Mass Spectrometric Study of Photoionization. XIII. Boron Trichloride and Diboron Tetrachloride

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Mass spectra and ion yield curves for the molecule ions and various fragment ions of BCl_3 and B_2Cl_4 are obtained by means of a combined vacuum ultraviolet monochromator and mass spectrometer. Shapes of ion yield curves, measured over the wavelength region from threshold to 600 Å, are discussed briefly. Ionization threshold values are used to calculate heats of formation of ions and radicals and to derive bond dissociation energies, including the boron–boron bond dissociation energy, $D_0(Cl_2B-BCl_2) = 3.80$ eV (87.6 kcal mol^{-1}), with estimated uncertainties of ± 0.04 eV.

Introduction

The heats of chlorination of diboron tetrafluoride and of diboron tetrachloride have been measured by Gunn and Green[1] and by Gunn, Green, and von Egidy,[2] respectively. By means of these data, Gunn and coworkers calculated heats of formation of the diboron halides and, assuming that the average B–X bond dissociation energy is the same in both BX_3 and B_2X_4, obtained B–B bond dissociation energies of 72.4 kcal mol^{-1} for the tetrafluoride and 79.0 kcal mol^{-1} for the tetrachloride. Gunn and Green[1] have remarked on the lesser validity of the calculations as applied to B_2F_4, and Urry[3] has noted the inconsistency of these results when compared with the known relative stability and the structural parameters of the two molecules B_2Cl_4 and B_2F_4.

In the preceding paper of this series, Dibeler and Liston[4] reported on a study of the photoionization of BF_3 and of B_2F_4. The observed threshold values for dissociative ionization of these molecules permitted calculations of various specific bond energies, including $D_0(F_2B-BF_2) = 4.47 \pm 0.04$ eV (103.1 $\pm$ 0.9 kcal mol^{-1}). Although the estimated uncertainty assigned to this value assumes the absence of systematic errors such as excess energy in the pertinent ionization processes, nevertheless it is considered in serious disagreement with the value obtained from the chlorination reaction. Therefore, it seemed desirable to extend the photoionization measurements to include the analogous chlorine compounds for a similar determination of the thermodynamic properties.

A number of electron impact studies of BCl_3 have been reported. Threshold values for the principal ions of BCl_3 observed by Marriott and Craggs[5] are in agreement with earlier work by Osberghaus[6] within their estimated uncertainties. However, in a more recent study, Koski, *et al.*,[7] reported threshold values for the same ions that are about 1 eV below the pre-

viously published values. Although Koski and coworkers discussed probable ionization processes at considerable length, the discrepancy is not explained.

A most recent study,[8] using photoelectron spectroscopy, reported the first and inner ionization energies for BCl_3, as well as BF_3 and BBr_3.

The mass spectrum and ionization thresholds of B_2Cl_4 have not been reported previously. As in the case of the fluorine compounds, concomitant studies of the related molecules, BCl_3 and B_2Cl_4, are required in order to interpret some of the results and to derive some of the thermodynamic properties.

Experimental Section

Data were obtained by means of the combined vacuum ultraviolet monochromator and mass spectrometer described previously[9] in detail. Briefly, the monochromator is a 1-m focal length, Seya-Namioka type, and, using a 1200-grooves/mm grating, has a calculated dispersion of 8.3 Å mm^{-1}. However, using 100-μm optical slits, the full width, half-height of the scanned 584-Å helium resonance line appeared to be about 1 Å. The grating could be rotated manually or by motor drive and set to any desired wavelength within the vacuum–uv region with an estimated reproducibility of 0.3 Å.

The wavelength region required for this study could not be covered by the emission from a single-continuum photon source. Therefore, those portions extending from 1300 to 1050 Å and from 1100 to 900 Å were covered by the argon continuum[10] and the many-lined hydrogen spectrum, respectively, both excited by a 2450-MHz, 800-W microwave generator. A Hinteregger source[11] was used to obtain the Hopfield continuum of helium in the range 950–600° Å.

The photon intensity was obtained by measuring the photoelectron current from a clean tungsten sheet mounted so as to intercept the photon beam after it traverses the ion source. Absolute measurements could not be obtained in this work. However, the uncertainty in the observed relative intensity at various wavelengths is estimated to be about 3% of the value.

Intensities of the ions resolved by the mass analyzer were measured by means of an electron multiplier, preamplifier, amplifier, and scaler. Except near the threshold of some ions, sufficient numbers of ions were counted at each wavelength to assure a statistical error in ion count of less than 1%.

The boron trichloride was supplied by Dr. T. D. Coyle of the Inorganic Chemistry Section. It was a sample of commercially

(1) S. R. Gunn and L. G. Green, *J. Phys. Chem.*, **65**, 178 (1961).
(2) S. R. Gunn, L. G. Green, and A. I. von Egidy, *ibid.*, **63**, 1787 (1959).
(3) G. Urry in "The Chemistry of Boron and Its Compounds," E. L. Muetterties, Ed., John Wiley & Sons, Inc., New York, N. Y., 1967.
(4) V. H. Dibeler and S. K. Liston, to be submitted for publication.
(5) J. Marriott and J. D. Craggs, *J. Electronics Control*, **3**, 194 (1957).
(6) O. Osberghaus, *Z. Phys.*, **128**, 366 (1950).
(7) W. S. Koski, J. J. Kaufman, and C. F. Pachucki, *J. Am. Chem. Soc.*, **81**, 1326 (1959).

(8) R. J. Boyd and D. C. Frost, *Chem. Phys. Letters*, 649 (1968).
(9) V. H. Dibeler and R. M. Reese, *J. Res. Natl. Bur. Std.*, **68A**, 409 (1964).
(10) P. G. Wilkinson and E. T. Byram, *Appl. Opt.*, **4**, 581 (1965).
(11) H. E. Hinteregger, "Vistas in Astronautics," M. Alpern and M. Stern, Ed., Pergamon Press Inc., New York, N. Y., 1958, p 146. See also R. G. Newburgh, L. Heroux, and H. E. Hinteregger, *Appl. Opt.*, **1**, 733 (1962).

available material shaken with mercury to remove chlorine and subjected to trap-to-trap distillation in a vacuum manifold. No special care was taken to preserve the sample during the measurements. However, the mass spectrum showed no impurities other than variable, small amounts of HCl. Presumably this resulted from the reaction of BCl_3 with water vapor absorbed occasionally on the inner walls of the sample-handling system.

The diboron tetrachloride was prepared by J. J. Ritter of the Inorganic Chemistry Section by means of the electric-discharge reduction of BCl_3.[12] The infrared spectrum of the material showed no detectable BCl_3 and only traces (<1%) of $SiCl_4$. The mass spectrum confirmed these observations.

The same procedures were used in the introduction of B_2Cl_4 to the mass spectrometer as were found[4] useful for B_2F_4. However, the lesser stability of B_2Cl_4 was qualitatively evident near the conclusion of these measurements in the appearance of a light straw color in the liquefied B_2Cl_4. Mass spectra, however, showed no measurable changes in composition throughout the course of the study. The following conversion factors are used in this report: 1 eV molecule^{-1} = 96.4870 kJ mol^{-1}, 1 kcal mol^{-1} = 4.1840 kJ mol^{-1}, 1 eV = 8065.73 cm^{-1}.

Results and Conclusions

(1) **Mass Spectra.**—The intensities of the positive ions in the mass spectra of boron trichloride and of diboron tetrachloride were measured at a constant ion accelerating voltage of 2.5 kV and a photon energy of 21.23 eV (584-Å resonance line of helium). The spectra are complicated by the presence of ions containing the nuclides ^{10}B, ^{11}B, ^{35}Cl, and ^{37}Cl. In the case of BCl_3, each ion peak in the spectrum is unicomponent; i.e., m/e 115 = $^{11}B^{35}Cl_3$, m/e 116 = $^{11}B^{35}Cl_3$, m/e 117 = $^{10}B^{35}Cl_2{}^{37}Cl$, m/e 118 = $^{11}B^{35}Cl_2{}^{37}Cl$, etc., and the spectrum that would be obtained if both boron and chlorine were anisotopic results from the summation of observed intensities of all ions having the same atomic composition. Although this convenience can be extended to B_2Cl_4, we have preferred to calculate the total ionization due to each species ($BCl_3{}^+$, $BCl_2{}^+$, etc., $B_2Cl_4{}^+$, $B_2Cl_3{}^+$, etc.) by multiplying the observed intensity of the principal peak in each ion group by the sum of the relative abundances of the appropriate isotopic ions. A tabulation of relative abundances of isotopic species similar to that published by Margrave and Polansky[13] for BCl_3 but using the isotope ratios $^{10}B/^{11}B$ = 0.2438 and $^{35}Cl/^{37}Cl$ = 3.0866 was made available to us by the Inorganic Chemistry Section from a computer program designed to include a variety of light-element inorganic species. The calculated mass spectra obtained thereby are given in Table I.

The mass spectrum of BCl_3 is compatible with previously published spectra[5-7] in consideration of the lower excitation energy used in the present work. No negative ions were observed and it is estimated that the intensity of any ion-pair process is less than 0.001 relative to the most abundant ion.

The mass spectrum of B_2Cl_4 has not been reported previously. Qualitatively, it is quite like the spectrum of B_2F_4, although quantitative differences are expected. The very weak $BCl_3{}^+$ ion is ascribed to a rearrangement process, rather than to an impurity on

(12) T. Wartik, R. Rosenberg, and W. B. Fox, *Inorg. Syn.*, **10**, 118 (1967).
(13) J. L. Margrave and R. B. Polansky, *J. Chem. Educ.*, **39**, 335 (1962).

TABLE I

MASS SPECTRA[a] OF BORON TRICHLORIDE AND OF DIBORON TETRACHLORIDE BY PHOTON ABSORPTION

Ion	Relative abundance[b]	
	BCl_3	B_2Cl_4
$B_2Cl_4{}^+$	...	0.34
$B_2Cl_3{}^+$	...	0.57
$B_2Cl_2{}^+$	...	0.14
$BCl_3{}^+$	0.59	<0.001
$BCl_2{}^+$	1.00	1.00
BCl^+	0.072	0.054
B^+	~0.001	...

[a] Spectra that would be obtained if boron and chlorine were anisotopic (see text). [b] At 584 Å (21.23 eV).

the basis of the analogy with B_2F_4 and the absence of change in relative abundance with increasing sample storage time. There is no evidence for the B_2Cl^+ or $B_2{}^+$ ion at this energy and no negative ions by ion-pair process were observed.

(2) **Ion Yield Curves and Threshold Energies. Boron Trichloride.**—Typical ion yield curves for the $^{11}B^{35}Cl_3{}^+$, $^{11}B^{35}Cl_2{}^+$, and $^{11}B^{35}Cl^+$ ions of BCl_3 are shown in Figure 1. The abscissas are given in ångstroms with the equivalent energy in electron volts at selected wavelengths. The ordinate is plotted as ions per photon transmitted through the ion source in arbitrary units. The respective ordinate scales for the $BCl_3{}^+$ and BCl^+ ions are 2 and 10 times that of the $BCl_2{}^+$ ion. Error bars represent the estimated uncertainty in yield at each wavelength.

The curve for the $^{11}B^{35}Cl_3{}^+$ ion exhibits a slightly tailing onset at 1069 Å (11.60 eV). The rapidly rising curve gives a clear indication of partially resolved peaks ascribed to the autoionization of Rydberg levels throughout the wavelength region 1050–856 Å. The abrupt change to a nearly flat continuum at about 865 Å (14.3 eV) suggests an approximate determination of a convergence limit of one or more Rydberg series and the threshold of an electronically excited state of the ion.[8] The remainder of the curve is apparently featureless at present optical resolution from 850 to 600 Å.

Initial portions (about 40 Å) of the ion yield curves for the isotopic ions $^{10}B^{35}Cl_3{}^+$ and $^{11}B^{37}Cl_3{}^+$ were also measured. Thresholds and curve shapes (at threshold) were indistinguishable (±0.01 eV) from those of the more abundant species.

The ionization threshold, $I(BCl_3)$ = 11.60 ± 0.01 eV, is within the estimated uncertainty of the electron impact value, 12.0 ± 0.5 eV, first reported by Osberghaus.[6] However, it is considerably outside the estimated uncertainties in the more recent electron impact values of 12.03 ± 0.02 eV[5] and 11.0 ± 0.2 eV.[7] It appears that uncertainties in the latter values are much greater than estimated. Although Boyd and Frost[8] give no estimate of uncertainties in their photoelectron spectroscopy results, our value is about 0.4 eV below their first ionization energy of 11.97 eV.

If we take the threshold value of 11.60 eV (267.5 kcal mol^{-1}) to be the ΔH_0 for the reaction BCl_3 +
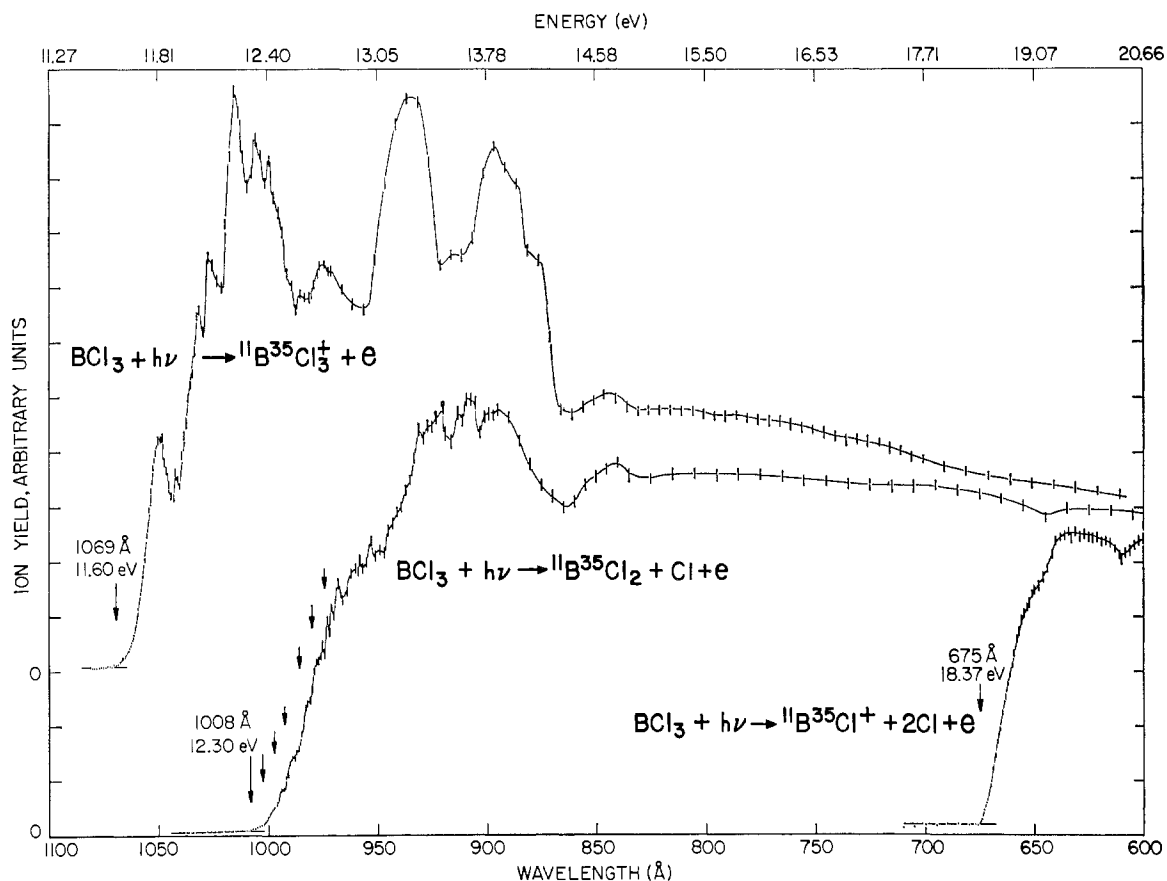
Figure 1.—Ion yield curves for the $^{11}B^{35}Cl_3{}^+$, $^{11}B^{35}Cl_2{}^+$, and $^{11}B^{35}Cl^+$ ions of boron trichloride. The respective ordinate scales (in arbitrary units) of the fragment ions are 2 and 10 times that of the molecule ion.

TABLE II

SUMMARY OF THRESHOLD ENERGIES AND THERMODYNAMIC PROPERTIES OF IONS AND RADICALS FROM BCl_3 AND B_2Cl_4

Ion process	Threshold energy, eV	$\Delta H_f{}^\circ{}_0$ (ion)[b]
$BCl_3 + h\nu \rightarrow BCl_3{}^+ + e$	11.60 ± 0.02^a	7.42₅ eV, 171.2 kcal mol⁻¹
$\rightarrow BCl_2{}^+ + Cl + e$	12.30 ± 0.02	6.88 eV, 158.6 kcal mol⁻¹
$\rightarrow BCl^+ + 2Cl + e$	18.37 ± 0.02	11.707 eV, 270.0 kcal mol⁻¹
		[$I(BCl) = 10.20$ eV]
$B_2Cl_4 + h\nu \rightarrow B_2Cl_4{}^+ + e$	10.32 ± 0.02	5.42 eV, 120.8 kcal mol⁻¹
$\rightarrow B_2Cl_3{}^+ + Cl + e$	11.52 ± 0.02	5.20 eV, 119.9 kcal mol⁻¹
		[$I(B_2Cl_3) \simeq 6.7$ eV]
$\rightarrow B_2Cl_2{}^+ + 2Cl + e$	17.24 ± 0.03	≃9.7 eV, 223 kcal mol⁻¹
		[$I(B_2Cl_2) \simeq 9.0$ eV]
$\rightarrow BCl_2{}^+ + BCl_2 + e$	11.32 ± 0.02	$\Delta H_f{}^\circ{}_0(BCl_2) = -0.64$ eV, -14.7 kcal mol⁻¹
		[$I(BCl_2) = 7.52$ eV, $D_0(Cl_2B-BCl_2) = 3.80$ eV]
$\rightarrow BCl^+ + BCl_3 + e$	13.71 ± 0.04	See text

^{a} Estimated uncertainty. ^{b} Except as noted.

$h\nu \rightarrow BCl_3{}^+ + e$; then, from the heat of formation,[14] $\Delta H_f{}^\circ{}_0(BCl_3) = -96.28$ kcal mol⁻¹ (-4.175 eV), we obtain $\Delta H_f{}^\circ{}_0(BCl_3{}^+) = 7.425$ eV (171.2 kcal mol⁻¹). This value and further calculations of thermodynamic properties are summarized in Table II.

The shape of the ion yield curve for the $BCl_2{}^+$ ion is remarkably similar to that of the molecule ion. The onset occurring at 1008 Å (12.30 ± 0.02 eV) is followed by a rapidly rising portion displaying evidence for step structure at intervals of about 10 Å, as indicated by the arrows (Figure 1). Although very little has been reported on vibrational excitation of

(14) D. D. Wagman, W. H. Evans, V. B. Parker, I. Halow, S. M. Bailey, and R. H. Schumm, NBS Technical Note 270-3, U. S. Government Printing Office, Washington, D. C., 1968.

boron halides, this is approximately equal to the ν_3 stretch frequency of the molecule.[15]

The broad band in the region 945–875 Å is very likely due to unresolved autoionization peaks from Rydberg series converging to a limit of about 860 Å. The similarity to the $BCl_3{}^+$ ion curve is noteworthy. Evidently the same Rydberg series can autoionize to produce either excited molecule ions or excited $BCl_2{}^+$ ions. As in the case of the molecule ion, the continuum is apparently featureless below 850 Å.

The threshold energy of 12.30 ± 0.02 eV for the $BCl_2{}^+$ ion is in approximate agreement with electron impact values, although not within the uncertainties

(15) L. P. Lindeman and M. K. Wilson, *J. Chem. Phys.*, **24**, 242 (1956).

reported for those experiments. Accepting our value as the more nearly correct ΔH_0 for the reaction $BCl_3 + h\nu \rightarrow BCl_2^+ + Cl + e$ and the heat of formation,[14] $\Delta H_f^{\circ}{}_0(Cl) = 28.68$ kcal mol^{-1} (1.244 eV), we obtain $\Delta H_f^{\circ}{}_0(BCl_2^+) = 6.88 \pm 0.02$ eV (158.6 $\pm$ 0.5 kcal mol^{-1}). This value assumes no excess energy in the dissociation process and ignores possible contribution of the internal energy of the molecule.[16]

No direct measurement has been made of the ionization energy of the BCl_2 radical, and, in view of the discrepancies in electron impact data, indirect determinations are suspect. As an approximation, however, we can calculate the average bond dissociation energy, $E(B-Cl) = 4.56$ eV (105.2 kcal mol^{-1}), from heats of formation.[14] Subtracting this average value from the threshold energy results in $I(BCl_2) = 7.74$ eV. This is similar to previously estimated[7] ionization energies of boron dihalides. However, further discussion on BCl_2 is deferred to the section on diboron tetrachloride.

The BCl^+ ion has a very sharp onset at 675 Å (18.37 $\pm$ 0.02 eV). The curve is quite smooth from a maximum at 640 Å to the practical limit of accessible wavelength. There is no indication of a correlative process in the curves of the larger ions. The threshold agrees well with the electron impact value of 18.54 $\pm$ 0.07 eV reported by Marriott and Craggs.[5] However, two values, 17.2 $\pm$ 0.2 and 20.0 $\pm$ 0.2 eV, were reported by Koski, et al.,[7] for $^{11}B^{35}Cl^+$ and $^{10}B^{35}Cl^+$, respectively. They are ascribed to two different ionization processes, not to the effects of isotopic composition. These two thresholds are not substantiated by our measurements. We assign our threshold value to the ΔH_0 for the reaction $BCl_3 + h\nu \rightarrow BCl^+ + 2Cl + e$ and calculate $\Delta H_f^{\circ}{}_0(BCl^+) = 11.707$ eV (270.0 $\pm$ 0.5 kcal mol^{-1}) with the same limitations as for the BCl_2^+ ion.

Again, no direct determination has been made of the ionization energy of the diatomic molecule BCl. However, the heat of formation can be calculated from spectroscopic data. Barrow[17] reported $D_0(BCl) = 127$ kcal mol^{-1} with a probable uncertainty of ± 1 kcal mol^{-1}. However, such a value is most likely an upper limit as our previous results[4] indicated in the case of $D_0(BF)$. Nevertheless, accepting the spectroscopic value and using $\Delta H_f^{\circ}{}_0(B)(g) = 133.3$ kcal mol^{-1}, we calculate $\Delta H_f^{\circ}{}_0(BCl) = 1.51 \pm 0.04$ eV (34.8 $\pm$ 1 kcal mol^{-1}). Subtraction from the threshold energy of BCl^+ results in $I(BCl) = 10.20 \pm 0.04$ eV. Although considerably more reliable, this is remarkably close to the lesser of the values 10.2_8 and 10.6_0 eV obtained from electron impact data.[7] The usual comparison with the ionization energies of isoelectronic molecules is favorable for SiO (10.8 $\pm$ 0.5 eV)[18] and AlF (9.7 $\pm$ 0.5 eV)[19] but not for CS (11.7 eV).[20] Nevertheless, the selected ionization process resulting in BCl^+ and

two atoms of chlorine is very probably correct. There is no evidence for the lower energy process yielding molecular chlorine. Furthermore, Barrow's value for $D_0(BCl)$ would seem to be preferred over the earlier determination of $D_0(BCl) = 4.2$ eV quoted by Herzberg.[21]

Diboron Tetrachloride.—Typical ion yield curves for the $B_2Cl_4^+$, $B_2Cl_2^+$, BCl_2^+, and BCl^+ ions are plotted in Figure 2 in the same manner as Figure 1. The curve for $B_2Cl_3^+$ is omitted and the ordinate for the BCl^+ ion is increased by a factor of 10 in order to simplify the figure. Specifically, $B_2Cl_4^+$, $B_2Cl_3^+$, and $B_2Cl_2^+$ were measured as ions appearing at $m/e = 164, 127,$ and 92, respectively. Thus the curves are rendered slightly ambiguous owing to the presence of isotopic species. However, we consider the effects on thresholds and curve shape to be entirely inconsequential in the present study.

The $B_2Cl_4^+$ ion shows a definite onset at 1201 Å (10.32 eV) followed by a slowly rising smooth curve to about 1100 Å. Some peak structure is observed in the region from 1100 to 900 Å. As before, this is attributed to unresolved autoionization of Rydberg levels in the molecule, converging to a limit somewhat below 900 Å. Thus, there appears to be a second onset at about 895 Å (13.85 eV) suggesting the presence of an electronically excited state of the ion.

The $B_2Cl_4^+$ threshold at 10.32 eV is assigned to the ΔH_0 for the reaction $B_2Cl_4 + h\nu \rightarrow B_2Cl_4^+ + e$. Although the tailing suggests an upper limit to the true value, we estimate an uncertainty of about ± 0.02 eV. From the heat of formation,[14] $\Delta H_f^{\circ}{}_0(B_2Cl_4) = -5.077$ eV (-117.09 kcal mol^{-1}), we obtain $\Delta H_f^{\circ}{}_0(B_2Cl_4^+) = 5.24$ eV (120.8 $\pm$ 0.5 kcal mol^{-1}). This value, together with other thermodynamic properties of ions and radicals of B_2Cl_4, is included in Table II.

The BCl_2^+ ion is not only the principal ion in the mass spectrum but shows a more abrupt onset than the molecule ion. However, the general shapes of the two curves are quite similar. Peak-like structure in the wavelength region 1000–900 Å is again ascribed to unresolved autoionization. A possible onset of an electronically excited state of the BCl_2^+ ion appears at about 895 Å. As in the case of BCl_3, the same Rydberg levels in the B_2Cl_4 molecule are apparently capable of autoionizing to produce excited states of the molecule or of the BCl_2^+ ion.

Unlike the BF_2^+ from the B_2F_4 molecule, the ion yield curve for BCl_2^+ from B_2Cl_4 shows no evidence for higher energy processes that would suggest further dissociation of neutral products. Therefore, the initial threshold at 1095 Å (11.32 $\pm$ 0.02 eV) is assigned to the ΔH_0 of the process $B_2Cl_4 + h\nu \rightarrow BCl_2^+ + BCl_2 + e$. Assuming no excess energy in this reaction or contribution from the internal energy of the molecule[16] and accepting $\Delta H_f^{\circ}{}_0(BCl_2^+)$ from the BCl_3 measurements, we calculate $\Delta H_f^{\circ}{}_0(BCl_2) = -0.64$ eV ($-14.7 \pm$

(16) W. A. Chupka and C. Lifshitz, *J. Chem. Phys.*, **48**, 1109 (1968).

(17) R. F. Barrow, *Trans. Faraday Soc.*, **56**, 952 (1960).

(18) R. F. Porter, W. A. Chupka, and M. G. Inghram, *J. Chem. Phys.*, **23**, 216 (1955).

(19) T. C. Ehlert, G. D. Blue, J. W. Green, and J. L. Margrave, *ibid.*, **41**, 2250 (1964).

(20) V. H. Dibeler and J. A. Walker, *J. Opt. Soc. Am.*, **57**, 1007 (1967).

(21) G. Herzberg, "Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1950.
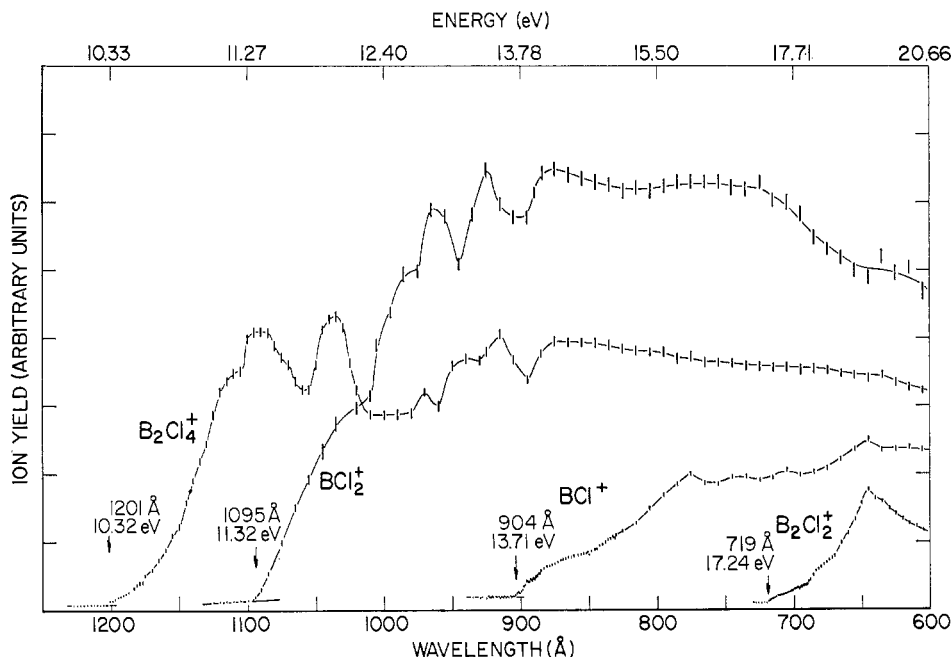
Figure 2.—Ion yield curves for the $B_2Cl_4^+$, $B_2Cl_2^+$, BCl_2^+, and BCl^+ ions of diboron tetrachloride. The ordinate scale for the BCl^+ ion is 10 times the scale for the other ions.

0.5 kcal mol^{-1}). The difference between the two heats of formation, of course, is the ionization energy, $I(BCl_2)$ = 7.52 eV. As this is very near, although considerably more accurate than, the value estimated from the average B–Cl bond dissociation energy in BCl_3 and the threshold of the BCl_2^+ ion from BCl_3, the result clearly supports the assumed ionization process and the absence of appreciable excess energy. Therefore, we can immediately calculate the boron–boron bond dissociation energy, $D_0(Cl_2B–BCl_2)$ = 3.80 eV (87.6 ± 0.5 kcal mol^{-1}). This is about 8 kcal mol^{-1} greater than the value reported by Gunn, et al.,[2] and is consistent with the conclusion regarding the boron–boron bond reached by Massey and Zwolenik[22] in a study of the flash photolysis of boron chlorides. On the other hand, our value for B_2Cl_4 is about 15 kcal mol^{-1} below the boron–boron bond dissociation energy in B_2F_4 (103 kcal mol^{-1}),[4] which is consistent with the well-known relative stability of the two compounds.

Returning to BCl_3, the determination of $\Delta H_f°_0(BCl_2)$ also permits us to calculate 4.78 eV (110.2 kcal mol^{-1}) for $D_0(Cl_2B–Cl)$. Furthermore, in conjunction with the heat of formation of BCl obtained from Barrow's spectra, we obtain the second B–Cl bond dissociation energy, $D_0(ClB–Cl)$ = 3.39 eV (78.2 kcal mol^{-1}). The several B–Cl bond dissociation energies in BCl_3 are summarized in Table III. The summation of the bond energies is found to be in good agreement with the calculated heat of atomization, thus giving considerable support to the several foregoing interdependent assumptions and calculations.

The $B_2Cl_3^+$ ion yield curve (not shown in Figure 2) exhibits a definite onset at 1076 Å (11.52 eV) followed by a slowly increasing portion. The curve approaches a maximum at 900 Å and thereafter remains essentially

(22) A. G. Massey and J. J. Zwolenik, *J. Chem. Soc.*, 5354 (1963).

Table III

Individual Bond Dissociation Energies in Boron Trichloride

Bond	Energy[a]	
	eV	kcal mol^{-1}
BCl_2–Cl	4.78	110.2
BCl–Cl	3.39	78.2
B–Cl[b]	5.51 ± 0.04	127 ± 1
Total	13.68	315.4
$BCl_3 \rightarrow B + 3Cl$	13.69[c]	315.6[c]

[a] Estimated uncertainties: ±0.02 eV (±0.5 kcal mol^{-1}).
[b] See ref 17. [c] Calculated from heats of formation.[14]

constant to about 600 Å with no striking features. The threshold energy of 11.52 eV is considered to be the ΔH_0 for the reaction $B_2Cl_4 + h\nu \rightarrow B_2Cl_3^+ + Cl + e$. From the known heats of formation, we calculate $\Delta H_f°_0(B_2Cl_3^+)$ = 5.20 eV (119.9 kcal mol^{-1}). Neither the heat of formation nor the ionization energy of the radical is known. However, if we assume the first B–Cl bond dissociation energy to be the same in BCl_3 and B_2Cl_4, we calculate $\Delta H_f°_0(B_2Cl_3)$ = −1.5 eV (−35 kcal mol^{-1}) and the ionization energy $I(B_2Cl_3)$ = 6.7 eV. The only observation to be made at present is that the difference between the ionization energies of the B_2Cl_3 radical and the B_2Cl_4 molecule is quite similar to the difference in analogous species in B_2F_4.

The assumption of equivalent dissociation energies for the first B–Cl bond in the BCl_3 and B_2Cl_4 molecules is observed approximately in the ions; i.e., $D(BCl_2^+–Cl)$ = 0.7 eV, whereas $D(B_2Cl_3^+–Cl)$ = 1.2 eV. This suggests that the electrons are photoejected from very similar orbitals in both cases; a situation unlike that observed in BF_3 and B_2F_4.

Only a short portion of the yield curve for the $B_2Cl_2^+$ ion is measurable (Figure 2). A definite onset

occurs at 719 Å (17.24 eV). If this is ascribed to the ΔH_0 for the reaction $B_2Cl_4 + h\nu \rightarrow B_2Cl_2^+ + 2Cl + e$, the usual summation of heats of formation results in $\Delta H_f{}^\circ{}_0(B_2Cl_2{}^+) = 9.7$ eV (223 kcal mol^{-1}). Estimating values for the first and second B–Cl bond dissociation energies in B_2Cl_4 results in $I(B_2Cl_2) = 9.0$ eV, an entirely reasonable value. If the neutral dissociation products were molecular chlorine rather than chlorine atoms, the ionization energy of B_2Cl_2 would be increased by about 2.5 eV. This would result in the improbable case of the ionization energy of the B_2Cl_2 radical being about 1.2 eV greater than that of the parent molecule.

Finally, the BCl^+ ion exhibits a definite onset at 904 Å (13.71 eV). There is some evidence of weak autoionization immediately in the region of threshold and at shorter wavelengths. The threshold value evidently includes some excess energy as the minimum-energy process $B_2Cl_4 + h\nu \rightarrow BCl^+ + BCl_3 + e$ results in a calculated heat of formation of BCl^+ of 12.8 eV compared with 11.7 eV from BCl_3.

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Carborane Formation in Alkyne–Borane Gas-Phase Systems. III. Flash Reactions of Small Boranes[1]

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Thermally induced flash reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene have been studied, and the volatile products, consisting almost exclusively of parent or alkyl closed-cage carboranes and hydrocarbons, have been individually isolated and characterized. Both the total carborane yield and the relative yields of B_3 and B_4 carboranes are largest in reactions of dimethylacetylene and least in those of acetylene. Derivatives of $1,2-C_2B_3H_5$ are formed in significant amounts from alkylacetylenes but not from acetylene. The results are compared with previous work on borane–alkyne systems, particularly the electric-discharge and flash reactions of diborane with acetylene, and implications in regard to reaction pathways are discussed. The pentaborane(11)–dimethylacetylene system is exceptional; flash reactions are not observed in 1:1 mixtures, but a 2:1 alkyne:borane ratio results in flash reaction below room temperature in which largely noncarborane products are obtained.

The gas-phase explosions or electric-discharge reactions of small boron hydrides with acetylene yield amorphous solids and volatile products consisting largely of polyhedral carboranes.[2–6] The carborane-forming processes in these systems are not understood and would constitute a formidable problem for any detailed investigation. However, in the course of exploratory studies of small-carborane chemistry it appeared useful to examine and compare the flash reactions of several small alkynes with boron hydrides in a search for possible correlations between the structures of reactants and products obtained. Accordingly, the 100° flash reactions of tetraborane(10) and pentaborane(11) with acetylene, methylacetylene, and dimethylacetylene were carried out in sealed bulbs under similar conditions. Volatile products were isolated by fractionation and vapor-phase chromatography and identified as described below.

Results

General.—With the exception of the B_5H_{11}–$C_2(CH_3)_2$ reaction, which proved anomalous (see below), mixtures of B_4H_{10} or B_5H_{11} with C_2H_2, HC_2CH_3, or $C_2(CH_3)_2$ flashed within 6 min at 100° without breakage of the Pyrex reactor. The products in each case consisted of dark nonhomogeneous solids, which were not investigated, and volatile species which were separated by glpc and individually characterized (Table I). The more significant results are summarized as follows.

(1) All organoboron products identified in these reactions are *closo*-carboranes or alkyl-*closo*-carboranes.

(2) The same carborane cage systems (not necessarily the same derivatives) which were produced in high-energy reactions of B_2H_6 and/or B_5H_9—*e.g.*, 1,5-

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