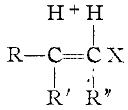
The decrease in rate of SN1 hydrolysis as well as the dipole moment results of Rogers can be attributed in large measure to the inductive effect of the H—C≡C— group.

Preliminary studies of the n.m.r. shifts in 1,1-dimethylpropargyl halides indicate somewhat different behavior, however. The relative methyl proton shifts with X = Br and X = Cl are opposite in direction from that expected on the basis of inductive withdrawal, but precisely this result has also been noted by Bothner-By for the β protons in alkyl halides,[9] and the latter has suggested resonance structures on the basis of which these data can be rationalized, *e.g.*



$$\mathrm{R{-}\underset{\displaystyle R'}{C}{=}\overset{\displaystyle H^{+}H}{\underset{\displaystyle R''}{C}}\,X^{-}}$$

Such forms can be expected to increase with the atomic number of X and to be favored by steric compression in secondary and tertiary halides. Shifts are also observed in the acetylenic protons, and like the methyl shifts, are opposite in order from the halogen electronegativities. In this connection it is noted that Rogers has measured the dipole moments of 1-methyl and 1,1-dimethylpropargyl bromides, obtaining values of 1.76 and 1.94 *D*, respectively.[27] The increased ionic character of the tertiary C-halogen bonds makes allenic resonance of the form I⟷II with consequent alteration of the terminal proton shielding more likely. The order of the shifts, as also evident in the β-methyl groups, appears to suggest that steric hindrance is more important than electronegativity in determining the relative contributions of these forms.

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[Contribution from the Department of Chemistry, The Johns Hopkins University and the Knolls Atomic Power Laboratory, General Electric Company]

A Mass Spectroscopic Appearance Potential Study of Some Boron Trihalides[1]

By W. S. Koski, Joyce J. Kaufman and C. F. Pachucki

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The appearance potentials of the positive ion fragments from BCl_3, BBr_3 and BI_3 were measured mass spectroscopically. These measurements permitted a determination of the average B–I bond dissociation energy in BI_3. The value obtained was 2.77 ± 0.2 e.v. A B–I bond length of 2.03 Å. was estimated independently. A plot of the bond energy *versus* bond length in the boron trihalides gave a linear relation. A set of apparently self-consistent ionization potentials for the boron trihalides and fragments formed from these molecules has been estimated and compared with ionization potentials of other BY_3 molecules as well as for BY_2 and BY fragments (where Y can be H, halogen or alkyl substituents). Comparison of the ionization potentials of BY_2 radicals indicates an interesting correlation between the ionization potentials and the nature of the group attached to the boron. CY_3 radicals exhibit a similar behavior. The mass spectra of the boron trihalides were also run at 70 e.v. ionizing voltage to obtain a set of fragmentation patterns under constant conditions.

The appearance potentials of the positive ion fragments from BCl_3, BBr_3 and BI_3 were measured mass spectroscopically. The purpose of this research was twofold. First, to calculate a value for the average B–I bond dissociation energy in BI_3 since there is no thermochemical data available on this subject. Second, to attempt to calculate a self-consistent set of ionization potentials for the boron trihalides and the fragments formed from these molecules.

The method of obtaining bond dissociation energies and ionization potentials by electron impact has had considerable success especially in the field of hydrocarbons and related organic compounds. If one represents the process taking place as

$$R_1 - R_2 + e \longrightarrow R_1^+ + R_2 + 2e$$

then by the equation

$$A(R_1^+) = D(R_1\text{–}R_2) + I(R_1)$$

where $A(R_1^+)$ is the mass spectrometrically measured appearance potential of R_1^+, $D(R_1\text{–}R_2)$ is the dissociation energy of R_1–R_2, and $I(R_1)$ is the ionization potential of R_1, either the bond dissociation energy R_1–R_2 or the ionization potential of R_1 may be calculated directly from the measured $A(R_1^+)$, provided that one knows the value for the other unknown in the equation. A necessary condition for the above equation to hold true is $I(R_1) < I(R_2)$.[2] If $I(R_1) > I(R_2)$ then $A(R_1^+) > D(R_1\text{–}R_2) + I(R_1)$. In order to interpret correctly the appearance potentials of fragment ions, it is necessary to know what other fragments are simultaneously formed, the states of electronic excitation of the fragments and the molecule ion and the excess kinetic or vibrational energy present. In hydrocarbon dissociations, only neutral fragments are simultaneously formed, but in dissociations of halogen containing compounds, there is always the possibility that an X^- ion can be formed since the halogen atoms have high electron affinities. The X^- ions can be produced in two ways: by a resonance dissociative attachment process

$$BX_3 + e \longrightarrow BX_2 + X^-$$

or by an ion pair process

$$BX_3 + e \longrightarrow BX_2^+ + X^- + e$$

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(1) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. AF 18(600)-1526. Reproduction in whole or in part is permitted for any purpose of the United States Government.

(2) D. P. Stevenson, *Disc. Faraday Soc.*, **10**, 35 (1951).

TABLE I

APPEARANCE POTENTIALS OF THE POSITIVE ION FRAGMENTS FROM THE BORON TRIHALIDES

Species	Appearance potential, e.v.					
	BCl_3		BBr_3		BI_3	
BX_3^+	$B^{10}Cl^{37}_2Cl^{35+}$	11.0 ± 0.2	$B^{11}Br^{81}_2Br^{79+}$	9.7 ± 0.2	$B^{11}I_3^+$	9.0 ± 0.2
	$B^{10}Cl^{35}_2Cl^{37+}$	10.9 ± .2	$B^{11}Br^{79}_2Br^{81+}$	9.7 ± .2		
	$B^{11}Cl^{35}_3{}^+$	10.9 ± .2				
	$B^{10}Cl^{35}_3{}^+$	10.6 ± .2				
BX_2^+	$B^{10}Cl^{37}_2{}^+$	12.0 ± .2	$B^{11}Br^{81}_2{}^+$	10.8 ± .2	$B^{11}I_2^+$	9.7 ± .2
	$B^{11}Cl_2^{35+}$	11.8 ± .2	$B^{11}Br^{79}Br^{81+}$	11.0 ± .2	$B^{10}I_2^+$	10.1 ± .2
			$B^{11}Br^{79}_2{}^+$	10.7 ± .2		
BX^+	$B^{11}Cl^{35+}$	17.2 ± .2	$B^{11}Br^{81+}$	10.7 ± .2	$B^{11}I^+$	14.4 ± .2
	$B^{10}Cl^{35+}$	20.0 ± .2	$B^{10}Br^{81+}$	11.8 ± .2	$B^{10}I^+$	14.6 ± .2
			$B^{11}Br^{79+}$	10.7 ± .2		
			$B^{10}Br^{79+}$	15.0 ± .2		
B^+	B^{11+}	19.5 ± .2	B^{11+}	19.6 ± .2	B^{11+}	16.6 ± .5
	B^{10+}	20.8 ± .5				

(X will always indicate a halogen atom: Cl, Br or I). To complicate matters still further, these X^- ions can be formed in conjunction with any of the lower fragmentation processes and apparently it is also possible to form X_2 molecules in some of the dissociations. However, it has been shown in many cases that the simplest set of assumptions will suffice for the interpretation of the data.

During the course of this investigation a paper on the appearance potentials of BF_3 and BCl_3[3] came to our attention. This report extended the measurements made previously on BF_3 and BCl_3[4] and BF_3.[5] In reference 3, the authors pointed out some of the possible processes which might have led to the appearance potentials observed; however, they made no attempt to decide what processes had actually taken place but simply reported that the ionization potentials could be one of several values.

In this study, therefore, results for these molecules are given as obtained from new measurements and combined with more recent and presumably more accurate values of the B–F and B–Cl bond dissociation energies.

A great disadvantage in the appearance potential studies of boron compounds is that there is so little independent thermochemical data available from which to calculate the energies of the possible states of combination in which the boron and other atoms may exist.

Experimental

The appearance potentials were deduced by the vanishing current method and the instrument, operating conditions and experimental procedure were similar to those used when the isotopically labeled diboranes were analyzed.[6] Due to the peaks present in the neon, argon and krypton regions, helium was used as the internal standard for BCl_3, BBr_3 and BI_3. The more predominant peaks of each fragment were run. The use of helium involved the change of focusing potentials which was not necessary when argon was used. Since there were some extreme changes in focusing potentials involved, some concern was felt that field penetration into the ionizing region of the ion source might give rise to erroneous results. Therefore, the argon appearance potential was checked, using the helium, and found to be 15.6 ± 0.1 e.v. as compared to the spectroscopic value 15.76 e.v. The appearance potentials of the B^+ and the BF_2^+ fragments from BF_3 were also measured using helium as an internal standard and then remeasured using argon as an internal standard. With the use of argon it was unnecessary to change the focusing potentials. Using helium as a standard the appearance potential of B^{11+} was 30.5 ± 0.5 e.v., whereas the argon standard gave 31.0 ± 0.5 e.v. compared with 30.6 ± 0.1 e.v. from the latest literature value.[3] $B^{11}F_2$ appearance potential was 15.9 ± 0.2 e.v. with the helium standard, 16.0 ± 0.2 with the argon standard compared with 16.17 ± 0.05 reported in reference 3. The results using helium or argon therefore seem to be consistent.

Since the m/e 392 peak of the BI_3 was not within the normal accelerating voltage range (2000 v.), the accelerating potential was lowered to 1000 v. to accommodate this higher mass. The helium standard was also used at this voltage.

The BI_3 was purified by vacuum subliming it twice over mercury and then was vacuum sublimed directly into an evacuated bulb.

The BBr_3 was purified by a vacuum distillation over mercury and then vacuum distilled into a bulb.

The BCl_3 was technical grade and was purified by vacuum distillation.

Calculations and Results

In Table I are presented the values for the appearance potentials of the positive ion fragments from the boron trihalides as measured in this study.

A. **Bond Dissociation Energy of BI_3.**—The average B–I bond dissociation energy in boron triiodide can be determined from the appearance potential of the B^+ ion if the process leading to this ion is

$$BI_3 + e \longrightarrow B^+ + 3I + 2e$$

$$A(B^+) = 3D(B\text{–}I) + I(B)$$

Since $I(I) = 10.44$ e.v. and $I(B) = 8.29$ e.v.,[7] the required inequality referred to above is satisfied here.

In view of the similarity between BI_3 and BBr_3, one might expect the same process in the latter case also to lead to the B^+ ion. The validity of the assumed process can be checked in the BBr_3 case since here D_{av}(B–Br) has been measured thermochemically.[8] The appearance potential $A(B^+)$ has been measured for BBr_3 in this study and found to be 19.6 ± 0.2 e.v. If one assumes that the process as outlined above is applicable, one finds a D_{av}(B–Br) in BBr_3 of 3.7_7 ± 0.1 e.v. The

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(3) J. Marriott and J. D. Craggs, *J. Electronics and Control*, **3**, 194 (1957).

(4) O. Osberghaus, *Z. Physik.*, **128**, 266 (1950).

(5) R. W. Law and J. L. Margrave, *J. Chem. Phys.*, **25**, 1086 (1956).

(6) W. S. Koski, Joyce J. Kaufman, C. F. Pachucki and F. J. Shipko, THIS JOURNAL, **80**, 3202 (1958).

(7) Charlotte E. Moore, "Atomic Energy Levels," Vol. I, National Bureau of Standards Circular 467, June 15, 1949.

(8) M. B. Wallenstein and E. J. Prosen, "Bond Energies and Heats of Formation of Some Boron Compounds," National Bureau of Standards Report 3455 (corrected) June 30, 1954.

thermochemically determined value is reported as 3.86 e.v.

The agreement between the two values is excellent and supports the assumption that at least in this case the process taking place corresponds to the simplest one possible. Extending this argument to BI_3 one obtains $D_{av}(B-I)$ as $2.7_7 \pm 0.2$ e.v., since $A(B^+)$ for BI_3 was measured as 16.6 ± 0.5 e.v. and $I(B)$ as 8.29 e.v.[7]

Empirical linear relationships have been noted between C–X bond dissociation energy and C–X bond distance in the methyl halides.[9] A similar linear relationship can be obtained for CF_3X and EtX molecules using reported literature values.[10–12] The B–X bond distances in BCl_3 and BBr_3 have been measured,[12] and the B–Cl bond distance in BCl_3 has been accurately remeasured recently.[13] However, no measured B–I distance in BI_3 has been reported. It was of interest to estimate the B–I distance in the latter compound independently. This can be done in the following manner.

Inspection of the M–X distances in all of the group III trihalides[12] (with the exception of the Al compounds which exist as dimeric bridged molecules), showed a surprising regularity. The difference between M–Cl and M–Br bond lengths was approximately constant at 0.12–0.13 Å. in every case, and the M–Br distance was about 0.16 Å. shorter than the M–I distance. Using this analogy, adding 0.16 Å. to the reported B-Br bond distance of 1.87 ± 0.02 Å. in BBr_3, one obtains a B–I distance of 2.03 ± 0.03 Å. in BI_3.

A plot of the above bond energies *versus* bond lengths for the three boron trihalides gives a straight line, Fig. 1. This linear relationship indicates the similarity between the bond length–bond energy behavior in the boron and carbon halogen compounds cited and establishes some confidence in the values for both the estimated bond length in BI_3 and the bond energy of BI_3 as calculated from the appearance potential measurements.

B. Calculated Ionization Potentials for BY_n Fragments.—In a previous article[6] on an appearance potential study of diborane, B_2H_6, the ionization potentials for all B_2H_n fragments were calculated and as a matter of academic interest an attempt was made to calculate ionization potentials for all the BH_n fragments. This was difficult because of the large number of possible combinations involved leading to a large number of choices for the correct values. Some trends seemed apparent in this series of calculated ionization potentials for the BH_n fragments, and it was of interest to make similar calculations for the boron trihalides and the fragments from these molecules.

There is little ambiguity about the appearance potentials of the parent ions—these are equal to the vertical ionization potentials of the molecules (where "vertical" is taken to mean the transition favored by the Franck–Condon principle).[14] The ionization potentials of the boron trihalides determined during the course of this study and the ionization potentials of several other BY_3 molecules (where Y can be hydrogen, halogen or alkyl substituents) are shown in Table II.

The trend in the ionization potentials in this series of compounds is the expected one.

Some correlation can be drawn between ionization potentials of boron compounds and those of carbon compounds, except that for compounds containing only one B atom, the correlation must be made between CY_4 molecules and BY_3 molecules since both of these have filled molecular orbital shells, although the ionization potentials of the carbon compounds will be expected to be higher in almost all cases. In the case of the ionization potentials of CY_3 radicals, comparison is made with BY_2 radicals since both of these fragments possess an odd electron.

The most interesting series of ionization potentials is that of the BY_2 radicals since this may indicate the effects of substituent groups on the ease with which the unpaired electron can be withdrawn assuming that the odd electron is the one involved in the ionization process. Using the average observed appearance potentials and the thermochemical B–Cl and B–Br bond energies[8] and the calculated B–I bond energy, the ionization potentials for the BX_2 fragments have been estimated. They are included in Table II with values calculated for several other BY_2 radicals for comparison.

These values were calculated assuming the process was

$$BX_3 + e \longrightarrow BX_2^+ + X + 2e$$

The following process

$$BX_3 + e \longrightarrow BX_2^- + X^- + e$$

was not used since the ionization potentials would have had to be raised by an amount equal to the electron affinity of each halogen: Cl, 3.72 e.v.; Br, 3.49 e.v.; and I, 3.14 e.v.[15] This would lead to extraordinarily high values for the ionization potentials, well above those for the parent molecules and this is not very probable. In every case where the ionization potentials of free radicals have been measured or calculated, they are always lower, usually by several e.v., than those of the parent molecules.

It will be noted from the data in Table II that the ionization potentials of the BX_2 radicals are about the same to within experimental error. This is not an unexpected behavior since electronegativities of the halogens—Cl, Br and I—are not too different. The calculated ionization potential of BH_2 is on the other hand about one electron volt higher than those of the corresponding boron dihalide radicals. This is very similar to the situation reported in CCl_3[16] and CH_3 radicals where the ionization potential of the CCl_3

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(15) G. Herzberg, "Atomic Spectra and Atomic Structure," Dover Publications, New York 44, N. Y., 1944.

(16) F. P. Lossing, J. B. Farmer and I. H. S. Henderson, 1954, unpublished (quoted in 16).

TABLE II

IONIZATION POTENTIALS OBTAINED FROM MASS SPECTROSCOPIC APPEARANCE POTENTIALS

BY_3 molecules		BY_2 radicals		CY_3 radicals		BY fragments	
Species	I(e.v.)	Species	I(e.v.)	Species	I(e.v.)	Species	I(e.v.)
BH_3[a]	11–12	BH_2[a]	8.12	CH_3[22]	9.96	BH[a]	10.06
BCl_3	10.9	BCl_2	7.20	CCl_3[16]	8.78	BCl	~10.44
BBr_3	9.7	BBr_2	7.06	C_2H_5[19]	8.78	BBr	9.25–10.14
BI_3	9.0	BI_2	7.13	*i*-C_3H_7[19]	7.90	BI	8.96
BMe_3[4]	8.8	BMe_2[b]	6.44	*t*-C_4H_9[23]	6.90	BMe[b]	9.28
BEt_3[4]	9.0	BEt_2[b]	5.98			BEt[b]	8.73

[a] Calculated from appearance potentials from B_2H_6.[6] [b] Calculated from appearance potentials in 4 using the B–Me and B–Et bond energies in 7.

radical is ~ 1 e.v. less than that of the methyl radical, and this can be explained on the basis of some interaction of the electrons in the 4 pπ nonbonding orbital of the Cl atoms and the $2p_z$ orbital of the central C atom, and also partially to the greater stability of the CCl_3^+ ion over the CH_3^+ ion.[17] Much the same type of behavior would be expected for the boron dihalide radicals. An inference can be drawn that the ionization potentials of the CCl_3, CBr_3 and CI_3 radicals may be very close and plans are under way to check this by experiment.

There are no spectroscopic values for the ionization potential of any boron containing free radicals although some such data have been obtained directly by electron impact and other values have been calculated from electron impact data.

Care must be exercized in picking ionization potentials of the CR_3 radicals because the ions may have isomeric configurations rather than the commonly postulated structures. Existing evidence suggests that some of the forms may differ little in energy,[18] however, the isomeric forms may differ considerably in ionization potential. It is definite that protons and other groups can migrate rather freely from one C atom to neighbors; and presumably the reason is that bridged or cyclic structures have small or possibly negative activation energies.

As an example of the ambiguities which may occur in assigning ionization potentials, the same values are calculated for the ionization potentials of C_3H_7 from alkanes or isoalkanes. This has led several investigators to conclude $C_3H_7^+$ ions from *n*-alkanes and isoalkanes have the same structure (formerly considered to be isopropyl). However, direct measurement of the ionization potential of the isopropyl radical[19] gave a value of 7.90 ± 0.05 e.v., significantly higher than the 7.43 ± 0.1 e.v.[20] derived from the appearance potentials of "*i*-$C_3H_7^+$" in mass spectra of isoalkanes and heats of formation. This discrepancy suggests that the $C_3H_7^+$ ions produced by electron impact of hydrocarbon molecules and those produced by ionization of isopropyl radicals do not have the same structure. A cationated cyclopropane ring or a different cyclic structure in which one hydrogen is shared between the two end carbon atoms have both been proposed for the $C_3H_7^+$ ion produced by electron impact.[20,21]

Table II shows the effect of substitution on the ionization potentials of the CY_3 radicals. All the values except that for the *t*-butyl radical were derived directly from electron impact of the free radicals themselves in order to lessen the possibility of ambiguity which would arise from rearrangements.

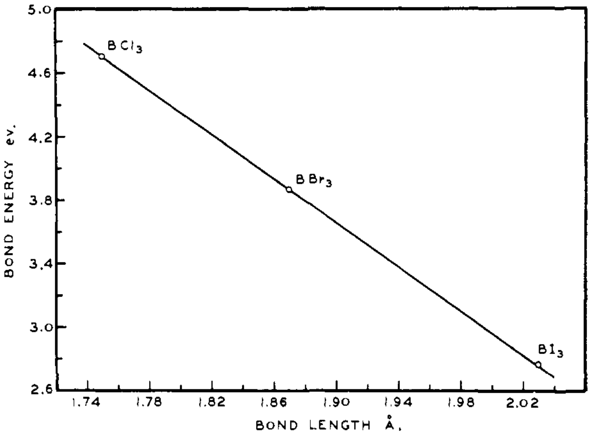

Fig. 1.—Plot of bond energies *versus* bond lengths for the boron trihalides.

From this table it can be seen that substitution of one methyl group on a CH_3 radical lowers the ionization potential by about 1 e.v.—this is in accord with the fact that a methyl group is electron donating. The mechanism by which this effect occurs has been postulated as a combination of strong hyperconjugation and charge redistribution.[18] The substitution of two methyl groups lowers the ionization potential by about 2 e.v. and three methyl groups lowers it by about 3 e.v. Therefore, one might expect that substitution of 2 methyl groups for the two H of BH_2 should lower the ionization potential by about 2 e.v.—and apparently it does.

This might imply that whatever is the correct mechanism by which the ionization potentials of the alkyl substituted CY_3 radicals are lowered, it is probably the same mechanism which accounts

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(23) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

for the lowering of ionization potentials of the alkyl substituted BY_2 radicals. An extension of this implication is that there may be hyperconjugation in the BR_2 radicals and ions. Substitution of 2 ethyl groups should lower the ionization potential a little more than substitution of two methyl groups—and apparently such is the case.

The ionization potentials of a series of methyl and ethyl halides obtained from accurate photoionization work[24] were studied and it was concluded that an ethyl group is more electron donating than a methyl group by 0.23 ± 0.02 e.v. Applying this figure to BMe_2 and BEt_2 one would expect a difference in ionization potentials of these two radicals of 0.46 e.v., which is just the value that is indicated in the table.

Substitution of three Cl atoms on a CH_3 radical lowers the ionization potential for the reasons described earlier—but substitution of three Cl atoms does not have as great an effect as substitution of three methyl groups.

An interesting corollary to this study is it appears possible to formulate a semi-quantitative method for the estimation of ionization potentials for even fairly complex substituted free radicals. Knowledge of the ionization potential of the parent free radical or that of any member of the series coupled with the observations of the effects of substituent groups on the ionization potentials of free radicals enable one to closely estimate the ionization potential of any other member of the series.

This approach can be carried even a little farther. The ionization potential of methane is 3 e.v. higher than that of the methyl radical and one might estimate that the ionization potential of BH_3 is about 3 e.v. higher than that of the BH_2 radical. Moreover, in the hydrogen and halogen substituted compounds, both in CH_4–BH_3 molecules, and in the series CY_3–BY_2 radicals there seems to be an almost constant difference in ionization potential of approximately 1.8 e.v.

The ionization potentials calculated for the BY fragments are those for which there is the greatest ambiguity. Inspection of the appearance potentials (Table I) for these fragments shows that there are at least two or three processes taking place which can give rise to these fragments in the case of BCl or BBr.

There seems to be less ambiguity in the case of the appearance potential of BI from BI_3 since the appearance potentials for the two isotopic species $B^{11}I^+$ and $B^{10}I^+$ were the same to within experimental error and no other appearance potential was observed.

The simplest process which could give rise to BI^+ is

$$BI_3 + e \longrightarrow BI^+ + 2I + 2e \qquad (1)$$

which would give

$$I(BI) = A(BI^+) - 2D(B\text{–}I)$$
$$= 8.96 \pm 0.3 \text{ e.v.}$$

This value for I(BI) seems reasonable and this would make the

$$I(BI) \cong I(BI_3)$$

The two other probable processes for the formation of BI are

$$BI_3 + e \longrightarrow BI^+ + I_2 + 2e \qquad (2)$$
$$BI_3 + e \longrightarrow BI^+ + I^- + I + e \qquad (3)$$

Process 2 would give an I(BI) of 10.5_1 e.v.

While this value of 10.5_1 is not completely unreasonable, the 8.9_6 e.v. is preferable especially in view of the fact that the ionization potentials for all molecules containing iodine are in the range of 9 e.v. (with the exception of HI which is 10.38 e.v. —and it is to be expected that the ionization potential of BI will be lower than that of HI).

The value for I(BI) calculated from process 3 is 12.1_0 e.v. and this value seems the least probable of the three since the ionization potentials for molecules containing iodine are usually much lower than this value.

There are three appearance potentials for BBr^+—10.7, 11.8 and 15.0 e.v. The low appearance potentials in part may be attributable to thermal dissociation of BBr_3 at the source filament

$$BBr_3 \longrightarrow BBr + Br_2$$

followed by

$$BBr + e \longrightarrow BBr^+ + 2e$$

For this reason the ionization potential of the BBr was calculated from the last value 15.0 e.v.

If the process taking place is presumed to be

$$BBr_3 + e \longrightarrow BBr^+ + 2Br + 2e \qquad (4)$$

then the $I(BBr) = 7.2_8$ e.v. This value seems too low, especially in view of the fact that the lowest calculated value for I(BI) is 8.9_6 e.v.

Therefore, the process taking place is assumed to be either

$$BBr_3 + e \longrightarrow BBr^+ + Br_2 + 2e \qquad (5)$$
$$BBr_3 + e \longrightarrow BBr^+ + Br^- + Br + e \qquad (6)$$

From (5) one obtains $I(BBr) = 9.2_5$ e.v.; and from (6) $I(BBr) = 10.1_4$ e.v. Both of these values are reasonable and it is assumed that I(BBr) lies somewhere between 9.2_5 and 10.1_4 e.v., with the value of 9.2_5 being slightly more preferable.

The two appearance potentials measured for $A(BCl^+)$ are 17.2 and 20.0 e.v. These two values differ by approximately the D(Cl–Cl) of 2.48 e.v. From the first value the process would be

$$BCl_3 + e \longrightarrow BCl^+ + Cl_2 + 2e$$

leading to an I(BCl) of 10.2_5 e.v.

From the second value the process would be

$$BCl_3 + e \longrightarrow BCl^+ + 2Cl + 2e$$

giving $I(BCl) = 10.6_0$ e.v. Therefore $I(BCl) \cong 10.4_4$ e.v.

The calculated ionization potentials for BY fragments are compared in Table II, but these values are not to be considered as anything more significant than a qualitative order.

The values (calculated and observed) for the ionization potentials of BY_n molecules and fragments begin to show promise of more than mere academic interest. In view of the scarcity of thermochemical data, a self-consistent set of ionization potentials might enable one to derive a fairly accurate idea of undetermined B–Y bond energies by the electron impact method using a properly

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[24] K. Watanabe, *J. Chem. Phys.*, **26**, 543 (1957).

TABLE III

MONOISOTOPIC MASS SPECTRA OF THE BORON TRIHALIDES RELATIVE ABUNDANCE

Species	BCl_3		BBr_3		BI_3	
BX_3^+	BCl_3^+	36.11	BBr_3^+	37.0	BI_3^+	Out of range
BX_3^{++}	BCl_3^{++}	1.11	BBr_3^{++}	5.31	BI_3^{++}	2.19
BX_2^+	BCl_2^+	100	BBr_2^+	100	BI_2^+	100
BX_2^{++}	BCl_2^{++}	3.71	BBr_2^{++}	0.27	BI_2^{++}	0
BX^+	BCl^+	7.63	BBr^+	48.91	BI^+	21.95
BX^{++}	BCl^{++}	0	BBr^{++}	1.03	BI^{++}	9.50
B^+	B^+	2.94	B^+	0.51	B^+	8.96
					Also evidence of BI_3^{+++} BI_3^{++++} BI_3^{+++++}	

chosen BY_3 molecule (in which the –Y's are different substituent groups) where the $I(BY_2)$ has been previously calculated from some known thermochemical data combined with electron impact experiments. There is also reason to believe that this approach can be extended to other types of compounds such as aluminum and silicon compounds in which there is a great deal of interest and a great scarcity of thermochemical data.

There are two instances in which this method should be of immediate interest in the field of boron compounds. First, to determine the B–X bond dissociation energy in molecules of the type BR_2X. Apparently the B–X bond dissociation energy in these molecules is not the same as the $(B–X)_{av}$ bond dissociation energy derived from BX_3 molecules. Second, to determine bond dissociation energies in BR_2R' molecules since a new method of preparation has made these mixed alkyl derivatives quite easy to prepare.

Finally, for comparison purposes, the fragmentation patterns for the boron trihalides were obtained at a constant ionizing voltage—70 e.v. From these, the monoisotopic mass spectra of the boron trihalides were calculated.

The values for BCl_3 check well with literature values.

It is of interest to note the greater abundance of multiply charged ions in the Br and I compounds. Evidence has been found for BI_3 ions with +3 and +4, and even +5 charges. This is in agreement with observation of multiply charged ions of Br and I compounds in radiation studies.[25]

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[25] R. H. Luebbe, Jr., and J. E. Willard, *J. Chem. Phys.*, **29**, 124 (1958).

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Thermodynamic Properties, Vibrational Assignment and Rotational Conformations of 2-Methyl-1-butene

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In a continuation of thermodynamic studies of monoölefins, values of the following thermodynamic properties of 2-methyl-1-butene were computed at selected temperatures between 0 and 1500°K.: $(F° - H°_0)/T$, $(H° - H°_0)/T$, $H° - H°_0$, $S°$, $C_p°$, $\Delta Hf°$, $\Delta Ff°$ and log Kf. A detailed vibrational and conformational analysis showed that the compound exists in two spectroscopically distinct conformations, one of which is predominant at room temperature.

In 1946 Kilpatrick, Prosen, Pitzer and Rossini[1] reported values of the thermodynamic properties of the six isomeric pentenes. The results of these authors were calculated from data for lower monoolefins by a method of increments, because values of heat of formation were the only experimental data then available for all isomers. Later, values of the entropy of all six pentenes,[2] the heat of vaporization and vapor heat capacity of three pentenes, and the thermodynamic functions of 2-methyl-2-butene[3] were reported from this Laboratory.

This paper presents values of the chemical thermodynamic properties of 2-methyl-1-butene calculated from previously published calorimetric, spectroscopic and molecular structure information. Values of entropy $S°$ and heat capacity $C_p°$, in the ideal gaseous state, taken from ref. 3, are collected in Table I. These results were used in the vibrational and conformational analysis of 2-methyl-1-butene.

Calculation of Thermodynamic Functions

For calculating the thermodynamic functions by the methods of statistical mechanics, a detailed vibrational assignment and an analysis of the effect of internal rotation were required. As previously noted,[3] 2-methyl-1-butene may exist in two spectroscopically distinct rotational conformations. Therefore, it was necessary to make a complete vibrational assignment for one conformation from spectroscopic data and to determine the relative stabilities of the two conformations from calorimetric data.

TABLE I

OBSERVED AND CALCULATED MOLAL ENTROPY AND HEAT CAPACITY OF 2-METHYL-1-BUTENE IN THE IDEAL GASEOUS STATE

	Entropy $S°$, cal. deg.$^{-1}$			Heat capacity $C_p°$, cal. deg.$^{-1}$	
T, °K.	Obsd.[a]	Calcd.	T, °K.	Obsd.[b]	Calcd.
277.96	79.41	79.39	320.66	27.76	27.79
298.16	81.14	81.15	362.51	30.68	30.66
304.32	81.67	81.69	407.11	33.61	33.65
			453.41	36.60	36.60
			502.21	39.52	39.51

[a] From Table V, ref. 3. [b] From Table I, ref. 3.

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[1] J. E. Kilpatrick, E. J. Prosen, K. S. Pitzer and F. D. Rossini, *J. Research Natl. Bur. Standards*, **36**, 559 (1946).

[2] S. S. Todd, G. D. Oliver and H. M. Huffman, THIS JOURNAL, **69**, 1519 (1947).

[3] D. W. Scott, G. Waddington, J. C. Smith and H. M. Huffman, *ibid.*, **71**, 2767 (1949).