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An Infrared Study of Hydroboration of Lower Olefins with Diborane on γ-Al_2O_3

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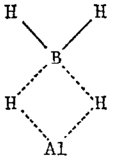
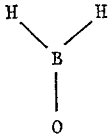
The hydroboration of ethylene and propylene as lower olefins with diborane on γ-Al_2O_3 was investigated by an infrared spectroscopic method. It has been confirmed that diborane is dissociatively adsorbed on the alumina and that the hydroboration proceeds by the collision of ethylene and propylene with the diborane thus adsorbed. This is compatible with the results of previous kinetic investigations. Two kinds of the adsorbed states of diborane, (I) and (II), may be considered to occur, and the bridge structure (I) is more reactive than (II) in the process of hydroboration.



(I)



(II)

The mechanism of hydroboration was considered. The triethyl or tripropyl boron adsorbed on the alumina is stable, so that it remains unchanged under vacuum at 80°C and is not affected by oxygen, although the vapor of the alkyl borons is easily attacked.

INTRODUCTION

The addition reaction of boron hydrides to the carbon–carbon double bond, the so-called hydroboration, was initiated by Hurd (*1*) and, afterward, was widely developed, mainly in the liquid phase, by Brown and others (*2*). The hydroboration proceeds almost quantitatively at a considerable rate in an ether-like solvent such as diglyme (*2*); but, in the gas phase, especially in a noncatalytic reaction, the rate of the reaction between ethylene and diborane at 100°C for 4 days, for instance, was so small that only a slight amount of triethyl boron was detected (*1*). Recently, using a Pd–carbon catalyst, the authors found that the reaction of diborane with ethylene and propylene under moderate conditions yields considerable amounts of triethyl and tripropyl boron (generally, trialkyl boron), and a report was made on the kinetic study of the catalytic hydroboration (*3*). It was further established that the hydroboration process was promoted by acidic catalysts (*4*). In this study, an infrared spectroscopic method is used to investigate the more detailed hydroboration mechanism on a γ-Al_2O_3 catalyst and also to investigate the adsorbed states of diborane and trialkyl boron on the catalyst.

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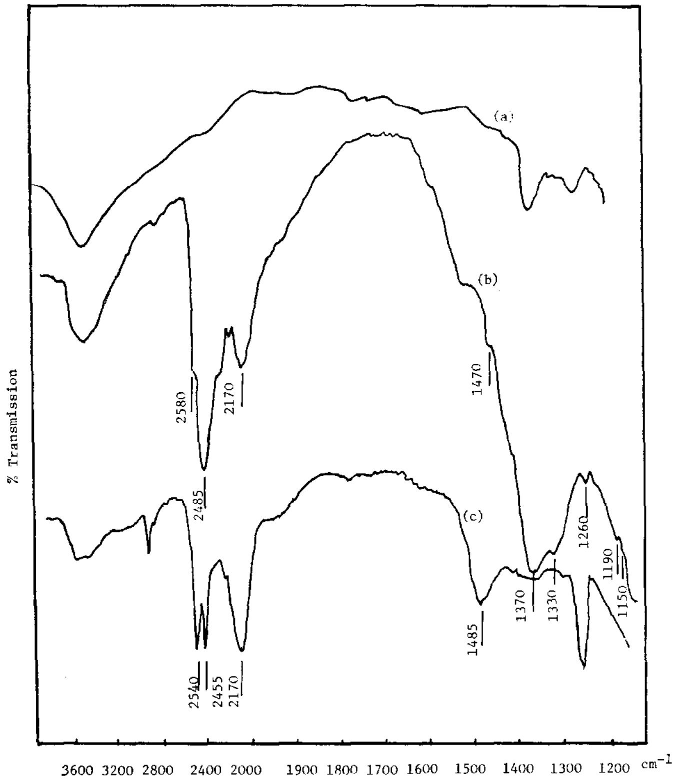


FIG. 1. The infrared adsorption spectra of: (a) γ-Al_2O_3 treated at 450°C for 6 hr under vacuum; (b) adsorbed B_2H_6; and (c) adsorbed $Al(BH_4)_3$. Spectra b and c were measured at room temperature after contact with 41.0 mm Hg of vapor for 15 hr and 30 min and degassing for 60 and 5 min, respectively.

EXPERIMENTAL METHODS

Diborane was prepared and purified in the same way as previously described (*3*). Before the diborane was adsorbed on the catalyst, it was condensed with liquid nitrogen and was pumped off in order to remove incondensable impurities.

Ethylene and propylene as olefins were also purified by the method described in the previous paper (*3*). Triethyl boron was prepared by a modification of the procedures of Brown and Rao (*5*) and Welch (*6*): A solution of the sodium borohydride of diglyme was placed in a flask through which ethylene was passed. A solution of the boron trifluoride–etherate of diglyme in a dropping funnel was added slowly to the solution in the flask. The temperature of the reaction was maintained at 40–50°C. The product was distilled to give triethyl boron (bp: 94.5 ~ 96°C). Tripropyl boron was prepared from *n*-propyl bromide, and boron trifluoride–etherate was prepared by Grignard's method and was purified by distillation (77 ~ 78°C at 40 mm Hg).

Aluminum borohydride was prepared by a method described in a previous paper (*7*). The mixture of $NaBH_4$ (12 g) and $AlCl_3$ (63 g) was placed in a 300-ml flask and was heated on a mantle heater by passing dry nitrogen. The reaction proceeded at the melting points of the compounds. The product, $Al(BH_4)_3$, was condensed in a trap cooled by a dry ice–alcohol solution and was purified by low-temperature distillation.

Powdered γ-alumina (surface area: 212 m^2/g), obtained from Shokubai Kasei Co., Ltd., was pressed into a thin disk of 1.5 cm diameter for infrared measurement. The

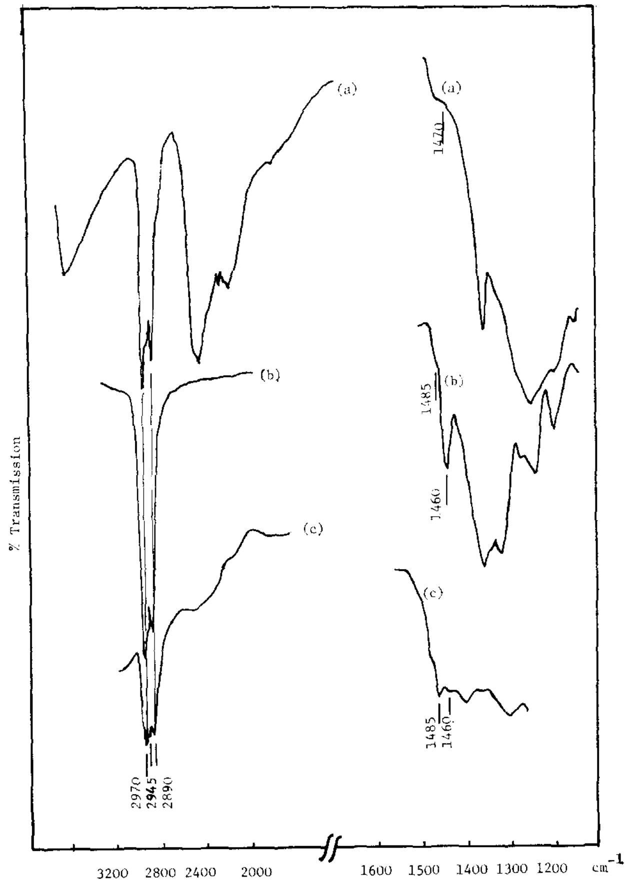


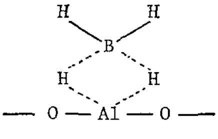
Fig. 2. The infrared adsorption spectra of (a) C_2H_4 (or C_3H_6) + B_2H_6 on γ-Al_2O_3; (b) $B(C_2H_5)_3$ in CCl_4; and (c) $B(C_2H_5)_3$ [or $B(n\text{-}C_3H_7)_3$] on γ-Al_2O_3.

disk was mounted in a quartz glass cell equipped with KBr windows. The disk was outgassed at 450°C for 4 hr under a conventional vacuum ($10^{-4} \sim 10^{-5}$ mm Hg) line and was then cooled to room temperature. Diborane, olefin, and a mixture of both were adsorbed on the alumina at room temperature, and the adsorbed states were examined with an infrared spectrometer (Nippon Bunko, Japan Spectroscopic, Model IRA-2), evacuating the ambient gas.

RESULTS

Adsorption of Diborane

Figure 1 shows the infrared spectra of the γ-Al_2O_3, diborane, and aluminum borohydride adsorbed on γ-Al_2O_3 at room temperature. The spectra of adsorbed diborane were very similar to those obtained by Mashchenko (*8*); the bands with frequencies at 2580, 2485, 2170, and 1470 cm^{-1} are associated with the B–H bond, and those at 1370, 1330, 1260, 1190, and 1150 cm^{-1} with B–O. According to Mashchenko (*8*), the bands at 2570, 2495, 2200, and 1460 cm^{-1}, which would correspond to the bands at 2580, 2485, 2170, and 1470 cm^{-1} in our findings, indicated borane compounds with the following bridge structure.



(I)

TABLE 1

Infrared Spectra of Adsorbed Triethyl and Tripropyl Boron and Their Assignments

Frequency (cm^{-1})		Assignment
Observed	Reference (*11*)	
2970	2970	Asymmetric CH stretch in CH_3
2945	2932	Asymmetric CH stretch in CH_2
2890	2880	Symmetric CH stretch in CH_3

In order to ascertain further the attribution of the infrared bands to the structure of (I), aluminum borohydride, having the same bridge structure as in (I) (*9*), was allowed to come in contact with the catalyst. The infrared spectrum in this case is shown in Fig. 1c. The bands at 2170 and 1485 cm^{-1} are very similar to those observed in the infrared spectra of the adsorbed diborane. Price (*9*) demonstrated that aluminum borohydride in the liquid phase exhibits bands at 2031 and 1500 cm^{-1}, due to BH_2Al bridge vibrations, each of which corresponds to the bands of the adsorbed species at 2170 and 1485 cm^{-1} in Fig. 1, respectively. Accordingly, it is concluded that diborane adsorbed on the alumina has the bridge structure (I). On the other hand, the intense bands in the region of 1600 and 2000 cm^{-1}, due to the bridge structure, $\mathrm{>BH_2B<}$, which is characteristic of the diborane molecule (*8, 10*), could not be observed in this case. This suggests that physically adsorbed diborane does not exist and that diborane is dissociatively adsorbed on the alumina surface, which has already been proposed based on the experiments of diborane adsorption reported in the previous paper (*3*). The frequencies of the terminal B–H bands at 2580 and 2485 cm^{-1} and the B–O bands in the 1150 and 1370 cm^{-1} region may suggest the existence of other possible adsorbed states of diborane as in (II).

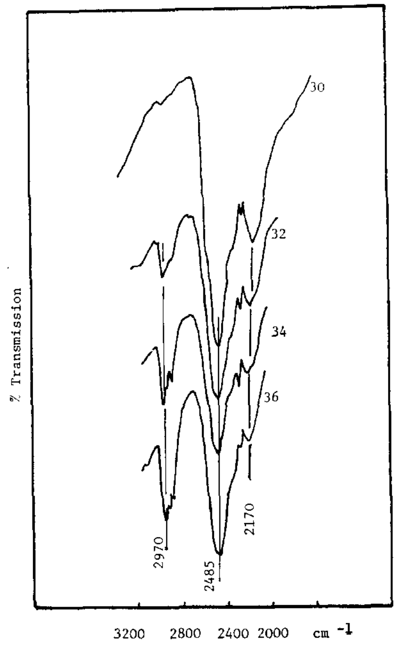
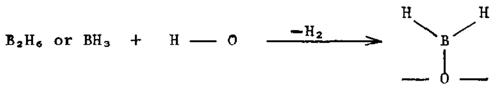


FIG. 3. The behavior of adsorbed species revealed in the ir spectra on admission of ethylene or propylene followed by degassing. Run 30: B_2H_6 (22.0 mm Hg) on γ-Al_2O_3, contact for 15 hr, degassing for 10 min; Run 32: admission of ethylene (50.7 mm Hg) after Run 30 for 2 min and degassing for 5 min; Run 34: further admission of ethylene (50.1 mm Hg) after Run 32, contact for 28 min, and degassing for 10 min; Run 35: standing overnight under vacuum; Run 36: admission of ethylene (50.3 mm Hg) after Run 35, contact for 60 min, and degassing for 60 min.



$$B_2H_6 \text{ or } BH_3 + H\text{—}O \xrightarrow{-H_2} \underset{\text{—}O\text{—}}{\overset{H\diagdown\ \diagup H}{B}}$$

(II)

State (II), which may be the dissociatively adsorbed state of diborane, would be formed by interaction with the hydroxylic sites on the alumina (*8*).

TABLE 2

Change in the Absorbance Ratios of C–H and B–H and of Terminal B–H and Bridge B–H bands with Contact Time

Run	Absorbance ratio $\frac{\text{C–H } (2970 \text{ cm}^{-1})}{\text{B–H } (2485 \text{ cm}^{-1})}$	Absorbance ratio $\frac{\text{Terminal B–H } (2485 \text{ cm}^{-1})}{\text{bridge B–H } (2170 \text{ cm}^{-1})}$	Contact time (min)	Pumping time (min)	Pressure[a] (mm Hg)
(A) Ethylene–diborane hydroboration					
32	0.24	1.59	2	5	50.7
34	0.44	1.80	28	25	50.1
35	0.45	1.82	Standing overnight under vacuum		—
36	0.54	2.04	60	60	50.3
(B) Propylene–diborane hydroboration					
17	0.76	2.06	2	5	81.2
18	0.76	2.06	Standing for 1 hr under vacuum		—
19	1.12	2.64	28	5	80.8
20	1.26	2.95	60	90	81.0

[a] Pressure of C_2H_4 in ethylene–diborane hydroboration and pressure of C_3H_6 in propylene–diborane hydroboration.

Adsorption of a Mixture of Diborane and an Olefin

Ethylene (50 mm Hg) or propylene (81 mm Hg) was individually allowed to come into contact with the alumina for 20 hr, but no bands, except γ-Al_2O_3, were detected in each case. Luochesi *et al.* (*11*) reported that the adsorption of ethylene was difficult to observe by conventional methods and that the spectroscopic identification of the surface species formed on an η-Al_2O_3 was supplemented only by hydrogenation. Avery (*12*) reached the same conclusion as did Luochesi *et al.* (*11*) in his spectroscopic investigations of the adsorption of olefin on Pd–SiO_2. The γ-Al_2O_3 was treated with hydrogen or olefin for more than 10 hr at room temperature and, afterward, was evacuated for a few minutes; then olefin or hydrogen was introduced and was followed by a brief degassing. No bands, except those of the γ-Al_2O_3, were detected in these cases. Mixed gases of hydrogen and ethylene or propylene were also admitted, but the results were similar.

The amount of olefin adsorbed on the alumina seemed so small that it could not be measured by the infrared method.

Upon admission of the mixture of diborane and ethylene or propylene, new bands at 2970, 2945, and 2890 cm^{-1} were observed as shown in Fig. 2. These bands could be assigned as due to the triethyl or tripropyl boron produced by olefin hydroboration. By the adsorption of triethyl or tri-*n*-propyl boron, bands with frequencies of the same wavenumbers as those of the new bands were observed (Fig. 2). The assignment of these bands is described in Table 1 on the basis of the results given previously (*11*), which demonstrates that the bands observed are due to the alkyl groups in the triethyl or tripropyl boron. Besides triethyl and tripropyl boron, R_2BH and RBH_2 ($R = C_2H_5$ or C_3H_7) may be produced, but it is impossible to distinguish between them using infrared spectroscopy. The only difference between the spectra of the systems of diborane–ethylene and –propylene was the ratio of the

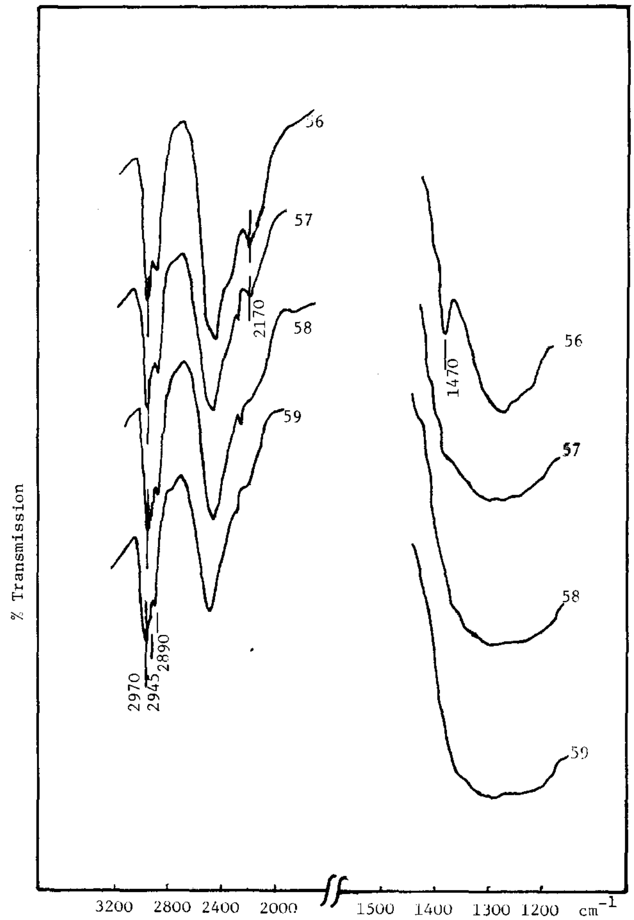


FIG. 4. Effect of oxygen on the mixture of C_2H_4 and B_2H_6. Run 56: reaction of B_2H_6 (22 mm Hg) and C_2H_4 (51 mm Hg) on γ-Al_2O_3 for 1 hr and then degassing for 15 min; Run 57: contact with oxygen after Run 56 for 2 min and then degassing for 5 min; Run 58: contact with oxygen after Run 57 for 15 min and then degassing for 5 min; Run 59: contact with oxygen after Run 58 for 1.5 hr and then degassing for 30 min.

absorbance [log (1/transmission)] of CH_3 (2970 cm^{-1}) and CH_2 (2945 cm^{-1}) in the alkyl radicals. The absorbance ratios, CH_3/CH_2, were 1.32 and 1.25 for ethylene and propylene hydroboration, respectively. When ethylene or propylene was admitted to alumina on which diborane had been preadsorbed and evacuated, the same new

TABLE 3

Effect of Oxygen on the Hydroboration of a Mixture of Ethylene and Propylene

Run	Absorbance ratio C–H (2970 cm^{-1}) / B–H (2485 cm^{-1})	Contact time (min)	Pumping time (min)	Pressure of oxygen (mm Hg)
56	0.67	60	15	—
57	0.73	2	5	100
58	0.76	15	5	100
59	0.78	90	30	100

bands as described above were observed. Successive treatment with ethylene or propylene adsorption and the pumping cycle showed that the bands of CH_3 and CH_2 in trialkyl boron increased with the cycle, whereas the band of the B–H bond decreased. These facts indicate that hydroboration proceeds by the successive admission of olefin. In Fig. 3 the behavior of the adsorbed species was examined spectroscopically when C_3H_6 was successively introduced onto the Al_2O_3 on which B_2H_6 had been preadsorbed, and similar behavior was observed in the cases of both ethylene and propylene. The absorbance ratios for C_3H_6 together with those for C_2H_4 are listed in Table 2. In Runs 35 and 18, the ratios showed hardly any changes, even when the mixture was kept standing overnight *in vacuo*, indicating that hydroboration did not occur without feeding the olefins, viz., there was no reaction between both the adsorbed diborane and olefin, which may be adsorbed in so small an amount as not to be detected by the infrared technique. The values in the third column of Table 2 will be explained later.

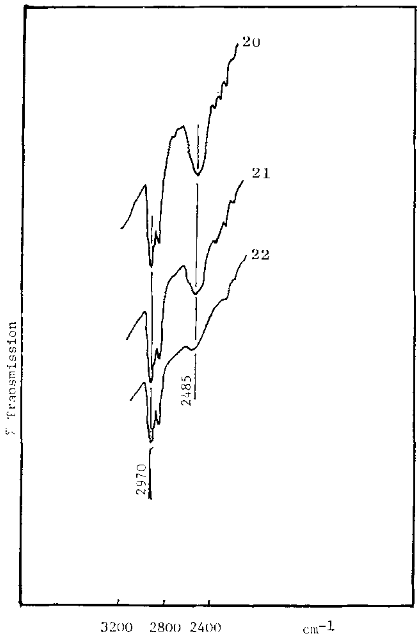


FIG. 5. Effect of heat treatment at 80°C. Run 20: propylene was introduced onto with the Al_2O_3 on which B_2H_6 was preadsorbed at room temperature; B_2H_6: 22.0 mm Hg, C_3H_6: 80.8 mm Hg, contact time: 28 min, and then degassing for 1 hr. Run 21: degassing for 5 min after Run 20. Run 22: further degassing for 25 min after Run 21.

TABLE 4

Absorbance Ratios of CH_3 (2970 cm^{-1}) and CH_2 (2945 cm^{-1}) in $(C_2H_5)_3B$ and $(C_3H_7)_3B$ on γ-Al_2O_3 and in CCl_4[a]

	Absorbance ratio
$(C_2H_5)_3B$ on γ-Al_2O_3	1.05
$(C_2H_5)_3B$ in CCl_4[a]	1.22
(n-$C_3H_7)_3B$ on γ-Al_2O_3	1.07
(n-$C_3H_7)_3B$ in CCl_4[a]	1.19

[a] The bands of CH_3 and CH_2 in CCl_4 solution are 2950 and 2920 cm^{-1}, respectively.

Effect of Oxygen

The mixed gas of ethylene and diborane was admitted on the alumina, and the ambient gas was then pumped off, which was followed by the admission of oxygen and pumping. The behavior of the adsorbed species upon addition of oxygen was studied by the infrared technique as shown in Fig. 4 and Table 3. The bands of triethyl boron and the B–H bond remained, and the absorbance ratios of C–H/B–H bands slightly increased with prolonged contact time with oxygen. Triethyl boron and diborane are so sensitive to oxygen that they decompose explosively in air (*2*), but, in the adsorbed state on alumina, they appear to be considerably stable to oxygen. On the other hand, the bands at 2170 and 1470 cm^{-1}, due to bridge structure (I), disappeared in Runs 58 to 59, indicating that the adsorbed species, as in (I), was rather sensitive to oxygen.

Effect of Temperature

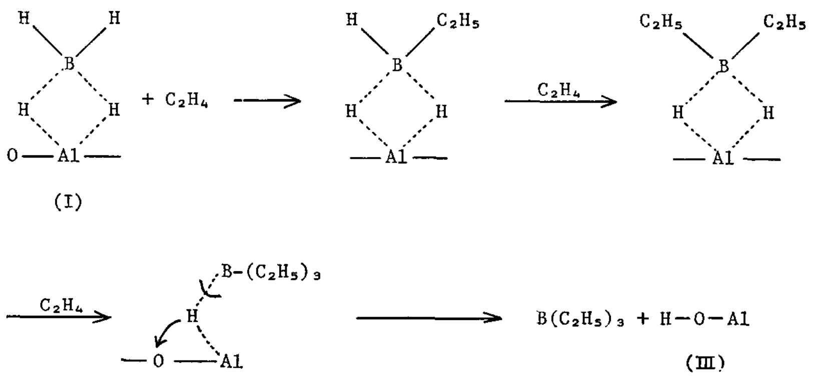
After the contact of C_3H_6 with the Al_2O_3 on which B_2H_6 had been preadsorbed, the ambient gas was evacuated at 80°C. The behavior of the adsorbed species during evacuation at higher temperatures is shown in Fig. 5. The experimental results demonstrate that the B–H bond is disrupted more easily than the B–C bond in trialkyl boron, because the absorbance due to tripropyl boron (2970 cm^{-1}, see Fig. 5) remains almost unchanged, whereas the B–H absorbance (2485 cm^{-1}) decreases with prolonged evacuation time. Fripiat and Tongelen (*10*) also showed that the B–H bond is easily disrupted by evacuation at 80°C.

Effect of 1-Butene

The trialkyl borons easily displace their alkyl groups with other alkyl groups of a higher carbon number in the liquid phase (*2*). Whether the exchange reaction between alkyl groups did or did not occur on solid catalysts was examined in the catalytic hydroboration. After adsorption of triethyl boron on alumina for 2 hr, followed by pumping for 5 min, 1-butene (250 mm Hg) was admitted and brought into contact for 15 hr, followed by pumping for 5 min. The absorbance ratios of CH_3/CH_2 before and after addition of 1-butene remained unchanged, viz., $CH_3/CH_2 = 1.06$, indicating that no exchange reaction occurred between the ethyl groups in the triethyl boron on the surface and the 1-butene in the gas phase.

DISCUSSION

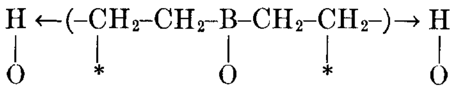
The adsorbed species of diborane as (I) and (II), as previously proposed, were considered. The question is which of the two species would be more reactive to the olefin hydroboration? When both C_2H_4 and C_3H_6 were brought into contact with Al_2O_3 on which B_2H_6 had been preadsorbed, the absorbance ratios of the terminal B–H (2485 cm^{-1}) and the bridge B–H (2170 cm^{-1}) bands were calculated as shown in the third column of Table 2. The ratio increased with prolonged contact time, indicating that the adsorbed species with the bridge structure (I) is more reactive, because the bridge B–H due to the adsorbed state (I) decreased relatively more rapidly than the terminal B–H (II). The reaction mechanisms producing triethyl boron from adsorbed diborane (I) and ethylene, for example, can be depicted as follows.



The hydroboration of olefin with diborane has been shown to correlate with the acidity of catalysts (*4*). On the acidic sites, diborane will be adsorbed by giving its electrons to the sites. As the adsorbed state, (I) is more reactive than (II), therefore, the hydroboration proceeds mainly on site (I). State (I) was originally formed by the reaction of the diborane and OH groups on the alumina surface (*8*).

It seems reasonable, therefore, to take the role of site (III) into consideration in the reaction mechanism. The hydroboration with the reaction of olefin and the adsorbed state of diborane as in (II) may occur through a similar mechanism.

The triethyl and tripropyl boron adsorbed on the alumina catalyst seem to be considerably stable because: (i) When evacuated at 80°C, the bands due to triethyl and tripropyl boron did not disappear; (ii) the bands were stable in oxygen; and (iii) no exchange reaction took place with 1-butene. When triethyl boron, for instance, was adsorbed on the alumina, the absorbance ratio of CH_3/CH_2 decreased from 1.22 to 1.06, which is the ratio of the liquid triethyl boron in CCl_4 solution (see Fig. 2 and Table 4). For reference, the frequency of the CH_3 and CH_2 groups in the carbon tetrachloride solution was 2950 cm^{-1}, which slightly shifted to the lower values in comparison to those on the alumina. The difference between the absorbance ratios on alumina and in CCl_4 may be explained by assuming that the ethyl group in triethyl boron is dissociatively adsorbed to split a hydrogen atom to form OH on the alumina surface, which may be schematically depicted as follows:



$$\begin{array}{ccccccc} H & \leftarrow(-CH_2 & -CH_2- & B & -CH_2- & CH_2-)\rightarrow & H \\ | & | & & | & & | & | \\ O & * & & O & & * & O \end{array}$$

In this case, the asterisk may be an alumina atom on the alumina surface.

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