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Exchange Reactions of Ethyldiboranes and Higher Boranes

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The exchange reactions of ethyldiborane and *sym*-diethyldiborane with tetraborane, pentaborane-9, pentaborane-11, and decaborane were studied. The reactions of pentaborane-11 with either ethyldiborane or *sym*-diethyldiborane took place with practically no degradation and can best be explained as an exchange of BH_3 and $C_2H_5BH_2$ to give ethylpentaborane-11 and diborane. Alternatively, it was shown that the reaction is reversible and ethylpentaborane-11 and diborane yield ethyldiborane and pentaborane-11. No exchange was observed in the reactions of *sym*-diethyldiborane with tetraborane, pentaborane-9, or decaborane.

Introduction

It has been shown[1] that the disproportionation reactions of the ethyldiboranes can be interpreted as the reversible associations of boranes which are produced by the reversible dissociation of diborane, eq. 1.

$$\begin{tikzcd} 2C_2H_5B_2H_5 \arrow[r, rightleftharpoons] & 2C_2H_5BH_2 \arrow[d, rightleftharpoons] & + & 2BH_3 \arrow[d, rightleftharpoons] & (1) \\ & \mathit{sym}(C_2H_5)_2B_2H_4 & & B_2H_6 & \end{tikzcd}$$

In studies of isotopic exchange between diborane and the higher boron hydrides, Koski, *et al.*,[2-7] found that the over-all picture is quire complex, involving at least three mechanisms. The self-exchange of diborane[6] appears to take place *via* borane, as the ratio of the deuterium rate to the boron-10 rate was 3. This is consistent with the mechanism given in eq. 1. In the case of the exchange of diborane with pentaborane-9[2,3,5] and decaborane,[4] only the terminal hydrogen atoms of the higher boron hydrides appear to be involved. However, in the exchange with pentaborane-11,[6] all of the borons and hydrogens of both diborane and pentaborane-11 appear to be involved. The exchange between diborane and tetraborane[7] appears to proceed by two different paths, one involving two hydrogen positions and the second involving the remaining eight hydrogens. This latter reaction also appears to involve boron atoms.

Since some of the postulated mechanisms for the exchange reactions involve the exchange of a borane intact, it was decided to study the reactions of ethyldiborane and *sym*-diethyldiborane with tetraborane, pentaborane-9, pentaborane-11, and decaborane as an approach to a better understanding of the reaction mechanisms and intermediates involved.

Results and Discussion

Reaction of Ethyldiborane with Pentaborane-11.— Since pentaborane-11 appeared to undergo complete exchange with diborane, this reaction was studied first. The results of a typical experiment are given in Table I.

TABLE I

REACTION OF ETHYLDIBORANE WITH PENTABORANE-11[a]

Reactants, mmoles	Products, mmoles
1.54 B_5H_{11}	2.64 B_2H_6
7.72 $C_2H_5B_2H_5$	3.81 $C_2H_5B_2H_5$
	1.34 *sym*-$(C_2H_5)_2B_2H_4$
	1.14 $C_2H_5B_5H_{10}$

[a] 30-min. reaction at 25° in a 130-cc. bulb.

The reaction took place with practically no degradation, as evidenced by no measurable amounts of hydrogen and no visible amounts of nonvolatile residue. Infrared spectral analysis of the diborane showed that neither ethane nor any other hydrocarbon was present in detectable quantities. It also appeared that the pentaborane-11 had reacted completely. The new compound, ethylpentaborane-11, was formed in 74% yield based on the pentaborane-11 consumed.

The reaction is complicated somewhat by the simultaneous disproportionation of ethyldiborane to yield diborane and *sym*-diethyldiborane. All of the data in Table I can be explained by the two reaction paths shown in eq. 2 and 3.

$$\begin{tikzcd} & 0.5\ B_2H_6 + 0.5\ \mathit{sym}\text{-}(C_2H_5)_2B_2H_4 \quad (2) \\ C_2H_5B_2H_5 \arrow[ur] \arrow[dr, "B_5H_{11}"'] & \\ & B_2H_6 + C_2H_5B_5H_{10} \quad (3) \end{tikzcd}$$

The net amount of ethyldiborane consumed was 7.72 − 3.81 = 3.91 mmoles. Since 1.14 mmoles of ethylpentaborane-11 was found, an equivalent amount of diborane would have been formed in reaction 3. This would leave 3.91 − 1.14 = 2.77 mmoles of ethyldiborane to react according to eq. 2. Thus, 1.39 mmoles of diborane and 1.39 mmoles of *sym*-diethyldiborane would be predicted. The actual amount of *sym*-diethyldiborane found was 1.34 mmoles. The total amount of diborane found was 2.64 mmoles, compared to the calculated value of 2.53 mmoles (1.14 mmoles from eq. 3 and 1.39 mmoles from eq. 2).

If the reaction of pentaborane-11 with ethyldiborane proceeded by a displacement of BH_3 by $C_2H_5BH_2$, the

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[1] I. J. Solomon, M. J. Klein, and K. Hattori, *J. Am. Chem. Soc.*, **80**, 4520 (1958).

[2] W. S. Koski and J. J. Kaufman, *J. Chem. Phys.*, **24**, 221 (1956).

[3] J. J. Kaufman and W. S. Koski, *ibid.*, **24**, 430 (1956).

[4] J. J. Kaufman and W. S. Koski, *J. Am. Chem. Soc.*, **78**, 5774 (1956).

[5] W. S. Koski, J. J. Kaufman, and P. C. Lauterbur, *ibid.*, **79**, 2382 (1957).

[6] P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1953).

[7] J. E. Todd and W. S. Koski, *J. Am. Chem. Soc.*, **81**, 2319 (1959).

reaction would probably be reversible, as is the disproportionation of ethyldiborane.[1] In order to investigate this possibility, the reaction of diborane and ethylpentaborane-11 was studied under the same conditions as the first reaction. The data are shown in Table II.

TABLE II

REACTION OF ETHYLPENTABORANE-11 AND DIBORANE AT 25°

Reactants, mmoles	Products, mmoles
8.75 B_2H_6	8.43 B_2H_6
0.86 $C_2H_5B_5H_{10}$	0.59 $C_2H_5B_5H_{10}$
	.29 $C_2H_5B_2H_5$
	.19 B_5H_{11}
	Trace *sym*-$(C_2H_5)_2B_2H_4$

It is seen that 0.32 mmole of diborane and 0.27 mmole of ethylpentaborane-11 were consumed to form 0.29 mmole of ethyldiborane and 0.19 mmole of pentaborane-11. Therefore, the reaction may be considered to be reversible. This provides a further indication that the initial reaction proceeds by a reversible displacement of BH_3 from pentaborane-11 by $C_2H_5BH_2$ as shown in eq. 4.

$$C_2H_5BH_2 + B_5H_{11} \rightleftharpoons BH_3 + C_2H_5B_5H_{10} \qquad (4)$$

The fact that no pentaborane-11 was recovered in the first reaction is probably due to the large excess of ethyldiborane employed, which would shift the equilibrium toward the ethylpentaborane-11.

Further evidence for the reversible nature of the exchange was obtained when the reaction was carried out in the presence of a large excess of diborane. In this case the yield of ethylpentaborane was much lower.

Reaction of *sym*-Diethyldiborane with Pentaborane-11.—The formation of ethylpentaborane-11 apparently proceeds by a displacement of BH_3 from pentaborane by $C_2H_5BH_2$, as shown in eq. 4. If the mechanism is correct, *sym*-diethyldiborane, which dissociates into two $C_2H_5BH_2$ units, should react with pentaborane-11 to yield ethylpentaborane. Two typical reactions, one with an excess of *sym*-diethyldiborane, are shown in Table III. In run 1 the *sym*-diethyldiborane fraction contained a considerable amount of unreacted pentaborane-11, whereas none was observed in run 2.

A material balance of the ethyl groups in run 1 indicated 0.45 mmole of unreacted pentaborane-11, which in turn gave a good balance with the starting quantity of pentaborane-11 and the alkylated product. When a large excess of *sym*-diethyldiborane was employed, run 2, the higher yields and good material balances reported with ethyldiborane were again obtained.

Reaction of *sym*-Diethyldiborane with Ethylpentaborane-11.—In the reactions described above, small amounts of less volatile, more highly alkylated materials were found. These could have been formed by further reaction of ethylpentaborane-11 as shown in eq. 5.

$$C_2H_5B_5H_{10} + sym\text{-}(C_2H_5)_2B_2H_4 \longrightarrow (C_2H_5)_2B_5H_9 + C_2H_5B_2H_5 \quad (5)$$

Therefore, an experiment was carried out in which ethylpentaborane-11 was treated with *sym*-diethyldiborane under the same conditions as the previous reactions. The data are shown in Table IV.

TABLE IV

REACTION OF *sym*-DIETHYLDIBORANE WITH ETHYLPENTABORANE-11

Reactants, mmoles	Products, mmoles
0.58 $C_2H_5B_5H_{10}$	0.01 B_2H_6
1.27 *sym*-$(C_2H_5)_2B_2H_4$	0.14 $C_2H_5B_2H_5$
	1.12 *sym*-$(C_2H_5)_2B_2H_4$
	0.39 $C_2H_5B_5H_{10}$
	0.11 $(C_2H_5)_2B_5H_9$

In this reaction 0.19 mmole of ethylpentaborane-11 and 0.15 mmole of *sym*-diethyldiborane were consumed, and 0.14 mmole of ethyldiborane and 0.11 mmole of diethylpentaborane-11 were found, which essentially is in agreement with eq. 5.

Reaction of *unsym*-Diethyldiborane with Pentaborane-11.—Since the formation of ethylpentaborane-11 derivatives appeared to take place by exchange of BH_3 with $C_2H_5BH_2$, the reaction of pentaborane-11 with *unsym*-diethyldiborane was studied to see whether $(C_2H_5)_2BH$ would also exchange with BH_3. In this case a diethylpentaborane-11 with both ethyl groups on the same boron atom should be formed. Under the same conditions as the previous reactions, no diethylpentaborane-11 was found. No pentaborane-11 was consumed, and only decomposition products of *unsym*-diethyldiborane were found. Therefore, it can be concluded that *unsym*-diethyldiborane does not exchange with pentaborane-11 in the same manner as ethyldiborane and *sym*-diethyldiborane, or at least that the equilibrium is much further to the left. It could also be a matter of rate or an indication that equilibrium had not been reached.

Reaction of Ethyldiboranes with Other Boron Hydrides.—The reactions of tetraborane with ethyldiborane and *sym*-diethyldiborane were also studied. No exchange was observed either under the conditions described above (0° and 0.5 hr.) or when the reaction time was extended to 1 hr., and the reactants were recovered quantitatively. Although some self-disproportionation reaction took place in the ethyldiborane

TABLE III

REACTION OF *sym*-DIETHYLDIBORANE WITH PENTABORANE-11[a]

	Reactants, mmoles		Products, mmoles				
Run	*sym*-$(C_2H_5)_2B_2H_4$	B_5H_{11}	B_2H_6	$C_2H_5B_2H_5$	*sym*-$(C_2H_5)_2B_2H_4$	$C_2H_5B_5H_{10}$	$C_2H_5B_5H_{10}$, %
1	1.47	1.39	0.08	0.72	1.14 (B_5H_{11})	0.83	60
2	5.03	1.26	0.07	1.22	3.77	0.97	77

[a] 0°, 0.5 hr., 80-cc. bulb.

experiments, tetraborane was not involved. When the temperature was raised to 120° and a hot–cold reactor[8] was used, some reaction occurred, but the only new product formed was ethylpentaborane-11. This was due to the synthesis of pentaborane-11 under these conditions.[8]

The reaction of ethyldiborane and pentaborane-9 was carried out for 2 hr. at 0°. The starting materials were recovered quantitatively.

No exchange was observed in a reaction of excess *sym*-diethyldiborane with decaborane in 24 hr. at 25°.

Conclusions

It appears that exchange reactions involving pentaborane-11 are unique among the higher boron hydrides in that they can be simply interpreted in terms of BH_3 reactions. This is consistent with the isotopic exchange studies in that all of the boron atoms and hydrogen atoms were observed to exchange only in the case of pentaborane-11.

The evidence for existence of the unstable B_4H_8 species appears to be mounting.[9] Therefore, a better interpretation of the observed reaction might involve the reversible cleavage of pentaborane-11, eq. 6, and the alkylated diborane, eq. 7.

$$B_5H_{11} \rightleftharpoons BH_3 + B_4H_8 \qquad (6)$$

$$RB_2H_5 \rightleftharpoons RBH_2 + BH_3 \qquad (7)$$

The observed product distribution would then be dictated by all of the equilibrium constants involved. The reason that $(C_2H_5)_2BH$ does not appear to exchange is probably due to steric factors, since it should form easily from the *unsym*-diethyldiborane. Further evidence of this steric restriction is manifested by the diethylpentaborane-11 which is formed from ethylpentaborane-11 when a second $C_2H_5BH_2$ group is introduced. This material, containing two ethyl groups on different boron atoms, is the same as the diethylpentaborane-11 formed from the reaction of pentaborane-11 and ethylene. Thus, this configuration appears to be preferred to one having both ethyl groups on the boron atom.

Experimental

The fractionation procedures were those generally used in high-vacuum techniques (10^{-5} mm.). All starting materials were purified to tensiometric homogeneity and were checked by infrared analysis. The diborane and ethyldiborane were obtained by fractionation of a mixture of ethyldiboranes supplied by the Callery Chemical Co. The diborane exhibited a vapor pressure of 69 mm. at −126°, and the ethyldiborane exhibited a vapor pressure of 7 mm. at −78°. The *sym*-diethyldiborane was prepared by disproportionation of ethyldiborane for 15–20 min. at 25°. The diethyldiborane produced in this manner is the pure symmetrical isomer with a vapor pressure of 36 mm. at 0°. Pure *unsym*-diethyldiborane was obtained from a mixture of diethyldiboranes by repeated expansion with diborane to remove the symmetrical isomer.[1] The resulting diethyldiborane was the pure unsymmetrical isomer with a vapor pressure of 46 mm. at 0°.

The tetraborane and the pentaborane-11 were prepared by means of a hot–cold tube method.[8] The tetraborane had a vapor pressure of 388 mm. at 0° and the pentaborane-11 had a vapor pressure of 52.5 mm. at 0°. The pentaborane-9 and the decaborane were obtained from Callery Chemical Co. The decaborane was purified by vacuum sublimation. Since infrared analysis of the pentaborane-9 indicated the presence of a small amount of pentaborane-11, the pentaborane-9 was passed repeatedly through a hot tube at 180°, and the final traces of pentaborane-11 were removed by reaction with trimethylamine. The material purified in this manner no longer showed evidence of pentaborane-11 in its infrared spectrum, and it had a vapor pressure of 69 mm. at 0°.

The ethylpentaborane-11 was identical in physical and chemical properties with the material obtained in the ethylene–pentaborane-11 reaction, and it was separated, purified, and identified as described earlier.[10]

The diethylpentaborane-11 appeared to be the same material found in the −23° condensates during the purification of ethyl pentaborane-11 prepared from ethylene and pentaborane-11.[10]

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(8) M. J. Klein, B. C. Harrison, and I. J. Solomon, *J. Am. Chem. Soc.*, **80**, 4149 (1958).

(9) B. C. Harrison, I. J. Solomon, R. D. Hites, and M. J. Klein, *J. Inorg. Nucl. Chem.*, **14**, 195 (1960).

(10) R. G. Maguire, I. J. Solomon, and M. J. Klein, *Inorg. Chem.*, **2**, 1133 (1963).