A Photoelectron Photoion Coincidence Study of the Vinyl Bromide and Tribromoethane Ion Dissociation Dynamics: Heats of Formation of $C_2H_3^+$, C_2H_3Br, $C_2H_3Br^+$, $C_2H_3Br_2^+$, and $C_2H_3Br_3$†

A. F. Lago and Tomas Baer*

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599-3290

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The threshold photoelectron photoion coincidence (TPEPICO) technique has been used to measure accurate dissociative photoionization onsets of vinyl bromide and 1,1,2-tribromoethane. The reactions investigated and their 0 K onsets are $C_2H_3Br + h\nu \rightarrow C_2H_3^+ + Br$ (11.902 ± 0.008 eV); $C_2H_3Br_3 + h\nu \rightarrow C_2H_3Br_2^+ + Br$ (10.608 ± 0.008 eV); and ($C_2H_3Br_3 + h\nu \rightarrow C_2H_3Br^+ + 2Br$ (12.301 ± 0.035 eV). The vinyl ion heat of formation ($\Delta_f H^\circ_{298K} = 1116.1 \pm 3.0$ kJ/mol) has been calculated using W1 theory and used as an anchor along with the measured dissociation energies to determine the heats of formation, $\Delta_f H^\circ_{298K}$, in kJ/mol, of the following bromine-containing species: C_2H_3Br (74.1 ± 3.1), $C_2H_3Br^+$ (1021.9 ± 3.1), $C_2H_3Br_2^+$ (967.1 ± 4.0), and $C_2H_3Br_3$ (53.5 ± 4.3). These results represent accurate and consistent experimental determinations of heats of formation for these bromine-containing species, which serve to correct the discrepancies in the literature for C_2H_3Br and $C_2H_3Br^+$ and provide the first experimental determination for the enthalpies of formation of $C_2H_3Br_2^+$ and $C_2H_3Br_3$.

1. Introduction

The chemistry of bromine-containing molecules in both neutral and ionic states has attracted increasing attention lately because of the important role that bromine plays in the catalytic depletion of the earth's protecting ozone layer in the stratosphere.[1,2] It has also been recognized that the tropospheric reactions of bromine atoms and bromine-containing radicals are more important than previously thought, especially in regions of the Arctic and marine boundary layers.[3−5] Reactions initiated by dissociative photoionization of bromine-containing molecules are a significant source of bromine atoms in the atmosphere.[6] In addition, the photodissociation of vinyl bromide (C_2H_3Br) is an important route for the production of the vinyl radical (C_2H_3) and its ionic species ($C_2H_3^+$). This hydrocarbon plays a fundamental role as an intermediate in hydrocarbon combustion chemistry,[7−9] and both C_2H_3 and $C_2H_3^+$ are believed to participate as reaction intermediates in interstellar media.[10] Understanding the chemistry of these brominated molecules and radicals in the atmosphere requires knowledge of their thermochemical properties.

Despite their importance, the thermochemistry of bromine-containing molecules is not well established in the literature. The only experimental value for the enthalpy of formation of the vinyl bromide available in the literature is $\Delta_f H^\circ_{298K}(C_2H_3Br) = 78.2 \pm 1.0$ kJ/mol, which was determined by Lacher et al.[11] from experiments on the catalytic hydrogenation of vinyl bromide. A reevaluation of this using updated ancillary heats of formation yields a value of 79.6 ± 1.9 kJ/mol.[12] This energy was corroborated by a theoretical G2 study of Glukhovtsev and Bach,[13] who reported a value of 79.7 kJ/mol. The vinyl bromide molecule has recently been investigated by pulsed field ionization (PFI) zero kinetic energy electron (ZEKE) spectroscopy by Qian et al.,[14] who obtained an ionization energy of 9.8200 ± 0.0015 eV and a dissociation energy to $C_2H_3^+ + Br$ of 11.9010 ± 0.0015 eV. No experimental value for the 1,1,2-tribromoethane molecule has been determined. An estimated value of $\Delta_f H^\circ_{298K}(C_2H_3Br_3) = 11$ kJ/mol[15] was derived by group additivity. However, because of the lack of thermochemical information about bromine-containing hydrocarbons in general, group additivity methods are not reliable here.

We have recently initiated an investigation into the dissociation dynamics and thermochemistry of halogenated molecules, the first result of which is a self-consistent set of heats of formation for all Cl-, Br-, and I-containing dihalomethane molecules.[16,17] A key advance in the threshold photoelectron photoion coincidence (TPEPICO) experiment and its analysis, which permits extraction of higher-energy dissociative photoionization onsets, has permitted us to obtain energetics with an accuracy of ±3 kJ/mol.[18] The present work is dedicated to the TPEPICO study of the dissociative photoionization and thermochemistry of 1,1,2-tribromoethane ($C_2H_3Br_3$) and vinyl bromide (C_2H_3Br). Whereas the higher energy onsets in the mixed dihalomethane reactions were competitive halogen loss steps, the higher-energy onset in the case of the $C_2H_3Br_3$ molecule is a sequential loss of Br atoms, which leads to the vinyl bromide ion as a product. The heats of formation of the two halide molecules are anchored to the heat of formation of the vinyl ion, $C_2H_3^+$, whose thermochemistry is reviewed.

2. Experimental Approach

The threshold photoelectron photoion coincidence (TPEPICO) apparatus have been described in detail elsewhere.[16,19,20] Some important improvements have been recently incorporated into our experimental apparatus, which substantially increased our collection efficiencies as well as our ability to quantitatively model higher-energy onsets. The room-temperature samples are introduced into the ionization region by means of a stainless steel capillary and ionized with VUV photons generated from

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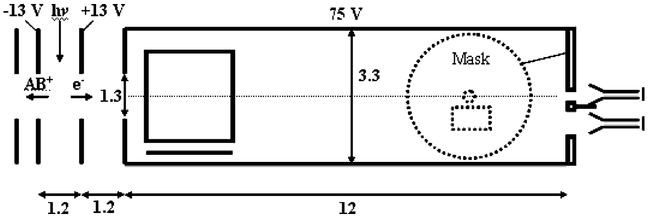

Figure 1. The approximately to scale representation of the threshold electron detection system. The dimensions are given in centimeters, and the typical voltages are indicated. Two deflection plates steer the threshold electrons through the 1.4 mm hole in the mask, shown by the dotted lines.

a hydrogen (H_2) discharge lamp dispersed by a 1 m normal incidence monochromator. The entrance and exit slits are set to 100 μm, which provides a photon resolution of 1 Å (8 meV at photon energy of 10 eV). The energy scale is calibrated by using the hydrogen Lyman-α resonance line. Ions and electrons are accelerated in opposite directions by a 20 V/cm extraction field. Electrons travel toward an electrode with a gridless 12.7 mm aperture located 6 mm from the center of the ionization region. A second gridless acceleration electrode, located 12 mm from the first one, accelerates the electrons to 75 eV after which they pass through a 12 cm field free flight tube.

A simpler and more effective method for the collection of on-axis and off-axis electrons has recently been installed. The electrons are collected by a pair of (7×3 mm^2 rectangular) Spiraltron electron multipliers (Burle Co.), one of them located on the central axis and the second located approximately 3 mm away from the center (see Figure 1). Threshold electrons, as well as any hot electrons with zero perpendicular velocity components, are focused onto a 1.5 mm aperture located in the center of the flight tube and are detected by the central Spiraltron electron multiplier, whereas the energetic (hot electrons) with a few millielectronvolts perpendicular to the extraction axis enter the (2×5 mm^2) off-axis rectangular aperture and are collected by the second Spiraltron (see mask in Figure 1). Two steering plates located at the beginning of the flight tube are adjusted to ensure that the threshold electrons pass through the 1.5 mm aperture. Because the electrons collected by the off-axis rectangular aperture are a good representation of the hot electrons at the central collector, we can subtract the off-axis electron signal from the central signal and thus obtain a pure threshold electron signal, as described in previous publications.[16,18,20]

The ions are accelerated over a 5 cm region before drifting 40 cm through the first field free region to a single-stage 20-cm-long reflectron, where they are decelerated, reflected, and then drifted for another 40 cm second drift region before being detected on tandem Burle MCP's. The electron and ion signals are used as start and stop pulses for obtaining the ion time-of-flight (TOF) spectrum. Separate ion TOF distributions are collected in coincidence with the two electron detectors. The collection efficiencies have been recently improved to about 40% for threshold electrons and 12% for ions. The samples of vinyl bromide and 1,1,2-tribromoethane were purchased from Sigma-Aldrich with purity better than 98% and were used without further purification.

3. Computational Methods

Ab initio molecular orbital calculations[21] were carried out by using the *Gaussian 03* system of programs.[22] The ground-state geometries of the neutral and ionic bromine-containing species studied in this work were fully optimized using density functional theory (DFT), with the Becke 3-parameter and Lee−Yang−Parr (B3LYP) functional[23,24] and the aug-cc-pVTZ basis set. The vibrational frequencies and rotational constants required for the Rice−Ramsperger−Kassel−Marcus (RRKM) analysis of the experimental breakdown diagrams were also obtained in these calculations.

TABLE 1: Energetics and Thermochemistry for Vinyl Radical and Cation Calculated at W1 Level of Theory

parameter	0 K energies[a]
E_{0K} ($C_2H_3^+$)	−77.56920
E_{zpe} ($C_2H_3^+$)	0.033586
$E_{thermal}$ ($C_2H_3^+$)	0.036959
E_{0K} (CH_4)	−40.479068
E_{0K} (CH_3^+)	−39.45277
E_{0K} (C_2H_4)	−78.554694
$\Delta_r H^\circ_{0K}$(reaction 1)	−107.1
$\Delta_f H^\circ_{0K}$($C_2H_3^+$)	1119.6

[a] Total energies are given in hartrees; $\Delta_r H^\circ_{0K}$ and $\Delta_f H^\circ_{0K}$ are in kJ/mol.

Because none of the brominated species in this study have well-established heats of formation, we anchored the derived energy scales to the $C_2H_3^+$ heat of formation. Although this is a simple closed-shell species, its heat of formation has also not been well established. However, it is sufficiently small so that high-level ab initio calculations can be applied to obtain an accurate heat of formation. To this end, we performed calculations on the $C_2H_3^+$ ion using the W1 level of theory. The W1 (Weizmann-1) theory[25,26] is known to provide accurate molecular atomization energies and consequently enthalpies of formation for first- and second-row molecules. It usually yields a mean absolute error on the order of 3 kJ/mol. This method requires more computational resources than the Gaussian G2 and G3 methods,[27,28] but it yields more accurate results. Although *Gaussian 03* does not implement the complete W1 method (they call it W1U), it should be the same as W1 for closed-shell molecules or ions in which spin contamination is not an issue. The following isodesmic reaction was used to calculate the vinyl ion enthalpy of formation:

$$CH_3^+ + C_2H_4 \rightarrow CH_4 + C_2H_3^+ \tag{1}$$

The W1 calculated reaction energies (Table 1) were combined with the well-established experimental $\Delta_f H^\circ_{0K}$(kJ/mol) for C_2H_4 (60.7), CH_4 (−66.8), and H (216.0) taken from Wagman et al.,[29] and CH_3^+ (1099.2) derived from the $CH_4 + h\nu \rightarrow CH_3^+ + H$ appearance energy of 14.323 ± 0.001 eV determined by Weitzel et al.[30] The overall error in the calculated enthalpy of formation of the vinyl cation obtained from reaction 1 was estimated to be about 3 kJ/mol. By using the isodesmic reaction scheme and closed-shell species, some of the systematic errors resulting from limitations in the theoretical treatment of the electron correlation energy and basis sets are compensated,[21] and spin contamination issues are avoided.

In the case of the $C_2H_3Br_3$ molecule, the hindered rotor correction has also been calculated. However, its contribution of less than 0.1 kJ/mol was considered negligible. The most stable geometry of the $C_2H_3Br_2^+$, cation calculated at DFT levels, corresponds to a nonplanar structure, where one bromine atom is bending out of the plane of the molecule, between the central carbon atoms (Figure 2).

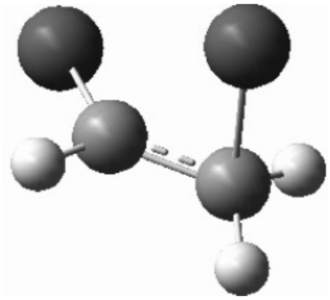

Figure 2. The calculated $C_2H_3Br_2^+$ ion geometry from DFT.

4. Results and Discussion

In this photoionization study, we measured the dissociative photoionization onsets for the following reactions:

$$C_2H_3Br + h\nu \rightarrow C_2H_3^+ + Br^\bullet \qquad (2)$$

$$1,1,2\text{-}C_2H_3Br_3 + h\nu \rightarrow 1,2\text{-}C_2H_3Br_2^+ + Br^\bullet \qquad (3)$$

$$1,2\text{-}C_2H_3Br_2^+ \rightarrow C_2H_3Br^+ + Br^\bullet \qquad (4)$$

Each of these reactions involves three species. If the energies of two of the species are known, then the third can be determined from the measured dissociation onset, by using eq 5

$$AB + h\nu \rightarrow A^+ + B + e^- \quad (E_0)$$

$$E_0 = \Delta_f H_o[A^+] + \Delta_f H_o[B] - \Delta_f H_o[AB] \qquad (5)$$

As mentioned before, none of the brominated species (aside from the bromine atom) have well-established heats of formation. Therefore, we rely on the vinyl ion heat of formation to anchor the energy scale.

4.1. Thermochemistry of the Vinyl Radical and Cation. The thermochemistry of the vinyl radical and its ion has been the object of considerable attention because of the importance of the vinyl radical in combustion processes. The two are related by the vinyl radical ionization energy, which in principle should be an easily measurable quantity. However, because of the dramatic change in structure from the classical radical to the hydrogen bridged ion structure, which results in a very poor Franck−Condon overlap for the 0−0 transition, the adiabatic ionization energy has not been determined with great precision.[31,32] The standard approach for obtaining the ion heat of formation is the dissociative photoionization: $C_2H_3X + h\nu \rightarrow C_2H_3^+ + X$. However, this procedure requires knowledge of the C_2H_3X heat of formation. The loss of H from C_2H_4 would appear to be a good candidate. Unfortunately, the lowest-energy channel for the ethane reaction is H_2 loss,[33] and the H-loss reaction proceeds via a barrier.[34,35]

Recent compilations of the experimental vinyl radical heat of formation[36−40] list its 298 K value at 299 ± 5 kJ/mol. This value is based on three independent experimental determinations which involve a positive ion cycle,[31,32,35] a negative ion cycle,[40] and a neutral kinetics measurement.[41] For various reasons outlined by Berkowitz et al.,[35] the precision of this value from the two ion cycles is not as high as the neutral kinetics data of Kaiser and Wallington,[41] which is based on the reaction of Cl and ethylene. As a result, Tsang recommended a value of 299 kJ/mol, based largely on the Kaiser and Wallington data. Unfortunately, the quoted value was based on a submitted manuscript. The actual publication of Kaiser and Wallington reported a $\Delta_f H^\circ_{298K}(C_2H_3^\bullet) = 295.4 \pm 1.7$ kJ/mol,[41] a value that is slightly lower than the ion cycle values and has a lower uncertainty. More recently, Parthiban and Martin[26] determined an identical value of 295.4 kJ/mol from calculations at the W1 level of theory. When this value is converted to 0 K, we obtain $\Delta_f H^\circ_{0K}(C_2H_3^\bullet) = 298.9 \pm 1.7$ kJ/mol.

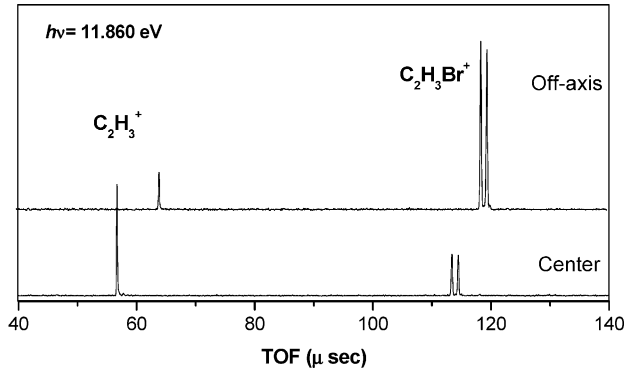

Figure 3. Center and off-axis ion TOF distributions for vinyl bromide at 11.86 eV. The ring spectrum shows the coincidence counts associated with energetic electrons. The off-axis spectrum is slightly shifted horizontally for presentation purposes.

To derive a vinyl ion heat of formation, we turn to ab initio calculations. Our direct calculation of the vinyl ion heat of formation using the isodesmic reaction 1 with the W1 level of theory yields a $\Delta_f H^\circ_{0K}(C_2H_3^+) = 1119.6 \pm 3$ kJ/mol (1116.1 ± 3 kJ/mol at 298 K). Our calculation is not only independent of the vinyl radical energy, but also involves only closed-shell species. The difference between the vinyl radical and ion heats of formation yields an ionization energy of 8.506 ± 0.03 eV. We can compare this value to a recently calculated ionization energy reported by Lau and Ng[42] who used coupled-cluster methods in the complete basis set limit, which leads to an IE(C_2H_3) of 8.485 eV. This calculated IE agrees with our derived IE to within 20 meV, but is slightly beyond the Lau and Ng suggested error of ±10 meV.

For this study, we take our calculated $\Delta_f H^\circ_{0K}(C_2H_3^+)$ value as the anchor for determining the thermochemistry of the alkyl bromides. In addition, we accept the Parthiban and Martin[26] and Kaiser and Wallington[41] vinyl radical heat of formation, $\Delta_f H^\circ_{298K}(C_2H_3^\bullet) = 295.4 \pm 1.7$ kJ/mol.

4.2. TOF Distribution and Breakdown Diagrams. Ion TOF distributions for vinyl bromide (C_2H_3Br) obtained with central and off-axis electron detectors are shown in Figure 3 at the energy of 11.860 eV. The narrow and symmetric peak shapes in those distributions indicate that the dissociation process is more rapid than we can measure, which means that the rate constant is faster than about 10^7 s^{-1}.[18] The photon energy of 11.860 eV is close to the dissociation limit to $C_2H_3^+ + Br$. Because the off-axis spectrum, in which the ions are collected in coincidence with energetic electrons, is associated with lower-energy ions, the fragment ion peaks are less intense than they are in the corresponding center spectrum. The TOF distributions recorded for the tribromoethane ($C_2H_3Br_3$) at 10.460 eV are presented in Figure 4. This photon energy is in the vicinity of the first dissociation limit $C_2H_3Br_2^+ + Br$. The second dissociation limit, corresponding to a sequential Br loss, occurs only at 1.693 eV in excess of the first dissociation limit. The clusters of peaks are a result of the 50:50 isotopic distributions of the mass 79:81 for the bromine isotopes.

The breakdown diagram, *B(I)*, which is a plot of the fragment and parent ion abundances as a function of the parent ion internal

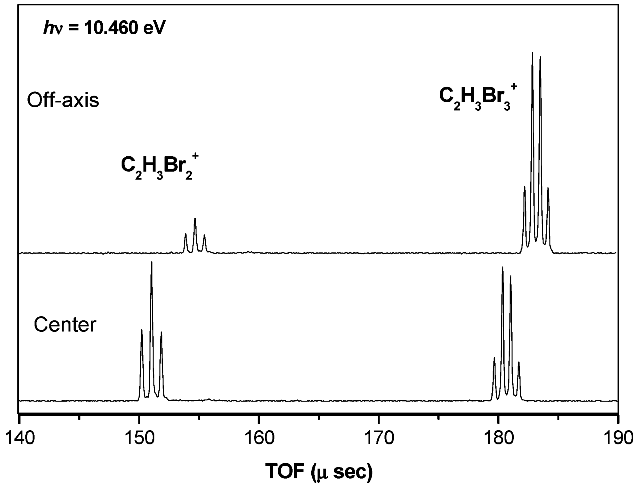

Figure 4. Center and off-axis TOF distributions for tribromoethane at 10.46 eV. The off-axis spectrum is slightly shifted horizontally for presentation purposes.

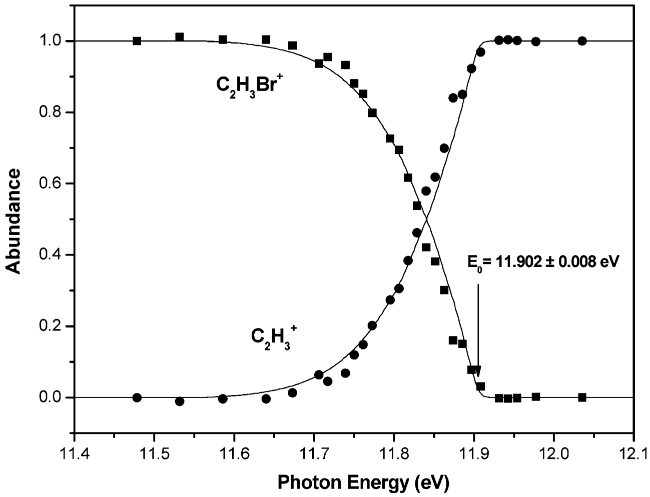

Figure 5. Breakdown diagram for vinyl bromide in the range 11.4−12.1 eV. Closed symbols are the experimental fractional abundances of parent and daughter ions. Solid lines represent the best calculated fit to the experimental data. The 0 K dissociation onsets obtained from modeling the data are indicated by the vertical arrows.

energy, is corrected for the presence of hot electrons by using eq 6[16]

$$B(I) = \frac{(I_c) - f(I_r)}{(T_c) - f(T_r)} \tag{6}$$

The terms I_c and T_c represent the integrated peak areas of a certain ion and the total area of the parent and daughter ions associated with the center electrode, respectively, and I_r and T_r are the corresponding quantities for the ring or off-axis data. The experimental subtraction factor, $f = 0.16$, is independent of the photon energy and of the molecule studied, as explained in previous publications.[16,18] We record a number of TOF distributions at different photon energies from which we obtained the fractional abundances of parent and ionic fragments, which are shown as points in Figures 5 and 6.

For a room-temperature sample, the ion energy is given by $h\nu + E_{th}$, where E_{th} is the thermal energy which is given by a distribution, $P(E) \propto \rho(E)\exp(-E/RT)$. The thermal energy distribution is obtained from the calculated or experimental vibrational frequencies of the parent molecule. The breakdown

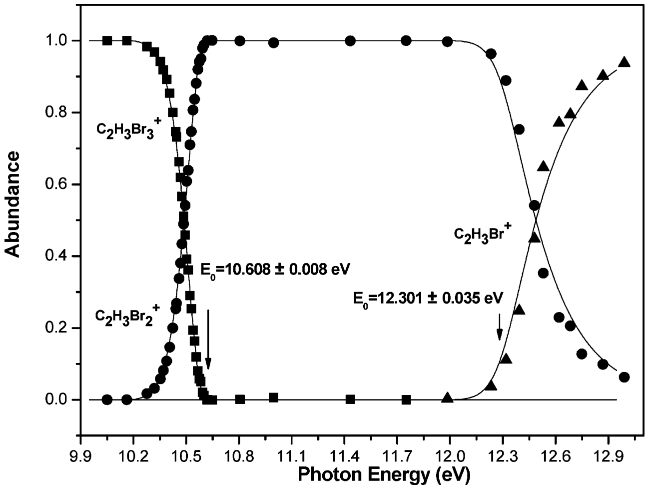

Figure 6. Breakdown diagram for 1,1,2-tribromoethane in the range 9.9−12.9 eV.

diagram for the first dissociation step can be calculated by eqs 7 and 8[18]

$$B_P(h\nu) = \int_0^{E_0 - h\nu} P(E)\,dE \quad \text{for } h\nu < E_o \qquad (B_P(h\nu) = 0 \text{ for } h\nu > E_o) \tag{7}$$

$$B_D(h\nu) = \int_{E_0 - h\nu}^{\infty} P(E)\,dE \quad \text{for } h\nu < E_o \qquad (B_D(h\nu) = 1 \text{ for } h\nu > E_o) \tag{8}$$

where B_P and B_D are the parent and daughter ion abundances. The one adjustable parameter in this modeled breakdown diagram is the 0 K dissociation onset, E_o, which is adjusted to achieve a best fit for the breakdown diagram. In the case of fast reactions such as this one, the 0 K onset is very close to the energy at which the parent ion signal goes to zero.

This analysis yields a 0 K onset for bromine loss from the vinyl bromide molecule of 11.902 ± 0.008 eV. This is essentially identical to the recent pulsed field ionization PEPICO study of Qian et al.,[14] who obtained the more accurate value of 11.901 ± 0.0015 eV from their high-resolution study. However, the onsets of 10.608 ± 0.008 eV and 12.301 ± 0.035 eV for the first and second Br loss, respectively, from the tribromoethane are the first measurements of these values.

The loss of the second Br atom from $C_2H_3Br_3^+$ is modeled in a similar manner, except that the internal energy distribution of the intermediate $C_2H_3Br_2^+$ ion is not given simply by a displaced 298 K thermal energy distribution. It is broadened by the loss of the first Br atom, which can carry away some translational energy. The microcanonical energy distribution of the intermediate ion, $P(E_i)$[18,43] is given by $P(E_i) = \rho(E_i)\rho_{rtn}(E_T - E_i)$, in which $\rho(E_i)$ is the density of states of the $C_2H_3Br_2^+$ ion and $\rho_t(E_T - E_i)$ is the density of states associated with the Br product. The latter only involves translational motion in the center of mass of the two departing fragments, which is given in the phase space theory as a two-dimensional distribution.[18,43] Its functional form is simply $(E_T - E_i)$. The only parameters required to evaluate the energy distribution are the vibrational frequencies of the $C_2H_3Br_2^+$. Thus, the second Br loss onset in Figure 6 is obtained again with only a single adjustable factor, which is the 0 K dissociation onset. It is interesting that the second Br loss onset at 12.301 ± 0.035 eV is not located at the energy at which the parent ion disappears. The reason for this is the translational energy (RT) carried away by the $C_2H_3Br_2^+$ + Br products. At the second dissociation limit, the products

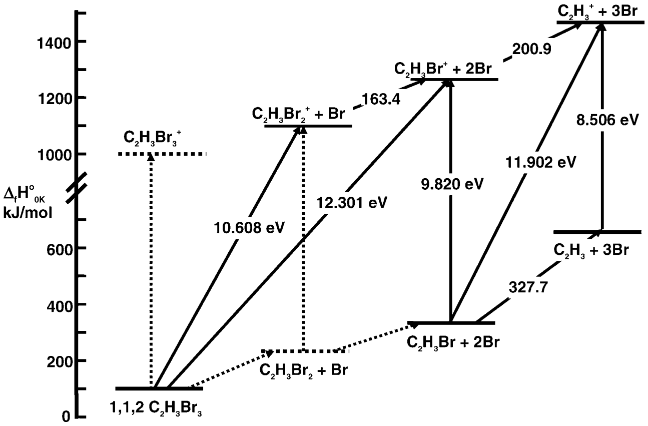

Figure 7. Summary of the experimental energies that relate the neutral and ionic species associated with 1,1,2-tribromoethane and vinyl bromide. All dissociation energies were measured by TPEPICO. The vinyl bromide ionization energy was measured by pulsed field ionization by Qian et al.[14] The vinyl radical energy was taken from Kaiser and Wallington,[41] and the IE is our calculated ionization energy. Bond energies at 0 K are given in kJ/mol. Dashed lines and arrows are unmeasured quantities.

TABLE 2: Summary of the Thermochemical Results (in units of kJ/mol)

species	$\Delta_f H^\circ_{0K}$	$\Delta_f H^\circ_{298K}$	$H_{298} - H_0$	$\Delta_f H^\circ_{298K}$ (lit.)
$C_2H_3^+$	1119.6	1116.1 ± 3.0	11.3	1117.2[a] 1120.3[b]
C_2H_3Br	89.1	74.1 ± 3.1	12.1	79.2[c] 79.6[d]
$C_2H_3Br^+$	1036.6	1021.9 ± 3.1	12.4	1024.8[e]
$C_2H_3Br_2^+$	991.1	967.1 ± 4.0	15.4	
$C_2H_3Br_3$	85.5	53.5 ± 4.3	19.5	11.0[f]

[a] Glukhovtsev and Bach.[51] [b] Qian at al.[14] [c] Pedley[12] (adjusted Lacher[11] value). [d] Glukhovtsev and Bach.[13] [e] Lias et al.[49] [f] Kolesov and Papina.[15]

partition a total of 1.7 eV of excess energy, of which the translational degrees of freedom amounts to about 0.23 eV, an average value that can be readily calculated using the Klots equation.[44] Thus, the sequential 0 K onset is located at the rising edge of the fragment ion signal, rather than at the break.

4.3. Thermochemistry of the Bromine-Containing Species. In this study, we have measured the 0 K dissociation onsets for reactions 2, 3, and 4. By using the calculated enthalpy of formation of the vinyl ion and the experimental onset, we can derive the heat of formation of the vinyl bromide molecule from reaction 2 ($C_2H_3Br \rightarrow C_2H_3^+ + Br$). In addition, the vinyl bromide ionization energy has been accurately measured by two groups using pulsed field ionization methods. Lee and Kim[45] reported an IE = 9.8171 ± 0.0006 eV and Qian et al.[14] reported a value of 9.8200 ± 0.0015 eV, which agree within 3 meV. The vinyl bromide IE combined with its heat of formation thus yields the vinyl bromide ion heat of formation. Because the vinyl bromide ion is the product of reaction 4, we obtain the enthalpy of formation of the 1,2-$C_2H_3Br_2^+$ ion. Finally, with this in hand, we can calculate the heat of formation of the tribromoethane molecule. The only ancillary heat of formation required is that of the Br atom, which is 117.92 kJ/mol at 0 K (111.86 kJ/mol at 298 K).[46] The measured energies (all at 0 K) are illustrated in the energy diagram of Figure 7, and the derived heats of formation are listed in Table 2.

The diagram presented in Figure 7 illustrates that, if the ionization energy for the $C_2H_3Br_2$ radical were to be measured, we would know all the successive C−Br bond energies for 1,1,2-tribromoethane. In addition, if the ionization energy of the parent molecule, which is close to 10 eV, were to be measured accurately, we would know all the successive ionic bond energies of this molecule. We could not accurately determine the IE of the tribromoethane molecule in this room-temperature study, because the onset is not very sharp. However, a laser spectroscopic measurement with a cold sample would most likely establish the 0−0 onset.

TABLE 3: Heats of Reaction (eq 9) and Enthalpies of Formation for Vinyl Bromide Calculated at Different Levels of Theory (in units of kJ/mol)

level of theory	$\Delta_r H^\circ_{0K}$	$\Delta_f H^\circ_{0K}(C_2H_3Br)$
PBE1PBE/aug-cc-pVTZ	−18.7	88.8
PBE1PBE/aug-cc-pVQZ	−19.0	88.5
B3LYP/aug-cc-pVQZ	−16.6	90.9
MP2/6-311+G*	−22.1	85.4
MP2/aug-cc-pVDZ	−20.8	86.7
G2	−18.6	88.9

The values for the 0 K enthalpies of formation can be converted to the corresponding 298 K values by means of the conventional thermochemical cycle, given by eq 9

$$\Delta_f H^\circ_{0K} = \Delta_f H^\circ_{298K} - [H^\circ_{298K} - H^\circ_{0K}](\text{molecule/ion}) + [H^\circ_{298K} - H^\circ_{0K}](\text{elements}) \quad (9)$$

We have used the $H^\circ_{298K} - H^\circ_{0K}$ values from the literature[46] for the atomic elements, and the calculated $H^\circ_{298K} - H^\circ_{0K}$ values for the molecules and fragment ions, from the vibrational frequencies obtained at B3LYP/aug-cc-pVTZ level of theory, which are in good agreement with the experimental values that could be found in the literature.[47,48] For the $H^\circ_{298K} - H^\circ_{0K}$ calculations, the heat capacity of the electron was chosen as 0.0 kJ/mol at all temperatures, according to the ion convention.[49] It should be noted that the bromine (Br_2) standard state changes from crystal at 0 K to liquid at 298 K, and the corresponding $H^\circ_{298K} - H^\circ_{0K}$ should be used. Table 2 lists both the determined 0 K and 298 K converted enthalpies of formation, which are compared to the available literature values.

The derived C_2H_3Br $\Delta_f H^\circ_{298K}$ of 74.1 ± 3.1 kJ/mol is about 5 kJ/mol lower than the updated experimental value of Lacher et al.[11] listed in Table 2. To test the reliability of our heat of formation, we performed a series of quantum mechanical calculations for vinyl bromide. We derived values for the enthalpy of formation of vinyl bromide by using ab initio and DFT calculations at different levels of theory, using the following isodesmic reaction:

$$C_2H_4 + CH_3Br \rightarrow C_2H_3Br + CH_4 \quad (10)$$

The well-known enthalpies of formation for C_2H_4, CH_3Br, and CH_4 were taken from the literature.[12] The outcome of these calculations, shown in Table 3, presents a remarkable consistency and yields an average 0 K value of 88.2 kJ/mol, which is just 0.9 kJ/mol lower than our experimentally derived value. The results obtained in this work strongly suggest that the literature enthalpies of formation of both C_2H_3Br and $C_2H_3Br^+$ should be adjusted.

From our results, it was also possible to determine the 298 K (C−Br) bond dissociation enthalpy, which is BDE(C_2H_3−Br) = 333.2 ± 3.1 kJ/mol, by using the well-known enthalpy of formation for the bromine atom (111.86 kJ/mol)[46] and eq 11.

$$\text{BDE}(C_2H_3 - Br) = \Delta_f H^\circ(C_2H_3) + \Delta_f H^\circ(Br) - \Delta_f H^\circ(C_2H_3Br) \quad (11)$$

Our derived BDE(C_2H_3−Br) agrees with the 332.2 ± 6.3 kJ/

mol bond enthalpy listed by Luo[50] (which is based on the Lacher et al.[11] vinyl bromide energy and the Tsang[36] vinyl radical energy) but reduces its uncertainty. Finally, our heats of formation of $C_2H_3Br_2^+$ (967.7 ± 4.0 kJ/mol) and $C_2H_3Br_3$ (53.5 ± 4.0 kJ/mol) are the first experimentally derived quantities available.

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References and Notes

(1) Albritton, D. L.; Watson, R. T. *Methyl Bromide: Its Atmospheric Science, Technology and Economics*; Montreal Protocol Assessment Supplement; UNEP: Nairobi, Kenya, 1993.

(2) Albritton, D. L.; Watson, R. T.; Aucamp, P. J. (assessment cochairs) *Scientific Assessment of Ozone Depletion: 1994*; World Meteorological Organization; Global Ozone Research and Monitoring Project, Report No. 37; World Meteorological Organization: Geneva, 1995.

(3) Le Bras, G.; Platt, U. *Geophys. Res. Lett.* **1995**, *22*, 599.

(4) Hausmann, M.; Platt, U. *J. Geophys. Res.* **1994**, *99*, 25399.

(5) Bierbach, A.; Barnes, I.; Becker, K. H. *Int. J. Chem. Kinet.* **1996**, *28*, 565.

(6) Barrie, L. A.; Bottenheim, J. W.; Schnell, R. C.; Crutzen, P. J.; Rasmussen, R. A. *Nature (London)* **1988**, *334*, 138.

(7) Gardner, W. C., Ed. *Combustion Chemistry*; Springer: New York, 1984.

(8) Miller, J. A.; Lee R. J.; Westbrook, C. K. *Annu. Rev. Phys. Chem.* **1990**, *41*, 345.

(9) Puri, L. K., Ed. *Environmental Implications of Combustion Chemistry Processes*; CRC Press: Boca Raton, FL, 1993.

(10) Smith, D. *Philos. Trans. R. Soc. London, Ser. A* **1988**, *324*, 257.

(11) Lacher, J. R.; Kianpour, A.; Montgomery, P.; Knedler, H.; Park, J. D. *J. Phys. Chem.* **1957**, *61*, 1125.

(12) Pedley, J. B. *Thermochemical Data and Structures of Organic Compounds*; Thermodynamics Research Center: College Station, TX, 1994.

(13) Glukhovtsev, M. N.; Bach, R. D. *J. Phys. Chem. A* **1997**, *101*, 3574.

(14) Qian, X. M.; Lau, K. C.; Ng, C. Y. *J. Chem. Phys.* **2004**, *120*, 11031.

(15) Kolesov, V. P.; Papina, T. S. *Russ. Chem. Rev. (Engl. Transl.)* **1983**, *52*, 425.

(16) Lago, A. F.; Kercher, J. P.; Bodi, A.; Sztaray, B.; Miller, B. E.; Wurzelmann, D.; Baer, T. *J. Phys. Chem. A* **2005**, *109*, 1802.

(17) Dávalos, J. Z.; Lago, A. F.; Baer, T. *Chem. Phys. Lett.* **2005**, *409*, 230.

(18) Baer, T.; Sztaray, B.; Kercher, J. P.; Lago, A. F.; Bodi, A.; Scull, C.; Palathinkal, D. *Phys. Chem. Chem. Phys.* **2005**, *7*, 1507.

(19) Baer, T.; Li, Y. *Int. J. Mass Spectrom.* **2002**, *219*, 381−389.

(20) Sztáray, B.; Baer, T. *Rev. Sci. Instrum.* **2003**, *74*, 3763−3768.

(21) Hehre, W. J.; Radom, L.; Schleyer, P. V. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

(22) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, Ö.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komáromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 03*; Gaussian, Inc.: Pittsburgh, PA, 2003.

(23) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652.

(24) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev.* **1988**, *B37*, 785−789.

(25) Martin, J. M. L.; de Oliveira, G. *J. Chem. Phys.* **1999**, *111*, 1843.

(26) Parthiban, S.; Martin, J. M. L. *J. Chem. Phys.* **2001**, *114*, 6014.

(27) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94*, 7221.

(28) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764.

(29) Wagman, D. D.; Evans, W. H. E.; Parker, V. B.; Schum, R. H.; Halow, I.; Mailey, S. M.; Churney, K. L.; Nuttall, R. L. The NBS Tables of Chemical Thermodynamic Properties. *J. Phys. Chem. Ref. Data*; NSRDS; U. S. Government Printing Office: Washington, DC, 1982; Vol. 11, Supplement 2.

(30) Weitzel, K. M.; Malow, M.; Jarvis, G. K.; Baer, T.; Song, Y.; Ng, C. Y. *J. Chem. Phys.* **1999**, *111*, 8267.

(31) Berkowitz, J.; Mayhew, C. A.; Ruscic, B. *J. Chem. Phys.* **1988**, *88*, 7396.

(32) Blush, J. A.; Chen, P. *J. Phys. Chem.* **1992**, *96*, 4138.

(33) Güthe, F.; Weitzel, K.-M. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 484.

(34) Hawley, M.; Smith, M. A. *J. Chem. Phys.* **1992**, *96*, 1121

(35) Berkowitz, J.; Ellison, G. B.; Gutman, D. *J. Phys. Chem.* **1994**, *98*, 2744.

(36) Tsang, W. Heats of Formation of Organic Free Radicals by Kinetics Methods. In *Energetics of Organics Free Radicals*; Simões, M. J. A., Greenberg, A., Liebman, J. F., Eds.; Chapman & Hall: London, 1996.

(37) *NIST Chemistry Webbook*, Standard Reference Database 2005; http://webbook.nist.gov/chemistry (accessed Aug 2005).

(38) Ruscic, B.; Boggs, J. E.; Burcat, A.; Császár, A. G.; Demaison, J.; Janoschek, R.; Martin, J. M. L.; Morton, M. L.; Rossi, M. J.; Stanton, J. F.; Szalay, P. G.; Westmoreland, P. R.; Zabel, F.; Bérces, T. *J. Phys. Chem. Ref. Data* **2005**, *34*, 573.

(39) Baulch, D. L.; Bowman, C. T.; Cobos, C. J.; Cox, R. A.; Just, T.; Kerr, J. A.; Pilling, M. J.; Stocker, D.; Troe, J.; Tsang, W.; Walker, R. W.; Warnatz, J. *J. Phys. Chem. Ref. Data* **2005**, *34*, 757.

(40) Ervin, K. M.; Gronert, S.; Barlow, S. E.; Gilles, M. K.; Harrison, A. G.; Bierbaum, V. M.; DePuy, C. H.; Lineberger, W. C.; Ellison, G. B. *J. Am. Chem. Soc.* **1990**, *112*, 5750.

(41) Kaiser, E. W.; Wallington, T. J. *J. Phys. Chem.* **1996**, *100*, 4111.

(42) Lau, K. C.; Ng, C. Y. *J. Chem. Phys.* **2005**, *122*, 224310.

(43) Baer, T.; Hase, W. L. *Unimolecular Reaction Dynamics: Theory and Experiments*; Oxford University Press: New York, 1996.

(44) Klots, C. E. *J. Chem. Phys.* **1973**, *58*, 5364.

(45) Lee, M.; Kim, M. S. *J. Chem. Phys.* **2003**, *119*, 5085.

(46) Chase, M. W. *NIST-JANAF Thermochemical Tables*; American Institute of Physics: New York, 1998.

(47) Sverdlov, L. M.; Kovner, M.; Karinov, E. *Vibrational Spectra of Polyatomic Molecules*; Wiley: New York, 1974.

(48) Lin-Vien, D.; Colthup, N. B.; Fateley, W. G.; Grasselli, J. G. *The Handbook of Infrared and Raman Characteristic Frequencies of Organic Molecules*; Academic Press: Boston, 1991.

(49) Lias, S. G.; Bartmess, J. E.; Liebman, J. F.; Holmes, J. L.; Levin, R. D.; Mallard, W. G. Gas Phase Ion and Neutral Thermochemistry. *J. Phys. Chem. Ref. Data*; NSRDS; U. S. Government Printing Office: Washington, DC, 1988; Vol. 17, Supplement 1.

(50) Luo, Y.-R. *Handbook of Bond Dissociation Energies in Organic Compounds*; CRC Press: Boca Raton, 2003.

(51) Glukhovtsev, M. N.; Bach, R. D. *Chem. Phys. Lett.* **1998**, *286*, 51.