technique for arriving at the displacement figure and no evidence is obtained by titration methods for reversibility.

Summary

1. Norris and Morton, from conductance measurements, considered the reaction between diphenylchloromethane and ethyl alcohol to be reversible. Ward, by a titration method, found the reaction to be irreversible.

2. The titration method has now been examined in greater detail. No evidence is obtained for reversibility.

SIR JOHN CASS TECHNICAL INSTITUTE
LONDON, ENGLAND

RECEIVED APRIL 18, 1935

[CONTRIBUTION NO. 47 FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF UTAH]

A New Method for the Preparation of Alkoxyboron Halides and their Reaction with Metals

BY CORLISS R. KINNEY, H. THERON THOMPSON AND LEE C. CHENEY

Alkoxyboron halides were first prepared by Gasselin[1] in 1894 by the action of methyl alcohol on boron trifluoride.

$$BF_3 + CH_3OH \longrightarrow \begin{matrix} CH_3OBF_2 \\ + \\ HF \end{matrix} + CH_3OH \longrightarrow \begin{matrix} (CH_3O)_2BF \\ + \\ HF \end{matrix}$$

In 1932 Bowlus and Nieuwland[2] observed that alcohols higher than methyl or ethyl did not produce fluoro esters, but a complex hydrocarbon mixture. The chloro esters were first investigated by Ramser and Wiberg[3] and later by Wiberg and Sütterlin[4] who prepared the methyl and ethyl derivatives from the corresponding alcohols or ethers and boron trichloride.

Preliminary experiments on the action of metals on diethoxyboron chloride indicated that larger groups would be desirable; consequently diisoamyloxyboron chloride was prepared and studied. The substance was prepared first using Wiberg and Sütterlin's method, but the yield was not satisfactory. Several attempts were made to prepare the substance from triisoamyl borate and dry hydrogen chloride, thionyl chloride, and phosphorus pentachloride[5] but the desired product was not obtained. With boron trichloride, however, the chloro ester was obtained and in much increased yields.

$$(C_5H_{11}O)_3B + BCl_3 \longrightarrow \begin{matrix} (C_5H_{11}O)_2BCl \\ + \\ C_5H_{11}OBCl_2 \end{matrix}$$

$$C_5H_{11}OBCl_2 + (C_5H_{11}O)_3B \longrightarrow 2(C_5H_{11}O)_2BCl$$

Diisoamyloxyboron chloride did not react with "molecular silver" at room temperature, but did react readily with sodium or zinc when warmed. The reaction was exothermic and became violent unless cooled. Unexpected gaseous products were observed even at 70° in a benzene solution. The gas contained hydrogen chloride and probably isoamylene and hydrogen. The liquid product did not react with water to form hydrogen, indicating that $(C_5H_{11}O)_2BNa$ or possibly $(C_5H_{11}O)_2$-$BB(OC_5H_{11})_2$ was absent. On distillation only triisoamyl borate and boric anhydride were obtained.

The reaction was obviously complex and involved secondary reactions. Without doubt the sodium removed the chlorine atom and the resulting radical, instead of combining with another of its kind, decomposed into an isoamyl radical and isoamyl metaborate.

$$(C_5H_{11}O)_2BCl + Na \longrightarrow (C_5H_{11}O)_2B\text{—} + NaCl$$
$$(C_5H_{11}O)_2B\text{—} \longrightarrow C_5H_{11}OBO + C_5H_{11}\text{—}$$

The unsaturated hydrocarbon gas and the hydrogen are accounted for by the decomposition of the isoamyl radical into isoamylene and nascent hydrogen, and the hydrogen chloride by the action of the hydrogen on another molecule of the chloro ester.

$$C_5H_{11}\text{—} \longrightarrow C_5H_{10} + H$$
$$(C_5H_{11}O)_2BCl + H \longrightarrow (C_5H_{11}O)_2B\text{—} + HCl$$

Finally, the isolation of triisoamyl borate and boric anhydride are to be expected because the attempt to isolate a metaborate by fractional distillation always results in the orthoborate and boric anhydride.

Experimental Part

The Reaction of Diethoxyboron Chloride with Metals.—Diethoxyboron chloride reacted readily with sodium or dry zinc dust when warmed slightly. Gases were evolved and a liquid product distilling between 110 and 150° was

---

[1] Gasselin, *Ann. chim. phys.*, [7] **3**, 83 (1894).

[2] Bowlus and Nieuwland, THIS JOURNAL, **54**, 2017 (1932).

[3] Ramser and Wiberg, *Ber.*, **63**, 1136 (1930).

[4] Wiberg and Sütterlin, *Z. anorg. allgem. Chem.*, **202**, 1 (1931).

[5] Schiff, *Ann. Suppl.*, **5**, 154 (1867).

obtained. The yield amounted to practically one-third the weight of chloro ester taken. Assuming that one molecule of the ester yields one third of a molecule of triethyl borate, the crude yield was 93%. Upon redistillation more than 75% of the product distilled between 112 and 114°, the boiling point of triethyl borate at 640 mm. The residue was boric anhydride.

The Preparation of Diisoamyloxyboron Chloride.—Upon adding dry isoamyl alcohol to boron trichloride dissolved in dry chloroform and cooled to −20°, a yield of only 15% of diisoamyloxyboron chloride was obtained. On the other hand, by mixing triisoamyl borate with boron trichloride in the ratio of two moles to one, allowing the mixture to stand for twenty-four hours and then fractionating, a yield of 45% was obtained. The yield was not increased by allowing the mixture to stand for a longer time or by heating it in a sealed tube to 100° for eleven hours. The compound distilled at 110 to 115° at 14 mm. pressure. The substance was analyzed by decomposing a weighed sample with water and titrating the hydrochloric and boric acids produced, using methyl orange and phenolphthalein as indicators.

Anal. Calcd. for $(C_5H_{11}O)_2BCl$: Cl, 16.1; B, 4.9. Found: Cl, 15.9; B, 4.9.

The Reaction of Diisoamyloxyboron Chloride with Metals.—Diisoamyloxyboron chloride reacted vigorously with sodium or zinc dust when warmed. In order to avoid excessive decomposition the reaction was carried out in a dry benzene solution. Twenty-two grams (0.1 mole) of the chloride was dissolved in 75 cc. of benzene dried over sodium and 4.5 g. of sodium shavings added. The flask was equipped with a reflux condenser to which a tube was attached to carry the evolved gases through a wash bottle containing water and then through another bottle containing a carbon tetrachloride solution of bromine. Upon heating the flask to 70° the sodium reacted slowly and bubbles of gas were evolved. The gas turned the water acidic in the first bottle and a test for chloride ion with silver nitrate was positive. On the other hand, a test for borate ion with turmeric paper was negative. After passing through the water the gas had an odor similar to that of gasoline, burned with a sooty flame and when passed into the bromine solution rapidly decolorized it. The residual gas was odorless and burned with a pale blue flame similar to that of hydrogen.

The reaction mixture was heated until no chlorine could be detected in the benzene solution, a period of seven hours being required. The dark red solution was filtered from the solid residue which dissolved completely in water leaving no residue of amorphous boron. Thirty grams of the total of seventy-five grams of the solution was treated with water in an apparatus designed to detect the liberation of gas, but none was evolved. The remainder of the solution was fractionated twice and 6.6 g. of pure triisoamyl borate boiling at 245 to 250° at 640 mm. pressure and 2.0 g. of boric anhydride were obtained.

Summary

1. Diisoamyloxyboron chloride has been prepared.
2. Dialkoxyboron halides react with metals forming extensive decomposition products.

SALT LAKE CITY, UTAH RECEIVED MAY 29, 1935

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Thermal Equilibrium of the Cis–Trans Isomers of Dichloroethylene at High Temperatures

BY WILLIAM MARONEY

In the investigation of the thermal and photochemical equilibria of the *cis–trans* isomers of dichloroethylene, Olson and Maroney[1] were limited by decomposition reactions to temperatures below 350°. In the present study, the temperature range has been extended to 975° by using a flow method and low pressures.

The method of preparing the materials and the method of analysis are the same as those described in the previous paper.

The experimental method consisted in passing mixtures of known composition of the gaseous isomers through a heated reaction tube, and finding the change in composition due to the thermal isomerization. The reaction tube used at 825° was a section of quartz tubing, 4.5 mm. inside diameter and the portion heated, 17 cm. long. The heating element was wound in five sections. The current through each section could be regulated separately. The temperature was measured by five thermocouples, one for each section. The reaction tube used at 975° was made in a similar manner. The inside diameter of the tubing was 2.5 mm., the heated portion, 12 cm. long. Three heating units and three thermocouples were used. It was found that the length and bore of the tubes employed could be changed without altering the values found for the equilibrium composition.

The pressure at each end of the reaction tube was measured by sulfuric acid manometers. Since the manometers were about 20 cm. from the

---

[1] A. R. Olson and William Maroney, THIS JOURNAL, **56**, 1320 (1934).