A Mass Spectrometric Investigation of the Exchange of Deuterium with Tetraborane(10) in the Gas Phase *

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Mass spectrometry has been used to establish direct exchange between dideuterium (D_2) and B_4H_{10} in the gas phase. In a mixture of stoicheiometry B_4H_{10} : $3D_2$ at 42 °C, *ca.* 7% of the hydrogen atoms were replaced by deuterium in 130 min. The possibility that the exchange might be occurring by an indirect or autocatalytic mechanism was eliminated by a series of experiments in which the rate of exchange was shown to be independent of small admixtures of the decomposition products. The present work resolves a troublesome inconsistency in the literature and strengthens the view that the equilibrium $B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2$ plays a key role in borane interconversion reactions.

The gas-phase thermolysis of B_4H_{10} has been the subject of numerous studies, although there is still disagreement in the literature about the steps involved in the initial stages of its decomposition. An early study [1] suggested that B_4H_{10} decomposes by two simultaneous first-order paths (1) and (2), leading to the formation of three highly reactive species $\{B_4H_8\}$, $\{B_3H_7\}$, and $\{BH_3\}$.† Subsequent kinetic studies[2,3] strongly implicated $\{B_4H_8\}$ as the reactive intermediate of prime importance. The observation [4] that $B_4H_8(CO)$ and dideuterium react to form $B_4H_8D_2$ was taken as strong evidence for the reverse of reaction (1).

$$B_4H_{10} \rightleftharpoons \{B_4H_8\} + H_2 \qquad (1)$$

$$B_4H_{10} \rightleftharpoons \{B_3H_7\} + \{BH_3\} \qquad (2)$$

Related studies [5-7] showed that B_4H_{10} and B_2D_6 exchange both deuterium and boron at 45 °C. Koski [7] argued that reaction (2) was probably the rate-controlling step of the fast exchange, and eliminated equilibrium (1) on the grounds that *no exchange* was observed between dideuterium and B_4H_{10} during a period of 130 min at 45 °C. More recently, Bond and Pinsky [8] have also favoured reaction (2) as the initial step, although they envisage this as part of a somewhat speculative chain mechanism.

Schaeffer and co-workers,[4,9,10] on the other hand, have cast considerable doubt on the original analysis of the B_2D_6/B_4H_{10} exchange data. In addition there is ample indication from other experiments of the importance of $\{B_4H_8\}$ as a reactive intermediate in tetraborane chemistry. Examples include the observation that B_4H_{10} reacts with ethylene to form $B_4H_8(C_2H_4)$,[11] and with deuteriated ethylene to form $B_4H_8(C_2D_4)$ in which all deuterium atoms in the product are attached to carbon.[12] There is also convincing mass-spectrometric evidence for $\{B_4H_8\}$ but not $\{B_3H_7\}$ or $\{BH_3\}$ in the thermolysis of B_4H_{10}.[13-16] In the light of this accumulation of evidence in favour of reaction (1), Koski's reported failure to observe exchange of dideuterium with this borane is seen as a worrying inconsistency in urgent need of reinvestigation. This is particularly so because Long,[17] in his synoptic re-assessment of the mechanisms of borane thermolyses and interconversions, rejected reaction (1) in favour of (2) largely on the basis of this piece of experimental evidence. There has been one attempt to resolve this problem but the results were inconclusive.[18]

We have therefore designed a careful series of experiments to establish unequivocally whether dideuterium exchanges directly with B_4H_{10} in the gas phase at moderate temperatures, and the results are presented below.

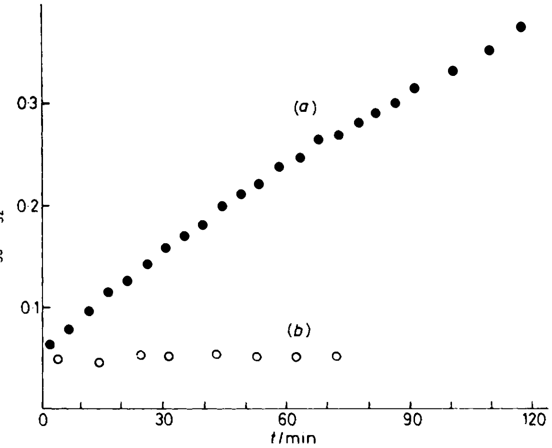

Figure 1. Reaction profiles for exchange in a clean Pyrex vessel at 42 °C: (*a*) plot of I_{53}/I_{52} *vs.* time for a mixture containing D_2 (12 mmHg) and pure B_4H_{10} (4 mmHg); (*b*) a similar plot for a control experiment with H_2 (12 mmHg) and pure B_4H_{10} (4 mmHg). Each mixture also contained He (100 mmHg) and Ar (5 mmHg) for calibration purposes

Results and Discussion

The results of an experiment in which D_2 (12 mmHg pressure) and B_4H_{10} (4 mmHg pressure) were heated together at 42 °C are shown in Figure 1. The vessel used for these particular reactions was a 1-dm³ Pyrex bulb, previously unexposed to boranes of any description. Figure 1(*a*) shows that the intensity ratio I_{53}/I_{52} ‡ increases steadily from the moment the two gases are brought into contact, and after 130 min the value has risen from 0.06 to 0.38, providing definitive evidence that substantial exchange has occurred even at this low temperature. In addition to the obvious change in the intensity ratio of the peaks at mass numbers 53 and 52, peaks corresponding to deuteriated fragments at mass numbers near the expected cut-off for B_4H_{10} (*m*/*z* 54) are observed in the mass spectrum. The assignment of these peaks to deuteriated tetra-

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* *Non-S.I. unit employed:* mmHg ≈ 133 Pa.

† Throughout this paper braces { } are used to indicate non-isolable reactive intermediates.

‡ See Experimental section for a definition of this ratio and for further details of the experimental procedures.

Table. Selected deuteriated fragments identified by high-resolution mass spectrometry *

Fragment	m/z Observed	m/z Calculated
$^{10}B_2{}^{11}B_2H_3D_6$	57.1518	57.1526
$^{10}B_1{}^{11}B_3H_2D_6$	57.1412	57.1411
$^{11}B_4H_3D_5$	57.1308	57.1312
$^{10}B_2{}^{11}B_2H_2D_6$	56.1448	56.1448
$^{10}B_1{}^{11}B_3H_3D_5$	56.1344	56.1348
$^{11}B_4D_6$	56.1225	56.1218

* Many other isotopomers below m/z 56 were observed and characterized with similar precision.

borane species was confirmed by accurate mass measurement of selected fragments under high resolution (Table).

The exchange was further demonstrated by a steady decrease with time of the measured pressure of deuterium and an accompanying increase in the pressures of H_2 and HD: after 130 min, *ca.* 11% of the D_2 originally present had entered the borane, implying that *ca.* 7% of the hydrogen atoms in B_4H_{10} had been replaced by deuterium.

Figure 1(*b*) shows the results of a control experiment in which a pressure of 12 mmHg of H_2 was substituted for the D_2. The intensity ratio I_{53}/I_{52} is seen to remain essentially constant, thereby ruling out any possibility that species other than deuteriated tetraborane(10) might be contributing to the increase in this ratio in the exchange experiment [Figure 1(*a*)]. The absence of any thermal decomposition in this experiment, and by implication in the D_2/B_4H_{10} exchange experiment also, was indicated by the near constancy of the intensity of the B_4H_{10} peak at m/z 50 relative to that of the argon internal standard peak at m/z 40.

Although there was no significant decomposition on a macro scale, trace amounts of B_5H_{11} and to a lesser extent B_2H_6 and higher boranes were nevertheless produced. This inevitably raises the possibility that deuterium might be incorporated into the B_4H_{10} *via* indirect routes involving such species. It is well known that, even in the process of being handled in vacuum lines at ambient temperature, boranes decompose slowly to produce solid polymeric deposits. The process is hastened at higher temperatures, and in the present work the Pyrex vessels invariably developed a characteristic coating after several experiments. During the course of this work we have discovered that the exchange reaction $H_2 + D_2 \rightleftharpoons 2HD$ is catalysed at room temperature in vessels conditioned in this way.* It was therefore deemed prudent to carry out further experiments to determine whether similar effects were operative in the D_2/B_4H_{10} exchange reaction.

Because it was not feasible to eliminate decomposition entirely, an approach was adopted whereby any possible effects the products might be having on the exchange reaction were assessed by deliberately introducing the species at the outset. The results of three such experiments on mixtures having a $D_2:B_4H_{10}$ ratio similar to that employed in the earlier runs are shown in Figure 2. The first run (filled circles) was carried out in a ' conditioned ' vessel (*i.e.* one which had been used previously in B_4H_{10} thermolysis experiments) to check specifically for any surface activity. The second run (open circles) refers to a reaction carried out under similar conditions but, before being mixed with D_2, the B_4H_{10} was heated for 3 min at *ca.* 75 °C to introduce a selection of thermolysis products. The major impurity was B_5H_{11} (*ca.* 5% by volume). The third run (open triangles) shows the results for a reaction in which the B_4H_{10} contained an admixture of *ca.* 2% by volume of B_2H_6. From a comparison with Figure 1(*a*) the rate of exchange is seen to be unaffected in all cases. This series of experiments therefore shows that exchange does not occur *via* an indirect route.

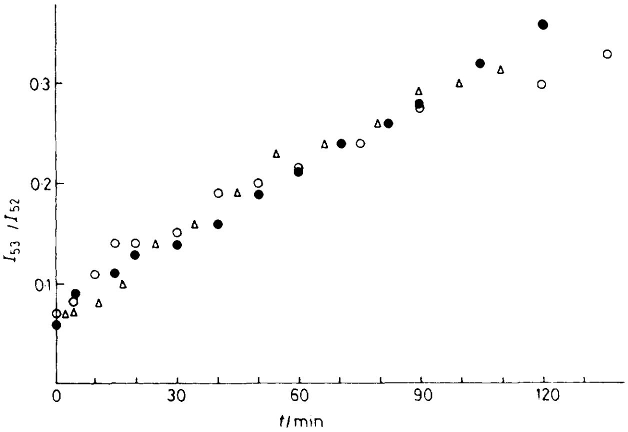

Figure 2. Plots of I_{53}/I_{52} *vs.* time for the exchange reactions at 42 °C for mixtures of similar composition to that in Figure 1 (*a*): ●, a run in a 'conditioned' vessel (see text); ○, the same except that the B_4H_{10} contained *ca.* 5% by volume of B_5H_{11}, together with smaller amounts of other B_4H_{10} thermolysis products; △, the B_4H_{10} contained *ca.* 2% by volume of B_2H_6

In summary, we have demonstrated unequivocally that D_2 undergoes direct exchange with B_4H_{10} in the gas phase at 42 °C. This result contradicts earlier reports that no such exchange occurs and thereby resolves a longstanding inconsistency in the literature. The possibility that the exchange might occur as a result of reaction (2) in conjunction with the postulated [17] reversible reaction (3) can be ruled out since reaction (3) is in

$$\{B_3H_9\} \rightleftharpoons \{B_3H_7\} + H_2 \qquad (3)$$

fact the rate-determining step in the decomposition of diborane which does not occur appreciably at temperatures below 100 °C. If it did contribute to the exchange processes, then this would imply stimultaneous and extensive decomposition of B_4H_{10}, which is not observed (at 42 °C). Furthermore it would be expected that the admixture of B_2H_6 with B_4H_{10} (see Figure 2) would affect the exchange rate if this route were involved. These considerations strengthen the view that reaction (1) is of major importance in the thermal decomposition of B_4H_{10} and that this equilibrium plays a key role in borane interconversion reactions. The possible significance of reaction (2) in thermal decomposition at elevated temperatures is not excluded and detailed kinetic studies of the thermolysis of B_4H_{10} are in progress to gain further insight into the mechanism of its decomposition.

Experimental

The boranes, B_2H_6 [20] and B_4H_{10},[21] were prepared by methods described in the literature, and purified by standard vacuum-line techniques. Particular care was necessary to render the B_4H_{10} free from B_5H_{11}: the mass spectrum indicated a B_5H_{11}-impurity level of <0.1% by volume, and the majority of this

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* In a typical reaction involving an equimolar mixture of H_2 and D_2, the individual pressures were each found to decrease from 10 to 6.3 mmHg in 60 min; on the basis of the value $K_p = 3.28$ given for the equilibrium constant at 298 K,[19] final pressures of 5.3 mmHg for H_2 and D_2 would be expected.

probably arose from decomposition in the source. CP Grade helium and Standard Grade argon were obtained from BOC Ltd., and dideuterium (95%) from Argo International Ltd.; all were used without further purification.

Mass Spectrometric Analysis.—The progress of each reaction was followed by two mass spectrometers: a Kratos MS30 double-beam instrument equipped with a DS55 data system to monitor the boranes, and an MS10S to analyse quantitatively for H_2, D_2, and HD. The MS30 was also used, in its high-resolution mode, to provide unambiguous identification of deuteriated fragments. The resolution (R = 150) available on the MS10S was just sufficient to enable the D_2 peak to be distinguished from the He peak at m/z 4, and a linear calibration curve of ion current *vs.* pressure for D_2 was established. The calibration curve for HD was determined by allowing known pressures of H_2 and D_2 to exchange in a ' conditioned ' vessel and recording the ion current at m/z 3 as the equilibration proceeded; the HD pressure at each point was estimated from the amount of H_2 and D_2 consumed. Tetraborane(10) and the various deuteriated species produced from it have not been analysed quantitatively; instead, exchange was monitored simply by observing changes in the relative intensities of peaks at m/z 53 and 52. This ratio (referred to throughout as I_{53}/I_{52}) is a very sensitive indicator of exchange, as can be seen by comparing the value of 0.05 found for B_4H_{10} with the value of 0.82 observed for $B_4H_8D_2$;[6] the value found under the present operating conditions for the pure material used in this work was 0.06.

Because of the intrinsic thermal instability of B_4H_{10}, traces of B_5H_{11} were always detectable in its mass spectrum. In order to minimize decomposition in the mass spectrometer, the source was cooled to *ca.* 80 °C by a constant flow of compressed air. In some experiments the temperature was reduced to 40 °C by first passing the dry cooling gas through copper coils immersed in solid CO_2, but this did not lead to a significant reduction in the impurity level.

Procedure.—The gas mixtures were prepared in calibrated bulbs on a high-vacuum line fitted with HP Rotoflo, glass/polytetrafluoroethylene, greaseless taps. The mixtures were then expanded into a 1-dm^3 Pyrex reaction vessel enclosed in an oven maintained at 42 ± 1 °C and this was taken as the zero reaction time. Samples were introduced without delay into the two mass spectrometers *via* separate 180-mm lengths of Veridia capillary tubing (diameter 0.1 mm) and scanning was initiated immediately. Approximately 1 min later, the reaction vessel was isolated by means of a long-distance-control, greaseless tap (Youngs Scientific Glassware Ltd.) which could be operated through the base of the oven. On the MS30, scans were recorded every 30 s; every ten scans were averaged and the mean value of the ratio I_{53}/I_{52} plotted at the midpoint of the time interval. The MS10S was used in its manual mode and the H_2, HD, D_2, and He signals were recorded alternately.

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