Boron Hydrides. On the Importance of Multiple Isotopic Substitution for the Observation of Primary Inverse Hydrogen Kinetic Isotope Effects*

By R. E. DAVIS, R. E. KENSON, C. L. KIBBY, and H. H. LLOYD
(*Department of Chemistry, Purdue University, West Lafayette, Indiana, 47907, U.S.A.*)

SINCE we first reported a primary inverse kinetic isotope effect of 0·70 for the aqueous hydrolysis of sodium borohydride and borodeuteride (Equation 1) at 25°, an alternative interpretation has been suggested.[1] In particular, it was suggested that it is very reasonable that deuteration on the boron should produce an inverse kinetic isotope effect since the weak B–H bond is being replaced by a stronger H–H bond in the transition state. It was stated that changes in the other bonds are of secondary importance.

$$BH_4^- + H^+ + 3\,H_2O \rightarrow 4\,H_2 + H_3BO_3 \qquad (1)$$

We report the results of new experiments that support the conclusions reached in our first papers,[2,3] namely that the inverse kinetic isotope effect is composed of two parts. The first effect is the *normal* kinetic isotope effect (k_H/k_D greater than 1) of the primary B–H bond breaking in the rate-determining step. The second effect is the secondary kinetic isotope effect of the other boron–hydrogen bonds which are not breaking in that rate-determining step. If the force constants of these other B–H bonds *increase* then the observed kinetic isotope effect *can* be less than one. A very simple method is used to make predictions with other boron and aluminium hydrides.

Firstly, Hawthorne and Lewis[4] have reported a normal isotope effect on the hydrolysis of diphenylpyridineborane at 40°. The B–H bond is breaking in the rate-determining step and there are no other B–H bonds in the activated complex. The normal isotope effect is 1·52.

$$Ph_2BH{\cdot}C_5H_5N + H_2O \rightarrow Ph_2BOH + H_2 + C_5H_5N \qquad (2)$$
$$k_H/k_D = 1{\cdot}52$$

Since hydrogen is formed in this reaction, it might be expected that the isotope effect would be

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* Previous paper, R. E. Davis, C. L. Kibby, and C. G. Swain, *J. Amer. Chem. Soc.*, in the press.

[1] E. A. Halevi, *Progr. Phys. Org. Chem.*, 1963, **1**, 214–216.
[2] R. E. Davis, E. Bromles, and C. L. Kibby, *J. Amer. Chem. Soc.*, 1962, **84**, 885.
[3] R. E. Davis, C. L. Kibby, and C. G. Swain, *J. Amer. Chem. Soc.*, 1960, **82**, 5950.
[4] M. F. Hawthorne, and E. S. Lewis, *J. Amer. Chem. Soc.*, 1958, **80**, 4296.

inverse if the only consideration would be the weak B–H bond being replaced by the stronger H–H bond.[1,6]

$$p\text{-R}{\cdot}C_6H_4{\cdot}BH_2{\cdot}C_5H_5N + 2\,H_2O \rightarrow p\text{-R}{\cdot}C_6H_4{\cdot}B(OH)_2 + 2\,H_2 + C_5H_5N \qquad (3)$$

Secondly, monoarylpyridineboranes have very interesting boron–hydrogen isotope effects (determined by competition experiments using an isotope-ratio mass spectrometer) for the acid-catalyzed aqueous hydrolysis at 25° C (k_H/k_D = $0{\cdot}95_2$ for R = H; $0{\cdot}92_3$ for R = Cl; and $1{\cdot}15_0$ for R = Me; the standard deviations of the data are ± 0·003). Thus at least two hydrogens must be present on the boron for an inverse effect. There is both a normal primary and an inverse secondary isotope effect in these systems. The secondary B–H bonds must stiffen the most in the *p*-chloro-derivative to compensate for the decreased electron density on the boron in the transition state. The small normal isotope effect for the *p*-methyl derivative shows the delicate balance of electronic and vibrational factors.

Preliminary data indicate a still larger k_H/k_D isotope effect for the *p*-methoxy-derivative of about 1·4. The kinetic isotope effect *decreases* from 1·4 to 0·9 in these derivatives as the B–H stretching frequency in the infrared spectra *increases*. The ^{11}BH stretches occur at 2353 cm.$^{-1}$ ± 1 for *p*-Cl, 2345 for *p*-H, 2331 for *p*-Me, and 2326 for the *p*-MeO derivative in $CHCl_3$ solvent at high resolution. This fits our original hypothesis.

Thirdly, sodium borohydride reduces a variety of materials (Table I) with an inverse isotope effect of about 0·7 at 25°, whether H–H or C–H bonds are formed in the reaction products in processes of greatly different enthalpies of reaction. The Brønsted general acid catalyst term, α, is 0·9. Thus the hydride is greatly transferred in the activated complex.

Calculations on a simple triatomic theoretical model show small *inverse primary* isotope effects are possible in such cases.[6]

Fourthly, the isotope effect of the alcoholysis

TABLE I

***Data** on* BH_4^- *at 25°*

Oxidant	ΔH (kcal./mole)	ΔH (kcal./mole)	k_H/k_D at 25°
H_3O^+	**−63·8**[a]	7·8[a]	0·70[a]
MeCOMe	**−128·2**[b]	7·6[c]	0·70[e]
PhCOMe	—	**11·6**[d]	0·69[e]
$PhOH_2^+$	—	—	0·63[f]
$MeOH_2^+$	—	6·2[g]	0·703[g]

[a] Ref. 2. Heat of reaction ± 0·2 kcal./mole, ΔH ± 0·5 kcal./mole.
[b] Ref. 7. Measured ΔH per mole of BH_4^- in 0·1 M-NaOH at 25°; ± 0·7 kcal./mole.
[c] Ref. 8.
[d] Ref. 10. ± 0·4 kcal./mole.
[e] In isopropyl alcohol at 25°. Unpublished data of Prof. H. C. Brown.
[f] Ref. 5. Measured at 35° in diglyme.
[g] $k_H/k_D = 1{\cdot}207e^{-321/RT} \pm 0{\cdot}002$ from 35° to −100° C in methanol (measured by Kibby).

TABLE II

Vibrational Bands in cm.$^{-1}$

BH_4^- [2,11]		BH_3 [12]
2264		2560
2251		2400
1210		1560
1089		1190
	— large upward shifts →	
	large inverse k_Hk_D	
$LiAlH_4$ [9]		AlH_3 [9]
1724		1778
1633		1600
760		772
702		771
	— small upward shifts →	
	small inverse k_H/k_D	

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[5] R. E. Dessy and E. Grannen, *J. Amer. Chem. Soc.*, 1961, **83**, 3953.
[6] J. Bigeleisen, *Pure Appl. Chem.*, 1964, **8**, 217.
[7] R. E. Davis and J. C. Carter, M.Sc. Thesis, Purdue University, 1965.
[8] W. H. Stockmayer, R. R. Miller, and R. J. Zeto, *J. Phys. Chem.*, 1961, **65**, 1076.
[9] R. Dautel and W. Zeil, *Z. Electrochem.*, 1960, **64**, 1234. Also measured by H. H. Lloyd in this study.
[10] H. C. Brown, O. M. Wheeler, and K. Ichikawa, *Tetrahedron*, 1957, **1**, 214.
[11] R. C. Taylor and A. R. Emery, *Spectrochim. Acta*, 1958, **10**, 419.
[12] J. R. Morrey, A. B. Johnson, U. Fu, and G. R. Hill, "Borax to Boranes," Advances in Chemistry Series, **32**, p. 157, American Chemical Society, Washington, D.C., 1961.

of lithium aluminium hydride has been measured in isopropyl alcohol–ether solvent. The smaller isotope effect arises from the smaller amount of bond stiffening occurring as AlH_3 is formed (Table II). Thus with X = H or D

$$\mathrm{LiAlX_4 + 4Pr^iOH \rightarrow 4XH + LiAl(OPr)_4} \qquad (4)$$

The results are:

$$k_{\mathrm{H}}/k_{\mathrm{D}} = 1{\cdot}264\, e^{-119\cdot7/RT} \pm 0{\cdot}004 \qquad (5)$$

measured from $-25°$ to $-110°$ c in isopropyl alcohol (mole fraction 0·197)–ether solvent. The experimental value of $k_{\mathrm{H}}/k_{\mathrm{D}}$ at $-78°$ c is 0·924 ± 0·003 [Equation (5) gives 0·929] and this value can be compared with the BH_4^- isotope effect of 0·528 ± 0·003 at the same temperature. In Table II the infrared frequencies are presented. Normal-co-ordinate analysis has shown that the BH force constant in BH_4^- is 2·77 mdynes/Å while in BH_3 the valence force constant is 3·41 mdynes/A.[11,12]

Lastly, the most important experiment has been completed. Synthesis of isotopically pure $NaBH_3D$ has been accomplished.

$$\mathrm{NaD + Et_3NBH_3 \xrightarrow[\Delta]{} NaBH_3D + Et_3N} \qquad (6)$$

The reaction of trimethylammonium chloride in ether with borohydride removed only one hydride.

$$\mathrm{BH_4^- + Me_3NH^+ \xrightarrow[25°]{ether} Me_3NBH_3 + H_2} \qquad (7)$$

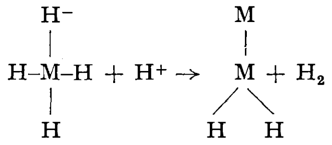
$$\mathrm{BH_3D^- + Me_3NH^+ \longrightarrow Me_3NBH_2D + H_2} \qquad (8)$$

$$\mathrm{BH_3D^- + Me_3NH^+ \longrightarrow Me_3NBH_3 + HD} \qquad (9)$$

The calculated isotope effects indicate that when the boron–deuterium bond breaks to form HD there is a *small normal* isotope of 1·18 effect [reactions (7) and (9)]. Yet a *small inverse* isotope effect results when the deuterium contributes only to the secondary isotope effect [reactions (7) and (8)].

These last results need not stand by analogy with the other boron hydride systems.

In conclusion the most consistent explanation of all of these inverse isotope effects is still that of inverse secondary effects of bond stiffening of the secondary Al–H or B–H bonds in the transition state which resembles borane or alane (or their derivatives) in all these bimolecular reactions.[13,14]



$$\begin{array}{c}\mathrm{H^-}\\ |\\ \mathrm{H{-}M{-}H}\\ |\\ \mathrm{H}\end{array} + \mathrm{H^+} \rightarrow \begin{array}{c}\mathrm{M}\\ |\\ \mathrm{M}\\ \diagup\ \diagdown\\ \mathrm{H\quad H}\end{array} + \mathrm{H_2}$$

Studies are under way to attempt to observe *primary inverse isotope* effects as postulated by Halevi and Bigeleisen.[6]

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[13] Detailed mechanistic and kinetic studies of all of the reactions discussed in this paper have been made and reported in the Ph.D. theses of C.L.K. (1964), R. E. K. (June 1965), and H.H.L. (in preparation).

[14] We wish to acknowledge an exchange of letters with Prof. E. A. Halevi. While a basic disagreement exists between Prof. Halevi and the authors, we have published our paper with new data and our hypothesis concerning isotope effects in these most unusual systems. Clearly further work is needed. It was the correspondence that led to our work with the mixed isotopic borohydrides.