

Table I. Isotope Effects on Hydrogen Exchange in Chloroform in Aqueous Solution at 25°

System <sup>a</sup>	$k_D/k_H$	
	Obsd	Theor
I. RT $\frac{LO^-}{L_2O} \rightarrow$ RL	1.48 ± 0.02	$\phi^\ddagger/\phi_h$
II. RL $\frac{LO^-}{L_2O} \rightarrow$ RT	2.10 ± 0.10	$\phi^\ddagger/\phi_s\phi_h$
III. RH $\frac{LO^-}{L_2O} \rightarrow$ RT	2.28 ± 0.03	1/ $\phi_h$
IV. RL $\frac{HO^-}{H_2O} \rightarrow$ RT	0.97 ± 0.04	$\phi^\ddagger/\phi_s$

<sup>a</sup> The symbol "L" is used to designate the hydrogens which are changed from H to D in the comparison, i.e., L = H or D.

present initially, in tracer amounts, in the solvent only, and rates of tritium incorporation rather than detritiation were determined; initial rate measurements were made where necessary in order not to alter the isotopic identity of the substrate.

These data lend themselves particularly well to analysis by the fractionation factor method. By this technique, solvent isotope effects become simple ratios of fractionation factors: those for all isotopically exchanged sites of the transition state divided by corresponding factors for the initial state. Thus, for system I,  $k_{D_2O}/k_{H_2O} = \phi^\ddagger/\phi_h$ , where  $\phi^\ddagger$  is the D-H fractionation factor, relative to the solvent, for the incoming hydrogen of the transition state (see eq 2), and  $\phi_h$  is the factor for the aqueous hydroxide ion in the initial state ( $\phi_h$  is a composite factor which includes the hydrogen of this ion as well as those of its solvating water molecules). Similar expressions may be written for the other three systems; these are listed in Table I. The additional symbol  $\phi_s$  is the fractionation factor for the exchanging hydrogen in the substrate.

These relationships and the corresponding experimental values of the isotope effects form a set with fewer unknowns ( $\phi^\ddagger$ ,  $\phi_h$ , and  $\phi_s$ ) than pieces of data. The model can therefore be tested for internal consistency. For example, the fractionation factor ratio for system II is equal to the product of those for systems III and IV, and it is significant therefore that  $(k_{D_2O}/k_{H_2O})_{III} \times (k_{D_2O}/k_{H_2O})_{IV} = (2.28 \pm 0.03) \times (0.97 \pm 0.04) = 2.21 \pm 0.09$ , in good agreement with  $(k_{D_2O}/k_{H_2O})_{II} = 2.10 \pm 0.10$ .

Solution of this system of equations gives  $\phi^\ddagger = 0.65 \pm 0.01$ ,  $\phi_h = 0.44 \pm 0.01$ , and  $\phi_s = 0.68 \pm 0.02$ . The fact that  $\phi^\ddagger$  is appreciably less than unity shows that there is appreciable isotopic fractionation in the incoming (or outgoing) water molecule of the rate-determining transition state (eq 2). This is a reasonable result, inasmuch as this molecule is in the process of forming a hydrogen bond to a localized carbanion; in this respect, it is similar to the water molecules which form the primary hydration shell of the hydroxide ion, and these are known to be subject to considerable isotopic fractionation.

As the fractionation factor expression for system I shows, the effect of  $\phi^\ddagger$  is to offset  $\phi_h$  and thereby to make the solvent isotope effect on detritiation smaller than the expected limiting value. It is only when *both* outgoing and incoming hydrogens remain unchanged, as in system III, that the full effect of  $\phi_h$  can be felt, and it is gratifying therefore that the isotope effect found for system III,  $k_{D_2O}/k_{H_2O} = 2.28 \pm 0.03$ , is in reasonably good agreement with the limiting or equilibrium value of 2.4.

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## References and Notes

- (1) This research was performed at the Illinois Institute of Technology and forms part of a thesis submitted there by A. C. Lin in partial fulfillment of the requirements for the Ph.D. degree.
- (2) Exchange is shown here as occurring via complete replacement of the original solvating water molecule generated by neutralization of the hydroxide ion. It could also be effected by a simple rotation of this water molecule which brings its other hydrogen into covalent bond-forming position, but the analysis of isotope effects using that mechanism would be no different from that presented here. The same is true of mechanisms in which the incoming and outgoing hydrogens are not equivalent.
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- (5) The value actually reported is 1.34. That, however, was calculated using isotope effects on the acid dissociation of biphosphate ion and the autoprotolysis of water which have since been superseded; when modern values are used, the result increases to 1.60.
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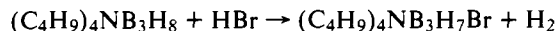
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## Halogenated Octahydroborate Salts. A New Route to Pentaborane(9)

Sir:

We wish to report the first preparation of halogen-substituted triborohydride salts and their use in a new and extremely convenient synthesis of pentaborane(9). The synthesis allows scale-up with simple equipment and provides a product from readily prepared starting materials in respectable yield and free of the bothersome pentaborane(11) contamination encountered with other methods.<sup>1,2</sup>

Tetrabutylammonium octahydroborate(-1), mp 217–218° was obtained from the oxidation of borohydride ion with iodine at 100°.<sup>3</sup> A 0.1561-g sample of the salt (0.552 mmol) dissolved in 0.8940 g of dry CH<sub>2</sub>Cl<sub>2</sub> in an evacuated tube produced a vapor pressure depression of 39 mmHg relative to pure solvent (353 mm at 20°), with a vapor volume of 310 ml. When bromine-free HBr gas (0.551 mmol) was condensed onto the sample, hydrogen gas was evolved rapidly on warming (0.557 mmol). Complete evaporation of the solvent left a solid residue and a weight gain of 0.0412 g, compared to a gain of 0.0418 g calculated on the basis of the equation



Return of the solvent now gave a vapor pressure depression of 37 mm. On the assumption that (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NB<sub>3</sub>H<sub>8</sub> and the product have the same Van't Hoff factor, these data correspond to a formula weight of 368 for the product, in good agreement with the value of 361 calculated for (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NB<sub>3</sub>H<sub>7</sub>Br. The nature of the reaction remained unchanged when diethyl ether was used as solvent. Evaporation of the solvent left a white crystalline solid which decomposed on heating. Anal. Calcd for (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NB<sub>3</sub>H<sub>7</sub>Br: C, 53.1; H, 12.0; N, 3.9; Br, 22.1. Found: C, 53.4; H, 12.1; N, 3.9; Br, 21.7.

These results were completely unexpected since it had been demonstrated that reaction of NaB<sub>3</sub>H<sub>8</sub> with HCl gives rapidly a B<sub>3</sub>H<sub>7</sub> intermediate,<sup>4</sup> and that (NH<sub>3</sub>)<sub>2</sub>BH<sub>2</sub>B<sub>3</sub>H<sub>8</sub>

Table I. Infrared Spectra of  $(C_4H_9)_4NB_3H_7X$  Salts

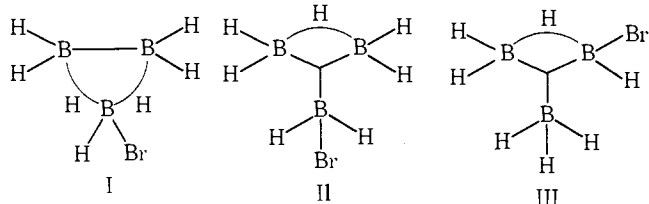
X	2500–2000 $cm^{-1}$	1020–900 $cm^{-1}$
H	2450 s, 2400 s, 2300 sh, 2130 m, 2080 m	1015 s, 930 w
Cl	2480 s, 2425 s, 2300 m, 2225 w	1015 m, 980 s, 930 w
Br	2495 s, 2435 s, 2300 m, 2230 sh	1015 m, 960 s, 930 sh

reacts even at  $-78^\circ$  with HCl or HBr to produce  $B_3H_7O(C_2H_5)_2$ .<sup>5,6</sup>

Similar experiments with hydrogen chloride and hydrogen iodide also gave quantitative evolution of hydrogen and a solid  $B_3H_7X^-$  salt without producing, at room temperature or below,  $B_3H_7$  or other volatile boron hydrides. Thus tetrabutylammonium ion apparently strongly stabilized the triborate ion with respect to halide loss which is perhaps not surprising in view of the relatively small Coulomb potential of this large cation.

Unlike the  $B_3H_8^-$  salt, the halogenated derivatives do not show resolved B–H resonances in the proton NMR spectrum. The  $^{11}B$  NMR also was not observed owing to extreme line broadening and to the fact that  $CH_2Cl_2$  solutions slowly decomposed with the stability decreasing from Cl to I derivatives.

The infrared spectra of the chloro and bromo derivative and of the starting material show, because of the presence of the  $(C_4H_9)_4N^+$  ion, many similarities and, in fact, only the regions from 2000 to 2500  $cm^{-1}$  and around 1000  $cm^{-1}$  exhibit any variation greater than 5  $cm^{-1}$  in the position of bands, in their number, or in their relative intensities. The pertinent data are given in Table I. The spectra reveal the absence of  $B_3H_8^-$  ion—or of  $BH_4^-$ , a possible disproportionation product—in the halogenation products. This, together with the vapor pressure depression data shows that the empirical formula  $B_3H_7X^-$  correctly represents the molecular identity as well. The new bands at 980 or at 960  $cm^{-1}$  can be assigned to the B–Cl or B–Br stretching mode, respectively. In the region 2000–2500  $cm^{-1}$  halogenation causes the loss of the weaker of the two doublets associated with the  $BH_2$  valence motions and replacement by a single band. Simultaneously there is a moderate shift to higher wave numbers for the remaining more intense doublet and a much larger shift of the new singlet with respect to the lost doublet. Both shifts are larger with bromine than with chlorine substitution. (The invariant band at 2300  $cm^{-1}$  does not appear in  $NaB_3H_8$ <sup>7</sup> and, therefore, is not associated with the B–H valence vibrations.) This suggests that the  $BH_2$  group associated with the less intense doublet is being substituted and that there remain two equivalent  $BH_2$  groups in the ion. The relative magnitudes of the shifts also are consistent with this notion, since amine– $BH_2X$  adducts<sup>8</sup> and boron cations<sup>9</sup> show similar shifts on substitution. Thus a 2013 *styx* formula<sup>10</sup> and a  $B_3H_8^-$  structure<sup>11</sup> substituted as in I is fully consistent with the infrared spectrum, whereas a 1104 structure is not easily reconciled. Neither substitution at the  $BH_3$  group (II), as in  $B_3H_7NH_3$ ,<sup>12</sup> nor at one of the two equivalent B atoms in III could be expected to produce the observed spectrum. In II the pattern of two doublets should be retained whereas in III an additional and strongly shifted singlet should appear at high wave numbers. Neither the observed bands nor their relative intensities agree with this prediction. The apparently inconsis-



quential changes in the part of the spectrum arising from skeletal vibrations and  $BH_2$  deformations also argue against a rearrangement to a 1104 structure.

The brominated tetrabutylammonium salt was resistant to substitution by ammonia at  $-78^\circ$  and reacted only slowly with  $NH_3$  at room temperature, without producing the expected  $B_3H_7NH_3$  in isolable quantities. Triphenylphosphine also reacted slowly at room temperature to give a mixture of products, one of which was  $Ph_3PBH_3$ . In the only clean substitution reaction 4.5 mmol of the compound and an equivalent quantity of  $NaBH_4$  in 20 ml of 1,2-dimethoxyethane at  $25^\circ$  slowly produced diborane. Treatment of the product with water, followed by extraction with  $CH_2Cl_2$  and precipitation with ether afforded a 73% yield of  $(C_4H_9)_4NB_3H_8$ , mp  $215-216^\circ$  dec, mmp  $216-217.5^\circ$ , identical in infrared spectrum to an authentic sample. This reaction not only confirms the structure assignment but also testifies to the enhanced acceptor strength of the  $B_3H_7$  fragment over that of  $BH_3$ , since hydride is transferred and bromine not retained.

For the synthesis of pentaborane(9) a 0.9556-g sample of  $(N-C_4H_9)_4NB_3H_8$  (3.375 mmol) contained in a 100-ml flask was dissolved on the vacuum line in 2 ml of  $CH_2Cl_2$ , which had been dried over Molecular Sieve 3A, and an equivalent quantity HBr was condensed onto the frozen solution. On warming with magnetic stirring to  $-78^\circ$  and then to room temperature there was removed by means of a Toepler pump over a 45-min period a total of 3.34 mmol of noncondensable gas ( $H_2$ ). After thorough evacuation for several hours to remove even traces of  $CH_2Cl_2$ , the system was heated to  $95-100^\circ$  for 1.5 hr while noncondensable gas was pumped off (1.53 mmol) and condensables were trapped, taking care to avoid splattering of the reaction mixture to the cool portions. Reaction apparently was complete.

The condensable product was then fractionated several times to cold traps at  $-78^\circ$  ( $B_5H_9$ , 0.746 mmol)  $-126^\circ$  ( $B_4H_{10}$ , trace identified by mass spectrum), and  $-196^\circ$  ( $B_2H_6$ , 0.902 mmol, identified by infrared spectrum). The yield was equivalent to 36.8% conversion of starting material to  $B_5H_9$ . The mass spectrum,<sup>13,14</sup> infrared spectrum,<sup>15</sup> and vapor pressure<sup>16</sup> of the  $B_5H_9$  fraction corresponded to published data, and no  $B_5H_{11}$  was detected in the product. A tenfold scale-up or a one-sixth scale down gave the same results.

## References and Notes

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