shows not only the results of the present work but also previous results.[1,2] The compounds containing one tin atom show an approximate linearity between $J_{C^{13}-H}$ and $J_{Sn^{119}-CH_3}$ which is indicated by a line in the figure. The substituent groups at the tin vary from simple alkyl to $-CH_3$ and $-Br$. Hexamethylditin[2] and triethyltrimethylditin are represented by the two points at the left of the figure, which are clearly anomalous. $J_{C^{13}-H}$ is representative of the product $|2s_C(0)|^2|1s_H(0)|^2$ where these symbols represent the s character probabilities at the respective nuclei.[6] The s character in the C–H bonds is thus seen to increase as the electronegativity of substituents at the tin increases. The highest value of $J_{C^{13}-H_3}$ is that obtained for $(CH_3)_2Sn(C_2F_4H)_2$.[1]

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The Interaction of Boron Trichloride with Diborane[1]

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Monochlorodiborane was identified by Stock[2] as a product resultant from the interaction of diborane and boron trichloride. Schlesinger and Burg[3] obtained monochlorodiborane by passing a mixture of boron trichloride and hydrogen through an electric arc. Monochlorodiborane was observed to decompose and form an equilibrium mixture containing diborane and boron trichloride. If the diborane were removed by distillation and the remaining material allowed to warm to 0°, a new equilibrium resultant from further decomposition was obtained. This could be continued until only a trace of monochlorodiborane remained. They observed that it was very difficult to get monochlorodiborane to decompose in the presence of a large excess of boron trichloride. Interaction of boron trichloride with diborane at 0°, followed by fractionation through a $-130°$ bath, showed that approximately one-eighth of the diborane had been consumed. On standing at 0°, the $-130°$ fraction had its vapor pressure increased from 58.0 to 685 mm. in 5 min., thus showing that equilibrium was attained very rapidly even at 0°. Hurd[4] prepared monochlorodiborane by passing mixtures of boron trichloride and hydrogen over active metals at elevated temperatures.

Urry, Wartik, Moore, and Schlesinger[5] suggest dichloroborane as a probable reaction intermediate formed in the reaction of diboron tetrachloride with hydrogen to form diborane. Lynds and Stern[6] obtained dichloroborane by passing a mixture of hydrogen and boron trichloride over magnesium at a temperature of 400–450°. They report that equimolar mixtures of boron trichloride and dichloroborane are relatively stable. Myers and Putnam[7] isolated monochlorodiborane using low temperature gas chromatography techniques. Contrary to previous reports they found the pure compound to be comparatively stable.

Experimental

Diborane was prepared by the reaction of boron trifluoride with sodium borohydride in diglyme (diethylene glycol dimethyl ether).

Boron trichloride, 99.8% pure (Stauffer Chemical Co.), was freed of phosgene by passage over boron carbide at 1000°.

The experiments were carried out in an all-glass high vacuum system using standard techniques.[8] Volumes of differing portions of the apparatus were determined using weighed quantities of carbon dioxide.

Measured portions of boron trichloride and diborane were mixed in differing portions of the apparatus at temperatures of 20.5 to 25.5°. If interaction did not take place an infrared spectrum of the gas mixture showed only the spectra of diborane and boron trichloride superimposed on each other.[9] If the gas mixture was fractionated through a $-131.5°$ trap into a $-196°$ trap, the starting quantity of diborane was obtained in the $-196°$ trap. When reaction occurred, an infrared spectrum such as that shown in Fig. 1 was obtained. When equimolar quantities of boron trichloride and diborane interacted approximately one-eighth of the diborane was consumed as shown by fractionation and by infrared analysis. Repeated observations of the infrared spectrum showed that equilibrium had been attained in the first observation.

The reaction product gases were measured and the number of moles of gas calculated. The results in Table I show that differing mole ratios of boron trichloride and diborane interact to form chloroboranes without any change in the number of moles of gas present. The results also show that change of pressure has little, if any, effect on the number of moles of gas present. This observation could be explained by equations such as

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_5Cl + BHCl_2 \qquad (1)$$

$$BCl_3 + 2B_2H_6 \rightleftarrows 2B_2H_5Cl + BH_2Cl \qquad (2)$$

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_4Cl_2 + BH_2Cl \qquad (3)$$

$$3BCl_3 + 2B_2H_6 \rightleftarrows 3BH_2Cl + 2B_2H_3Cl_3 \qquad (4)$$

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(1) The original concept and experimental work were supported by the research program of Stauffer Chemical Company, Richmond, Calif. Support for the completion of the work was provided by the Lockheed Independent Research Fund.

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(3) H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, **53**, 4321 (1931).

(4) D. T. Hurd, *ibid.*, **71**, 20 (1949).

(5) G. Urry, T. Wartik, R. Moore, and H. I. Schlesinger, *ibid.*, **76**, 5293 (1954).

(6) L. Lynds and D. R. Stern, *ibid.*, **81**, 5006 (1959).

(7) H. W. Myers and R. F. Putnam, *Inorg. Chem.*, **2**, 655 (1963).

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

(9) This was only observed to happen when the reactants were mixed in a new, clean vacuum system. Possibly traces of a boron oxide are needed to catalyze the reaction.

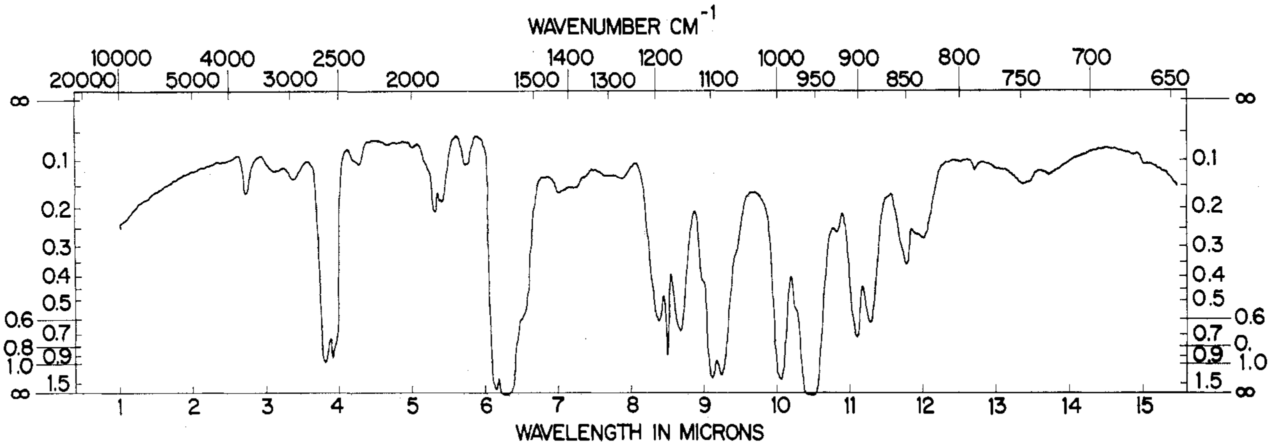

Fig. 1.—Spectrum of diborane–boron trichloride reaction product mixture.

TABLE I

Moles of BCl_3	Moles of B_2H_6	Total no. of moles	No. of moles of mixture obsd.	Pressure, mm.
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.77×10^{-3}	107.5
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.77×10^{-3}	122
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.77×10^{-3}	226.7
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.75×10^{-3}	291.5
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.74×10^{-3}	422.4
3.56×10^{-4}	3.41×10^{-3}	3.77×10^{-3}	3.71×10^{-3}	726.5
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.17×10^{-3}	134.8
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.14×10^{-3}	117.0
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.13×10^{-3}	246.6
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.12×10^{-3}	315.9
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.13×10^{-3}	462.1
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.10×10^{-3}	785.2
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.17×10^{-3}	340.5
7.25×10^{-4}	3.41×10^{-3}	4.14×10^{-3}	4.16×10^{-3}	508.4
1.26×10^{-3}	3.41×10^{-3}	4.67×10^{-3}	4.67×10^{-3}	150.1
1.26×10^{-3}	3.41×10^{-3}	4.67×10^{-3}	4.64×10^{-3}	514.7
3.01×10^{-3}	3.41×10^{-3}	6.42×10^{-3}	6.47×10^{-3}	207.5
3.01×10^{-3}	3.41×10^{-3}	6.42×10^{-3}	6.42×10^{-3}	374.5
6.51×10^{-3}	3.41×10^{-3}	9.92×10^{-3}	10.0×10^{-3}	320.9
6.51×10^{-3}	3.41×10^{-3}	9.92×10^{-3}	9.95×10^{-3}	564.6
13.57×10^{-3}	3.41×10^{-3}	16.98×10^{-3}	16.98×10^{-3}	467.8
6.51×10^{-3}	4.2×10^{-4}	6.93×10^{-3}	6.99×10^{-3}	525.4

$$4BCl_3 + 2B_2H_6 \rightleftarrows 2B_2H_3Cl_3 + 2BHCl_2 + 2BH_2Cl \quad (5)$$

$$BCl_3 + B_2H_5Cl \rightleftarrows BHCl_2 + B_2H_4Cl_2 \quad (6)$$

and possibly others.

Reactions involving only dichloroborane or monochlorodiborane such as

$$B_2H_6 + 4BCl_3 \rightleftarrows 6BHCl_2 \quad (7)$$

$$5B_2H_6 + 2BCl_3 \rightleftarrows 6B_2H_5Cl \quad (8)$$

would require either an increase or a decrease in the number of moles of gas present.

The spectrum of the boron trichloride–diborane reaction product mixture shown in Fig. 1 shows peaks identified by Lynds and Stern[6] and Myers and Putnam[7] for the spectrum of pure dichloroborane and for pure monochlorodiborane by Myers and Putnam[7] superimposed upon the spectrum of boron trichloride and diborane. This evidence shows that eq. 1 plays a major role in the observed equilibria.

If the boron trichloride–diborane–chloroborane reaction mixture is fractionated through a −131.5° trap into a −196° trap and the −131.5° fraction of boron trichloride and chloroboranes is allowed to warm to room temperature, forming a new equilibrium mixture, then the number of moles present plus the number of moles of diborane in the −196° trap equal the number of moles present in the initial reaction mixture. This shows that the material in the −131.5° trap also forms a new equilibrium mixture without change in the number of moles present. This new mixture would contain the same components as were present before fractionation, only the mole fractions would be different.

A mixture of 46.8% boron trichloride and diborane which had reacted to form the chloroborane species was fractionated through a −131.5° trap into a −196° trap. A −80° bath was placed about the −131.5° fraction for 0.5 hr. and the vapor pressure remained constant. At −63° the vapor pressure also remained constant. A −45° bath showed a slow increase in vapor pressure, indicating an equilibrium shift, and at −23° the observed equilibrium shift was fairly rapid. The mixture was allowed to warm to room temperature so that the equilibrium shift could go to completion. The vapor pressures at −23, −45, −63, and −80° were taken. The vapor pressures before and after equilibrium shift had occurred are shown in Table II.

Thus it is seen that removal of one of the components results in the remaining components interacting to form a new equilibrium consisting of a mixture of components with a higher vapor pressure. This is similar to the observations of Schlesinger and Burg.[3]

TABLE II

Temp., °C.	Vapor pressure, mm. Before equil. shift	After equil. shift
−80	8.5	53
−63	29	74
−45	80	127
−23	158–226	254

Discussion and Conclusions

Boron trichloride and diborane react to form chloroboranes without change in the number of moles of gas present. This may be explained by equilibria such as

$$BCl_3 + B_2H_6 \rightleftarrows B_2H_5Cl + BHCl_2$$

Of the possible reactions which may be written, this involves the simplest mechanism. One molecule of boron trichloride and one molecule of diborane come together and exchange a chlorine atom for a hydrogen atom. The reaction products of this interaction are monochlorodiborane and dichloroborane. These have been identified in the infrared spectrum. One may view this equilibria as a sort of gaseous ion exchange where hydrogen and chlorine are continuously being exchanged at the boron exchange site.

Monochlorodiborane and dichloroborane are relatively stable in the product equilibrium mixture. They do not spontaneously disproportionate, but instead they interact with the other species present in the reaction mixture by exchange of hydrogen and chlorine atoms until equilibrium is established. Previous reports of the instability of monochlorodiborane and dichloroborane may have been observations of reaction product mixtures containing these compounds trying to attain equilibrium. If one of the equilibrium components is removed by fractionation, the remainder of the equilibrium mixture will then react until a new equilibrium mixture is formed.

One would expect that pure monochlorodiborane would have a stability similar to diborane in an environment of diborane. Dichloroborane would also be fairly stable in an environment of boron trichloride since the proposed equilibria would permit only small concentrations of diborane and monochlorodiborane at equilibrium.

Some diborane syntheses may produce reaction products which are rich in boron–hydrogen bonding and others produce reaction products which contain a large quantity of boron–chlorine bonding. This could explain the differences of opinion in the literature. Reaction product mixtures which are mostly diborane and monochlorodiborane can have only small concentrations of boron trichloride and dichloroborane present in the equilibrium mixture. In like manner, reaction products rich in boron–chlorine bonding would have low concentrations of diborane and monochlorodiborane at equilibrium. Fractionation or distillation would yield the desired diborane product by shifting the equilibrium.

The exchange of hydrogen and chlorine atoms may be similar to that observed by Keller and his coworkers[10] for the interaction of boron trichloride and boron tribromide and by Porter, *et al.*,[11] for boron trichloride and boron trifluoride.

The interaction of boron trichloride with silane reported by Edwards and Pearson[12] may proceed through a similar hydrogen–chlorine exchange. They found that when a 4:1 excess of boron trichloride was used, the disproportionation of dichloroborane was inhibited so that most of the hydrogen bonding remained as dichloroborane. Conceivably, a large excess of silane would yield monochlorodiborane and diborane and little dichloroborane and boron trichloride.

If a chemical species is added which interacts with and removes one or more of the equilibrium components, the remaining components interact to set up new equilibria until the reaction has gone to completion. Examples of this may be found in the work of Brown and Tierney,[13] Onak, Landesman, and Shapiro,[14] and others.

Perhaps current methods of infrared analysis should be evaluated in the light of these findings.

It is hoped that these observations may prove useful in catalysis reactions involving boron and similar compounds.

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Reactions of Alkylgermanium Alkanesulfonates[1]

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Triphenylgermanium benzenesulfonate, b.p. 160° (1.3 mm.), white needles of m.p. 38°, the only previously known organogermanium compound with a sulfonate group, is the product of a 6-hr. reflux of triphenylgermane with benzenesulfonic acid in toluene[2] solution.

A rapid transesterification such as $2R_3GeOCOR' + H_2SO_4 = [R_3Ge]_2SO_4 + 2HOCOR'$, involving a distillation for 15 min. in equipment of at least five theoretical plates, is adequate in the preparation of $[(n\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 370°,[3] $[(i\text{-}C_3H_7)_3Ge]_2SO_4$, b.p. 380°,[4] $[(i\text{-}C_3H_7)_2GeSO_4]_2$, m.p. 115° dec.,[3] and $[(C_2H_5)_3Si]_2SO_4$, b.p. 278°.[5] This procedure offers many advantages

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[1] Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

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