

Characterization of the $C_3H_6O^{+\cdot}$ Ion from 2-Methoxyethanol. Mixture Analysis by Dissociation and Neutralization–Reionization*

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The $C_3H_6O^{+\cdot}$ ion formed upon the dissociative ionization of 2-methoxyethanol is identified by a combination of several tandem mass spectrometry methods, including metastable ion (MI) characteristics, collisionally activated dissociation (CAD), and neutralization–reionization mass spectrometry (NRMS). The experimental data conclusively show that 2-methoxyethanol molecular ion, namely, $HOCH_2CH_2OCH_3^+$, loses H_2O to yield mainly the distonic radical ion $\cdot CH_2CH_2OCH_2^+$ along with a smaller amount of ionized methyl vinyl ether, namely, $CH_2=CHOCH_3^+$. Ring-closed products, such as the oxetane or the propylene oxide ion are not observed. The proportion of $\cdot CH_2CH_2OCH_2^+$ increases with decreasing internal energy of the 2-methoxyethanol ion, which indicates a lower critical energy for the pathway leading to this product than for the competitive generation of $CH_2=CHOCH_3^+$. The present study also uses MI, CAD, and NRMS data to assess the structure of the distonic ion $^+(CH_3)CHOCH_2\cdot$ (ring-opened ionized propylene oxide) and evaluate its isomerization proclivity toward the methyl vinyl ether ion. (*J Am Soc Mass Spectrom* 1995, 6, 1030–1036)

The unimolecular chemistry and ion–molecule reactions of gaseous $C_3H_6O^{+\cdot}$ cations have been studied extensively by theory [1–3] as well as mass spectrometry experiments [4–20] for over two decades now. Several of these investigations concerned the structure of the $C_3H_6O^{+\cdot}$ ion(s) arising via H_2O elimination from ionized 2-methoxyethanol (ME) [4, 5, 12–14]. This bifunctional precursor ion can undergo competitive fragmentations that yield different $C_3H_6O^{+\cdot}$ product ions (Scheme I; [8, 21]).

By using collisionally activated dissociation (CAD) [22], van de Sande and McLafferty [4] first identified the $C_3H_6O^{+\cdot}$ product from ME as a mixture of ionized oxetane (**b**) and methyl vinyl ether (**c**). Later, Holmes and co-workers [12] showed by deuterium labeling that the cleaved H_2O molecule incorporates the hydroxylic H atom and one H atom from either the methyl group or the methylene group next to the ether oxygen (see Scheme I). CAD on the fragment ion showed further that transfer of the methyl hydrogen leads to ionized oxetane (**b**) whereas transfer of the methylene hydrogen generates ionized propylene oxide (**e**); no complete H-atom randomization was detected during these reactions [12]. Similar labeling studies of Audier et al. [13] confirmed that the methylene group adjacent to the hydroxyl substituent of

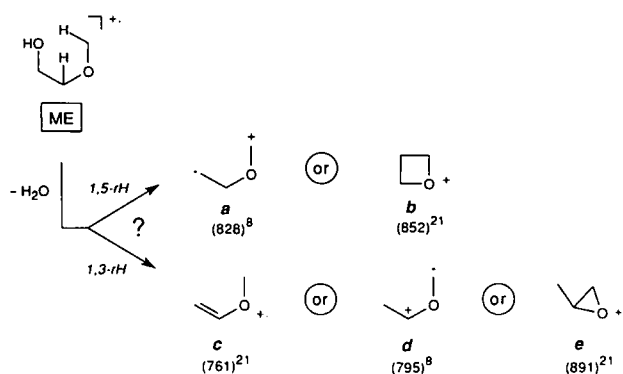
2-methoxyethanol does not participate in the water loss. These authors proposed, however, that the cleavage of H_2O proceeds after 6 H atoms (namely, $HO-$, CH_2-O- , and $-O-CH_3$) have lost their positional identity through equilibration with three distonic isomers, ultimately giving rise to ionized oxetane (**b**) [13] and/or its distonic ring-opened isomer **a** [14].

The problems encountered in the characterization of the $[ME - H_2O]^{+\cdot}$ ion partly originate from the fact that certain cationic isomers cannot be distinguished adequately by metastable ion (MI) or CAD spectra alone [22, 23]. In such cases, ion–molecule reactions and/or neutralization–reionization (NR) [24–26] may offer the additional information needed to determine or confirm the unknown structure(s). For example, NR and ion–molecule reactions have significantly helped to distinguish the distonic ion **a** from the conventional radical ion **b** [15, 17, 19, 20]. Here, we employ NR together with MI and CAD characteristics to elucidate the structure of the $C_3H_6O^{+\cdot}$ radical cation from 2-methoxyethanol.

These methods also are used to interrogate the unimolecular chemistry of ions **c**, **d**, and **e** whose ion–molecule reactions and photodissociation have led to contradictory conclusions. Bouma et al. [2] observed that ion **d**, formed from 4-methyl-1,3-dioxolane, transfers CH_2^+ to acetonitrile, whereas ion **e** does not, and they deduced from this result that ionized propylene oxide maintains the cyclic structure **e**. In a more recent study, van de Guchte and van der Hart [18] subjected

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Scheme 1. C₃H₆O⁺⁺ fragment ions from ionized 2-methoxyethanol. ΔH_f° values (kJ/mol) are given in parentheses. The superscript numbers that follow the parentheses denote reference numbers.

ions **c**, **d**, and **e** to ion-molecule reactions with pyridine and 1-hexene. Their results suggested that ionized propylene oxide undergoes complete rearrangement to ionized methyl vinyl ether, via **e** → **d** → **c**, and that distonic ion **d** partly isomerizes to **c**. Supporting evidence for such a situation was obtained from photodissociation at ~ 480 nm. This photon energy efficiently dissociates the distonic ion $\cdot\text{CH}_2\text{OCH}_2^+$ (ring-opened ethylene oxide), but only a fraction of **d** and none of **e**, consistent with partial (for **d**) or complete (for **e**) isomerization of these ions to **c**, which is transparent at 480 nm [18]. The elegant study of Tureček and McLafferty [6] on the dissociation mechanism of metastable propylene oxide ions showed that ions **c**–**e** with sufficient internal energy for decay indeed equilibrate. The present study sheds more light on the rearrangement proclivity of nondecomposing **c**–**e** and partially resolves the controversy about these C₃H₆O⁺⁺ cations.

Experimental

All experiments were performed with a modified VG AutoSpec (VG Analytical Ltd., Manchester, UK) tandem mass spectrometer of E₁BE₂ geometry [27]. This instrument contains three collision cells, one in the field-free region that follows the ion source (FFR-1) and two more between the magnet and E₂ (FFR-3). In MS/MS studies (MI, CAD, or NR) [22, 23], the first two sectors were employed as MS-1 and the second electrostatic analyzer as MS-2. In MS³ measurements [22, 23b] a fragment formed in FFR-1 was transmitted by E₁B to FFR-3, where it underwent dissociation or neutralization–reionization.

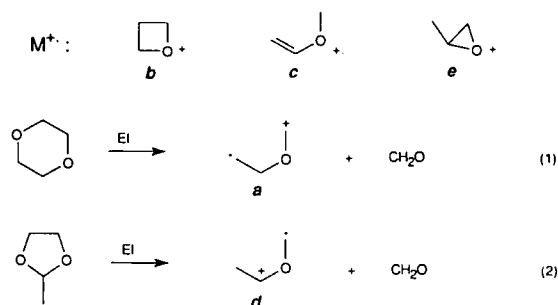
The samples were ionized by electron impact at 70 eV, and the ions so formed were accelerated to 8 keV (or as stated) upon exiting the ion source. The desired precursor ion (formed in the ion source or in FFR-1) was then mass-selected for acquisition of its MI, CAD, and NR spectra, which were recorded as described in detail elsewhere [15, 27]. The collision gases used were O₂ for CAD and reionization, and Xe or trimeth-

ylamine (TMA) for neutralization. The transmittance adjusted with each target effected ~ 20% attenuation of the precursor ion abundance. For MI fragments, kinetic energy releases were calculated from peak widths at half height ($T_{0.5}$) by using established procedures [23].

The spectra shown represent multiscan summations and are reproducible within $\pm 10\%$. The samples were acquired from Matheson Gas Products (Secaucus, NJ) and Aldrich Chemical Co. (Milwaukee, WI) and were introduced into the mass spectrometer without further alteration.

Results and Discussion

The structure of the C₃H₆O⁺⁺ product from 2-methoxyethanol was ascertained by comparison of its MI, CAD, and NR mass spectra to reference spectra of cations **a**–**e**. Molecular ions **b**, **c**, and **e** were formed from the corresponding neutral molecules, whereas distonic ions **a** and **d** were produced by dissociative ionization of 1,4-dioxane and 2-methyl-1,3-dioxolane, respectively (eqs 1 and 2):



Metastable Ion Dissociation

Our MI spectrum of C₃H₆O⁺⁺ from 2-methoxyethanol is very similar to that reported by Holmes and co-workers [12], displaying fragments of m/z 57 (H· loss; 100%), 43 ($\cdot\text{CH}_3$ loss; 58%), and 30 (CO loss; 8%). The peaks at m/z 57 and 30 are of gaussian type with $T_{0.5}$ values equal to 300 and 30 meV, respectively, whereas the signal at m/z 43 is flat-topped, with $T_{0.5} = 660$ meV. Analogous characteristics also were found for the distonic ion **a**, except that pure **a** forms much less m/z 43 [15]. The extra amount of m/z 43 fragments in the [ME – H₂O]⁺⁺ beam suggests that an additional isomer, which can contribute to this product, is cogenerated. Most likely candidates are ions **c**, **d**, or **e**, whose MI spectra are dominated by broad, flat-topped m/z 43 peaks (as was shown for isomers **c** and **e** by Tureček and McLafferty [6] as well as Lifshitz [10]). Which C₃H₆O⁺⁺ ions are actually formed from 2-methoxyethanol is more precisely revealed by CAD and NR analysis.

Collisionally Activated Dissociation

The CAD spectrum of $[\text{ME} - \text{H}_2\text{O}]^{++}$ (Figure 1a) is most similar to the CAD spectrum of distonic ion **a** (Figure 1b), which substantiates that ring-opened oxetane is the major $\text{C}_3\text{H}_6\text{O}^{++}$ isomer arising upon H_2O loss from ionized 2-methoxyethanol. Note that both these spectra include a prominent product of m/z 44 (CH_2 elimination), which is diagnostic for the $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ connectivity [15]. Such a fragment is either absent or much less abundant in the reference CAD spectra of isomers **b** (Figure 1c) and **c-e** (Figure 2). Other important CAD features of the ring-opened ion **a**, which are duplicated upon CAD of $[\text{ME} - \text{H}_2\text{O}]^{++}$, are the formation of $\text{C}_3\text{H}_6\text{O}^{++}$ dications (m/z 29) and the very low abundance of $\text{C}_3\text{H}_{0-3}^+$ (m/z 36-39). In sharp contrast, the ring-closed ion **b** shows the opposite characteristics (Figure 1a,b versus 1c) [15]. Also, this ion yields a sizable m/z 55 fragment that is much smaller for **a** and $[\text{ME} - \text{H}_2\text{O}]^{++}$. Undoubtedly H_2O cleavage from ME^{++} yields the distonic ion **a**, but oxetane radical ion (i.e., **b**) is not formed in any appreciable extent.

The CAD spectra of $[\text{ME} - \text{H}_2\text{O}]^{++}$ (Figure 1a) and **a** (Figure 1b) are not identical. For example, the former contains more abundant m/z 15 and 42-43 peaks, which verifies that 2-methoxyethanol must coproduce other $\text{C}_3\text{H}_6\text{O}^{++}$ isomer(s) [12]. The differences between Figure 1a and b can be accounted for if some **c**, **d**, or **e**

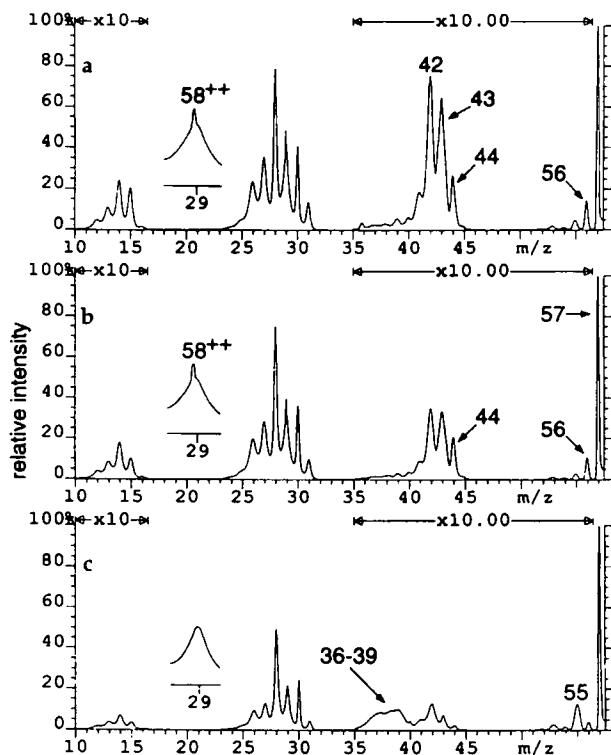


Figure 1. CAD spectra of (a) the $\text{C}_3\text{H}_6\text{O}^{++}$ ion from 2-methoxyethanol, $[\text{ME} - \text{H}_2\text{O}]^{++}$; (b) distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$, **a**, and (c) cyclic oxetane ion, **b**. The insets show the peak of m/z 29 in expanded scale.

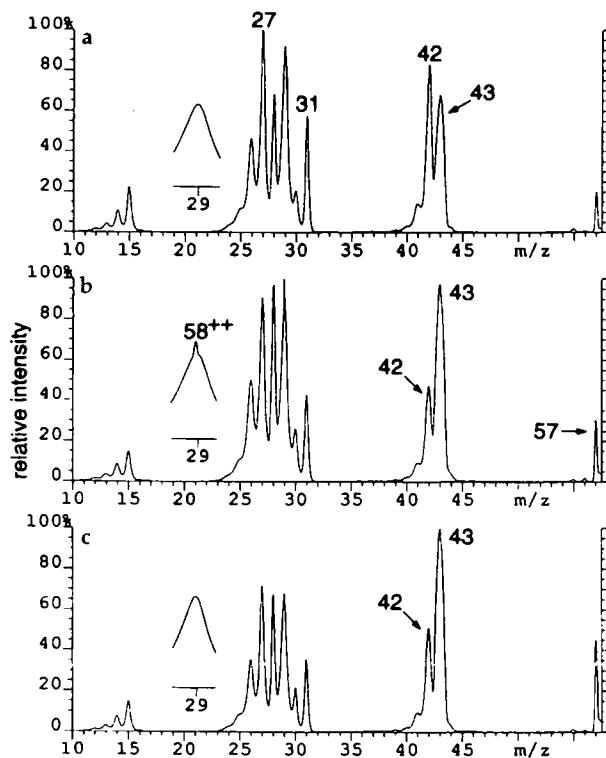


Figure 2. CAD spectra of (a) methyl vinyl ether ion, **c**, (b) distonic ion $^+(\text{CH}_3)\text{CHOCH}_2$, **d**, and (c) cyclic propylene oxide ion, **e**. The insets show the peak of m/z 29 in expanded scale.

is cogenerated. CAD of these latter isomers (Figure 2) leads to substantially more m/z 15 and 42-43 than CAD of ion **a** and, hence, any admixture of **c-e** would explain the mentioned discrepancies. Unfortunately, the CAD spectra of **c-e** are not sufficiently distinct from each other to unequivocally pinpoint which ion is present in $[\text{ME} - \text{H}_2\text{O}]^{++}$. Based on the abundance ratio $[m/z 42]:[m/z 43]$ observed for the unknown isomer (Figure 1a), ionized methyl vinyl ether (Figure 2a) is the best match. It must be kept in mind, however, that the relative abundance of m/z 43, which is the major metastable product of ions **c-e** (vide supra), could be sensitive to internal energy effects too. For this reason, we can conclude only tentatively at this point that isomer **c** is the second $\text{C}_3\text{H}_6\text{O}^{++}$ structure that emerges from the 2-methoxyethanol ion. Corroborating proof is provided by the NR spectra.

Neutralization-Reionization

The NR Xe/O_2 spectra of ring-opened ion **a** (Figure 3b) and of cyclic ion **b** (Figure 3c) have been discussed in detail previously [15]. They differ markedly from each other owing to the different stabilities of the corresponding neutral intermediates. Neutralization of **a** yields the weakly bound diradical $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2\cdot$ that decomposes extensively and with large kinetic energy release to $\text{CH}_2=\text{CH}_2$ (28 u) + $\text{O}=\text{CH}_2$ (30 u) [15]. As a result, substantial peak broadening is

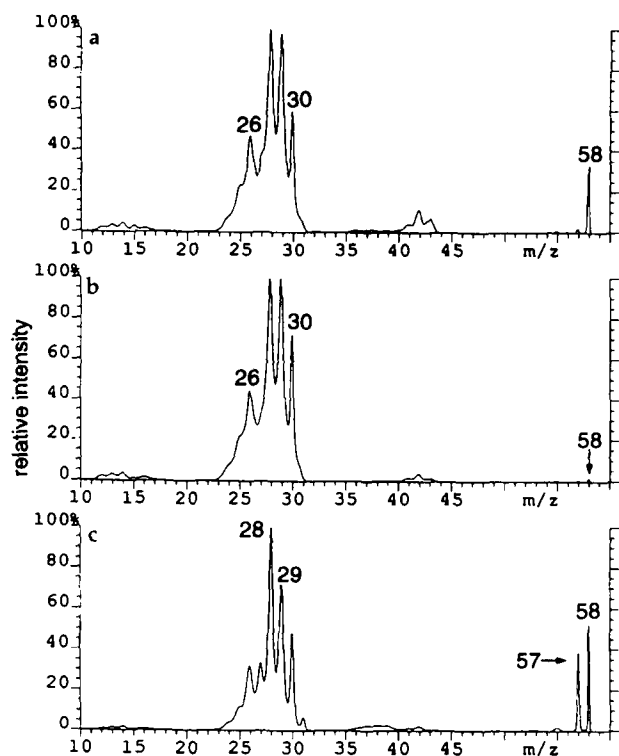


Figure 3. NR Xe/O₂ spectra of (a) the C₃H₆O⁺ ion from 2-methoxyethanol, [ME - H₂O]⁺; (b) distonic ion ·CH₂CH₂OCH₂⁺, a, and (c) cyclic oxetane ion, b.

observed after reionization for m/z 24–30. Only a small fraction of neutralized a survives intact based on the minuscule relative intensity of the survivor ion (m/z 58) and of the fragments above m/z 30 in Figure 3b. Neutralization of ion b, on the other hand, produces the stable oxetane molecule. Its reionization yields a large survivor ion (Figure 3c) and a fragmentation pattern quite similar to that in the CAD spectrum of b, in keeping with negligible dissociation of the intermediate neutral [15]. Of importance for the present study is the striking similarity of peak shapes and relative abundances for m/z 24–30 in the NR spectra of [ME - H₂O]⁺ (Figure 3a) and the distonic ion a (Figure 3b). This analogy reinforces the earlier conclusion that distonic ion a is the major constituent of [ME - H₂O]⁺.

Compared to the reference spectrum of a (Figure 3b), the NR spectrum of [ME - H₂O]⁺ (Figure 3a) contains more abundant fragments above m/z 30 and a larger survivor ion. These features affirm that at least one more C₃H₆O⁺ isomer is formed from 2-methoxyethanol. This isomer cannot be ionized oxetane (b) because this ion generates, inter alia, a much greater m/z 57 fragment than actually seen; compare Figure 3a vis à vis 3c. In contrast, isomers c, d, or e are possible candidates. All three yield little m/z 57, but substantial amounts of m/z 41–43 and 58, as does [ME - H₂O]⁺ (Figure 4 vis à vis 3a). Note, however, that the relative abundances of m/z 41–43 and 58 in the NR spectrum of [ME - H₂O]⁺ agree well only

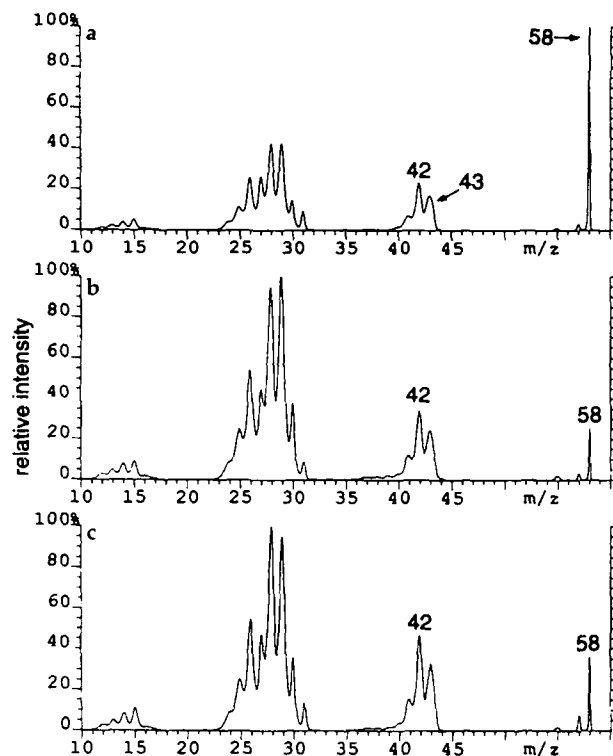


Figure 4. NR Xe/O₂ spectra of (a) methyl vinyl ether ion, c, (b) distonic ion ⁺(CH₃)CHOCH₂, d, and (c) cyclic propylene oxide ion, e.

with those found for ionized methyl vinyl ether, c. Hence, c must be the additional C₃H₆O⁺ isomer in the [ME - H₂O]⁺ beam.

Supporting evidence that the second C₃H₆O⁺ product from 2-methoxyethanol is cation c comes from the neutralization-reionization yield (i.e., absolute abundance) of the survivor ion (Table 1). The intensity of C₃H₆O⁺ (m/z 58) in the NR spectrum of [ME - H₂O]⁺ is 4.5×10^{-5} times lower than that of the [ME - H₂O]⁺ precursor ion that is subjected to NR (Table 1). This yield is larger than the yield observed for pure a (2.2×10^{-6}), which is the predominant component of [ME - H₂O]⁺ (vide supra). Admixtures of ions d and/or e cannot increase 2.2×10^{-6} to the observed value of 4.5×10^{-5} ; this is only possible with ions b and c, which exhibit superior NR efficiencies. However, b is incompatible with the NR spectrum of [ME - H₂O]⁺ (cf. Figure 3c versus 3a). Consequently, only ionized methyl vinyl ether, c, can be the minor constituent of the C₃H₆O⁺ ions generated from 2-methoxyethanol. The absolute abundance of the survivor ion in Figure 3a is consistent with [ME - H₂O]⁺ being a mixture of ~86% distonic ion a and ~14% methyl vinyl ether ion c; the intensities of all other ions in the NR spectrum agree well with this composition.

H₂O Loss from Metastable 2-Methoxyethanol Ions

Metastable 2-methoxyethanol ions, which possess internal energies lower than ME⁺ dissociating in the ion

Table 1. Neutralization-reionization (NR) yields for survivor ions (m/z 58)^a

Precursor molecule	Incipient $C_3H_6O^{++}$ ion	NR yield ^b	
		Xe/O ₂	TMA/O ₂
2-Methoxyethanol		4.5×10^{-5}	
1,4-Dioxane	a	2.2×10^{-6}	
Oxetane	b	1.2×10^{-4}	
Methyl vinyl ether	c	3.0×10^{-4}	7.3×10^{-4}
2-Methyl-1,3-dioxolane	d	2.3×10^{-5}	5.9×10^{-5}
Propylene oxide	e	3.8×10^{-5}	1.0×10^{-4}

^a Intensity of the $C_3H_6O^{++}$ survivor in the NR spectrum divided by the intensity of the $C_3H_6O^{++}$ precursor ion undergoing NR [27]. Estimated error, $\pm 20\%$.

^b In the notation A/B, A and B denote the neutralization and reionization targets, respectively.

source [22, 23], produce a distinct $C_3H_6O^{++}$ mixture. This is evident from a comparison of the CAD and NR spectra of metastably generated $[ME - H_2O]^{++}$ (Figure 5) to the corresponding spectra of source-generated $[ME - H_2O]^{++}$ (Figures 1a and 3a, respectively). $C_3H_6O^{++}$ precursor ions formed in the metastable window yield less m/z 42-43 upon CAD and fewer ions above m/z 30 upon NR. Such CAD and NR products are characteristic for ionized methyl vinyl ether, **c** (see above sections). Hence, ME ions of low internal excitation generate a larger proportion of distonic ion **a** and a smaller proportion of methyl vinyl ether ion **c**. Specifically, the absolute intensity of the survivor ion (m/z 58) in the NR spectrum of Figure 5b points out that metastably formed $[ME - H_2O]^{++}$ is composed of $\sim 98\%$ **a** and $\sim 2\%$ **c**.

The molecular ion of methyl vinyl ether, **c**, is thermodynamically 67 kJ/mol more stable than the distonic ion **a** (Scheme 1). The predominant formation of ion **a** at lower internal energy indicates, therefore, that

its formation must require a smaller barrier than formation of the more stable ion **c**. These two $C_3H_6O^{++}$ products may arise from ionized 2-methoxyethanol through a 1,5- or 1,3-H rearrangement, respectively (Scheme 1). The discrimination against isomer **c** at low internal energy could then result from the higher activation energy of the route involving the 1,3-H shift vis à vis the route commencing with the 1,5-H migration. [The metastable ME^{++} ions that lead to $\sim 98\%$ **a** and $\sim 2\%$ **c** dissociate in FFR-1 (see Experimental) and have an average lifetime of 1 μ s. Metastable ME^{++} ions that decompose in FFR-3 have a much longer lifetime (12 μ s) and thus a substantially lower internal energy. They give rise to a simple gaussian $C_3H_6O^{++}$ signal with $T_{0.5} = 23$ meV. The peak shape and $T_{0.5}$ value observed suggest that only ion **a** is formed at threshold. Generation of ion **c**, which requires a higher barrier and is more stable, would have led to a considerably broader signal]. The possibility that **c** originates from isomerization of energetically excited **a** can be excluded based on our recently reported study of distonic ion **a**, which clearly documented that **a** of higher internal energy content maintains its structure [15]. Also the labeling data of Holmes and co-workers [12] would be incompatible with **c** being formed via $ME^{++} \rightarrow a \rightarrow c$.

Distonic Radical Ion $^+(CH_3)CHOCH_2$ (**d**)

Ionized propylene oxide (**e**), its C—C ring-opened form (**d**), and methyl vinyl ether ion (**c**) behave very similarly upon CAD (Figure 2). Except for m/z 43, which is the major metastable fragment of these $C_3H_6O^{++}$ isomers (vide supra) [6, 10], all other singly charged CAD products are generated with practically superimposable relative abundances. There is, however, a noticeable difference: only distonic ion **d** gives rise to a recognizable charge-stripping product— $C_3H_6O^{++}$ of m/z 29 (Figure 2b). Generally, distonic ions produce more dications upon CAD than do their conventional (e.g., ring-closed) isomers [15, 28]. The presence of $C_3H_6O^{++}$ in Figure 2b affirms therefore that **d** represents a stable, distinct $C_3H_6O^{++}$ species that is separated by a finite barrier from the more stable cation **c** [3, 18].

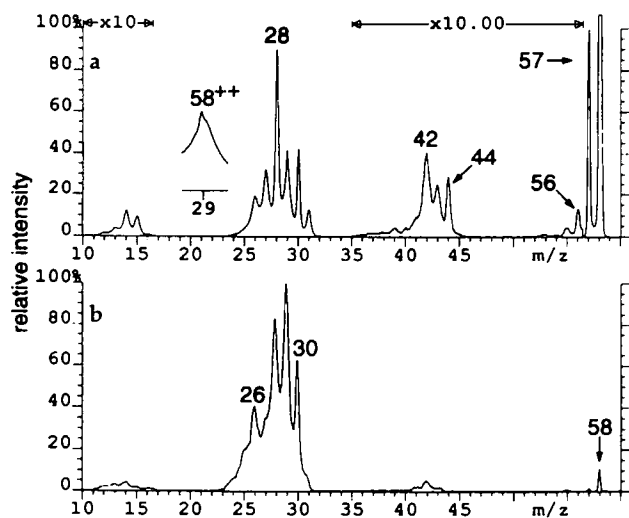
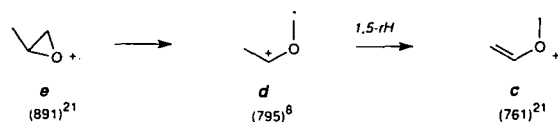


Figure 5. (a) CAD and (b) NR spectra of $C_3H_6O^{++}$ formed from metastable 2-methoxyethanol ions. This $C_3H_6O^{++}$ cation has a kinetic energy of 6.1 keV. The NR yield of the survivor ion (m/z 58) in (b) is 2.9×10^{-6} . For comparison, the 6.1-keV NR yields of isomers **a** ($\cdot CH_2CH_2OCH_2^+$) and **c** ($CH_2=CHOCH_2^+$) are 9.5×10^{-7} and 1.2×10^{-4} , respectively. The inset in (a) shows the peak of m/z 29 in expanded scale.

More information about the fate of ions **c–e** is disclosed by NR spectra, acquired by using either xenon or trimethylamine (TMA) for neutralization and O₂ for reionization (Figures 4 and 6, respectively). NR of cation **c** consistently yields the largest survivor ion and the fewest fragments, in line with the higher stability of ion **c** over ions **d** and **e** (Scheme II) and of neutral methyl vinyl ether [21] over the propylene oxide molecule [21] and diradical $\cdot(\text{CH}_3)\text{CHOCH}_2\cdot$ (neutral counterpart of **d**; $\Delta H_f^\circ(\cdot(\text{CH}_3)\text{CHOCH}_2\cdot) = 126$ kJ/mol; estimated from $\Delta H_f^\circ(\text{CH}_3\text{CH}_2\text{OCH}_3) = -216$ kJ/mol [21] and the C–H bond dissociation energies compiled by McMillen and Golden [29]). This difference indicates that the proportion of nondissociating **d** and **e** that has isomerized to **c**, which is the most stable of these three isomers, must be small (vide infra).

The presence of a survivor ion (m/z 58) in the NR spectra of **d** (Figures 4b and 6b) suggests that the diradical $\cdot(\text{CH}_3)\text{CHOCH}_2\cdot$, which is accessed in the neutralization step, may be a bound species. Related diradicals that have been found to reside in energy wells are $\cdot\text{CH}_2\text{OCH}_2\cdot$ [30], $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2\cdot$ [15], and $\cdot\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\cdot$ [31]. We cannot, however, exclude the possibility that a small fraction of **d** isomerized to **c** and that the survivor ion in Figures 4b and 6b is mainly due to this admixture of **c**. An upper limit of the relative amount of **c** contained in the C₃H₆O⁺ beam of **d** can be calculated from the absolute abundances (i.e., NR yields) of m/z 58 in the NR



Scheme II. Ions **c–e**. ΔH_f° values (kJ/mol) are given in parentheses. The superscript numbers that follow the parentheses denote reference numbers.

spectra of **c** and **d** (Table 1). Based on the NR Xe/O₂ data, distonic ion **d** contains at most $\sim 8\%$ **c**; the same value is obtained from the TMA/O₂ data. Similarly, the absolute abundances of m/z 58 in the NR spectra of **e** (Figures 4c and 6c) point out that the C₃H₆O⁺ beam from propylene oxide contains $< 14\%$ **c**.

Comparison of Figures 4 and 6 further reveals that the NR spectra of **c–e** change when the neutralization target is replaced. TMA leads to larger survivor ions and hence less overall fragmentation than does Xe; changes also are observed in relative fragment ion abundances. The exact reason(s) for these variations are unknown. Two plausible explanations follow: (1) The neutralizing collision may cause some concomitant CAD [24–26]. Any neutral fragments formed during this CAD will overlap (upon ionization) with the fragments that arise from the reionized precursor itself, thus leading to an apparent decrease of the survivor ion. Thus, the higher fragment ion intensities with Xe could be due to the higher CAD efficiency of this target vis à vis TMA. This recently was shown to be the case for C₆₀⁺ precursors [32]. (2) The lower fragmentation degree with TMA (Figure 6) than with Xe (Figure 4) also may be due to the deposition of lower average internal energies on NR TMA/O₂ versus NR Xe/O₂ [15, 33].

Conclusions

Combined MI, CAD, and NR experiments conclusively identify the C₃H₆O⁺ ions that arise by water loss from ionized 2-methoxyethanol as a mixture of the distonic ion $\cdot\text{CH}_2\text{CH}_2\text{OCH}_2^+$ (**a**, ring-opened ionized oxetane) and the methyl vinyl ether ion (**c**). The predominant component is ion **a**. The minor component **c** is thermodynamically more stable but must require a higher critical energy, because it is formed with a lower yield from metastable precursor ions than from the more excited precursor ions that decompose in the ion source. We find no evidence for the generation of ionized oxetane (**b**), propylene oxide (**e**), or ring-opened propylene oxide (**d**).

The MI spectra of ions **c**, **d**, and **e** are indistinguishable. The CAD and NR spectra of these C₃H₆O⁺ isomers present, however, two structurally significant differences: (1) only **d** yields a discernible charge stripping product upon CAD and (2) the absolute and relative abundances of neutralized–reionized m/z 58 (survivor ion) are ~ 10 times higher for **c** than for **d** or **e**. [No additional information is obtained by charge

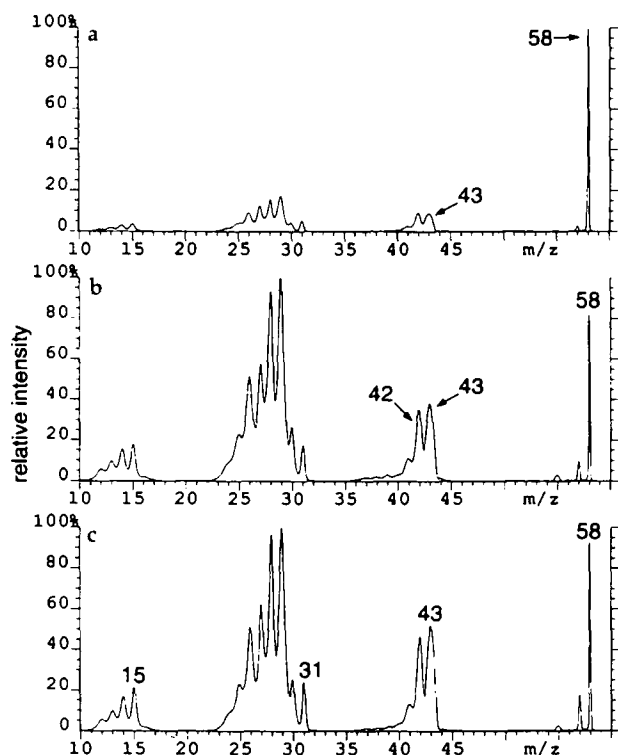


Figure 6. NR TMA/O₂ spectra of (a) methyl vinyl ether ion, **c**, (b) distonic ion $\cdot(\text{CH}_3)\text{CHOCH}_2^+$, **d**, and (c) cyclic propylene oxide ion, **e**.

reversal of c-e [15] or by collision-induced dissociative ionization [25, 26] of the neutral losses released upon CAD of c-e ("neutral fragment-reionization"). The charge-reversal mass spectra mainly show products of m/z 43, 41, 31, 25, and 16. The neutral fragment-reionization spectra are dominated by m/z 24-30.] Our CAD and NR results verify the predicted stability of distonic ion **d** and indicate that < 8% of **d** and < 14% of **e** rearrange to more stable methyl vinyl ether ion, **c**. The absence of a charge-stripping product in the CAD spectrum of **e** suggests that nondissociating ionized propylene oxide does not isomerize appreciably to **d**. Hence, the majority of **e** (> 86%) either retains its incipient structure or rearranges to another yet unknown C₃H₆O⁺ cation.

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