

TABLE I

VALUES OF ΔE , ΔH^\ddagger , ΔF^\ddagger , ΔS^\ddagger , (AT 300°K.) FOR PROTON

Reaction	TRANSFER IN WATER				
	ΔE	ΔH^\ddagger (kcal. mole ⁻¹)	ΔF^\ddagger	ΔS^\ddagger (e.u.)	A (sec. ⁻¹)
H ₂ O ⁺ + H ₂ O	+2.6	+2.0	+3.8	-5.8	9.4×10^{11}
OH ⁻ + H ₂ O	+4.7	+4.1	+4.1	-0.1	1.7×10^{12}
	+5.0	+4.4	+4.3	+0.5	2.3×10^{12}
H ₂ O ⁺ + OH ^{-a}	+2.5	+1.9	+2.3	-1.3	9.0×10^{12}

^a Approximate values calculated from ΔE and k_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 $T_1 = T_1(\text{max})/\eta$ where $T_1(\text{max})$ is equal^{3b,8} to

TABLE II

VALUES OF T_1 AND T_2 (IN SEC.) IN VERY ACIDIC OR BASIC WATER (25°)

	pH	T_1	T_2	T_1
		(meas.)	(meas.)	(calcd.)
Ordinary water	~ 0	2.54	2.52	2.52
Ordinary water	~14	2.24	2.17	2.11
H ₂ O ¹⁷ enriched water (0.6%)	0.86	2.39	2.36	

2.6 and η 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^{1,2}

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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 HBF₂ 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 information⁵ concerning the strength of the boron-carbon 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 RBF₂ (R = CH₃-, C₂H₅-, CH₂:CH- and (CH₃)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

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.⁶ 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 impurity, 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 ¹¹B isotope. The data were evaluated by the vanishing current method,⁷ 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.

(6) F. E. Brinckman and F. G. A. Stone, *J. Am. Chem. Soc.*, **82**, 6218 (1960).

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

(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 Natl. 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.

TABLE I

APPEARANCE POTENTIALS OF SOME ORGANOBORON DIFLUORIDES							
<i>m/e</i>	Ion	CH ₃ BF ₂ Rel. abs. (%)	A _p (e.v.)	<i>m/e</i>	Ion	CH ₂ :CHBF ₂ Rel. abs. (%)	A _p (e.v.)
64	CH ₃ BF ₂ ⁺	13.0	12.54 ± 0.03 ^a	76	C ₂ H ₃ BF ₂ ⁺	100	11.06 ± 0.03 ^a
49	BF ₂ ⁺	100	13.62 ± .02	57	C ₂ H ₄ BF ⁺	30.0	11.9 ± .2
45	CH ₃ BF ⁺	19.7	15.05 ± .1	56	C ₂ H ₂ BF ⁺	27.4	15.5 ± .2
44	CH ₂ BF ⁺	15.7	13.38 ± .02	49	BF ₂ ⁺	87.4	12.69 ± .05
15	CH ₃ ⁺	6.4	14.8 ± .1	27	C ₂ H ₃ ⁺	65.0	14.8 ± .1
14	CH ₂ ⁺	4.8	16.9 ± .1	26	C ₂ H ₂ ⁺	40.1	14.25 ± .05
							13.75 ± .1
<i>m/e</i>	Ion	C ₂ H ₃ BF ₂ Rel. abs. (%)	A _p (e.v.)	<i>m/e</i>	Ion	(CH ₃) ₂ CHBF ₂ Rel. abs. (%)	A _p (e.v.)
78	C ₂ H ₃ BF ₂ ⁺	3.3	11.8 ± 0.05 ^a	92	C ₃ H ₇ BF ₂ ⁺	3.0
59	C ₂ H ₃ BF ⁺	9.6	12.1 ± .2	77	C ₂ H ₄ BF ₂ ⁺	19.8	12.58 ± 0.05 ^a
			15.6 ± .2				
58	C ₂ H ₄ BF ⁺	2.1	12.6 ± .2	76	C ₂ H ₃ BF ₂ ⁺	8.4	12.80 ± .05
57	C ₂ H ₃ BF ⁺	8.6	12.0 ± .2	57	C ₂ H ₃ BF ⁺	33.0	11.8 ± .1
			14.9 ± .2				
56	C ₂ H ₂ BF ⁺	4.9	12.0 ± .2	49	BF ₂ ⁺	32.3	14.6 ± .2
			15.0 ± .2				
49	BF ₂ ⁺	19.0	14.3 ± .2	43	C ₃ H ₇ ⁺	51.0	12.05 ± .05
29	C ₂ H ₃ ⁺	14.9	13.1 ± .2	42	C ₃ H ₆ ⁺	100	11.48 ± .02
28	C ₂ H ₄ ⁺	100	12.08 ± .01	27	C ₂ H ₃ ⁺	39.4	14.8 ± .1

^a ± 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 RBF₂ compounds studied are listed in Table I, together with the relative abundances of the ions as calculated for the ¹¹B and ¹²C 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.⁸ or 15.5 e.v.^{5b} 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 π-electrons with the vacant p_π-orbital of the BF₂ group. Indeed, the position of the ionization potential of vinylboron difluoride, when considered with the series of ethylenic ionization potentials discussed recently,⁹ is in agreement with the known electron withdrawing character of the BF₂ 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 R₁-R₂ bond from the appearance potential *A_p* of the R₁⁺ ion and the ionization potential *I* of the R₁ radical is limited by the possibility of excess energy. Stevenson¹⁰ has stated the useful empirical rule that if *I*(R₁) < *I*(R₂) the R₁⁺ ion is more likely to be formed without excess energy than if *I*(R₁) > *I*(R₂). 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.¹¹ No ionization potential is known for the BF₂ radical, but as discussed below it may be estimated from the appearance potentials of boron trifluoride.^{5b,8}

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.^{11c} As a result of formation of the ions C₂H₃⁺, C₂H₅⁺ and C₃H₇⁺ 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, C₂H₃BF₂ and (CH₃)₂-CHBF₂ with the appearance potentials of the corresponding BF₂⁺ ions gives for *I*(BF₂) values of 10.0, 9.9 and 10.4 e.v., respectively. However, since the ionization efficiency curves for the BF₂⁺ ions showed marked tailing, often associated with excess energy,¹² these values must be regarded as upper limits. With methylboron difluoride the tailing situation was reversed; the CH₃⁺ curve tailed while the BF₂⁺ plot was parallel to that of argon. Thus, to arrive at a value for the boron-carbon bond dissociation energy in the methyl compound, it is necessary to estimate a value for the ionization potential of the BF₂ 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^{5b,8} of the BF_2^+ ion from boron trifluoride and assuming that the thermochemical bond energy term¹³ $E = 154 \text{ kcal. mole}^{-1}$ represents a reasonable lower limit to $D(\text{F}_2\text{B}-\text{F})$. The resulting upper limit for $I(\text{BF}_2)$ is then calculated to be about 9.5 e.v., and thus we feel that the most probable range for $I(\text{BF}_2)$ is 9.3–9.5 e.v. This also gives a reasonable value for $D(\text{H}_3\text{C}-\text{BF}_2)$ when compared with the other boron-carbon bond dissociation energies in the RBF_2 series and satisfies the requirements of Stevenson's rule, $I(\text{BF}_2)$ being higher than $I(\text{C}_2\text{H}_5)$ and $I(\text{iso-C}_3\text{H}_7)$, about equal to $I(\text{C}_2\text{H}_5)$ but below $I(\text{CH}_3)$.

Our results show that the B-C bond strength in the vinyl compound $\text{CH}_2:\text{CHBF}_2$ lies significantly above that of the B-C bonds in alkylboron 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 π -interaction, further indicated by other work.¹⁴ In the absence of bond dissociation data for comparable compounds, the range of 95 to 101 kcal. mole⁻¹ for the methyl-, ethyl- and *iso*-propylboron difluorides is not unreasonable. The only related data available in the literature is the thermochemical bond energy term E for the boron-carbon bond in several trialkylboron compounds. The most recent work on this subject^{5a} gives $E = \sim 84 \text{ kcal. mole}^{-1}$. 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.

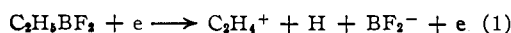
TABLE II

BOND DISSOCIATION ENERGIES AND HEATS OF FORMATION OF SOME ORGANOBORON DIFLUORIDES

Compound	ΔH_f (kcal. mole ⁻¹)	$I(\text{R})$ (e.v.)	D (R-BF ₂) (kcal. mole ⁻¹)	D (H-BF ₂) (kcal. mole ⁻¹)
CH_3BF_2	-199 ± 3	9.3–9.5 ^a	95–100	
$\text{CH}_2:\text{CHBF}_2$	-171^b	9.45 ^c	111	99
$\text{C}_2\text{H}_5\text{BF}_2$	-209^b	8.72 ^d	101	106
<i>i</i> - $\text{C}_3\text{H}_7\text{BF}_2$	-212^b	7.90 ^e	96	99

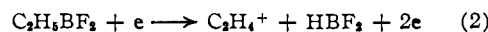
^a $I(\text{BF}_2)$. ^b Calculated assuming $I(\text{BF}_2) = 9.4 \text{ e.v.}$, result probably accurate to $\pm 8 \text{ kcal. mole}^{-1}$. ^c From ref. 11c. ^d From ref. 11b. ^e From ref. 11d.

Inspection of the mass spectra of ethyl- and *iso*-propylboron difluoride reveals the interesting fact that in both cases the ion formed by loss of both H and BF_2 predominates over that formed by loss of BF_2 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 difluoride these may be written as

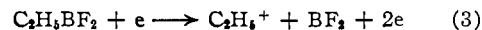


(13) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

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



(1) is unlikely since it would require an unrealistically high value (106 kcal. mole⁻¹) for the electron affinity of the BF_2 radical to account for the difference in appearance potentials of C_2H_4^+ and C_2H_5^+ . Furthermore, Marriott and Craggs⁸ reported no BF_2^- 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_2 molecule, the existence of which has been postulated as a chemical intermediate.¹⁵ When (2) is considered in conjunction with the process



one obtains

$$\Delta H_f(\text{BF}_2) - \Delta H_f(\text{HBF}_2) = -A_p(\text{C}_2\text{H}_4^+) + A_p(\text{C}_2\text{H}_5^+) + \Delta H_f(\text{C}_2\text{H}_4^+) - \Delta H_f(\text{C}_2\text{H}_5^+)$$

furthermore

$$D(\text{F}_2\text{B}-\text{H}) = \Delta H_f(\text{BF}_2) - \Delta H_f(\text{HBF}_2) + \Delta H_f(\text{H})$$

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,⁷ with the exception of $\Delta H_f(\text{C}_2\text{H}_3^+)$ where the more recent value of Harrison and Lossing^{11c} was used. The resulting $D(\text{F}_2\text{B}-\text{H})$ 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_3^+ ion. The average value of about 101 kcal. mole⁻¹ compares favorably with the bond energy term $E(\text{B}-\text{H})$ of about 93 kcal. mole⁻¹ in BH_3 given by McCoy and Bauer.¹⁶

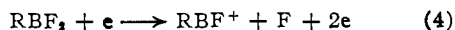
The appearance potential of the BF_2^+ ion from methylboron difluoride, together with the known BF_2^+ appearance potential^{5b,8} from boron trifluoride, and the heat of formation $\Delta H_f(\text{BF}_3(\text{g})) = -270 \text{ kcal. mole}^{-1}$ ¹⁷ allow calculation of the heat of formation of methylboron 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 $\sim 9.4 \text{ e.v.}$ 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_2 compounds cannot be easily deduced by direct measurement.

(15) (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.

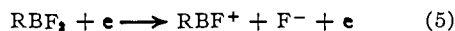
(16) R. E. McCoy and S. H. Bauer, *J. Am. Chem. Soc.*, **78**, 2061 (1956).

(17) 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

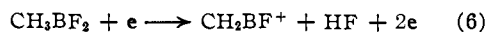


or

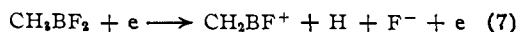


That both processes occur with the ethyl and vinyl compounds is evident from the observation of two appearance potentials for $\text{C}_2\text{H}_5\text{BF}^+$ and $\text{C}_2\text{H}_3\text{BF}^+$, respectively, the difference in both cases being 3.6 e.v., which is almost exactly the electron affinity¹⁸ of the fluorine atom. Only a single process was observed leading to CH_3BF^+ from methylboron difluoride. Its relatively high appearance potential of 15.0 e.v. implies process 4 above. The $\text{C}_3\text{H}_7\text{BF}^+$ 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^+ ion produced by loss of F. The correct process thus must be one of the following, using methylboron difluoride as an example

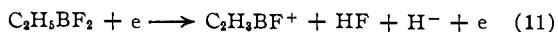
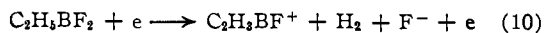
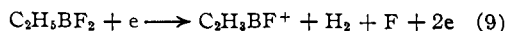


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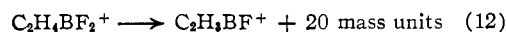
Although sufficient information is not available in each case to allow a definite choice on energetic grounds, it is possible, as discussed below, to correlate the appearance potentials of the $\text{C}_2\text{H}_2\text{BF}^+$ ion from ethylboron difluoride with the same ion from vinylboron difluoride 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, $\text{C}_2\text{H}_3\text{BF}^+$, from vinylboron difluoride as formed by process 5, using the heats of formation of the compounds (Table II). Possible processes are



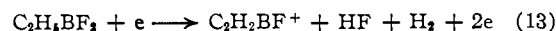
The appearance potentials predicted for the processes (8-11) are 15.9, 17.2, 13.5 and 13.6 e.v., respectively. None of these results is as low as the lower observed value. It is possible that the failure to predict sufficiently low values arises from the presence of excess energy in the reference process.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

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 ^{11}B - ^{10}B isotopes, corresponding to the transition

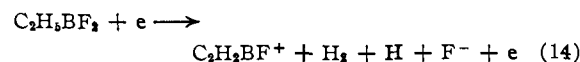


indicating that reaction 8 occurs. Thus equations 8 and 10 provide reasonable explanations for the higher and lower appearance potentials, respectively.

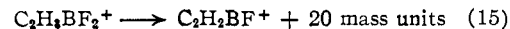
The appearance potential of the $\text{C}_2\text{H}_2\text{BF}^+$ ion from ethylboron difluoride was also measured, leading to two values, 12.0 and 15.0 e.v. These relatively low potentials suggest



and

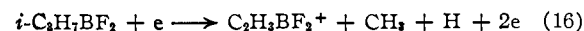


as the two most likely processes involved. Using process 6 as a standard, the calculated appearance potentials are 14.3 and 16.6 e.v., respectively, while process 7 as a reference yields 12.1 and 14.3 e.v., respectively. Other possible processes lead to much higher values. The agreement between the observed 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

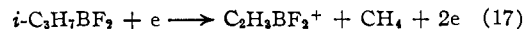


This further supports the idea that process 13 occurs. The above arguments indicate that (7) provides a more likely explanation than (6) for the decomposition of vinylboron difluoride.

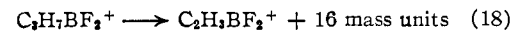
Only the mass spectrum of *iso*-propylboron difluoride contains peaks of carbon and boron containing ions formed by loss of a hydrocarbon fragment which are sufficiently intense to permit accurate measurements. The ion $\text{C}_2\text{H}_4\text{BF}_2^+$ must be formed by simple loss of a methyl group, while $\text{C}_2\text{H}_3\text{BF}_2^+$ may be formed either by



or



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



also support the occurrence of (17).

(18) H. O. Pritchard, *Chem. Revs.*, **53**, 529 (1953).

