Ion Chemistries in Triethylborane

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Abstract

The absolute total and partial cross sections of electron ionization on triethylborane (TEB) are measured in an electron energy range of 6.6-200 eV. The total cross section reaches a maximum of $2.2 \times 10^{-15} \text{ cm}^2$ in 65-85 eV energy region. Product ions from the electron ionization include $\text{C}_2\text{H}_{2.5}^+$, BCH_4^+ , $\text{BC}_2\text{H}_{2,4,6}^+$, $\text{BC}_3\text{H}_{4,6}^+$, $\text{BC}_4\text{H}_{8,10}^+$ and $\text{BC}_6\text{H}_{15}^+$, among which $\text{BC}_6\text{H}_{15}^+$, $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ are the most abundant ions. Gas-phase reactions between TEB and certain major ions from the electron ionization of TEB are studied. Common products from the ion-molecule reactions are $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ , as well as association products for certain heavy-ion reactions. The mechanisms of forming $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ in ion-molecule reactions are believed to be simple ethide transfer and ethide transfer followed by dissociation (loss of C_2H_4), respectively.

1. Introduction

Boron-containing compounds are distinctive electron-deficient species and are therefore of great interest in basic research because of their unusual chemistries.^[1,2] While the development of boron chemistry is still in its infant stage compared to organic chemistry, it has become an exciting research field in recent decades.^[3,4] Boron-containing compounds are also finding an increasing number of applications. Alkylboranes, mainly triethylborane (TEB), have been used as radical initiators in many chemical reactions because of their ability to yield alkyl radicals in the presence of oxygen molecule.^[5-9] TEB is an excellent ignition source for liquid fuel ramjet combustor and is used as a hypergolic igniter in air-breathing jet engines and rocket engines.^[10-13]

Aimed toward providing more data to understand basic boron chemistry and plasma processes involving TEB; this paper reports our recent study on the electron ionization of TEB and the reactions of the ions from TEB with their parent molecule. Total and partial ionization cross sections and ion-molecule reaction rates are presented, and the reaction mechanisms of forming major product ions are discussed.

2. Experimental

All of the experiments were performed using a modified FTMS equipped with a cubic ion cyclotron resonance trapping cell (5 cm on a side) and a 2 T superconducting magnet.^[14] For the electron ionization cross section measurements, triethylborane (TEB) (95+%, Sigma-Aldrich) was mixed with Ar (99.999%, Matheson) in a pressure ratio of ~1:1 to a total pressure of ~25 Torr, as determined by capacitance manometry. The mixture was then admitted through a precision leak valve (Varian variable leak valve) into the FTMS system. Ions were formed by electron impact in the trapping cell at pressures in the 10^{-7} Torr range. An electron gun (Kimball Physics ELG-2A, Wilton, NH) irradiated the cell with a few hundred picocoulombs of electrons at a varying energy within the range of 6.6-200 eV, with a spectral width of ± 0.6 eV. The motions of the product ions were constrained radially by the superconducting magnetic field and axially by an electrostatic potential applied to the faces of the cubic trapping cell that were perpendicular to the magnetic field. Ions of all mass-to-charge ratios, in a range of 10 to 500 amu, were simultaneously and coherently excited into cyclotron orbits by applying a Stored Waveform Inverse Fourier Transform (SWIFT)^[15] to two opposing trap faces that were parallel

to the magnetic field. Following cyclotron excitation, the image currents induced on the two remaining faces of the trap were amplified, digitized and Fourier analyzed to yield a mass spectrum. In this study, the intensity ratios of the ions from TEB to Ar^+ gave cross sections relative to those for electron ionization of Ar ,^[16] since the pressure ratio of TEB to Ar was known.

The pressure ratio of TEB to Ar in the trapping cell region mentioned above is assigned to be equal to the pressure ratio in the manifold, based on the following reasoning. Given the pressures in the manifold and the trapping cell region, the leak valve opening, i.e., the gap between the sapphire and the metal gasket, is estimated to be on the order of submicron. The gap is therefore smaller than the mean free path of atoms/molecules in the manifold, which is on the order of a micron, and therefore diffusion of the gas through the leak valve is characterized by molecular flow, which is proportional to $P_m M^{-0.5}$, where P_m is the manifold pressure and M the species atomic/molecular mass. At the low pressures in the trapping cell region, flow to the cryopump (1500 l/s) is likewise molecular with a conductance of approximately 65 l/s through the connecting vacuum lines. Therefore the pump rate out of the trapping cell is proportional to $P_t M^{-0.5}$, where P_t is the pressure in the trapping cell. In summary, at equilibrium P_t depends on P_m and the leak valve aperture but not M because both in-flow and out-flow are diffusive and the atomic/molecular mass effect is cancelled out. The absence of mass discrimination in the pressure ratio of the trapping cell region is confirmed by experiments in which a mixture of Ar and Xe gases is used and the measured ion intensity ratio is compared to the known ionization cross sections of these gases.^[17] A typical experiment is finished during a timeframe in which there is no significant pressure change in the manifold so that the pressure ratio is constant.

Due to the limits of electronic parameters used in the current FTMS system that set the lower mass limit at 10 amu, H^+ is not detectable in our experiments. The partial ionization cross section of H^+ is expected to be negligible; however, this ion is absent in the mass spectrum of TEB made by the NIST measurement that allows H^+ to be detected.^[18]

To study the reactions between ions from TEB electron ionization and the parent molecule, a mixture of TEB and Ar with a pressure ratio of $\sim 1:20$ was used. The ion to be studied was selected by using SWIFT to eject other ions out of the trapping cell, followed by a cooling period in which the ion underwent collisions with Ar at a total pressure of $\sim 1 \times 10^{-5}$ Torr for various times, typically 500 ms. SWIFT was used again to select the ion to be studied from others that

were formed during the cooling period, followed by a programmed reaction time selectable typically from 0 to 2000 ms. The pressure of Ar and the length of the cooling period were adjusted so that at the end of the cooling period there were still sufficient reactant ions to study and their reaction showed a single exponential decay to the end of the reaction time at which only a few percent of the reactant ions were left over. With the high Ar partial pressure, Ar^+ was overpopulated during the normal electron ionization procedure, resulting in a significant space charge effect. To eliminate this effect, an RF waveform with the appropriate single-frequency for Ar^+ cyclotron resonance was applied during the electron beam event to continuously and selectively eject Ar^+ out of the trapping cell, for the purpose to reduce the Ar^+ population in the trapping cell.

3. Results and Discussion

3.1 Electron ionization

Two issues cause difficulties in analyzing the mass spectrum of TEB: (a) the two boron isotopes with appreciable natural abundances: boron-11 (^{11}B , 80.1%) and boron-10 (^{10}B , 19.9%), and (b) the possible isobaric ions due to the boron-containing species and non-boron-containing species. For example, at m/z 27, there can be three possible ions: C_2H_3^+ , $^{11}\text{BCH}_4^+$ and $^{10}\text{BCH}_5^+$, with exact masses of 27.0229, 27.0401 and 27.0515 amu, respectively. These isobaric ions often make qualitative and quantitative determination of species difficult. In a mass spectrometry study on boron chemistry a few decade ago, a technique of isotopic variation of the two boron isotopes was used to deduce numbers of boron atoms in particular ions.^[19] When the isobaric ions (the boron-containing and non-boron-containing species) overlap, however, this technique will be difficult to implement to determine the accurate distribution of boron isotopes. In this FTMS study on TEB, by means of the high-mass-resolution spectrum to distinguish the isobaric ions, we have identified and quantitatively measured the following ions produced from the electron ionization of TEB, listed in the order of increasing ions mass-to-charge ratio that is shown in the parentheses in the unit of amu:

Certain other ions are observed, but their intensities are rather insignificant to be quantitatively measurable. The ion mass shown above in parentheses assumes any boron is the main isotope

^{11}B , but when assigning the ion identities and ion intensities used to derive partial ionization cross sections (see below), B in the formulae then represents both isotopes of boron. The same issue also applies for C (^{12}C and ^{13}C). This implication applies elsewhere in the text unless a specific isotope is indicated. By exact mass measurements, the existence in any significant amount of many possible isobaric ions from TEB has been ruled out. For example, in the region of m/z 26 as shown in figure 1, there are only C_2H_2^+ and $^{10}\text{BCH}_4^+$; $^{11}\text{BCH}_3^+$ is negligible. In the regions of m/z 28 and 29, there are only C_2H_4^+ and C_2H_5^+ , respectively, and $^{11}\text{BCH}_5^+$ and $^{11}\text{BCH}_6^+$ are absent, respectively. The absence of these boron-carbon species will be discussed later. At m/z 68 there is mostly $^{10}\text{BC}_4\text{H}_{10}^+$, with a minor amount of $^{11}\text{BC}_4\text{H}_9^+$. As seen from the above list, there is only one pair of isobaric ions: C_2H_3^+ and BCH_4^+ at m/z 27, and there appears to be a trend: heavy ions are exclusively boron-carbon species, while the light ions are essentially non-boron-containing species, with a boron-containing isobaric ion at m/z 27. The absence of large non-boron-containing ions seems to indicate that, during the fragmentation of the parent ion, no new C-C bond is formed to produce hydrocarbon ions larger than C_2H_5^+ .

No noteworthy doubly-charged ions are observed, but the possible ones that have the same mass-to-charge ratios as the singly charged ions listed above cannot be excluded; these doubly and singly charged ions having the same mass-to-charge ratios are not distinguishable by mass spectrometry methods. Certain amounts of the singly charged ions listed above may be formed by dissociative double ionization and thus carry significant amounts of kinetic energy. In our experiments, as described in more details previously,^[20] with a pair of screen electrodes and 10 V trapping potential, we expect to be able to trap most of the energetic ions with energies up to a few eV. For example, 97% of the ions with 5 eV kinetic energy are expected to be detected. Since the energetic ions are of minor population, a missing few percents of the energetic ions should not severely affect the measurement of the total cross section within its error margins.

The total and partial electron ionization cross sections as functions of the electron energy in a range from 6.6 to 200 eV are shown in figures 2 and 3. The peak of the total cross section is located in the 65-85 eV region, with a value of $2.2 \times 10^{-15} \text{ cm}^2$. The uncertainty of the cross section data includes $\pm 14\%$ of estimated possible errors in FTMS experiments,^[21] and an additional $\pm 3.5\%$ for the Ar cross section^[16] calibration. As shown in figure 3, the most abundant ions are the parent ion $\text{BC}_6\text{H}_{15}^+$ and fragment ions $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ ; together the three ions account for more than four-fifths of the ion population throughout the energy range studied. The

formation of the parent ion has the onset energy at 9.6 eV. At higher energies after the parent ion onset, the fragment ion $\text{BC}_4\text{H}_{10}^+$ appears, with the onset energy of 9.8 eV, formed by loss of a ligand (C_2H_5 radical) of B in the parent ion, resulting in a valence structure of $(\text{C}_2\text{H}_5)\text{-B}^+\text{-(C}_2\text{H}_5)$. At 11.4 eV, the fragment ion BC_2H_6^+ emerges, which is expected to be formed by further dissociation of $\text{BC}_4\text{H}_{10}^+$ via loss of C_2H_4 , with an H atom from a cleaved ethyl group attaching itself to the B atom,^[19] resulting in a valence structure of $(\text{C}_2\text{H}_5)\text{-B}^+\text{-H}$.

The valence structures for $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ mentioned above can be attributed to the preferred oxidation number of B: +3; the singly-charged B atom can only bind to two ligands. Based on this argument, we propose the valence structure of BCH_4^+ to be $(\text{CH}_3)\text{-B}^+\text{-H}$, and the absence of BCH_5^+ and BCH_6^+ mentioned earlier can be explained by the fact that the oxidation number of B in these two ions would exceed +3 in these two hypothetical valence structures, respectively: $[(\text{CH}_3)\text{-BH}_2]^+$ and $[(\text{CH}_3)\text{-BH}_3]^+$.

3.2 Ion-molecule reactions

Gas-phase reactions between TEB and certain major ions from the electron ionization of TEB are summarized in table 1. Also included in the table is the reaction of Ar^+ with TEB. After 70-eV electron ionization to produce the ions, the ion to be studied is isolated and thermalized by collisions with Ar gas under $\sim 1 \times 10^{-5}$ Torr pressure for a certain length of time, typically 500 ms, followed by its reaction with TEB. Listed in table 1 are the reaction rates relative to the Ar^+ reaction, the product ions and their branching ratios. We didn't isolate the two isobaric reactant ions at m/z 27, C_2H_3^+ and BCH_4^+ , because their masses are too close for us to isolate one from the other. Although we can determine the individual decay rate of each isobaric ion to derive its reaction rates, we cannot resolve the product branching ratios from each of them; the branching ratios shown in table 1 for m/z 27 ions are the combined values for C_2H_3^+ and BCH_4^+ . Similarly, the reactant ions at m/z 26 are a mixture of isobaric ions C_2H_2^+ and $^{10}\text{BCH}_4^+$, and thus the branching ratios presented are also combined values from the two isobaric ions. Due to the high pressures used in experiments to study ion molecule reactions, the mass resolution of spectra is only high enough to distinguish certain isobaric ions of low masses, such as those mentioned above, but not high enough to distinguish the possible isobaric ions of high masses, such as the association products (ions containing two boron atoms) listed in table 1; please note that in FTMS the resolving power (ΔM) is dependent of M^2 (M is the mass of the peak). The formulae

of the product ions shown in table 1 are proposed based on our reasonable guess, which are not all confirmed by the exact mass measurement; other possible isobaric ions for the same mass-to-charge ratio as the formulae shown in table 1 have not been excluded.

One can see from table 1 that all reactant ions from TEB have slower reaction rates with neutral TEB than Ar^+ , and there is a trend of faster reaction rates for lighter reactant ions.

The reaction of Ar^+ with TEB produces $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ . It is expected that a dissociative charge transfer between Ar^+ and TEB produces $\text{BC}_4\text{H}_{10}^+$ and C_2H_5 , and the former in turn undergoes further dissociation forming BC_2H_6^+ by loss of C_2H_4 :

As seen in Table 1, $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ are the common and major products in many reactions: all ions smaller than $\text{BC}_4\text{H}_{10}^+$ reacting with TEB to form $\text{BC}_4\text{H}_{10}^+$, and all ions (except C_2H_5^+) smaller than BC_2H_6^+ also reacting with TEB to form BC_2H_6^+ . The mechanisms that produce these two major product ions will be discussed later. For the two hydrocarbon reactant ions, C_2H_2^+ and C_2H_4^+ , which have ionization potentials (IPs) of 11.4 and 10.507 eV,^[22] respectively, which are higher than TEB (IP=9.6 eV^[22]), there is a charge transfer product, $\text{BC}_6\text{H}_{15}^+$. The charge transfer product is absent in the reactions of C_2H_3^+ and C_2H_5^+ , which have IPs of 8.9 and 8.13 eV^[22], respectively. For reactant ions larger than BC_2H_2^+ , there are formed the association product ions containing two boron atoms. Certain secondary product ions (not shown in table 1) due to further reactions of the primary product ions with TEB, are observed, such as m/z 87 ion (formula not identified) for the reactions of C_2H_5^+ or smaller ions. Certain minor products not listed in table 1 include ions at m/z 125 and 127 from the reaction of $\text{BC}_4\text{H}_{10}^+$ and the reaction of $\text{BC}_6\text{H}_{15}^+$ with TEB.

It is noteworthy to point out that when $^{11}\text{BC}_6\text{H}_{15}^+$ is isolated and reacted with a mixture of $^{11}\text{BC}_6\text{H}_{15}/^{10}\text{BC}_6\text{H}_{15}$, $^{10}\text{BC}_6\text{H}_{15}^+$ (m/z 97) was produced among other products, indicating a symmetric charge transfer reaction between $\text{BC}_6\text{H}_{15}^+$ and BC_6H_{15} :

Here a symmetric reaction means a reaction in which the products are chemically the same as the reactants and thus the enthalpy of reaction is zero if there is no isotope effect. Similarly there is a symmetric reaction of $^{11}\text{BC}_4\text{H}_{10}^+$ with $^{10}\text{BC}_6\text{H}_{15}$ producing $^{10}\text{BC}_4\text{H}_{10}^+$ (m/z 68), which cannot be

explained by a dissociative charge transfer reaction because it would be endothermic. This reaction is therefore expected to proceed via a symmetric ethide (C_2H_5^-) transfer mechanism:

The ethide transfer reaction is likewise observed when $^{10}\text{BC}_4\text{H}_{10}^+$ is isolated; it reacts with $^{11}\text{BC}_6\text{H}_{15}$ forming $^{11}\text{BC}_4\text{H}_{10}^+$. It is also noteworthy to note that no other symmetric reactions are observed from other reactant ions. For example, the following symmetric reaction was not observed on BC_2H_6^+ :

The above hypothetical symmetric reaction is a C_4H_9^- transfer, and its absence appears to indicate that it is not a prospective reaction mechanism in reactions of TEB, probably due to the fact that C_4H_9^- transfer requires two boron-ligand bonds to be cleaved. As a comparison, C_2H_5^- transfer only requires one boron-ligand bond cleavage. Similar analysis of reactions of other reactant ions enables us to conclude that other alkyl transfers, except ethide transfer, also are not prospective channels in reactions of TEB.

Based on the above discussion, we propose the mechanism of forming the common product ion $\text{BC}_4\text{H}_{10}^+$ in table 1 as an ethide transfer, as shown in the following equation for the reaction of BCH_4^+ as an example:

The neutral product in 6 is expected to have a valence structure of $(\text{CH}_3)\text{-BH-(C}_2\text{H}_5)$. One may explain the formation of $\text{BC}_4\text{H}_{10}^+$ by a dissociative charge transfer, but it is not likely based on the thermochemical consideration; the reaction is endothermic, at least for certain reactant ions that have ionization potentials available in literature for enthalpy calculations. For example, for the following dissociative charge transfer:

the enthalpy of reaction $\Delta H = \text{AP}(\text{BC}_4\text{H}_{10}^+) - \text{IP}(\text{C}_2\text{H}_5) = 1.7 \text{ eV}$, where the IP value (8.13 eV) is taken from reference [22] and the AP value ($9.8 \pm 0.6 \text{ eV}$) is taken from the threshold of $\text{BC}_4\text{H}_{10}^+$ in our ionization cross section measurement data. The kinetic shift should be insignificant for $\text{BC}_4\text{H}_{10}^+$ as it is one of the most abundant and most readily formed ion from electron ionization, and therefore its threshold energy is expected to be close to its AP value. A similar discussion also applies to the threshold energy of BC_2H_6^+ which is cited below. On the other hand, if the reaction proceeds via the ethide transfer mechanism, shown in the following equation,

the enthalpy of reaction will be -2.0 eV, calculated using additional thermochemical data from reference [22].

We further propose that another common product ion in table1, BC_2H_6^+ , is formed by dissociation of $\text{BC}_4\text{H}_{10}^+$ (by loss of C_2H_4) after its formation from the ethide transfer. For example, the reaction of C_2H_4^+ produces BC_2H_6^+ via the following equation:

The above proposal is based on the following thermochemical consideration. The enthalpy of reaction (ΔH) for the equation 9 can be expressed in terms of the heat of formation ($\Delta_f H$):

$$\Delta H = \Delta_f H(\text{n-C}_4\text{H}_9) + \Delta_f H(\text{C}_2\text{H}_4) + \Delta_f H(\text{BC}_2\text{H}_6^+) - \Delta_f H(\text{C}_2\text{H}_4^+) - \Delta_f H(\text{BC}_6\text{H}_{15}). \quad \underline{\mathbf{10}}$$

Because the value of $\Delta_f H(\text{BC}_2\text{H}_6^+)$ is not available from the literature, we choose to use the relevant data item, the appearance energy of BC_2H_6^+ or $\text{AP}(\text{BC}_2\text{H}_6^+)$, and relate it to our threshold measurement for BC_2H_6^+ , which is assumed to be formed by the following dissociative electron ionization (see the second last paragraph of section **3.1**):

$$\text{AP}(\text{BC}_2\text{H}_6^+) = \Delta_f H(\text{BC}_2\text{H}_6^+) + \Delta_f H(\text{C}_2\text{H}_4) + \Delta_f H(\text{C}_2\text{H}_5) + \Delta_f H(e) - \Delta_f H(\text{BC}_6\text{H}_{15}) . \quad \underline{\mathbf{12}}$$

Another relevant data item, the ionization energy of C_2H_4 , or $\text{IP}(\text{C}_2\text{H}_4)$, is also used:

$$\text{IP}(\text{C}_2\text{H}_4) = \Delta_f H(\text{C}_2\text{H}_4^+) + \Delta_f H(e) - \Delta_f H(\text{C}_2\text{H}_4) \quad \underline{\mathbf{13}}$$

Combined with 12 and 13, equation 10 becomes:

$$\Delta H = \text{AP}(\text{BC}_2\text{H}_6^+) - \text{IP}(\text{C}_2\text{H}_4) + \Delta_f H(\text{n-C}_4\text{H}_9) - \Delta_f H(\text{C}_2\text{H}_4) - \Delta_f H(\text{C}_2\text{H}_5) \quad \underline{\mathbf{14}}$$

which is calculated to be -0.1 eV, by using thermochemical data of IP and $\Delta_f H$ from reference [22] and $\text{AP} = 11.4 \pm 0.6$ eV from the threshold of BC_2H_6^+ in our ionization cross section measurement data. On the other hand, other reaction mechanisms to form BC_2H_6^+ , including dissociative charge transfer and C_4H_9^- transfer as shown by the following two equations, respectively, are not considered to be probable as argued later:

The neutral products in eq. 15 reflect the consecutive dissociation processes following the charge transfer, as shown by equations 17-19:

in a similar manner as the dissociative electron ionization discussed in section 3.1. While the C_4H_9^- transfer process (16) is not likely as we discussed earlier (it requires two boron-ligand bonds to be cleaved), the dissociative charge transfer (15) is endothermic and therefore also unlikely. The enthalpy of reaction for equation 15 is calculated to be: $\Delta H = \text{AP}(\text{BC}_2\text{H}_6^+) - \text{IP}(\text{C}_2\text{H}_4) = 0.9 \text{ eV}$, using the IP value ($10.507 \pm 0.004 \text{ eV}$) from reference [22].

4. Summary

With exact mass measurements using FTMS, the product ions from electron ionization of TEB in the energy range of from 6.6 to 200 eV have been identified as $\text{C}_2\text{H}_{2.5}^+$, BCH_4^+ , $\text{BC}_2\text{H}_{2.4,6}^+$, $\text{BC}_3\text{H}_{4,6}^+$, $\text{BC}_4\text{H}_{8,10}^+$ and $\text{BC}_6\text{H}_{15}^+$. The heavy product ions (m/z 37 or heavier) are exclusively boron-carbon species, while the light ions are all non-boron-containing species except a boron-containing isobaric ion at m/z 27. The major product ions in the energy range studied are the parent ion $\text{BC}_6\text{H}_{15}^+$ and fragment ions $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ . The absolute total and partial ionization cross sections are measured. The total cross section is found to peak at a value of $2.2 \times 10^{-15} \text{ cm}^2$ in the electron energy region of 65-85 eV.

Gas-phase reactions between TEB and certain major ions from the electron ionization of TEB are studied. A trend is observed that faster reaction rates result from lighter reactant ions. Product ions $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ are found to be common among reactions of small reactant ions (smaller than BC_3H_6^+), while association product ions are significant for the large reactant ions. Symmetric reactions are observed for reactant ions $\text{BC}_6\text{H}_{15}^+$ and $\text{BC}_4\text{H}_{10}^+$. Based on this observation and on the thermochemical consideration, the reaction mechanisms forming the two common product ions, $\text{BC}_4\text{H}_{10}^+$ and BC_2H_6^+ , are proposed to be simple ethide transfer and ethide transfer followed by dissociation (loss of C_2H_4), respectively.

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Table 1. Gas-phase ion-molecule reactions of TEB with selected ions from electron ionization of TEB, listed in the order of the increasing masses of reactant ions. Also included is the Ar^+ reaction with TEB. Reaction rates relative to the Ar^+ reaction, product ions and their branching ratios (in parentheses) are shown.

Reactant ion	Relative rate	Product ion
m/z 40 Ar^+	1.00	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (61%) m/z 41 BC_2H_6^+ (39%)
m/z 26 C_2H_2^+	0.84	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (85%) ^a m/z 41 BC_2H_6^+ (11%) ^a m/z 98 $\text{BC}_6\text{H}_{15}^+$ (4%) ^a
m/z 27 C_2H_3^+ BCH_4^+	0.76 0.69	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (82%) m/z 55 BC_3H_8^+ (8%) m/z 41 BC_2H_6^+ (7%) m/z 29 C_2H_5^+ (3%)
m/z 28 C_2H_4^+	0.54	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (71%) m/z 41 BC_2H_6^+ (17%) m/z 98 $\text{BC}_6\text{H}_{15}^+$ (12%)
m/z 29 C_2H_5^+	0.61	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (81%) m/z 55 BC_3H_8^+ (19%)
m/z 37 BC_2H_2^+	0.63	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (84%) m/z 41 BC_2H_6^+ (19%) m/z 39 BC_2H_4^+ (3%)
m/z 39 BC_2H_4^+	0.62	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (86%) m/z 41 BC_2H_6^+ (9%) m/z 108 $\text{B}_2\text{C}_6\text{H}_{14}^+$ (5%)
m/z 41 BC_2H_6^+	0.35	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (100%)
m/z 53 BC_3H_6^+	0.32	m/z 69 $\text{BC}_4\text{H}_{10}^+$ (52%) m/z 109 $\text{B}_2\text{C}_6\text{H}_{15}^+$ (48%)
m/z 69 $\text{BC}_4\text{H}_{10}^+$	0.023	m/z 155 $\text{B}_2\text{C}_{10}\text{H}_{13}^+$ (~100%)
m/z 98 $\text{BC}_6\text{H}_{15}^+$	0.067	m/z 155 $\text{B}_2\text{C}_{10}\text{H}_{13}^+$ (~100%)

^a. We did not isolate isobaric reactant ions C_2H_2^+ and $^{10}\text{BCH}_4^+$, and therefore the branching ratios shown here are the combined results from both reactions of these two ions (See the text).

Figure Captions:

Figure 1. A high resolution mass spectrum at m/z 26 showing multiple isobaric ions.

Figure 2. Total electron ionization cross section of TEB.

Figure 3. Log plots of partial cross sections for major product ions from electron ionization of TEB. For visual clarity data are presented in three graphs, in which scales are set to the same for easy comparison of the amplitudes for different ionization channels. The display mode of lines-between-points is used, except for certain ions: BCH_4^+ in (a), BC_4H_8^+ in (b) and C_2H_4^+ in (c), which are presented using dots at points, for the purpose of easy distinguishing data for different ions.

Figure 1

Figure 2

Figure 3

Graphical Abstract