The spectrum of the *iso*-propyl compound also contains a relatively intense peak due to the $C_2H_3BF^+$ ion. The very low appearance potential of 11.8 e.v. suggests one of these three reactions

$$i\text{-}C_3H_7BF_2 + e \longrightarrow C_2H_3BF^+ + CH_3 + HF + 2e \quad (19)$$

$$i\text{-}C_3H_7BF_2 + e \longrightarrow C_2H_3BF^+ + CH_4 + F^- + e \quad (20)$$

$$i\text{-}C_3H_7BF_2 + e \longrightarrow C_2H_3BF^+ + CH_3F + H + 2e \quad (21)$$

Using the appearance potential of $C_2H_3BF^+$ from vinylboron difluoride, one can calculate values of 15.1 and 12.9 e.v. for the appearance potentials of equations 19 and 20, respectively. The absence of a known heat of formation for methyl fluoride[19] precludes a similar calculation for (21), but one would expect a value higher than that of (19) due to the greater strength of the H–F bond in HF than of the C–F bond in methyl fluoride.[13] Equation 20 thus represents the most likely reaction. The failure to obtain a calculated appearance potential as low as the observed value may be due to the presence of excess energy in the formation of the $C_2H_3BF^+$ ion from vinylboron difluoride, already suggested above. A study of the negative ions in the mass spectra of these compounds, together with a determination of the kinetic energy of the various positive ions, would no doubt cast further light on these modes of decomposition.

The dissociation energies of about 100 kcal. mole^{-1} found for the boron–carbon bonds in the organoboron difluorides are unusually high for single covalent bonds not involving hydrogen and are in marked contrast to the relatively weak bonds found in many organometallic compounds. That most of the known chemical reactions of the organoboron difluorides proceed without cleavage of the boron–carbon bonds is readily understandable in terms of the results presented in this paper.

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[19] We are indebted to a referee for calling our attention to a value for $\Delta H_f(CH_3F) = -59 \pm 2$ kcal. mole^{-1} deduced from electron impact data. See J. L. Margrave, *J. Chem. Phys.*, **24**, 475 (1956). The appearance potential for equation 21 can then be calculated as 16.2 e.v. in agreement with our conclusion.

[Contribution from the Department of Chemistry, William M. Rice University, Houston, Texas]

The Mechanism of Hydride Transfer. II. Details of Isotope Effects in Pyridine–Diphenylborane Hydrolysis[1,2]

By E. S. Lewis and R. H. Grinstein[3]

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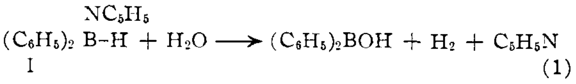
Previously measured deuterium isotope effects in the hydrolysis of pyridine diphenylborane in acetonitrile solution have been extended by studying the variation with temperature and the tritium isotope effects. The effect of isotopic substitution in the water is normally large and almost all attributable to a difference in activation energy. Isotopic substitution of the borane hydrogen leads to a smaller effect which is temperature independent ($k_H/k_D = 1.4$, $k_H/k_T = 1.7$). It is shown that the deuterium and tritium isotope effects are consistent with each other and with a previously proposed triangular transition state, which is not unambiguously proven, however.

Introduction

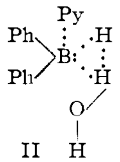
In the first paper of this series,[1] the hydrolysis of pyridine diphenylborane (I) in acetonitrile solution was shown to be first order in the borane, first order in water, and independent of added pyridine; the reaction 1 was followed



$$\underset{\text{I}}{(C_6H_5)_2}\overset{NC_5H_5}{B}\text{–}H + H_2O \longrightarrow (C_6H_5)_2BOH + H_2 + C_5H_5N \quad (1)$$

by an iodimetric analysis for I. On the basis of these results, some general considerations of electrophilic substitutions, substituent effects and isotope effects, a non-linear transition state for the attack of the water proton on the B–H bond was proposed. The proposed transition state can be modified by assuming that the oxygen of the water is becoming bound to boron as the BH bond is broken in a type of SNi[4] reaction as proposed by Hawthorne,[5] on the basis of the small negative value of Hammett's ρ.

The partial transition state, II, avoids this question; we shall use this ambiguous model since the results presented here do not give evidence on this possibility of B–O bonding.



II

Py = pyridine
Ph = phenyl

The study of hydride transfer mechanisms through measurements of isotope effects would be facilitated if the source and magnitudes of isotope effects were well established in some reaction readily studied. We have chosen for this purpose to study in more detail the isotope effects in the

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[1] Paper I, M. F. Hawthorne and E. S. Lewis, *J. Am. Chem. Soc.*, **80**, 4296 (1958).

[2] From the Ph.D. thesis of R. H. Grinstein, Rice University, 1961.

[3] Humble Oil and Refining Co. Predoctoral Fellow, 1960–1961.

[4] The applicability of the SNi mechanism (W. A. Cowdrey, E. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1252 (1937)) as a one-step mechanism has been seriously questioned since many examples show characteristics of an ion-pair intermediate (C. E. Boozer and E. S. Lewis, *J. Am. Chem. Soc.*, **74**, 6307 (1952); **76**, 794 (1954); D. J. Cram, *ibid.*, **75**, 332 (1953)), but a true cyclic mechanism apparently is found in the gas phase although ionic character contributes (E. S. Lewis and W. C. Herndon, *ibid.*, **83**, 1961 (1961)); it is therefore proper to consider this mechanism even though it usually appears to require high activation energies.

[5] M. F. Hawthorne, paper presented before the division of organic chemistry, 135th meeting A.C.S., 1959. The abstract, p. 40 O, does not mention this point.

pyridine diphenylborane reaction for the reasons: (1) the isotopically labelled substances are readily prepared; (2) the rate is convenient and easily controlled; (3) there is only one reactive hydridic hydrogen so that it is not necessary to be concerned with secondary isotope effects (this contrasts to the studies on the borohydride ion hydrolysis[6]); (4) only one mechanism appears operative under the conditions studied, again in contrast to the borohydride reactions.[7]

The suggestion that the triangular transition state, II, for hydride transfer leads to an expectation of a small isotope effect is not disputed, but the converse statement that non-linearity may be deduced if the isotope effect is small is definitely wrong. By small isotope effect we shall mean one substantially smaller in magnitude than that calculated on the basis of the loss of the zero-point energy of the stretching vibration of the bond to hydrogen.[8] Thus, even with a linear transition state, lower isotope effects can be predicted from a consideration of the existence of new real vibrations in the activated complex, among which Melander[9] and Westheimer[10] have emphasized a linear vibration sometimes closely related to the stretching vibration of the reagent, whereas Bell[11] has mentioned the two bending modes, usually presumed to be closely related to the bending of the bond in the reagent. A factor influencing the magnitude of isotope effects, especially with hydrogen compounds is the possibility of tunneling, but this increases the usual effect of k_H/k_D, since the light hydrogen will penetrate the barrier more extensively than the heavier isotopes. Bell[11] has proposed empirical tests for the existence of substantial tunneling, the most sensitive of these is that if the experimentally determined pre-exponential factor of the Arrhenius equation for the deuterium compound is substantially greater than that for the protium compound, tunneling is indicated. The mass dependence of the extent of tunneling is not simple from Bell's treatment and is even less accessible from the calculations based upon more realistic potential barriers.[12] The calculation of the mass dependence of tunneling in cases more complicated than in the linear H_3 transition state and related systems of Reference 12 presently seems out of the question. It seems likely that this function will be such that the relation between deuterium and tritium isotope effects will be different from that predicted on the basis of vibrational differences alone. This latter prediction has been put in the convenient form of eq. 2 by

$$k_H/k_T = (k_H/k_D)^{1.442} \qquad (2)$$

Swain and his co-workers.[13] In this paper therefore we have investigated both the deuterium and tritium isotope effects as a function of temperature.

Methods, Results and Discussions

The isotope effects were measured competitively, allowing a greater precision than in the direct measurements of ref. 1. A mixture of deuterated and undeuterated material (either water or the borane) was allowed to react to a small extent and the deuterium content of the gas was then determined by thermal conductivity. The isotope effect was calculated from the approximate equation 3, in which $A_H{}^0$ and $A_D{}^0$ are the numbers of moles of hydrogen and deuterium compounds respectively in the starting material, and P_H and P_D are the numbers of moles in the product. This equation

$$k_H/k_D = A_D{}^0\,P_H/(A_H{}^0P_D) \qquad (3)$$

is exact for the first infinitesimal product gas and is a good approximation for small extents of completion. In our system, no more than 4% of labelled borane, nor more than 0.5% of labelled water was consumed, leading to errors substantially smaller than 1%, within the limits of reproducibility. The equation 3 of course also applies to tritium, which we determined with an ionization chamber.

Table I shows the isotope effects for the reaction of pyridine diphenylborane with isotopically substituted water in acetonitrile solution. Each entry is the average of at least two runs. Also shown are the rate constants for the reaction with ordinary water measured in the same apparatus by the increase of hydrogen pressure. The apparatus was not designed for rate measurements so these rates are not very precise. Since the isotope effect from eq. 2 is not a function of extent of completion, it is not necessary to know the rate precisely. Nevertheless, the rate of 39.9° of 2.4 × 10^{-4} l./mole-sec. is in reasonable accord with the value 2.14 × 10^{-4} from ref. 1. The similarly imprecise isotope effect $k_H/k_D = 5.2$ should be directly compared to the value 6.90 of ref. 1, and the discrepancy is again not serious. Comparison between the competitive results and the directly measured numbers is complicated by the possibility of a secondary isotope effect from the second hydrogen on the water. A secondary effect would contribute to the directly measured isotope effects, but not to the competitive one, since the average environments are identical for both isotopes in the reacting position. Assuming that the values at 39.9° are both precise, the secondary isotope effect contribution is k_H/k_D about 1.15. This estimate is rough, but the result is in a reasonable range for reactions in which the influence of a neighboring atom is be-

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(6) R. E. Davis, C. L. Kibby and C. G. Swain, *J. Am. Chem. Soc.*, **82**, 5950 (1960). In connection with the inverse isotope effect observed by these authors, it is interesting that the triangular transition state proposed in ref. 1, when applied to borohydride ion hydrolysis, would suggest that the bending vibrations of the unattacked protons might be more seriously influenced than even in the S_N2 reactions of CH_3X, leading to a prediction of an even larger inverse secondary isotope effect than has been observed with the reactions of methyl esters (R. R. Johnson and E. S. Lewis, *Proc. Chem. Soc.*, 52 (1958)).

(7) R. E. Davis and C. G. Swain, *ibid.*, **82**, 5949 (1960).

(8) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(9) L. Melander, "Isotope Effects on Reaction Rates," Ronald Press, New York, N. Y., 1960.

(10) F. H. Westheimer, *Chem. Revs.*, **61**, 265 (1961).

(11) R. P. Bell, "The Proton in Chemistry," Cornell University Press, Ithaca, N. Y., 1960.

(12) R. E. Weston, Jr., *J. Chem. Phys.*, **31**, 892 (1959); I. Shavitt, *ibid.*, **31**, 1359 (1959); H. S. Johnson and D. Rapp, *J. Am. Chem. Soc.*, **83**, 1 (1961).

(13) C. G. Swain, E. C. Stivers, J. F. Reuwer, Jr., and L. J. Schaad, *J. Am. Chem. Soc.*, **80**, 5885 (1958).

ing removed.[14] Whatever the reason for this discrepancy, it is not large enough to be clearly significant.

Table I also yields three Arrhenius equations by the application of the method of least squares, the first of low precision.

$$k_H = 4.99 \times 10^{11} e^{\frac{-20,400}{RT}} \quad (4)$$

$$k_H/k_D = (0.940 \pm 0.06) e^{\frac{1150 \mp 40}{RT}} \quad (5)$$

$$k_H/k_T = (0.784 \pm 0.12) e^{\frac{1700 \mp 100}{RT}} \quad (6)$$

The last two show estimated errors which are 90% confidence limits, based of course on too few data for a really meaningful statistical treatment. Table I also shows the values calculated by equations 5 and 6.

TABLE I

REACTION OF PYRIDINE DIPHENYLBORANE WITH ISOTOPICALLY SUBSTITUTED WATER

Temp., °C.	$k_H \times 10^5$, l.[a]/mole sec.	k_H/k_D[b] Obsd.	k_H/k_D[b] Calcd.[c]	k_H/k_T[b] Obsd.	k_H/k_T[b] Calcd.[d]
0.00				17.7	18.0
8.50		7.38	7.31		
10.2				16.7	16.0
20.0	3.1	6.78	6.75	13.9	14.5
29.9	10	6.45	6.32	12.6	13.3
34.9	17				
39.9	24	6.04 (5.2[e])	5.96	12.4	12.1
45.0	52				
50.1	79				
51.4		5.59	5.57		

[a] Imprecise value from gas evolution. [b] Measured competitively. [c] From eq. 5. [d] From eq. 6. [e] From direct gas evolution rates in reaction with D_2O.

Table II shows the isotope effects for the reaction of hydride labelled pyridine diphenylborane with ordinary water. Both deuterium and tritium isotope effects appear to be temperature independent, and the value within experimental error of $\sqrt{2}$ for the deuterium compound is interestingly confirmed by the value for tritium within experimental error of $\sqrt{3}$. The deuterium result can now be compared with the value 1.52 from ref. 1 and again an imprecise value from gas evolution kinetics of 1.3. The discrepancies are not serious.

TABLE II

HYDROLYSIS OF ISOTOPICALLY SUBSTITUTED PYRIDINE DIPHENYLBORANE

Temp., °C.	k_H/k_D	k_H/k_T
0.00	1.40	1.79
20.9	1.41	
29.9	1.39	1.71
39.9	1.40 (1.3[a])	1.77
49.8	1.41	

[a] Derived from direct gas evolution kinetics.

The value of the study of temperature variation together with the study of both isotopes is shown by the data of the tables. Without the temperature coefficients, one might be tempted to ascribe the B–H isotope effect to a zero-point energy effect. The tritium isotope effects lead to the same conclusion as the deuterium isotope effects, showing that no particularly unusual effects are contributing. In fact, the tritium isotope effect on water substitution is very close to that predicted by equation 2, thus at 39.9° the equation predicts $k_H/k_T = 13.4$, compared with 12.6 observed. The exponential factor is also in agreement. Thus Swain's arguments lead to the prediction that $Ea_T - Ea_H = 1.442\ (Ea_D - Ea_H)$, and we find the factor 1.48 ± 0.10. Both these are within the limits of precision justified by the derivation of the equation and the accuracy of the data.

The application of Bell's criterion to equations 5 and 6 indicates that tunneling is no more than a minor contributor to the reaction, in agreement with expectation for a reaction with a large activation energy. The less than unit pre-exponential factors in these equations (barely significant for deuterium, but confirmed for tritium) do not lend themselves to ready explanation. Bell, using a model in which the hydrogen is unbound, found the possibility of a pre-exponential factor for deuterium of $^1/_2$, but this is quite unrealistic. The model can nevertheless be approached continuously from a realistic one, thus pre-exponential factors smaller than one are conceivable. Alternatively, there may be a small amount of tunneling, reducing a near-unit pre-exponential factor to the ones observed. The entire isotope effect arising from substitution in the water molecule can be adequately explained by assuming that most of the zero-point energy of the OH stretch is lost in the transition state. Both Melander[9] and Westheimer[10] have shown that this sort of statement is not inconsistent with the requirement that one mode of vibration of the transition state be entirely missing.

The complete temperature independence of the isotope effects in Table II is worthy of comment. It is, of course, impossible to demonstrate experimentally that there is no temperature dependence, but within our experimental error, the entire isotope effect is found in the pre-exponential term. Bigeleisen and Wolfsberg[15] have shown that in certain simplifications of the general equation for isotope effects the square root of the reduced mass of the system undergoing the imaginary vibration appears as a pre-exponential factor. In order to have the reduced mass corresponding to any vibration equal to that of a single particle, it is necessary that only this particle move significantly in this vibration. In the present case, the implication is that the borane hydrogen is not firmly bound but that the water hydrogen still is. Since the force constant for bending the BH bond are small, whereas that for stretching the OH bond is large, this conclusion

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(14) A. Streitwieser, R. H. Jagow, F. C. Fahey and S. Suzuki, *J. Am. Chem. Soc.*, **80**, 2326 (1958); L. S. Bartell, *Tetrahedron Letters*, **6**, 13 (1960).

(15) J. Bigeleisen and M. Wolfsberg, "Advances in Chemical Physics," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1958, Chapter 1.

is consistent with the triangular transition state II. We have not attempted to apply the Bigeleisen equations rigorously to this proposed transition state, since the difficulties even in the treatment of the three body one-dimensional model for the substitution reaction remain substantial. Even the greatest simplification could reduce the non-linear transition state II only to a four body two-dimensional problem. Without this rigorous treatment, it is not certain that the proposed model can fit the observations, but the qualitative arguments above make it probable that the model could fit the data without recourse to any unusual dimensions or force constants, nor is it necessary to call upon large tunnel corrections.

Experimental

Materials.—Pyridine Diphenylborane.—The method of Hawthorne[16] was followed except that it was not found necessary to use a column in the distillation of ethyl diphenylborinate, only a 50% excess of pyridine was used in its reduction and the final crystallization was from benzene and petroleum ether.

Pyridine Diphenylborane-*d*.—This followed exactly the synthesis of the normal compound except that lithium aluminum deuteride was the reducing agent.

Pyridine Diphenylborane-*t*.—Lithium aluminum hydride (5 mg., 5 mc.) containing tritium (New England Nuclear Co.) was added to 50 ml. of an ether solution which already contained a small amount of lithium aluminum hydride. The solution was cooled to −70°, 1 ml. of pyridine was added, followed by half of a solution of ethyl diphenylborinate in dry ether, and the system was stirred for 2 hr. Then lithium aluminum hydride (5 g.), dissolved in 500 ml. of ether was added, followed by 9 ml. of pyridine and the remainder of the ethyl diphenylborinate. The remainder of the procedure followed that of Hawthorne.[16] The product was obtained in normal yield and showed an activity of about 31,000 counts/min./mg. in the solution scintillation counter, which normally counts tritium with 10–15% efficiency. Since this method was not used quantitatively, the absolute activity was not established.

Acetonitrile.—Practical grade acetonitrile was fractionally distilled repeatedly from phosphorous pentoxide, until it showed no contamination by gas chromatography. It was redistilled from phosphorous pentoxide shortly before use.

Apparatus.—The apparatus for measuring the isotope effects is in three parts: the reaction vessel, the device for analysis of H_2–HD mixtures by thermal conductivity and an ion chamber for tritium analysis. These were connected to a high-vacuum line and the gas from the reaction vessel could be sent either to the deuterium or tritium analysis. The 250 cc. ion chamber was evacuated, then filled partially by opening it to the chilled reaction vessel. The pressure was read on an oil manometer, then the chamber was filled with ordinary hydrogen to a pressure of 770 mm. before isolating it from the system and measuring the rate of charge with an electrometer (Cary Model 32). Gas from the runs with deuterium was passed into the thermal conductivity cell (Victory Engineering Co., Type M-128) by means of a Toepler pump. A pressure of 30 mm. was used in the cell. Assorted manometers, storage bulbs and vessels of known volume allowed the storage of HD (made from heavy water and lithium aluminum hydride) and the preparation of known mixtures of this with tank hydrogen. It was shown that tank hydrogen was indistinguishable in the thermal conductivity apparatus from that made with lithium aluminum hydride and water. The thermal conductivity cell was connected in a bridge circuit as recommended by the manufacturer, and the imbalance was read on a 0–100 microampere meter, connected with a reversing switch so that the over-all range was 200 microamperes. A plot of current *vs.* % HD was not quite linear, but the curvature was small and the accuracy of interpolation between known points was greater than the over-all reproducibility. The device was calibrated for each analysis. The precision and accuracy obtained was slightly better than ± 1% HD absolute. Details of construction may be found in the thesis of ref. 2, they are not given here since the construction is being substantially improved.

The ratio A_D^0/A_H^0 of eq. 3 was determined for the water by mixing weighed amounts of 99+ % D_2O with ordinary water. The remaining uncertainty of less than 1% was partially cancelled by the use of the same water in preparing the standards for thermal conductivity measurements. The same ratio for the borane was also fixed gravimetrically, assuming that the pyridine diphenylborane was isotopically pure. A sample resulting from complete reaction of one of these mixtures compared to the standard H_2–HD mixtures prepared as described above showed no discrepancy. Thus the assumption is as good as the analysis; the results, since the isotope effect is small, are not sensitive to a minor failure in the assumption. The ratio P_H/P_D of eq. 3, measured as described above, is most accurate when it is about 1. The ratios A_D^0/A_H^0 were chosen using preliminary values of the isotope effect to approach the optimum mixture.

The ratio A_T^0/A_H^0 was determined using the ion chamber. The tritiated borane was allowed to react to completion with ordinary water to give a sample representative of the whole sample; the tritiated water was separately allowed to react quantitatively with lithium aluminum hydride to give a sample of hydrogen of HT content identical to the tritium content of the water.

The reactions were in all cases carried out in thoroughly degassed systems, carefully checked for vacuum tightness. This precaution is especially important with the deuterium analysis since all contaminating gases have a lower thermal conductivity than hydrogen and therefore can give a fictitiously high deuterium analysis. The reaction vessel in the earlier studies was a 2-necked flask, one of which led to the gas handling system, the other contained a dropping funnel with a gas bypass equipped with a stopcock so that pressure could be equalized or not, at will. While this device worked, the total of 3 ground joints and two stopcocks, one wet with organic solvent, is conducive to leakage, and several runs had to be discarded for this reason. Leakage could be detected not only by meaningless thermal conductivities but also by a pressure increase in the closed system easily measurable on a McCleod gauge.

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(16) M. F. Hawthorne, *J. Am. Chem. Soc.*, **80**, 4293 (1958).