306-mmole sample of B_2H_5Cl was admitted to the gas cell and the spectrum recorded. Liquid nitrogen was placed around a remote tip of the U-trap, causing all the B_2H_5Cl to condense there. As the tip was warmed to 25°, the gas returning to the cell passed through the B_2O_3 a second time. The infrared spectrum then showed only B_2H_6 (0.235 mmole) to be present in the gas cell. After evacuating the B_2H_6 , the B_2O_3 was heated to 100° as an infrared scan was recorded. A spectrum of BCl_3 then was observed. After evacuating the BCl_3 , analysis of the resulting B_2O_3 showed no Cl to be present.

Reaction of B_2H_5Cl with Excess HCl .—To a 0.415-mmole sample of B_2H_5Cl contained in an infrared gas cell, a 5.302-mmole sample of HCl was introduced at 25°. An infrared scan of the 1500 to 1650 cm^{-1} region was begun and showed that B_2H_5Cl had immediately disappeared. Gas chromatographic and gasometric analysis of the mixture showed 2.052 mmoles of H_2 and 0.851 mmole of BCl_3 to be present in the remaining HCl .

Acknowledgment.—This work was performed under Contract No. AF33(600)-35780 with the United States Air Force, Aeronautical Systems Division, Manufacturing Technology Laboratory, Wright-Patterson Air Force Base, Ohio.

CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS, WASHINGTON, D. C., AND THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON, WISCONSIN

The Nature of the Compound Obtained from Aqueous Cesium Chloride Solution and Hydrogen Chloride

By ARTHUR G. MAKI AND ROBERT WEST

Received January 17, 1963

In 1957 one of us reported the preparation of a new compound from aqueous cesium chloride solution saturated with hydrogen chloride.¹ On the basis of partial

(9) H. G. Nadeau and D. M. Oaks, Jr., *Anal. Chem.*, **32**, 1481 (1960).

(10) T. Onak, H. L. Landesman, and I. Shapiro, *J. Phys. Chem.*, **62**, 1605 (1958).

(1) R. West, *J. Am. Chem. Soc.*, **79**, 4568 (1957).