# Ethylene bromonium and 1-bromoethyl cations and their neutral and anionic counterparts: a tandem mass spectrometry study of dissociations and gas phase redox reactions

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The unimolecular chemistry of ethylene bromonium cation (cyclo-$CH_2CH_2Br^+$, **1$^+$**) and 1-bromoethyl cation ($CH_3CH^+Br$, **2$^+$**) has been probed by metastable ion (MI) characteristics, collisionally activated dissociation (CAD) and neutral fragment reionization ($N_fR$). These isomers undergo many common decompositions but can, nevertheless, be distinguished based on the structurally indicative $^•CH_3$ *vs.* $CH_2$ losses. Neutralization–reionization (NR) experiments have further shown that the gas phase reduction of **1$^+$** and **2$^+$** leads to 2-bromoethyl ($^•CH_2CH_2Br$, **3**) and 1-bromoethyl ($CH_3\dot{C}HBr$, **2**) radicals, respectively, both of which are stable species. However, from the incipient $C_2H_4Br^-$ anions emerging upon charge reversal of **1$^+$** and **2$^+$**, only $CH_3CH^-Br$ (**2$^-$**) is found to be a bound anion.

## Introduction

Three-membered cyclic bromonium cations are intermediates in the electrophilic addition of bromine to olefins.[1] Their formation in solution has been confirmed by low temperature NMR spectroscopy in superacidic media.[1,2] The importance of bromonium ions in organic synthesis[1,3] has prompted a number of gas phase studies about the simplest homolog, *viz.* the ethylene bromonium ion cyclo-$CH_2CH_2Br^+$ (**1$^+$**).[4–11] So far, these studies have concentrated on the ion–molecule reactions and thermochemistry of **1$^+$** whose behavior was compared to that of the isomeric 1-bromoethyl cation $CH_3CH^+Br$ (**2$^+$**).
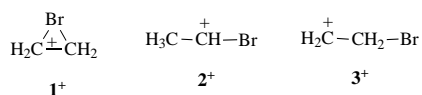


*Ab initio* calculations predict **1$^+$** and **2$^+$** as distinct, bound $C_2H_4Br^+$ isomers.[12] Bridged ion **1$^+$** is the global minimum.[12] Linear ion **2$^+$** is placed 6 kJ mol$^{-1}$ higher in energy and is separated from **1$^+$** by an interconversion barrier of 105 kJ mol$^{-1}$.[12] According to theory, ring-opened **1$^+$**, *i.e.* the 2-bromoethyl cation $^+CH_2CH_2Br$ (**3$^+$**), is unstable,[12] lying 121 kJ mol$^{-1}$ above **1$^+$** to which it collapses without any activation energy.[12] The heats of formation of **1$^+$** and **2$^+$** derived experimentally (from appearance energies) are 864 and 870 kJ mol$^{-1}$, respectively;[7,8] these values differ by 6 kJ mol$^{-1}$, in excellent agreement with the theoretical prediction.[12] The bimolecular reactivity of ions **1$^+$** and **2$^+$** has been studied extensively (*vide supra*).[4–6,9–11] In contrast, the unimolecular chemistry of **1$^+$** and **2$^+$** has remained largely unexplored and is determined here by metastable ion (MI) characteristics,[13,14] collisionally activated dissociation (CAD),[15] neutral fragment reionization ($N_fR$),[16] neutralization–reionization (NR)[17–19] and charge reversal (CR).[20] MI and CAD examine the ionic fragments arising from $C_2H_4Br^+$ that dissociate spontaneously or after collisional activation, respectively. $N_fR$ probes the neutral fragments generated upon CAD. NR and CR provide information on the gas phase redox properties of **1$^+$** and **2$^+$** and also examine the stability and reactivity of the neutral and anionic forms, respectively, of **1$^+$** and **2$^+$**.

$C_2H_4Br^-$ anions have never been characterized before. A few studies of $^•C_2H_4Br$ radicals have, however, been reported.[21–25]

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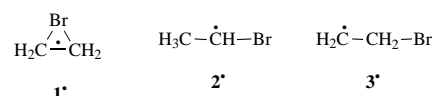
EPR experiments and photochemical reactions involving $^•C_2H_4Br$ identified the linear radicals **2$^•$** and **3$^•$** as distinct, stable species;[21–24] these studies also suggested that the bromine atom in **3$^•$** can migrate between the two carbon atoms *via* the bridged radical **1$^•$** which represents the transition state of this rearrangement. A more recent appearance energy study determined the heats of formation of **2$^•$** (114 kJ mol$^{-1}$) and **3$^•$** (135 kJ mol$^{-1}$) to establish the stabilizing effect of bromine on ethyl radicals.[25] The latter study also mentioned briefly that **2$^•$** and **3$^•$** can be accessed in NR experiments. This paper presents in detail the NR features of these $^•C_2H_4Br$ isomers, which reflect the different stabilities and reactivities of radicals **2$^•$** and **3$^•$**.

## Experimental

For all tandem mass spectra in this study, $E_1B$ served as MS-1 (precursor ion selector) and $E_2$ as MS-2 (product ion analyzer). The interface region between MS-1 and MS-2 houses two collision cells (C-1 and C-2) and an intermediate ion deflector.[26] CAD and CR spectra were measured using C-2; the collision gases were $O_2$ (80% transmittance) and trimethylamine (TMA; 60% transmittance), respectively. $N_fR$ and NR utilized both collision cells. In $N_fR$,[16] the precursor ion was subjected to CAD with He in C-1 (80% transmittance), the ionic fragments and undissociated precursors were removed by the ion deflector and the remaining neutral fragments were reionized by collision-induced dissociative ionization (CIDI)[18,19,28] with $O_2$ in C-2 (80% transmittance). NR was effected in an analogous manner by replacing He (in C-1) with TMA. The gaseous targets used in C-1 provide optimum yields for the respective processes; specifically, He minimizes the extent of charge exchange (owing to its high ionization energy), whereas TMA maximizes it (due to its lower ionization energy and, probably, poorer CAD efficiency).[16]
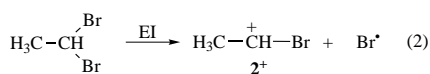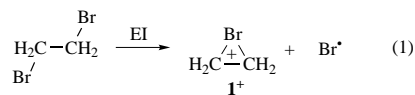
Kinetic energy releases were measured from peak widths at

half-height ($T_{0.5}$) using established procedures.[14] The $C_2H_4Br^+$ precursor ions were formed by electron impact at 70 eV and were accelerated to 8 keV upon leaving the ion source. The spectra shown are multiscan summations of *ca.* 20 scans for MI and CAD, *ca.* 400 scans for $N_fR$ and NR and *ca.* 600 scans for CR data (all reproducible within ±15%). $C_2H_4{}^{79}Br^+$ and $C_2H_4{}^{81}Br^+$ give rise to identical spectra; those obtained with the $^{79}Br$ isotopomers are included in the figures. 1,2-Dibromoethane (precursor of $1^+$) and 1,1-dibromoethane (precursor of $2^+$) are available from T.C.I. America and Acros Organics USA, respectively, and were introduced into the mass spectrometer as received.

## Results and discussion

According to the ion–molecule reaction and thermochemistry studies of $C_2H_4Br^+$ reported so far, bridged $1^+$ and linear $2^+$ are

$$H_2C-CH_2 \ (Br, Br) \xrightarrow{EI} H_2C \overset{+}{\underset{\diagdown}{-}} CH_2 \ (Br) + Br^\bullet \quad (1)$$
$$\mathbf{1^+}$$

$$H_3C-CH \ (Br, Br) \xrightarrow{EI} H_3C-\overset{+}{CH}-Br + Br^\bullet \quad (2)$$
$$\mathbf{2^+}$$

produced in isomerically pure form upon the dissociative electron ionization of 1,2- and 1,1-dibromoethane, respectively [reactions (1) and (2)].[4-11] The same precursors were utilized here for the investigation of the unimolecular chemistry of these $C_2H_4Br^+$ cations.

### Metastable $C_2H_4Br^+$
The only dissociation of metastable $1^+$ and $2^+$ is formation of $C_2H_3{}^+$ ($m/z$ 27) + HBr. Both isomers give rise to Gaussian and narrow $m/z$ 27 signals with similar widths ($T_{0.5} \approx 10$ meV). The very small kinetic energy releases point out that there is essentially no reverse activation energy.[14] Hence, the critical energies for $1^+/2^+ \to C_2H_3{}^+ + HBr$ must be very close to the corresponding reaction endothermicities which are 212 and 206 kJ mol$^{-1}$, respectively.[7,8,29] The latter values are considerably higher than the isomerization barrier for $2^+ \to 1^+$ (105 kJ mol$^{-1}$).[12] For this reason, metastable $1^+$ and $2^+$, *i.e.* long-lived ions with sufficient internal energy to decompose,[13,14] can interconvert to a common structure prior to HBr elimination, explaining their similar MI characteristics. The situation is different for stable ions, *i.e.* ions lying below their dissociation threshold. The isomerization degree of stable $1^+$ and $2^+$ [which depends on the height of the interconversion relative to the decomposition barrier and the internal energy distribution of the ions generated in reactions (1) and (2)] can be examined by collisionally activated dissociation (following section).[14,15]

### Ionic fragments from collisionally excited $C_2H_4Br^+$
The ionic fragments arising upon collisional activation of $1^+$ and $2^+$ give rise to the CAD spectra depicted in Fig. 1. Several fragments are formed with similar relative abundances, *inter alia* $C_2H_3{}^+$ ($m/z$ 27), $H_{0-2}Br^+$ ($m/z$ 79–81), $CBr^+$ ($m/z$ 91) and $C_2H_{0-3}Br^+$ ($m/z$ 103–106). However, there are also substantial and structurally diagnostic differences. Cyclic ion $1^+$, which carries $CH_2$ groups, produces both more $CH_2{}^{\bullet+}$ ($m/z$ 14) and more $CH_2Br^+$ ($m/z$ 93) than does linear ion $2^+$. In contrast, $2^+$ yields more abundant $CH_3{}^+$ ($m/z$ 15) and $[C_2H_4Br - CH_3]^{\bullet+}$ ($m/z$ 92, $CHBr^{\bullet+}$), in keeping with the presence in it of a methyl substituent. The CAD differences observed verify that stable $1^+$ and $2^+$ do not interconvert freely, in agreement with the high isomerization barrier calculated by theory (105 kJ mol$^{-1}$).[12] Based on the abundance ratio [$m/z$ 93]:[$m/z$ 15] in the CAD spectra of $1^+$ (>24) and $2^+$ (<1.3), <5% of $2^+$ that reach the collision cell (lifetime $\approx$ 14 $\mu$s) have rearranged to the more stable bridged ion $1^+$.
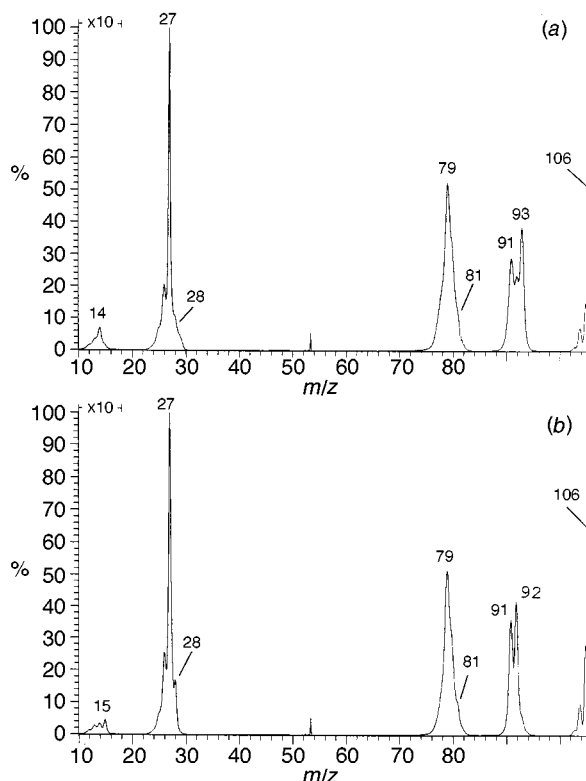
**Fig. 1** Collisionally activated dissociation (CAD) spectra of (*a*) ethylene bromonium cation $1^+$ and (*b*) 1-bromoethyl cation $2^+$. CAD promotes the dissociation of stable ions, *i.e.* ions without enough internal energy for spontaneous decay. The spectra display the ionic fragments generated upon CAD of $1^+$ and $2^+$.

It has been noticed for both $C_2H_4Br^+$ isomers that generation of $Br^+$ ($m/z$ 79) is preferred over elimination of $^\bullet Br$ (to give $C_2H_4{}^{\bullet+}$, $m/z$ 28), even though $Br^+ + C_2H_4$ ($\Sigma\Delta_fH^\circ = 1304$ kJ mol$^{-1}$) lies higher in energy than $C_2H_4{}^{\bullet+} + Br^\bullet$ (1178 kJ mol$^{-1}$).[29] Possibly, collisional activation populates excited electronic states of $1^+$ and $2^+$ which preferentially decompose to $Br^+$; the large kinetic energy release accompanying $Br^+$ formation, as revealed by the considerable peak width of $m/z$ 79 (Fig. 1), supports such a proposition.[14,15] The $m/z$ 79 peak appears to be broader for $1^+$ than $2^+$.[30] The same trend is observed for the complementary fragment, $C_2H_4{}^{\bullet+}$ ($m/z$ 28), whose signal is clearly wider for $1^+$ than for $2^+$. These differences suggest that $Br^+$ and $C_2H_4{}^{\bullet+}$ emerge from unique excited states of $1^+$ and $2^+$, respectively, which do not communicate.

### Neutral losses from collisionally excited $C_2H_4Br^+$
The neutral fragments released upon CAD of $C_2H_4Br^+$ can be made visible by collision-induced dissociative ionization (CIDI).[19,28] Notice that several different neutrals are eliminated during the CAD process and that each of them gives rise to a unique CIDI spectrum. The ultimately observed neutral fragment reionization ($N_fR$) spectra of $1^+$ and $2^+$ (Fig. 2) are, thus, a convolution of the CIDI spectra of all neutral losses from the selected $C_2H_4Br^+$ precursor ion.[16]

Both $N_fR$ spectra are dominated by $Br^+$ ($m/z$ 79) and $HBr^{\bullet+}$ ($m/z$ 80), originating mainly from the losses of HBr and $^\bullet Br$ which are cleaved upon dissociation to $C_2H_3{}^+$ (basepeak in the CAD spectra of Fig. 1) and $C_2H_4{}^{\bullet+}$, respectively. Marked differences are observed in the relative intensities of the $N_fR$ products at $m/z$ 14–15 and 92–93. As discussed above, the loss of $CH_2$ (14 u) is more prominent for isomer $1^+$, while the loss of $^\bullet CH_3$ (15 u) is more prominent for isomer $2^+$. The $N_fR$ spectra corroborate this reactivity by the significantly larger intensity ratio [$m/z$ 14]:[$m/z$ 15] for $1^+$ *vis à vis* $2^+$ (*cf.* Fig. 2). Similarly, the $N_fR$ spectra of $1^+$ and $2^+$ differ in the abundances of $CH_2Br^+$ ($m/z$ 93) and $CHBr^{\bullet+}$ ($m/z$ 92). The greater [$m/z$ 93]:
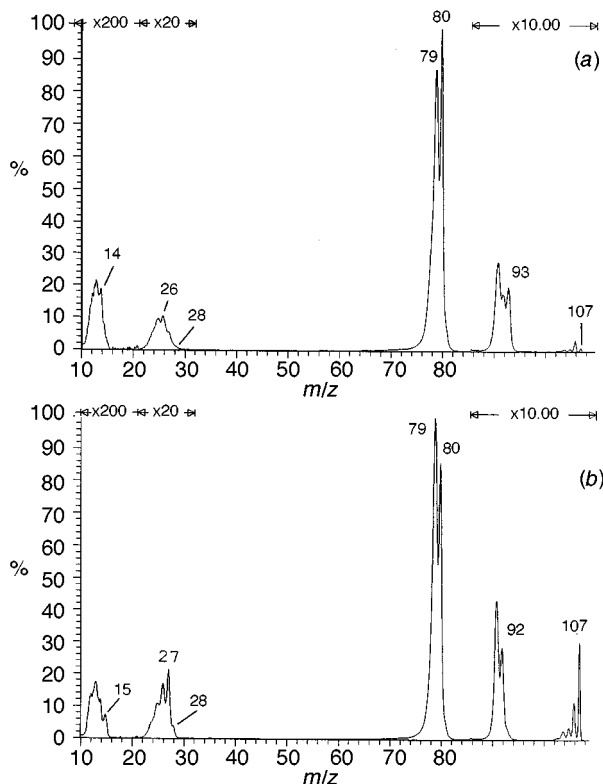
**Fig. 2** Neutral fragment reionization (N$_f$R) spectra of (*a*) ethylene bromonium cation **1**$^+$ and (*b*) 1-bromoethyl cation **2**$^+$. The spectra arise from the neutral fragments generated upon CAD of **1**$^+$ and **2**$^+$.

[*m/z* 92] ratio for **1**$^+$ *vs.* **2**$^+$ indicates a larger proportion of $^{\bullet}$CH$_2$Br (93 u), as compared to CHBr (92 u), in the neutral loss mixture from **1**$^+$ *vs.* **2**$^+$, as expected from the abundances of the complementary ionic fragments CH$_2$$^{\bullet+}$ and CH$_3$$^+$ in the CAD spectra.

The C$_2$H$_{0-4}$$^+$ peaks in the N$_f$R spectra (at *m/z* 24–28 in Fig. 2) probably result from the C$_2$H$_{2-4}$ losses co-produced with the CAD ions H$_{0-2}$Br$^+$ (*m/z* 79–81 in Fig. 1). Finally, the high-mass N$_f$R ions at *m/z* 103–107 (C$_2$H$_{0-4}$Br$^+$) are attributed to the small fraction of **1**$^+$ and **2**$^+$ that underwent neutralization and not CAD with the He targets (*vide infra*).

## C$_2$H$_4$Br$^+$ reduction to C$_2$H$_4$Br$^-$ anions

Charge reversal (CR) of **1**$^+$ and **2**$^+$ by collision with trimethyl-amine (TMA) targets leads mainly to Br$^-$ anions (*m/z* 79), *cf.* Fig. 3. Important and structurally diagnostic differences are also observed in the *m/z* 91–107 region. Consistent with its CH$_2$-bearing structure, **1**$^+$ yields a sizable CH$_2$Br$^-$ (*m/z* 93) fragment corresponding to CH$_2$ loss. On the other hand, CH$_3$-carrying **2**$^+$ produces a much more abundant CHBr$^{\bullet-}$ fragment (*m/z* 92; $^{\bullet}$CH$_3$ loss). In addition, CR of **2**$^+$ generates a recovered C$_2$H$_4$Br$^-$ peak (*m/z* 107), indicating that the 1-bromoethyl anion, *viz.* CH$_3$CH$^-$Br (**2**$^-$), is a stable species. In sharp contrast, no surviving C$_2$H$_4$Br$^-$ is formed upon CR of **1**$^+$, pointing out that this cation cannot be reduced to a bound negative ion.

Charge reversal of multi-atomic cations, such as C$_2$H$_4$Br$^+$, has been shown to proceed by sequential reduction, *via* cation→neutral→anion.[31] Thus, the CR spectra also depend on the stabilities and chemical properties of the intermediate neutrals arising after the first electron attachment.[32] The observed stability of **2**$^-$ reveals that the intermediate 1-bromo-ethyl radical, CH$_3$ĊHBr (**2**$^{\bullet}$), is stable and has a positive electron affinity (otherwise it would have been unable to form a surviving anion). Similarly, the instability of **1**$^-$ suggests that the intermediate neutral is either unstable or has a negative electron affinity (and, hence, cannot support a negative charge
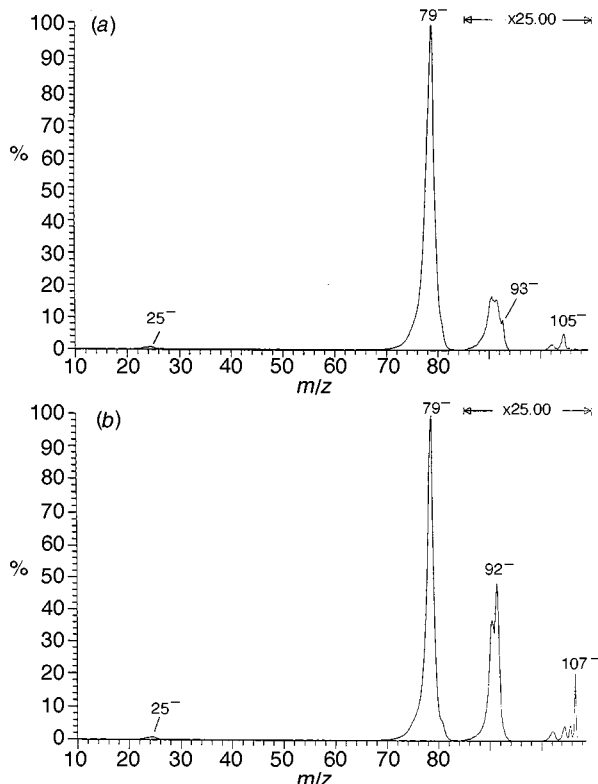


**Fig. 3** Charge reversal (CR) spectra of (*a*) ethylene bromonium cation **1**$^+$ and (*b*) 1-bromoethyl cation **2**$^+$

even if it is stable). The absence of a surviving anion from **1**$^+$ and the large differences in the *m/z* 91–107 regions of the CR spectra of **1**$^+$ and **2**$^+$ exclude, however, that neutralized **1**$^+$, *i.e.* the incipient radical **1**$^{\bullet}$, rearranges to the 1-bromoethyl radical **2**$^{\bullet}$. This information will be very useful in the interpretation of the neutralization–reionization (NR) spectra of **1**$^+$ and **2**$^+$ (*vide infra*), which provide more definitive information about the identity of the radical emerging from neutralization of cyclic ion **1**$^+$.

## Radicals formed upon reduction of C$_2$H$_4$Br$^+$

The NR spectra of **1**$^+$ and **2**$^+$ (Fig. 4) are strikingly different. That of the 1-bromoethyl cation contains a large recovery peak (*m/z* 107) and is fairly similar to the corresponding CAD spectrum [*cf.* Figs. 4(*b*) and 1(*b*)]. Hence, the 1-bromoethyl structure is preserved upon neutralization–reionization, in agreement with the high stability of the intermediate 1-bromoethyl radical **2**$^{\bullet}$.[24,25] Notice that the relative fragment ion abundances in the CAD and NR spectra of **2**$^+$ do not match exactly, presumably because of the different internal energy distributions deposited in these processes. NR, which provides higher average internal energies to the precursor ion,[33] discriminates against slow rearrangements, such as the formation of C$_2$H$_3$$^+$ (*m/z* 27) which was favored at threshold (see MI section).

A recovery peak is also present in the NR spectrum of bridged ion **1**$^+$ [Fig. 4(*a*)]. Thus, neutralization of **1**$^+$ creates, at least in part, a bound radical. Because this radical does not produce a surviving anion (*vide supra*), it cannot be **2**$^{\bullet}$. The incipient radical arising by electron addition to **1**$^+$ should be the bridged radical **1**$^{\bullet}$. There is no theoretical data on **1**$^{\bullet}$. According to EPR studies in solution, **1**$^{\bullet}$ is an intermediate in the migration of bromine between the two carbons of 2-bromo-ethyl radical (**3**$^{\bullet}$). This migration proceeds rapidly at temper-atures as low as 100 K,[22,23] suggesting that **1**$^{\bullet}$ and **3**$^{\bullet}$ ($\Delta_f H^{\circ} = $ 135 kJ mol$^{-1}$)[25] lie close in energy. Thus, nascent **1**$^{\bullet}$ should be capable of rearranging to **3**$^{\bullet}$ well below the dissociation limit to C$_2$H$_4$ + $^{\bullet}$Br ($\Sigma \Delta_f H^{\circ} = $ 164 kJ mol$^{-1}$),[29] *cf.* reaction (3). It is, therefore, concluded that neutralization of **1**$^+$ ultimately
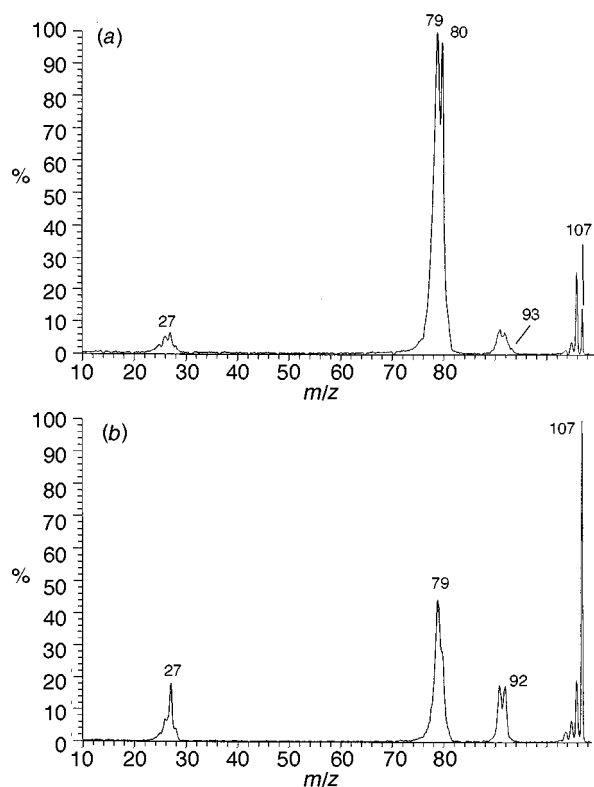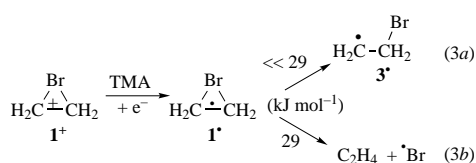
**Fig. 4** Neutralization–reionization (NR) spectra of (*a*) ethylene bromonium cation **1**$^+$ and (*b*) 1-bromoethyl cation **2**$^+$



yields the 2-bromoethyl radical **3**$^{\bullet}$, as inferred by Holmes and Lossing.[25]

Some **1**$^{\bullet}$ or **3**$^{\bullet}$ may decompose to $C_2H_4 + {}^{\bullet}Br$ [reaction (3*b*)]. Upon reionization, these neutrals would contribute to the $C_2H_{0-4}^+$ (*m/z* 24–28) and Br$^+$ (*m/z* 79) signals present in the NR spectrum of **1**$^+$ [Fig. 4(*a*)]; the same signals can also arise from dissociations of reionized **3**$^{\bullet}$. Reionization of **3**$^{\bullet}$ gives the 2-bromoethyl cation **3**$^+$ which is unstable.[12] Any **3**$^+$ formed below the dissociation threshold would collapse back to bridged ion **1**$^+$, as the cyclization **3**$^+ \rightarrow$**1**$^+$ requires no activation energy;[12] the remaining amount of **3**$^+$ decomposes to yield the fragments observed in the NR spectrum. Dissociating **3**$^+$ should lose $CH_2$ more readily than ${}^{\bullet}CH_3$; indeed, the [*m/z* 93]:[*m/z* 92] ratio is higher in the NR spectrum of precursor ion **1**$^+$ (whose redox sequence leads to **3**$^+$) than in the NR spectrum of precursor ion **2**$^+$ (Fig. 4).

Several factors can account for the differences between CAD and NR spectra of bromonium ion **1**$^+$ [Fig. 1(*a*) *vis à vis* 4(*a*)], *inter alia* (*a*) internal energy effects,[33,34] (*b*) partial dissociation of neutral **1**$^{\bullet}$ (*vide supra*)[35] and (*c*) the fact that the NR spectrum also samples ion **3**$^+$ while the CAD spectrum does not.

Electron exchange at keV translational energies is a vertical (Franck–Condon) transition, completed within femtoseconds.[17–19] The cross-sections of such reactions depend on their Franck–Condon factors, which in turn are influenced by the bond lengths and angles in the equilibrium structures of reduced and oxidized forms. Since the NR sequence **1**$^+ \rightarrow$**1**$^{\bullet} \rightarrow$**3**$^{\bullet} \rightarrow$**3**$^+ \rightarrow$**1**$^+$ involves more substantial structural changes than the NR sequence **2**$^+ \rightarrow$**2**$^{\bullet} \rightarrow$**2**$^+$, it should suffer from a poorer efficiency. Table 1 confirms this expectation. The NR yield for recovered $C_2H_4Br^+$ (*m/z* 107) is 30 times smaller

**Table 1** Neutralization–reionization yields in the NR (TMA/O$_2$) spectra of $C_2H_4Br^{+}$ [a]

| Precursor ion | Recovery peak | Total ions |
|---|---|---|
| $H_2C \overset{Br}{\underset{+}{\diagup}} CH_2$   **1**$^+$ | $2.4 \times 10^{-6}$ | $1.9 \times 10^{-4}$ |
| $H_3C - \overset{+}{C}H - Br$   **2**$^+$ | $7.2 \times 10^{-5}$ | $4.9 \times 10^{-4}$ |

[a] Calculated by dividing the flux of the recovery peak or the flux of all NR products by the flux of the unattenuated precursor ion being subjected to neutralization–reionization (peak areas, ± 30%).

for **1**$^+$ than for **2**$^+$. The total ion flux resulting after NR (*m/z* 24–107) is also smaller for **1**$^+$ than for **2**$^+$ (by *ca.* three-fold).

## Conclusions

$C_2H_4Br^+$ isomers **1**$^+$ and **2**$^+$ undergo the same threshold decomposition, *viz.* HBr loss to yield $C_2H_3^+$. On the other hand, their collision-induced dissociations as well as their charge permutation reactions differ substantially, allowing for an unequivocal distinction. The NR spectra of bridged ion **1**$^+$ and linear ion **2**$^+$ are consistent with the generation of 2- and 1-bromoethyl radicals (**3**$^{\bullet}$ and **2**$^{\bullet}$), respectively, upon neutralization. Radical **3**$^{\bullet}$ arises from an incipient bridged radical **1**$^{\bullet}$, which appears to lie close in energy to **3**$^{\bullet}$, rearranging to **3**$^{\bullet}$ without appreciable activation energy ($\ll$29 kJ mol$^{-1}$). Upon further reduction of radicals **2**$^{\bullet}$ and **3**$^{\bullet}$, a stable surviving $C_2H_4Br^-$ anion is observed only for **2**$^{\bullet}$.

## Acknowledgements

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