

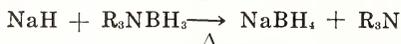
Boron Hydrides. XII. The Synthesis and Infrared Spectra of NaBH_3D and NaBD_3H

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In continuing our studies on the unusual kinetic isotope effects and exchange reactions observed in simple boron hydrides (as BH_4^- and amine boranes) (2, 3, 4, 5, 6, 7), it seems important to prepare the isotopically mixed borohydrides ($\text{BH}_{4-x}\text{D}_x^-$) in pure form. Mixtures (with $x=0$ to 4) have been prepared by Jolly using a high temperature exchange reaction of deuterium gas with solid potassium borohydride (11). The pure materials are described in the present article.

Synthesis of the isotopic borohydride ions was based on a procedure due to Koester (10). He reported the reaction (all hydrogen):



which has been modified in the present investigation by the use of NaD or R_3NBD_3 in the reaction.

The infrared spectra of the product of the reaction of NaD with triethylamine borane and the product of NaH with $(\text{C}_2\text{H}_5)_3\text{NBD}_3$ were obtained. In Table 1 the spectra of NaBH_4 , NaBH_3D and NaBD_4 in solution are reported. The calculated frequencies for NaBH_4 and NaBD_4 were obtained from the FG matrix calculation of Taylor (8). Table 1 also contains the results of our calculations for NaBH_3D using the force constants reported by Taylor.

The infrared spectrum of sodium borohydride-*d* was also measured in potassium bromide pellet. The bands were observed at $1702 \pm 5 \text{ cm}^{-1}$ (ν_1), 1214 (ν_2), 2298 (ν_{3a}), 2235 (ν_{3bc}), 1127 (ν_{4a}) and 953 (ν_{4bc}). Thus the bands of A_1 symmetry decrease in frequency as the change is made from the solid phase to solution. The symmetric A vibrations must be greatly perturbed by the asymmetric ionic environment within the crystalline state. The bands in the pellet are somewhat broader than those in the liquid phase but a band splitting is not clearly detectable.

The infrared spectrum of sodium borohydride-*d*₃ was obtained in a Nujol mull. The bands were observed at 1727 cm^{-1} (ν_1), 1090 (ν_2), 2320 (ν_{3a}), 1781 (ν_{3bc}), 825 (ν_{4a}) and 855 (ν_{4bc}). The same shifts with A and E bands observed in NaBH_3D were observed with NaBD_3H .

In a future paper the kinetic isotope effects for hydrolysis of these mixed ions will be reported.

Experimental

Synthesis of Sodium Borohydride-*d*.

A 250 ml three-neck round-bottom flask was fitted with a condenser and a nitrogen-inlet tube. The system was purged with nitrogen and 90

1. (a) Alfred P. Sloan Fellow 1962-1966. (b) Purdue Research Foundation XL Fellow 1964-65. Taken in part from the Ph.D. Thesis, June, 1965. The computer program is listed in this thesis in Fortran II for the IBM 7094.

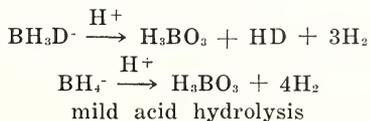
TABLE 1. Comparison of the Experimental Frequencies in Solution with the Calculated Values in cm^{-1}

BH_4^-	Experimental $\pm 3 \text{ cm}^{-1}$	Calculated
ν_1	2264 ^a	2267
ν_2	1210 ^a	1210
ν_3	2244	2251
ν_4	1080	1089
BH_3D^-		
ν_1	1646	1643
ν_2	1214	1172
ν_{3a}	2277	2264
ν_{3dc}	2259	2251
ν_{4a}	1102	1072
ν_{4dc}	952	957
BD_4^-		
ν_1	1571 ^a	1603
ν_2	855 ^a	856
ν_3	1696	1686
ν_4	823	819

(a) Raman value, Ref. 11.

ml of methylecyclohexane was added, followed by careful addition of 2.5 g (0.05 moles) of sodium deuteride dispersion (Metal Hydrides—51% sodium deuteride) and 8 ml (0.056 moles) of liquid triethylamine borane. The reaction mixture was heated to 100° C under nitrogen. After a day the solvent was evaporated, and more was added. For the next four days the system was purged with nitrogen every few hours to remove the free triethylamine. The odor of amine was noticeable. The solid product was removed by filtration. The unreacted triethylamine borane was recovered by extraction with ether. The solid was then extracted with isopropylamine. The product was obtained upon evaporation *in vacuo* of the amine. Sodium borohydride-*d* (0.60 g, 39% of theory) was recovered. The infrared spectrum was determined on a Perkin-Elmer 221 high resolution ($\pm 3 \text{ cm}^{-1}$) infrared spectrophotometer. The observed bands corresponded well to the expected spectrum of sodium borohydride-*d*.

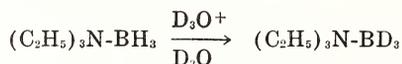
Since the two infrared active bands of BH_4^- are so close to two of the infrared active bands of BH_3D^- , the presence of BH_4^- in sample cannot be detected. The analysis of the sample by mass spectra of the gas produced on complete acid hydrolysis gave a ratio of H_2/HD of 4.90, indicating a mixture of 67% NaBH_3D and 33% NaBH_4 . Since no infrared bands were seen in the region of 1600 cm^{-1} , it has been concluded that little or no BH_2D_2^- was present.



Synthesis of Sodium Borohydride- d_3

The preparation of triethylamine borane - d_3 was required as a preliminary step. Triethylamine borane (12 g, 0.0104 moles) was dissolved in 150 ml of ether. This was stirred with 100 ml of 1.7 normal DCl-D₂SO₄ solution. This acid solution is prepared from heavy water (99.73% D) and sulfuric chloride. The preparation is discussed in another paper (6, 9).

After eight hours the ether layer was separated and dried over potassium carbonate. The ether was removed *in vacuo* by use of a Rinco flash evaporator and the infrared spectrum of the liquid amine borane determined as liquid film on a Perkin-Elmer 221 high-resolution infrared spectrophotometer. The procedure was repeated twice until the boron-deuterium bands present indicated that the amine borane had been at least ninety percent deuterated on the boron atom.



The deuterated triethylamine borane, (6.4 g, 0.056 moles) was reacted with 2.5 g (0.05 moles) of sodium hydride (51% by weight in oil, Metal Hydrides) in 90 ml of methylcyclohexane at 100° C (under the same procedure as sodium borohydride- d) for one week. The yield was 0.1 g or 13 percent of theory. The infrared spectrum was taken on a Perkin-Elmer 221 high resolution infrared spectrophotometer as a Nujol mull after the potassium bromide pellet method failed. The spectrum corresponds to that of sodium borohydride- d_3 while the background bands exist that may be other borohydrides as BH₂D₂.

Calculations

The F and G matrix method (1, 12) has been used to obtain the results of the present investigation using an IBM 7094 computer.

Acknowledgement

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