Re <b>ac</b> tion	$\Delta E_{(\mathbf{k})}$	∆H <sup>‡</sup> cal. mole	$\Delta F^{\pm}$	Δ <i>S</i> ‡ (e.u.)	A (sec. ~1)
$H_{3}O^{+} + H_{2}O$	+2.6	+2.0	+3.8	-5.8	$9.4 \times 10^{11}$
$OH^- + H_2O$	+4.7	+4.1	+4.1	-0.1	$1.7 \times 10^{13}$
	+5.0	+4.4	+4.3	+0.5	$2.3 \times 10^{13}$
H <sub>2</sub> O + + OH − <sup>a</sup>	+2.5	+1.9	+2.3	-1.3	$9.0 \times 10^{12}$

 $^a$  Approximate values calculated from  $\Delta E$  and  $k_{\rm R}$  given by Eigen and deMaeyer.²

limits of experimental error and that the two decrease together. Table II summarizes some of the results. The decrease of  $T_1$  and  $T_2$  at high acid and base concentrations is due to the increase of the viscosity under these conditions. Table II includes values of  $T_1$  calculated by the formula  $T_1 = T_1(\max)/\eta$  where  $T_1(\max)$  is equal<sup>3b,8</sup> to

					Т	able II	I				
VALUES	OF	$T_1$	AND	$T_2$ (	IN	SEC.) I	N	Very	Acidic	or	BASIC
WATER (25°)											

		$T_1$	$\mathcal{T}_{2}$	$T_1$
	pН	(meas.)	(meas.)	(calcd.)
Ordinary water	$\sim$ 0	2.54	2.52	2.52
Ordinary water	$\sim 14$	2.24	2.17	2.11
H <sub>2</sub> O <sup>17</sup> enriched water				
(0.6%)	0.86	2.39	2.36	

2.6 and  $\eta$  is the specific viscosity. Thus, this effect is not related in any way to the proton transfer reaction since the latter would give rise to a difference between  $T_2$  and  $T_1$ .

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

## An Electron Impact Investigation of Some Organoboron Difluorides<sup>1,2</sup>

BY W. C. Steele,<sup>3</sup> L. D. Nichols<sup>4</sup> and F. G. A. Stone

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The appearance potentials of the major positive ions in the mass spectra of methyl-, vinyl-, ethyl- and iso-propylboron difluoride have been measured. The boron-carbon bond dissociation energy has been calculated in each of the four cases, and an indirect measurement of the boron-hydrogen bond dissociation energy in the  $HBF_2$  molecule is reported. The heat of formation of methylboron difluoride has been calculated, and estimates are given for the other three compounds. The various processes for dissociation under electron impact are discussed.

Continued interest in preparative boron chemistry during the last two decades has emphasized the lack of molecular thermodynamic data for boron compounds in general. In particular, little information<sup>5</sup> concerning the strength of the boroncarbon bonds in organoboron compounds is available, and this has limited our understanding of the bonding in these substances and the factors governing the course of their reactions. To remedy this situation in the case of the lower organoboron difluorides  $RBF_2$  (R =  $CH_{3-}$ ,  $C_2H_{5-}$ ,  $CH_2$ :  $CH_{-}$ and  $(CH_3)_2CH_{-}$ , a mass spectrometric study of these halides was made. The appearance potentials obtained in this work, taken in conjunction with the appropriate free radical ionization potentials, allowed a direct calculation of boron-carbon bond strengths without many of the difficulties attendant

(1) (a) Part VII of the series "Organoboron Halides." For Part VI see J. R. Phillips and F. G. A. Stone, J. Chem. Soc., in press; for Part V see S. L. Stafford and F. G. A. Stone, J. Am. Chem. Soc., 82, 6238 (1960). (b) Also Part VII of the series "Spectroscopic Studies on Organometallic Compounds"; for Part VI see E. Pitcher and F. G. A. Stone, Spectrochim. Acta, 17, 1244 (1961).

(2) This research was supported by the Directorate of Chemical Sciences, Air Force Office of Scientific Research.

(3) Postdoctoral Fellow, Harvard University

(4) Fellow of the General Electric Educational and Charitable Fund, 1959–1961.

(5) (a) The thermochemical bond energy term E has been calculated for the boron-carbon bond in several trialkylboron compounds from their heats of combustion, the most recent refinements being those of W. H. Johnson, M. V. Kilday and E. J. Prosen, J. Research Nail. Bureau Standards, **65A**, 215 (1961); (b) The appearance potentials of trimethyl- and triethyl-boron have been measured by R. W. Law and J. L. Margrave, J. Chem. Phys., **25**, 1086 (1956), but no attempt was made to interpret results in terms of bond dissociation energies. upon a calorimetric investigation of compounds containing both boron-carbon and boron-halogen bonds.

### Experimental

The organoboron difluorides used in this work were prepared by treating the appropriate tetraorganotin compound with boron trifluoride.<sup>6</sup> The compounds were manipulated in a high vacuum system, and their purity was determined from their infrared and mass spectra. A small amount of boron trifluoride was the most common inpurity, but was easily reduced to below 1%.

Appearance potentials were measured using a Consolidated Electrodynamics Corporation Model 21-103C mass spectrometer, modified to allow magnetic scanning. All measurements of ions containing boron were made on the peak corresponding to the <sup>11</sup>B isotope. The data were evaluated by the vanishing current method,<sup>7</sup> using semi-log plots where possible. Some of the ionization efficiency curves failed to yield semi-log plots parallel to the standard curves, in which case the appearance potentials were obtained by a conventional extrapolation to zero intensity on linear paper or by the essentially equivalent "extrapolated voltage difference" method. Argon (I = 15.76 e.v.) and krypton (I = 14.00 e.v.) were used as standards and were introduced simultaneously with the sample in each case.

Since organoboron difluorides are highly reactive towards water, it was necessary to thoroughly flush the mass spectrometer and sample system with sample material prior to its final introduction, in order to prevent a build-up of hydrolysis products during the appearance potential determinations. Fortunately, the occurrence of this hydrolysis could be detected immediately in the mass spectrum.

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<sup>(6)</sup> F. E. Brinckman and F. G. A. Stone, J. Am. Chem. Soc., 82, 6218 (1960).

<sup>(7)</sup> See F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press. Inc., New York, N. Y., 1957.

#### Table I

CH2:CHBF2 Rel. abs. (%) CH3BF2 Rel, abs. (%)  $A_n$  (e.v.) m/e Ion An (e.v.) m/e Ion  $12.54 \pm 0.03^{a}$ 76  $C_2H_3BF_2^+$ 100  $11.06 \pm 0.03^{a}$ 64 CH3BF2+ 13.0100 13.62 ± .02 57C<sub>2</sub>H<sub>3</sub>BF<sup>+</sup> 30.0  $11.9 \pm .2$  $BF_2^+$ 49 $15.5 \pm .2$  $12.69 \pm .05$ 56  $C_2H_2BF^+$ 27.445CH₃BF+ 19.7 $15.05 \pm .1$ CH<sub>2</sub>BF+ 15 7  $13.38 \pm .02$ 49  $BF_2^+$ 87.4  $14.8 \pm .1$ 44  $C_{2}H_{3}^{+}$ 65.0 $14.25 \pm .05$ 15CH<sub>3</sub>+ 6.4  $14.8 \pm .1$ 27 $13.75 \pm .1$  $CH_2$ + 4.8 $16.9 \pm .1$  $\mathbf{26}$  $C_2H_2^+$ 40.114 (CH8)2CHBF2 Rel. abs. (%) C2H3BF2 Rel. abs. (%)  $A_p$  (e.v.) m/e Ion Ap (e.v.) m/e Ion  $11.8 \pm 0.05^{a}$ 92  $C_3H_7BF_2^+$ 3.0 78  $C_2H_5BF_2$  + 3.3. . . . . . . . . . 59C<sub>2</sub>H<sub>5</sub>BF<sup>+</sup> 9.6  $12.1 \pm .2$ 77 $C_2H_4BF_2^+$ 19.8  $12.58 \pm 0.05^{a}$  $15.6 \pm .2$ 76 $C_2H_3BF_2^+$ 8.4  $12.80 \pm .05$  $12.6 \pm .2$ C<sub>2</sub>H<sub>4</sub>BF+ 2 1 5857C<sub>2</sub>H<sub>3</sub>BF<sup>+</sup> 8.6  $12.0 \pm$ .2 57C<sub>2</sub>H<sub>3</sub>BF + 33.0  $11.8 \pm .1$  $14.9 \pm$ .2 $12.0 \pm .2$ 49  $BF_2^+$ 32.3 $14.6 \pm .2$  $C_2H_2BF^+$ 56 4.9 $15.0 \pm .2$  $12.05 \pm .05$  $BF_2^+$ 19.0  $14.3 \pm .2$ 43C<sub>3</sub>H<sub>7</sub>+ 51.049 $C_{3}H_{6}^{+}$  $C_2 H_5^{+}$  $13.1 \pm .2$ 100  $11.48 \pm .02$ 2914.942  $14.8 \pm .1$ 28 100  $12.08 \pm .01$ 27 $C_{2}H_{3}^{+}$ 39.4 $C_{2}H_{4}$  +

## Appearance Potentials of Some Organoboron Difluorides

 $^{a}$   $\pm$  figures in each case represent reproducibility of three to five replicate measurements.

### Results and Discussion

The appearance potentials of the major positive ions in the mass spectra of the four  $RBF_2$  compounds studied are listed in Table I, together with the relative abundances of the ions as calculated for the <sup>11</sup>B and <sup>12</sup>C isotopes only.

All three of the ionization potentials which could be measured (Table I) are considerably lower than the value of 15.7 e.v.<sup>8</sup> or 15.5 e.v.<sup>5b</sup> for boron trifluoride but differ from those of the corresponding hydrocarbon RH by at most 0.6 e.v. The vinyl compound shows the greatest elevation of ionization potential relative to the parent hydrocarbon, perhaps reflecting interaction of its  $\pi$ -electrons with the vacant  $p_{\pi}$ -orbital of the BF<sub>2</sub> group. Indeed, the position of the ionization potential of vinylboron difluoride, when considered with the series of ethylenic ionization potentials discussed recently,<sup>9</sup> is in agreement with the known electron withdrawing character of the BF<sub>2</sub> group.

The relation

$$A_{p}(R_{1}^{+}) = D(R_{1} - R_{2}) + I(R_{1})$$

normally used to calculate the dissociation energy D of the  $R_1$ - $R_2$  bond from the appearance potential  $A_p$  of the  $R_1$ <sup>+</sup> ion and the ionization potential I of the  $R_1$  radical is limited by the possibility of excess energy. Stevenson<sup>10</sup> has stated the useful empirical rule that if  $I(R_1) < I(R_2)$  the  $R_1$ <sup>+</sup> ion is more likely to be formed without excess energy than if  $I(R_1) > I(R_2)$ . The ionization potentials of the hydrocarbon radicals are known accurately, having been measured directly by electron impact,

(8) J. Marriott and J. D. Craggs, J. Electron. Control, 3, 194 (1954).
(9) R. Bralsford, P. V. Harris and W. C. Price, Proc. Roy. Soc. (London), 258, 459 (1960).

(10) D. P. Stevenson, Discussions Faraday Soc., 10, 35 (1951).

mainly by Lossing and his co-workers.<sup>11</sup> No ionization potential is known for the BF<sub>2</sub> radical, but as discussed below it may be estimated from the appearance potentials of boron trifluoride.<sup>5b,8</sup>

The ethyl and *iso*-propyl ions had appearance potential curves which were very nearly parallel to the inert gas curve. The vinyl ion showed a slight departure from parallelism, which interestingly was almost exactly the same as that of the vinyl ion from ethylene as described by Harrison and Lossing.<sup>11c</sup> As a result of formation of the ions  $C_2H_3^+$ ,  $C_2H_5^+$  and  $C_3H_7^+$  by apparently simple processes, the boron–carbon bond dissociation energies for vinyl-, ethyl- and *iso*-propylboron difluoride could be calculated (Table II) directly from the appearance potentials of the hydrocarbon ions (Table I) and the free radical ionization potentials (Table II).

Combination of the boron-carbon bond dissociation energies for CH2: CHBF2, C2H5BF2 and (CH3)2-CHBF<sub>2</sub> with the appearance potentials of the corresponding  $BF_2^+$  ions gives for  $I(BF_2)$  values of 10.0, 9.9 and 10.4 e.v., respectively. However, since the ionization efficiency curves for the  $BF_2^+$ ions showed marked tailing, often associated with excess energy,<sup>12</sup> these values must be regarded as upper limits. With methylboron difluoride the tailing situation was reversed; the CH<sub>3</sub>+ curve tailed while the  $BF_2^+$  plot was parallel to that of argon. Thus, to arrive at a value for the boroncarbon bond dissociation energy in the methyl compound, it is necessary to estimate a value for the ionization potential of the  $BF_2$  radical. This (11) (a) F. P. Lossing, K. U. Ingold and I. H. S. Henderson, J. Chem. Phys. 22, 621 (1954); (b) J. B. Farmer and F. P. Lossing, Can. J. Chem., 33, 861 (1955); (c) A. G. Harrison and F. P. Lossing, J. Am. Chem. Soc., 82, 519 (1960); (d) F. P. Lossing and J. B. deSousa. ibid., 81, 283 (1959).

(12) J. A. Morrison, Revs. Pure and Applied Chem., 5, 22 (1955).

can be accomplished by using the appearance potential<sup>5b,8</sup> of the BF<sub>2</sub><sup>+</sup> ion from boron trifluoride and assuming that the thermochemical bond energy term<sup>13</sup> E = 154 kcal. mole<sup>-1</sup> represents a reasonable lower limit to  $D(F_2B-F)$ . The resulting upper limit for  $I(BF_2)$  is then calculated to be about 9.5 e.v., and thus we feel that the most probable range for  $I(BF_2)$  is 9.3–9.5 e.v. This also gives a reasonable value for  $D(H_3C-BF_2)$  when compared with the other boron-carbon bond dissociation energies in the RBF<sub>2</sub> series and satisfies the requirements of Stevenson's rule,  $I(BF_2)$  being higher than  $I(C_2H_3)$  but below  $I(CH_3)$ .

Our results show that the B-C bond strength in the vinyl compound CH2: CHBF2 lies significantly above that of the B-C bonds in alkyl-boron difluorides. This increase will in part be due to the change in hybridization of the bonded carbon atom but also is probably related to vinylboron  $\pi$ -interaction, further indicated by other work.<sup>14</sup> In the absence of bond dissociation data for comparable compounds, the range of 95 to 101 kcal. mole-1 for the methyl-, ethyl- and isopropylboron difluorides is not unreasonable. The only related data available in the literature is the thermochemical bond energy term E for the boroncarbon bond in several trialkylboron compounds. The most recent work on this subject<sup>5a</sup> gives E = $\sim$ 84 kcal. mole<sup>-1</sup>. However, the quite different character of dihalo- and dialkylboron groups, coupled with the transition from dissociation energies to bond energy terms, renders impossible any quantitative comparison between the two.

#### TABLE II

### BOND DISSOCIATION ENERGIES AND HEATS OF FORMATION OF SOME ORGANOBORON DIFLUORIDES

Δ <i>H</i> 1 (kcal. mole <sup>-1</sup> )	<i>I</i> (R) (e.v.)	D. (R-BF1) (kcal. mole <sup>-1</sup> )	D. (H-BF2) (kcal. mole <sup>-1</sup> )
$-199 \pm 3$	$9.3 - 9.5^{n}$	95-100	
-171 <sup>b</sup>	$9.45^{\circ}$	111	99
-209 <sup>b</sup>	$8.72^{d}$	101	106
$-212^{b}$	7.90''	<b>9</b> 6	99
	$\Delta H_1$ (kcal. mole <sup>-1</sup> ) -199 ± 3 -171 <sup>b</sup> -209 <sup>b</sup> -212 <sup>b</sup>	$ \begin{array}{c} \Delta H_1 & I(\mathbf{R}) \\ (\mathbf{kcal. mole^{-1}}) & (\mathbf{e}.\mathbf{v}.) \\ -199 \pm 3 & 9.3 - 9.5^a \\ -171^b & 9.45^c \\ -209^b & 8.72^d \\ -212^b & 7.90^c \end{array} $	$\begin{array}{c} D.\\ (R-BFt)\\ (kcal.\ mole^{-1}) & I(R)\\ (kcal.\ mole^{-1}) & (e.v.) & mole^{-1} \end{array} \\ \hline -199 \pm 3 & 9.3 - 9.5^{a} & 95 - 100\\ -171^{b} & 9.45^{c} & 111\\ -209^{b} & 8.72^{d} & 101\\ -212^{b} & 7.90^{e} & 96 \end{array}$

<sup>a</sup>  $I(BF_2)$ . <sup>b</sup> Calculated assuming  $I(BF_2) = 9.4$  e.v., result probably accurate to  $\pm 8$  kcal. mole<sup>-1</sup>. <sup>c</sup> From ref. 11c. <sup>a</sup> From ref. 11b. <sup>e</sup> From ref. 11d.

Inspection of the mass spectra of ethyl- and *iso*propylboron diffuoride reveals the interesting fact that in both cases the ion formed by loss of both H and BF<sub>2</sub> predominates over that formed by loss of BF<sub>2</sub> alone. Moreover, the energy required to produce these ions is less than that needed for the corresponding alkyl ions. This eliminates the possibility of their formation by loss of hydrogen from the alkyl ion. Two other mechanisms are possible. For ethylboron diffuoride these may be written as

 $C_2H_bBF_2 + e \longrightarrow C_2H_4^+ + H + BF_2^- + e$  (1)

$$C_2H_5BF_2 + e \longrightarrow C_2H_4^+ + HBF_2 + 2e \qquad (2)$$

(1) is unlikely since it would require an unrealistically high value (106 kcal. mole<sup>-1</sup>) for the electron affinity of the BF<sub>2</sub> radical to account for the difference in appearance potentials of  $C_2H_4^+$  and  $C_1H_5^+$ . Furthermore, Marriott and Craggs<sup>8</sup> reported no BF<sub>2</sub><sup>-</sup> ion in their study of the negative ions of boron trifluoride. Therefore, (2) is taken to be the correct description of the process. This affords a unique opportunity for calculation of the boron-hydrogen bond dissociation energy in the HBF<sub>2</sub> molecule, the existence of which has been postulated as a chemical intermediate.<sup>16</sup> When (2) is considered in conjunction with the process

$$C_2H_5BF_2 + e \longrightarrow C_2H_5^+ + BF_2 + 2e \qquad (3)$$

one obtains

$$\Delta H_{\mathbf{f}}(\mathrm{BF}_{\mathbf{2}}) - \Delta H_{\mathbf{f}}(\mathrm{HBF}_{\mathbf{2}}) = -A_{p}(\mathrm{C}_{\mathbf{2}}\mathrm{H}_{\mathbf{4}}^{+}) + A_{p}(\mathrm{C}_{\mathbf{2}}\mathrm{H}_{\mathbf{5}}^{+}) + \Delta H_{\mathbf{f}}(\mathrm{C}_{\mathbf{2}}\mathrm{H}_{\mathbf{4}}^{+}) - \Delta H_{\mathbf{f}}(\mathrm{C}_{\mathbf{2}}\mathrm{H}_{\mathbf{5}}^{+})$$

furthermore

$$D(F_2B-H) = \Delta H_f(BF_2) - \Delta H_f(HBF_2) + \Delta H_f(H)$$

Similar equations hold for the *iso*-propyl and vinyl compounds. Heats of formation of the hydrocarbon ions were taken from the tables of Field and Franklin,<sup>7</sup> with the exception of  $\Delta H_{\rm f}({\rm C_2H_3^+})$  where the more recent value of Harrison and Lossing<sup>11e</sup> was used. The resulting  $D({\rm F_2B-H})$  values are listed in Table II. No value was calculated from the data for the methyl compound due to the apparent presence of excess energy in the formation of the CH<sub>3</sub><sup>+</sup> ion. The average value of about 101 kcal. mole<sup>-1</sup> compares favorably with the bond energy term  $E({\rm B-H})$  of about 93 kcal. mole<sup>-1</sup> in BH<sub>3</sub> given by McCoy and Bauer.<sup>16</sup>

The appearance potential of the  $BF_2^+$  ion from methylboron difluoride, together with the known  $BF_2^+$  appearance potential<sup>5b,8</sup> from boron trifluoride, and the heat of formation  $\Delta H_{\rm f}({\rm BF}_{3({\rm g})}) = -270$  kcal. mole<sup>-1</sup> <sup>17</sup> allow calculation of the heat of formation of methylboron difluoride. Unfortunately, this method cannot be applied directly to other members of the series due to the apparent presence of excess energy in the formation of  $BF_{2}^{+}$ in these cases. However, it is possible to calculate a value based on the hypothetical appearance potential obtained by adding the appropriate value of D and the ionization potential of  $BF_2$ , estimated above as  $\sim 9.4$  e.v. These values are listed in Table II. While these latter three values cannot be regarded as accurate, the internal consistency should be as good as that of the bond dissociation energies, and they are useful in consideration of the other dissociation processes discussed below. Furthermore, the heats of formation of the RBF<sub>2</sub> compounds cannot be easily deduced by direct measurement.

<sup>(13)</sup> T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

<sup>(14)</sup> T. D. Coyle, S. L. Stafford and F. G. A. Stone, J. Chem. Soc., 3103 (1961); and references cited therein.

<sup>(15) (</sup>a) B. Bartocha, W. A. G. Graham and F. G. A. Stone, J. Inorg. Nuclear Chem., 6, 119 (1958): (b) F. G. A. Stone, "Advances in Inorganic Chemistry and Radiochemistry," Ed. Emeléus and Sharpe, 2, 279 (1960), Academic Press, Inc., New York, N. Y.

<sup>(16)</sup> R. E. McCoy and S. H. Bauer, J. Am. Chem. Soc., 78, 2061 (1956).

<sup>(17)</sup> W. H. Evans, D. D. Wagman and E. J. Prosen, N.B.S. Report #6252, December 15, 1958.

The ions nineteen mass units below the parent peak can be formed by either of two processes

$$RBF_{1} + e \longrightarrow RBF^{+} + F + 2e \qquad (4)$$

or

$$RBF_{2} + e \longrightarrow RBF^{+} + F^{-} + e \qquad (5)$$

That both processes occur with the ethyl and vinyl compounds is evident from the observation of two appearance potentials for  $C_2H_5BF^+$  and  $C_2H_3BF^+$ , respectively, the difference in both cases being 3.6 e.v., which is almost exactly the electron affinity<sup>18</sup> of the fluorine atom. Only a single process was observed leading to CH3BF+ from methylboron difluoride. Its relatively high appearance potential of 15.0 e.v. implies process 4 above. The  $C_3H_7BF^+$  peak in the mass spectrum of iso-propylboron difluoride was too small to permit accurate measurement of its appearance potential.

The ions twenty mass units below the parent peak were characterized by simple ionization efficiency curves and lead to appearance potentials below those observed for process 4. This lower value excludes the possibility of their formation by elimination of a hydrogen atom from an RBF<sup>+</sup> ion produced by loss of F. The correct process thus must be one of the following, using methylboron difluoride as an example

or

$$CH_3BF_2 + e \longrightarrow CH_2BF^+ + HF + 2e$$
 (6)

$$CH_{3}BF_{3} + e \longrightarrow CH_{2}BF^{+} + H + F^{-} + e \quad (7)$$

Although sufficient information is not available in each case to allow a definite choice on energetic grounds, it is possible, as discussed below, to correlate the appearance potentials of the C<sub>2</sub>H<sub>2</sub>BF+ ion from ethylboron difluoride with the same ion from vinylboron difluoride only by assuming that the ion from the vinyl compound is formed by process 7.

The ion formed by elimination of one fluorine atom and two hydrogen atoms from the parent molecule was measured only for ethylboron difluoride. Two appearance potentials are observed at 12.0 and 14.9 e.v., and it is interesting to attempt a comparison with the appearance potential of the same ion, C<sub>2</sub>H<sub>3</sub>BF+, from vinylboron difluoride as formed by process 5, using the heats of formation of the compounds (Table II). Possible processes are

$$C_2H_5BF_2 + e \longrightarrow C_2H_3BF^+ + HF + H + 2e \quad (8)$$

$$C_2H_5BF_2 + e \longrightarrow C_2H_3BF^+ + H_2 + F + 2e \quad (9)$$

$$C_2H_5BF_2 + e \longrightarrow C_2H_3BF^+ + H_2 + F^- + e \quad (10)$$

$$C_2H_5BF_2 + e \longrightarrow C_2H_3BF^+ + HF + H^- + e \quad (11)$$

The appearance potentials predicted for the processes (8-11) are 15.9, 17.2, 13.5 and 13.6 e.v., respectively. None of these results is as low as the lower observed value. It is possible that the failure to predict sufficiently low values arises from the presence of excess energy in the reference process. To account for the lower observed ap-

(18) H. O. Pritchard, Chem. Revs., 52, 529 (1953).

pearance potential, process 10 is more likely than (11), due to the greater electron affinity of fluorine than that of hydrogen. It should also be noted that metastable ions are observed at m/e of 42.3 and 41.3, in the correct intensity ratio for the <sup>11</sup>B-<sup>10</sup>B isotopes, corresponding to the transition

$$C_2H_4BF_2^+ \longrightarrow C_2H_3BF^+ + 20$$
 mass units (12)

indicating that reaction 8 occurs. Thus equations 8 and 10 provide reasonable explanations for the higher and lower appearance potentials, respectively.

The appearance potential of the  $C_2H_2BF^+$  ion from ethylboron difluoride was also measured, leading to two values, 12.0 and 15.0 e.v. These relatively low potentials suggest

$$C_2H_{\bullet}BF_2 + e \longrightarrow C_2H_2BF^+ + HF + H_2 + 2e \quad (13)$$

 $C_2H_5BF_2 + e \longrightarrow$ 

and

100

$$C_2H_2BF^+ + H_2 + H + F^- + e$$
 (14)

as the two most likely processes involved. Using process 6 as a standard, the calculated appearance potentials are 14.3 and 16.6 e.v., respectively, while process 7 as a reference yields 12.1 and 14.3 e.v., respectively. Other possible processes lead to much higher values. The agreement between the observed values and those calculated using equation 7 as standard is very good, substantiating the occurrence of reactions 13 and 14. Furthermore, metastable ions are observed at m/e =41.3 and 40.4, in the correct intensity ratio for the boron isotopes, corresponding to the transition

$$C_2H_3BF_2^+ \longrightarrow C_2H_2BF^+ + 20 \text{ mass units} (15)$$

This further supports the idea that process 13 occurs. The above arguments indicate that (7) provides a more likely explanation than (6) for the decomposition of vinylboron difluoride.

Only the mass spectrum of iso-propylboron difluoride contains peaks of carbon and boron con-taining ions formed by loss of a hydrocarbon fragment which are sufficiently intense to permit accurate measurements. The ion  $C_2H_4BF_2^+$  must be formed by simple loss of a methyl group, while  $C_2H_3BF_2^+$  may be formed either by

$$i-C_{2}H_{7}BF_{2} + e \longrightarrow C_{2}H_{3}BF_{2}^{+} + CH_{3} + H + 2e$$
 (16)  
or

$$i-C_3H_7BF_2 + e \longrightarrow C_2H_3BF_2^+ + CH_4 + 2e$$
 (17)

For these two reactions the calculated appearance potentials are 16.5 and 12.0 e.v., respectively, using the measured ionization potential of vinylboron difluoride. Since the experimentally observed appearance potential for iso-propylboron difluoride is 12.8 e.v., equation 17 must represent the reaction which takes place. Metastable ions at m/e = 62.7 and 61.6 corresponding to the process

 $C_{2}H_{7}BF_{2}^{+} \longrightarrow C_{2}H_{3}BF_{2}^{+} + 16 \text{ mass units}$  (18)

also support the occurrence of (17).

The spectrum of the *iso*-propyl compound also contains a relatively intense peak due to the  $C_2H_3$ -BF<sup>+</sup> ion. The very low appearance potential of 11.8 e.v. suggests one of these three reactions

$$i - C_3 H_7 BF_2 + e \longrightarrow C_2 H_3 BF^+ + CH_3 + HF + 2e$$
 (19)

$$i - C_3 H_7 BF_2 + e \longrightarrow C_2 H_3 BF^+ + CH_4 + F^- + e$$
 (20)

 $i-C_3H_7BF_2 + e \longrightarrow C_2H_3BF^+ + CH_3F + H + 2e$  (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<sup>19</sup> precludes a similar calculation for (21), but one would expect a value higher than that of (19) due

(19) We are indebted to a referee for calling our attention to a value for  $\Delta H_f(CHsF) = -59 \pm 2$  kcal. mole<sup>-1</sup> 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.

to the greater strength of the H–F bond in HF than of the C–F bond in methyl fluoride.<sup>13</sup> 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<sub>2</sub>H<sub>3</sub>BF<sup>+</sup> 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.

[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<sup>1,2</sup>

By E. S. LEWIS AND R. H. GRINSTEIN<sup>3</sup>

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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 ( $k_{\rm H}/k_{\rm D} = 1.4$ ,  $k_{\rm H}/k_{\rm T} = 1.7$ ). 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,<sup>1</sup> 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

$$\begin{array}{c} \mathrm{NC}_{\delta}\mathrm{H}_{\delta} \\ (\mathrm{C}_{\delta}\mathrm{H}_{\delta})_{2} \ \mathrm{B}\mathrm{-H} \ + \ \mathrm{H}_{2}\mathrm{O} \longrightarrow (\mathrm{C}_{6}\mathrm{H}_{\delta})_{2}\mathrm{B}\mathrm{O}\mathrm{H} \ + \ \mathrm{H}_{2} \ + \ \mathrm{C}_{\delta}\mathrm{H}_{\delta}\mathrm{N} \\ \mathrm{I} \end{array}$$
(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<sup>4</sup> reaction as proposed by Hawthorne,<sup>5</sup> on the basis of the small negative value of Hammett's  $\rho$ .

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.

$$Ph = Py$$

$$Ph = H$$

$$Ph = Py$$

$$Ph = pyridine$$

$$O = Ph = phenyl$$

$$H$$

$$H$$

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

(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.

<sup>(1)</sup> Paper I, M. F. Hawthorne and E. S. Lewis, J. Am. Chem. Soc., 80, 4296 (1958).

<sup>(2)</sup> From the Ph.D. thesis of R. H. Grinstein, Rice University, 1961.

<sup>(3)</sup> 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

<sup>(</sup>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 apparen'ly 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.