[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

Infrared Study of the Exchange of Deuterium between Decaborane and Diborane[1]

BY JOYCE J. KAUFMAN AND W. S. KOSKI

RECEIVED JUNE 18, 1956

An infrared spectroscopic study of partially deuterated decaborane samples prepared by exchanging deuterium between diborane and decaborane at 100° has been made. These spectra have been compared with those of partially deuterated decaborane in which the deuteriums are randomly distributed. This comparison shows that the exchange proceeds on the terminal hydrogens in decaborane and that the bridge hydrogens are not involved at all in the reaction under the experimental conditions.

Introduction

If deuterated diborane is mixed with decaborane ($B_{10}H_{14}$) at 100° there is an exchange of deuterium. A preliminary kinetic study[2] of this reaction indicated that not all of the hydrogens in decaborane were involved in the exchange; however, the number of hydrogens involved could not be determined unambiguously from the kinetic study alone because of extensive decomposition of diborane for long reaction times. We have therefore made an infrared spectroscopic study of the partially deuterated decaborane resulting from the exchange reaction and established the positions into which deuterium is entering.

In some previous investigations[3,4] we have made a study of the corresponding reaction involving pentaborane (B_5H_9) and found that the exchange proceeded preferentially in the non-bridge positions. It was therefore of interest to see if a similar phenomenon occurs with other boron hydrides and this paper is a report of our results on decaborane.

The structure of decaborane has been determined[5] and the molecule has ten terminal hydrogens and four bridge hydrogens. Some of the vibrational frequencies of decaborane of normal isotopic constitution have been assigned[6] and a comparison of the spectra of $B_{10}H_{14}$ and $B_{10}D_{14}$ enabled us to correlate a sufficient number of absorption peaks in the latter compound to achieve the main objectives of this investigation.

Experimental

The diborane used in this work was prepared by treating $LiAlH_4$ or $LiAlD_4$ with boron trifluoride–ethyl ether and was purified by the method outlined by Shapiro, *et al.*[7]

The decaborane was prepared by pyrolysis of diborane at 125°. The pyrolysis was carried out in a Pyrex vessel, the main part of which was heated to 125° while a cold finger was kept at room temperature. The reaction was permitted to continue for two days with the decaborane subliming out as it was formed. The resulting decaborane was purified by pumping off all non-condensables at room temperature and then vacuum subliming the remaining decaborane. The partially deuterated decaboranes, in which the deuterium was distributed randomly, were prepared by pyrolysis of deuterated diborane containing the appropriate amount of deuterium. In this manner decaborane samples containing 12.9, 30.1 and 48.3% deuterium were prepared. Partially deuterated decaborane samples were also prepared by exchange of deuterium between decaborane and deuterated diborane. In these cases decaborane samples containing 10.5, 19.6 and 29.8% deuterium were prepared by heating 6.5 mg. of decaborane with 6.00 cm. of B_2D_6 for 1 hour, 6.5 mg. of decaborane with 6.00 cm. of B_2D_6 for 2 hours, and 6.5 mg. of decaborane with 5.97 cm. of B_2D_6 for 3 hours, respectively. The reaction temperature was 100° and the volume of the reaction vessels was approximately 80 cc. The non-condensables were pumped off at room temperature and the decaborane was sublimed out of the reaction bulb.

The total deuterium content of the decaborane was determined by decomposing the decaborane in quartz bulbs at 525° and then analyzing the resulting hydrogen for its deuterium content by a thermal conductivity method.[8]

A Perkin-Elmer Model 21 double-beam infrared spectrometer was used in this experiment. A pair of microcells, matched to within 1%, were used in the sample and the reference beams. The $B_{10}H_{14}$ samples were dissolved in CCl_4 at a concentration of 2 mg. in 0.5 ml. The weights of the partially deuterated decaborane samples were adjusted so that there were the same number of moles of decaborane per ml. of solution as in the reference solution. Spectra were run of partially deuterated decaborane samples in the sample beam against CCl_4 and against $B_{10}H_{14}$ solution in the reference beam.

Results and Discussion

In this study two types of partially deuterated samples were prepared. One set of samples was prepared by pyrolysis of partially deuterated diborane and had a statistical distribution of deuteriums. This set of samples gave us the variations of the intensities of the absorption peaks due to B–D and B–D–B bridge vibrations as a function of the percentage of deuterium in the non-bridge and bridge positions, respectively. With this information, calibration curves were constructed and infrared measurements were made on the samples prepared by exchange, and the amount of deuterium that had gone into the non-bridge and bridge positions was determined. These figures were then compared with the results obtained by thermal conductivity analysis.

One favorable region in the decaborane spectrum for observation of the entrance of deuterium into the non-bridge positions is the 5.17μ absorption band which is due to a B–D stretch vibration. The data obtained from observations on this peak are summarized graphically in Fig. 1, and it is evident from this plot that decaborane having 19.6% deuterium due to exchange absorbs almost as strongly as decaborane containing 30.1% deuterium statistically distributed, while decaborane having 29.8% deuterium due to exchange absorbs much more strongly than a sample containing 30.1% deuterium statistically distributed. These ob-

---

[1] This research was supported by the United States Air Force through the Office of Scientific Research of the Air Research and Development Command.

[2] P. C. Maybury and W. S. Koski, unpublished work.

[3] W. S. Koski, J. J. Kaufman, L. Friedman and A. P. Irsa, *J. Chem. Phys.*, **24**, 221 (1956).

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

[5] Kasper, Lucht and Harker, *Acta Cryst.*, **3**, 436 (1950).

[6] W. E. Keller and H. L. Johnston, *J. Chem. Phys.*, **20**, 1749 (1952).

[7] Shapiro, Weiss Skolnik and Smith, THIS JOURNAL, **74**, 901 (1952).

[8] W. S. Koski, P. C. Maybury and J. J. Kaufman, *Anal. Chem.*, **26**, 1992 (1954).

servations indicate that, qualitatively, the exchange is proceeding preferentially in the non-bridge positions. If we make the assumption that all of the deuterium entering the decaborane molecule by exchange is going into the non-bridge positions, then the per cent. deuterium as determined by thermal conductivity multiplied by 1.4 gives the percentage of non-bridge positions occupied by deuterium. Comparison of this figure with the infrared deduced percentage of non-bridge positions occupied by deuterium shows reasonable quantitative agreement as evidenced from the data in Table I. To within experimental error all of the deuterium that has entered the decaborane molecule by exchange can be accounted for by the amount of deuterium in the non-bridge positions, indicating that the exchange reaction proceeds preferentially into these positions.

TABLE I

DEUTERIUM ANALYSIS OF PARTIALLY DEUTERATED DECABORANE OBTAINED FROM THE B_2D_6–$B_{10}H_{14}$ EXCHANGE

Per cent. deuterium By thermal conductivity[a]	By infrared spectra (5.17 μ) (non-bridge positions)
14.7	16.6
27.4	29.1
41.7	40

[a] Calculated from thermal conductivity measurements assuming that all of the deuterium enters the non-bridge positions.

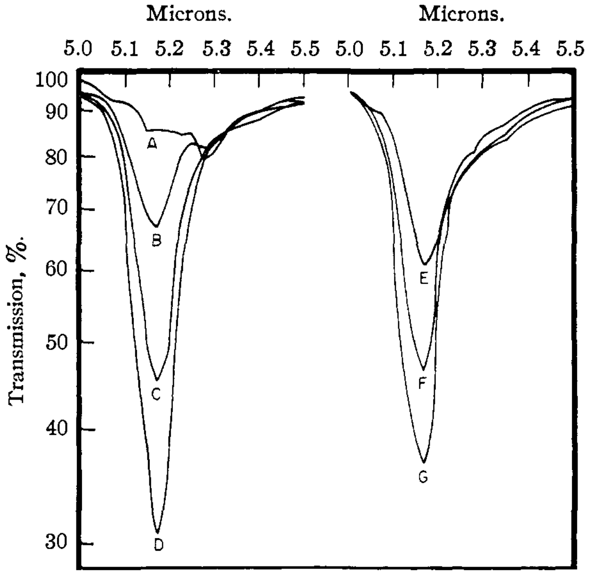

Fig. 1.—Infrared absorption of partially deuterated decaborane: A, $B_{10}H_{14}$ of normal isotopic content; B, C and D are samples of decaborane in which the deuterium is statistically distributed and have 12.9, 30.1 and 48.3% total deuterium, respectively. E, F and G are samples of decaborane prepared by exchange and contain 10.5, 19.6 and 29.8% total deuterium, respectively.

Another region in the spectrum which can be observed fairly well is an absorption band at 8.72μ due to a B–D–B bridge vibration. For statistical samples this B–D–B band rises almost linearly with increasing deuterium content. However, for exchange samples there is no rise in this peak at all. This fact constitutes further proof that the deuterium entering the decaborane molecule by the exchange reaction is not going into the bridge positions.

BALTIMORE, MD.

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Energetics of the Boranes. II. Kinetic Consequences of the Diborane–Borane Equilibrium. Comments on the Decomposition of OC:BH_3

BY S. H. BAUER

RECEIVED MAY 25, 1956

The equilibrium $B_2H_6 \rightleftarrows 2BH_3$ has been assumed to play a dominant role in many reactions involving diborane. Eight independent kinetic studies have been analyzed to determine whether these data impose mutually consistent conditions on this dissociation. It is demonstrated that if the postulate is introduced that the rate of association of boranes is comparable to that for methyl groups ($k_{\text{assoc}} \approx 10^{14}$ mole^{-1} cc. sec.$^{-1}$) six experiments lead to mutually compatible upper bounds for the heat of dissociation of diborane; the two smallest bracket the previously published thermochemical value of 28.4 ± 2 kcal. The remaining kinetic experiments do not give clear-cut estimates. With the introduction of an additional assumption one of these can be interpreted to give a lower bound which is consistent with the lack of a directly observable equilibrium dissociation pressure, and with the other studies listed above. The published mechanism for the decomposition of OC:BH_3 is shown to be incorrect and an alternate mechanism is proposed which does give the correct form for the observed pressure–time dependence. Comments are appended for the existence of activation energies for some primary acid–base associations.

In the first paper of this series[1] we reported a value for the heat of dissociation $B_2H_6(g) = 2BH_3(g)$, based on measured heats of reaction between diborane and tetramethyldiborane with several amines. Since the entropy increment for this reaction has been computed with adequate certainty (34.2 e.u.),[2] the equilibrium concentration of BH_3 may be estimated readily. This equilibrium has been utilized in eight postulated mechanisms describing the kinetic behavior of mixtures containing diborane. In five of these it is assumed as a first step

$$B_2H_6 \underset{k_d}{\overset{k_a}{\rightleftarrows}} 2BH_3 \qquad \text{(a)}$$

followed by

$$BH_3 + X \underset{k_x}{\longrightarrow} \text{products} \qquad \text{(b)}$$

---

(1) R. M. McCoy and S. H. Bauer, THIS JOURNAL, **78**, 2061 (1956).

(2) A. Shepp and S. H. Bauer, *ibid.*, **76**, 265 (1954).