

The Boron Number is a measure of the fraction of diborane on alumina in silica-alumina and can be used to calculate the fraction of total hydroxyl groups on alumina. To make this calculation it is necessary to know the exact value of the hydrogen to diborane ratio for reaction with hydroxyl groups attached to aluminum and silicon atoms in silica-alumina. Using the values obtained experimentally with the separate oxide gels, *i.e.*, 1:1 for alumina and 3:1 for silica, the fraction of hydroxyl groups on alumina can be calculated from the formula: $f(\text{Al}) = B_n/[B_n + 1.5(1 - B_n)] = B_n/[1.5 - 0.5B_n]$, where B_n is the Boron Number. Further work is indicated to determine whether the absolute values for fraction of hydroxyls on alumina shown in Table II are real. However, relative to one another the changes are significant. It can be seen from Table II that the OH sites on silica-alumina are associated with both silicon and aluminum atoms when the catalyst has been heated at 250°. The hydroxyl ratios also show that heating to higher temperatures tends to eliminate the silica hydroxyl groups at a faster rate than those associated with the alumina. The fact that the Boron

Number and Hydroxyl Ratio drops on long-time heating at 500° indicates that water is now being eliminated from the aluminum or that hydroxyls may be transferring from aluminum to silicon atoms. In addition to the change in Boron Number, the above conclusions are supported by the following corroborating evidence: (1) the hydrogen-diborane ratios decrease with increasing drying temperatures until they approach the limiting ratio (1:1) of alumina and, (2) the exchange reactions for catalyst dried at low temperatures exhibit the slow rate characteristic of silica, while for samples heated to higher temperatures this rate of exchange increases (as in alumina).

Other exchange studies, involving diborane-catalyst adducts, are currently being studied and will be reported separately. The utility of the concept of Boron Number for studies on silica-alumina has been demonstrated for this particular work on activation temperatures. The possibility that Boron Number and catalyst activity may be related is also being examined.

PASADENA, CAL.

[CONTRIBUTION FROM THE RESEARCH LABORATORY, OLIN MATHIESON CHEMICAL CORPORATION]

Boron Exchange between Diborane and Pentaborane-9 in the Presence of Alumina Catalysts

BY H. G. WEISS, J. A. KNIGHT AND I. SHAPIRO

RECEIVED OCTOBER 29, 1958

Boron exchange between diborane and pentaborane occurs in the presence of γ -alumina at 90°; no such exchange takes place under comparable conditions in the absence of the catalyst. The role of the alumina has been elucidated by use of isotopic techniques. The alumina provide sites for the formation of a diborane-catalyst complex, which is capable of exchanging boron atoms with either diborane or pentaborane-9. The exchange of the catalyst complex with pentaborane-9 is slower than with diborane.

Mixtures of isotopically different diboranes are known to reach equilibrium distributions quickly at room temperature.¹ This exchange, of course, arises from the rapid equilibrium between diborane and borane, *viz.*, $\text{B}_2\text{H}_6 \rightleftharpoons \text{BH}_3$. Of the exchange reactions reported between diborane and higher molecular weight boron hydrides only the unstable hydrides,² B_4H_{10} and B_5H_{11} , have shown boron participation. The boron exchange of diborane with these molecules has been explained² on the basis of fragmentation of the B_4H_{10} or B_5H_{11} molecules. The stability of pentaborane-9 and decaborane (relative to B_4H_{10} and B_5H_{11}) is such that boron exchange with diborane should be considerably less than in the case of B_4H_{10} or B_5H_{11} . In fact, it was found that there was no boron exchange between diborane and pentaborane-9^{3,4} at 80° or between diborane and decaborane⁵ at 100°, although there was hydrogen exchange under these conditions. The tendency of the stable boron hydrides to resist boron exchange even at high temperatures is illus-

trated in the self exchange of pentaborane⁶ at 250° (vapor phase); in this case no boron exchange was observed even though considerable decomposition had occurred.

In our Laboratory, boron exchange was observed between pentaborane-9 and B^{10} -enriched diborane on exposure to a chrome-alumina catalyst at 90°. Similar results were obtained under the same conditions on platinum-alumina and on γ -alumina. The reactions discussed here were carried out using platinum on alumina. Pentaborane-9 was found to exchange with diborane through a mechanism involving a catalyst-diborane complex, which also exchanged with diborane vapor. Relative rates of the two exchange reactions are such that diborane (vapor) was essentially in equilibrium with the complex at all times.

Experimental

1. **Reagents.** 0.3% Platinum on Alumina Catalyst.—Baker and Co., Inc., $1/8''$ pellets were dried *in vacuo* at 450° prior to use.

Diborane.— B^{10} -enriched diborane was prepared by reaction of lithium aluminum hydride with B^{10} -enriched boron trifluoride etherate.⁷

(6) I. Shapiro and B. Keilin, *ibid.*, **77**, 2663 (1955).

(7) I. Shapiro, H. G. Weiss, M. Schmich, S. Skolnik and G. B. L. Smith, *ibid.*, **74**, 901 (1952).

(1) P. C. Maybury and W. S. Koski, *J. Chem. Phys.*, **21**, 742 (1955).

(2) W. S. Koski, *Résumés de Communications, 16th Internat. Cong. Pure and Appl. Chem. (Paris)*, 1957.

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

(4) J. J. Kaufman and W. S. Koski, *ibid.*, **24**, 403 (1956).

(5) J. J. Kaufman and W. S. Koski, *THIS JOURNAL*, **78**, 5774 (1956).

Pentaborane.—Pentaborane was prepared by pyrolysis of diborane and was purified by conventional high vacuum techniques. The pentaborane was found to be spectroscopically pure by mass spectral analysis.

2. **Procedure.**—Catalyst samples (1.5 g. each) were heated in a glass reactor under vacuum at 450° for 7 hr. Then a measured quantity of B¹⁰-enriched diborane (96% B¹⁰) was added and the reactor was removed from the vacuum line. The reactor was shaken at intervals to ensure thorough mixing, and after *ca.* 20 minutes at room temperature, the residual diborane was removed and measured to determine the amount of complex formed. Isotopically normal pentaborane was then added, and the reactor was placed in an oil-bath (maintained at 90°) for the desired period of time. The conditions were such that no liquid pentaborane could be present. After reaction the pentaborane was collected and analyzed mass spectrometrically with a Consolidated Model 21-103 Mass Spectrometer operated at an ionizing potential of 70 volts.

Results and Discussion

In initial experiments mixtures of pentaborane-9 vapor and B¹⁰-diborane were heated at 90° in the presence of alumina catalysts for various lengths of time, and the B¹⁰ content of the pentaborane-9 was then measured. Inconsistent results were obtained at first, but then it was noted that with pre-treatment of the catalyst with diborane reproducible results could be obtained. Since the initial reaction of diborane with the catalyst is exothermic, it appears that the inconsistent results obtained with untreated catalyst were caused by local temperature variations on the catalyst surface. With the pretreated catalyst there was measurable exchange between diborane and pentaborane-9 at 90°, and for runs of short duration no reactants were lost. Longer exposure, however, produced small losses of diborane and gave high values for the B¹⁰ content of the pentaborane. This indicates pyrolysis of diborane to pentaborane.

The initial reaction between diborane and silica gel is known to involve reaction of diborane with the bound water in the catalyst.⁸ The same was found to be true here with alumina catalysts⁹; also, the borane surface that formed was found to exchange with diborane vapor. Measurable exchange of the surface complex with diborane vapor occurred both at room temperature and at 90°. At both temperatures the diborane gas was completely recovered. At 90° the exchange reaches equilibrium after two or three minutes, and the equilibrium value attained corresponds to participation of half of the boron on the catalyst. Details of this exchange as compared with boron exchange on silica gel and on silica-alumina are reported separately.⁹

Since pentaborane-9 also was found to exchange

(8) I. Shapiro and H. G. Weiss, *J. Phys. Chem.*, **57**, 219 (1953).

(9) H. G. Weiss, J. A. Knight and I. Shapiro, *THIS JOURNAL*, **81**, 1823 (1959).

with the borane-alumina complex, it was possible to run exchange reactions in the absence of diborane vapor. Thus the complication of pyrolysis of the diborane could be eliminated. The experiments consisted of pre-treatment of the catalyst with B¹⁰-diborane followed by exposure to pentaborane-9 vapor. A plot of the B¹⁰ content of pentaborane *vs.* time of exchange for reaction at 90° is shown in Fig. 1. It can be seen from this curve that exchange

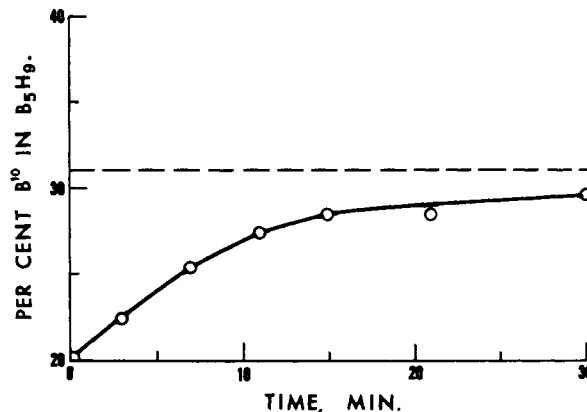


Fig. 1.—Pentaborane exchange at 90°: - - - -, calculated equilibrium for 50% boron exchange.

with pentaborane-9 occurs at a slower rate than with diborane, equilibrium being attained only after 15–20 minutes. Essentially all of the pentaborane-9 can be recovered. As in the case of diborane, the curve in Fig. 1 again approaches a value which represents participation of half of the available boron on the catalyst surface. This would signify two independent exchange reactions involving the same catalyst-diborane species. Hence, in the exchange of diborane with pentaborane-9 over the catalyst at 90° diborane would be essentially in equilibrium with the surface borons, while pentaborane-9 exchange with the surface is much slower and would be rate determining. In experiments carried out in the absence of catalysts under conditions comparable to the above there was no boron exchange between diborane and pentaborane-9, so all exchange in the presence of the catalyst must involve the catalyst complex.

In summary, boron exchange between diborane and pentaborane-9 over alumina catalysts involves two independent reactions: (1) a relatively fast reaction between diborane and a catalyst-diborane complex, and (2) a slower rate-determining reaction between pentaborane-9 and the catalyst-diborane complex.

PASADENA, CAL.