
Fragmentation of 1- and 3-Methoxypropene Ions

Another Part of the $C_4H_8O^+$ Potential Energy Surface

J. R. Cao, M. George, and John L. Holmes

Department of Chemistry, University of Ottawa, Ottawa, Canada

The fragmentation mechanisms of metastable ionized 1- and 3-methoxypropene have been examined in detail by using ionization and appearance energy measurements, metastable ion and collisional activation mass spectra, and a variety of isotopically labeled molecules. These metastable $C_4H_8O^+$ ions fragment by loss of H, CH_3 , and H_2CO , and the experimental observations allowed the construction of the potential energy diagram which describes their interconversion and the participation of four other distonic and carbene $C_4H_8O^+$ ions. It was found that these two methyl alkenyl ether ions had no common reaction channel with either the 2-methoxy isomer or with any of the alcohol, keto, or enol $C_4H_8O^+$ isomers which previously have been extensively studied. (*J Am Soc Mass Spectrom* 1992, 3, 99-107)

The gas-phase ion chemistry of isomeric C_4H_8O species has been investigated for many years and their present status has recently been thoroughly reviewed [1]. In brief summary, most metastable $C_4H_8O^+$ ions that have alcohol, aldehyde, ketone, and enol structures decompose largely by rearranging to ionized 2-butanone or to the methyl vinyl alcohol ion and then losing methyl or ethyl with small kinetic energy releases (as measured from the half-height widths of the metastable peaks), $T_{0.5} = 10-40$ meV. Mechanisms for the isomerization of these ions and their potential energy surface have been proposed [2], in which keto-enol tautomerism, involving interalia, distonic ions, plays an important role. However, conspicuously absent is any apparent connection between the many keto and enol-type $C_4H_8O^+$ ion structures and their alkenyl ether isomers. To explore this aspect of $C_4H_8O^+$ ion chemistry we have studied in detail the energetics and fragmentation behavior of the isomers allyl methyl ether (3-methoxypropene), $CH_2=CHCH_2OCH_3$, 1, and 1-methoxy propene, $CH_3CH=CHOCH_3$, 2,

by standard procedures [4]. Appearance energies using energy-selected electrons were measured with an apparatus that comprised an electron monochromator together with a quadrupole mass analyzer and mini-computer data system [5]. Metastable peak appearance energies were measured on a Kratos-AEI MS902S mass spectrometer as described earlier [6]. Kinetic energy release distributions were evaluated by an analytical method [7]. $CD_3OCH_2CH_2CH_2OH$ and $CH_3OCH_2CH_2CH_2OH$ were obtained from another study [8]; $CH_2CHCH_2O^{13}CH_3$ and $CH_2CHCH_2OCD_3$ were prepared by reacting $^{13}CH_3I$ and CD_3I with CH_2CHCH_2ONa in excess allyl alcohol. $CH_3CHCHOCH_3$ was prepared by reacting $CH_2=CHCH_2OCH_3$ with $(CH_3)_3COK$. The $CD_2CHCH_2OCH_3^+$ ion was generated from ionized $CH_3OCH_2CH_2CD_2OH$ (by loss of H_2O); the latter compound was prepared by the reaction of $CH_3OCH_2CH_2C(O)OCH_3$ with $LiAlD_4$. Isotopic purity was checked by nuclear magnetic resonance (NMR) or mass spectrometric analyses.

Experimental

Mass spectrometric measurements were performed by using a modified VG Analytical (Winsford, UK) ZAB-2F mass spectrometer [3]. Metastable ion (MI) and collisional activation (CA) mass spectra were recorded

Results and Discussion

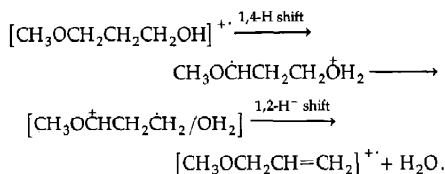
Allyl Methyl Ether

The low energy electron ionization (EI) mass spectra of this compound and related larger molecules have very recently been reported [9] together with some proposed reaction mechanisms. The MI and CA mass spectra of ionized allyl methyl ether, 1, are shown in

Address reprint requests to John L. Holmes, Department of Chemistry, University of Ottawa, 32 George Gliniski, Ottawa, Ontario, Canada K1N 6N5.

Table 1. The MI mass spectrum contains three peaks: at m/z 71, H⁺ loss (kinetic energy release calculated from the half-height width of the metastable peak, $T_{0.5} = 136$ meV); at m/z 57, CH₃ loss ($T_{0.5} = 443$ meV); and at m/z 42, CH₂O loss, ($T_{0.5} = 21.5$ meV). These dissociations are quite different from those of the keto/enol C₄H₈O⁺ isomers [1, 2], all of which show major losses of CH₃ and C₂H₅ with small kinetic energy releases. It is already clear then, that the low energy ether ions have nothing in common with some of the other thoroughly investigated C₄H₈O⁺ isomers. The ionization energy (IE) of allyl methyl ether was measured to be 9.22 ± 0.05 eV, replacing an earlier value by ourselves [10], which at 9.56 eV, was too high. The ΔH_f° value for ionized **1** is thus 785 kJ mol^{-1} , using $\Delta H_f^\circ[\text{CH}_2\text{CHCH}_2\text{OCH}_3] = -105 \text{ kJ mol}^{-1}$ (by additivity) [11]. The appearance energy (AE) values for the three daughter ions were measured using energy-selected electrons (see Experimental) and were 10.20, 9.92, and 9.90, all ± 0.05 eV, for the H⁺, CH₃⁺, and CH₂O losses, respectively. These transition state energies are shown in the energy diagram (Figure 1) as TS3, TS2, and TS1, respectively.

The allyl methyl ether ion is also generated by the loss of H₂O from ionized 3-methoxy-propanol, with the resulting m/z 72 ion having the same MI and CA mass spectral characteristics as ion **1**⁺. The AE of m/z 72 was measured to be 9.78 ± 0.05 eV, leading to $\Delta H_f^\circ[\text{C}_4\text{H}_8\text{O}]^{+} = 800 \text{ kJ mol}^{-1}$ ($\Delta H_f^\circ[\text{CH}_3\text{OCH}_2\text{CH}_2\text{CH}_2\text{OH}] = -386 \text{ kJ mol}^{-1}$ [11], $\Delta H_f^\circ[\text{H}_2\text{O}] = -242 \text{ kJ mol}^{-1}$ [11]). The relatively large kinetic energy release for the above loss of H₂O, $T_{0.5} = 42$ meV, is in keeping with the ΔH_f° value of 800 kJ mol^{-1} , which is 15 kJ mol^{-1} above $\Delta H_f^\circ[\text{1}]^+$. A mechanism for this reaction is shown below



The deuterium-labeled precursors CD₃OCH₂CH₂CH₂OH and CH₃OCH₂CH₂CH₂OD lost only H₂O and HDO, respectively, indicating a lack of isotope positional mixing between the hydroxyl group and the remainder of the ion and no involvement of methyl hydrogen atoms in the water loss.

It is now necessary to consider the structure of the three fragment ions generated from **1**⁺. The ΔH_f° value for the C₃H₅⁺ ion produced by the CH₂O loss is calculated to be 959 kJ mol^{-1} using the above AE value, showing that it must have the propene structure ($\Delta H_f^\circ = 959 \text{ kJ mol}^{-1}$ [10]) rather than ionized cyclopropane ($\Delta H_f^\circ = 1004 \text{ kJ mol}^{-1}$ [10]).

For the [C₃H₅O]⁺ ion, thermochemical data are of little help because the large kinetic energy release

Table 1. Principal peaks in the metastable ion (MI) and collisional activation (CA)^a mass spectra of C₄H₈O⁺ ions

m/z	CH ₂ =CH-CH ₂ -OCH ₃ ⁺		CH ₃ -CH=CH-OCH ₃ ⁺	
	MI	CA	MI	CA
71	100	100	100	100
57	94	71	82	45
45		3		12
44		1		4
43	6	5	10	8
42	55	45	53	41
41		14		67
39		11		37
29		8		32
27		5		19
15		1		4

^a Collision gas, helium. CA mass spectrum was recorded at 10% beam reduction.

shows that the reaction must have a significant reverse energy barrier (see Figure 1). Two structures which are compatible with the transition state energy

are CH₃CH₂CH₂⁺ and CH₂CHCHOH⁺ whose heats of formation are 591 and 642 kJ mol⁻¹ [10], respectively. The MI and CA mass spectra of these two isomeric ions were compared with that of the ion produced from **1**. The results are shown in Tables 2 and 3. The metastable peak for the generation of m/z 29 from CH₃CH₂CH₂⁺ ions is very narrow (Table 2) and corresponds only to the loss of CO from ions of structure CH₃CH₂CH₂⁺ [12]. The broadest metastable peak, that from the C₃H₅O⁺ ion from CH₂CHCHOH(OH)CH₃⁺, **7**, has been shown to arise from loss of both CO and C₂H₄ from ions of structure CH₃CH₂CH₂⁺ and CH₂CHCHOH⁺, respectively [12, 13], with the latter as the major species present. The C₃H₅O⁺ ions from **1**, **2**, and **10** have slightly lower $T_{0.5}$ values (Table 2) indicating a greater proportion of CH₃CH₂CH₂⁺ relative to that formed by **7**. The kinetic energy release distribution for the metastable dissociation of C₃H₅O⁺ ions from **1** is shown in Figure 2 and the presence of the two components is clearly visible, and discernible in the metastable peak itself. The metastable peaks and kinetic energy release distributions for the same process for ions from **2**, **7**, and **10** are not shown here but are essentially similar to that for **1**. Careful inspection of the metastable peak for **7**, assuming that the peak is composed only of signals corresponding to the above CO and C₂H₄ losses, showed that for these ion source generated species at least 95% of them must have the CH₂CHCHOH⁺ structure. For the ions derived from **1**, the corresponding estimate is 90-95%. The CA mass spectra (Table 3) can be similarly rationalized; again, for these ion-source generated C₃H₅O⁺ ions, small differences between the spectra are observable, compatible with a mixture of the two C₃H₅O⁺ ions. Based on the low energy mass spectra

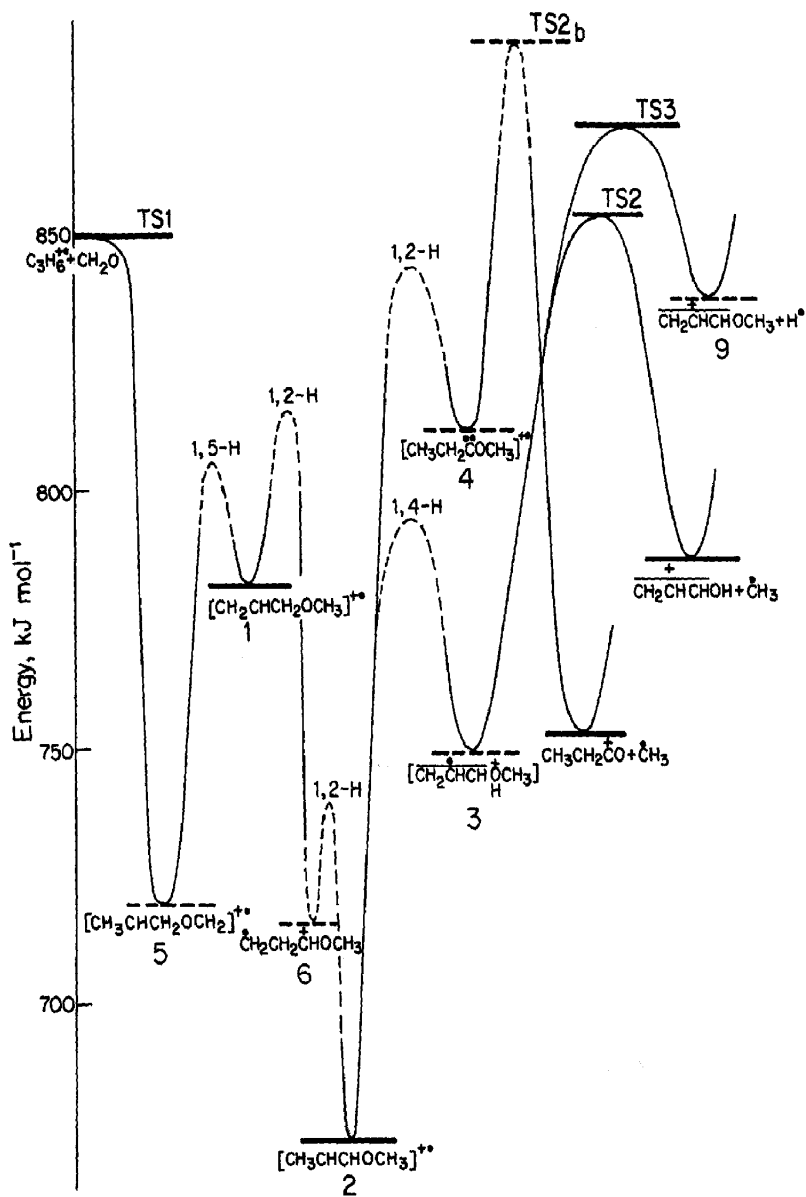


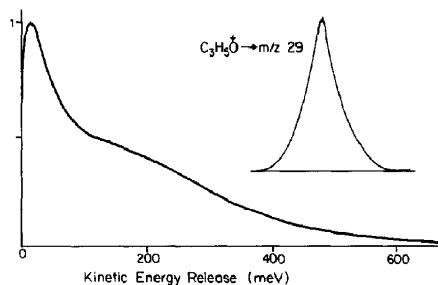
Figure 1. Potential energy surface for $C_4H_8O^+$ ions derived from 1- and 3-methoxypropene. Broken lines are for estimated energies, solid lines are from experimental measurements. The nature of the various H shifts is discussed in the text.

Table 2. Kinetic energy releases (meV) accompanying the metastable dissociation of $[C_3H_5O]^+$ ions from various precursor molecules

	CH_2CHCH_2OH 10	$CH_2CHCH_2OCH_3$ 1	$CH_2CHCH(OH)CH_3$ 7	$CH_3CHCHOCH_3$ 2	$CH_3CH_2C(O)OCH_3$ 8
	↓ -H	↓ -CH ₃	↓ -CH ₃	↓ -CH ₃	↓ -OCH ₃
	$C_3H_5O^+$	$C_3H_5O^+$	$C_3H_5O^+$	$C_3H_5O^+$	$CH_3CH_2\dot{C}O$
	↓ -(C ₂ H ₄ + CO)	↓ -(C ₂ H ₄ + CO)	↓ -(C ₂ H ₄ + CO)	↓ -(C ₂ H ₄ + CO)	↓ -CO
	<i>m/z</i> 29	<i>m/z</i> 29	<i>m/z</i> 29	<i>m/z</i> 29	<i>m/z</i> 29
<i>T</i> _{0.5}	43.6	46.2	54.4	46.4	2.1

of allyl methyl ether and labeled isotopomers Bowen et al. [9] proposed similar reactions.

Next, the $C_4H_7O^+$ ion produced by H[•] loss must be considered. The MI mass spectrum of this ion from allyl methyl ether has four peaks, loss of H[•]; H₂O, CO/C₂H₄, and H₂CO. Five isomeric $C_4H_7O^+$ ions and their MI and CA mass spectral characteristics have been described by Laderoute et al. [14]. These were $CH_2=CHC(OH)CH_3^+$, $CH_3CH=CHCH(OH)^+$, $CH_2=C(CH_3)CHOH^+$, $CH_3CH_2CH_2CO^+$, and $(CH_3)_2CHCO^+$, none of which displayed all of the above four fragmentations in their MI mass spectra. Therefore, either a mixture of ions is produced from $1^{+•}$ or a new, hitherto unexamined $C_4H_7O^+$ isomer is involved. The MI mass spectra of $C_4H_7O^+$ ions generated from four different precursors are shown in Table 4. The $C_4H_7O^+$ ion from 1 is clearly not that derived from 2-methyl-tetrahydrofuran. The MI mass spectra of the $C_4H_7O^+$ ions produced from 3,3-dimethylprop-1-ene-3-ol (by CH₃ loss) and but-1-ene-3-ol (by H[•] loss) [14] are similar to that from 1 except that they lack a peak at *m/z* 41. The MI and CA mass spectra of $C_4H_7O^+$ ions from a variety of precursor molecules have also been reported by Bouchoux et al.

**Figure 2.** Kinetic energy release distribution for the loss of 28 u from $C_3H_5O^+$ ions produced from allyl methyl ether. Inset is the corresponding metastable peak.

[15] but none of them had the dissociation characteristics identical with those of the ion from 1. Further consideration of the structure(s) to be assigned to this ion is best left to the next section, in which are discussed the mechanisms by which CH₂O, CH₃, and H[•] losses take place, together with the roles of other $C_4H_8O^+$ isomers on the potential surface.

Table 3. CA mass spectra of $C_3H_5O^+$ ions generated from five different precursors

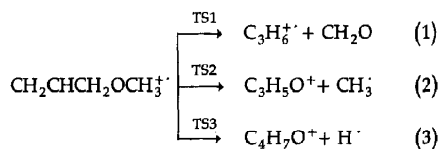
Neutral lost	CH_2CHCH_2OH S10 H [•]	$CH_2CHCH_2OCH_3$ 1 H [•]	$CH_2CHCH(OH)CH_3$ 7 CH ₃	$CH_3CHCHOCH_3$ 2 CH ₃	$CH_3CH_2C(O)OCH_3$ 8 CH ₃ OCH ₃
<i>m/z</i>					
55	14	14	26	20	1.6
53	2.7	3.0	4.3	4.6	1.4
42	4.2	4.9	3.8	4.9	6.5
41	1.5	1.6	0.8	1.7	1.8
39	5.7	5.7	10	9.8	1.3
38	3.9	4.3	7.1	6.9	1.1
37	3.0	3.4	5.2	3.0	1.3
31	7.2	7.1	14	9.2	0.1
30	1.2	1.2	1.9	1.2	< 0.1
29	100	100	100	100	100
28	5.7	5.9	3.3	4.3	7.9
27	14	15	18	18	11
26	6.6	7.3	8.1	6.9	5.7
25	1.5	1.8	1.9	1.4	1.4
15	0.3	0.8	0.5	0.6	0.7
14	0.3	0.8	0.5	0.5	0.8

Table 4. Relative abundances and kinetic energy releases ($T_{0.5}$, meV) accompanying metastable dissociation of $C_4(H, D)_7O^+$ ions generated from different precursors

m/z	$CH_2CHCH_2OCH_3$ 1 ↓ -H		$CH_2CHCH_2OCD_3$ 1 ↓ -H		$CH_2CH_2OCH(CH_3)CH_2$ ↓ -CH ₃		$CH_2CHC(CH_3)_2OH$ ↓ -CH ₃	
	$CH_2CHCHOCH_3^+$		$CH_2CHCHOCD_3^+$		$CH_2CH_2OCHCH_2^+$		$CH_2CHC(CH_3)OH^+$	
	MI	$T_{0.5}$	MI	$T_{0.5}$	MI	$T_{0.5}$	MI	$T_{0.5}$
56			25	30				
55			16	29				
53	22	29					24	20
46			100	88				
45			7	400				
44			13	400				
43	100	124	25	21	100	113	100	360
42			41	21				
41	38	21						

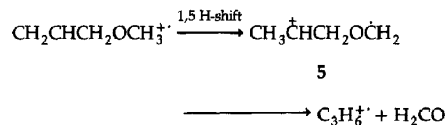
Fragmentation Mechanisms

The three reactions for which mechanisms must be proposed are



Reaction (1) proceeded at the calculated thermochemical threshold for the production of ionized propene plus H_2CO . The results on metastable, deuterium and ^{13}C -labeled 1^+ ions are shown in Table 5. First it is evident that there is a significant loss of positional

identity among H and D atoms prior to each metastable dissociation, but not to full randomization. However, the carbon atom which is lost as CH_2O and CH_3 is uniquely from the methyl group, as shown by the MI mass spectrum of ionized $CH_2CHCH_2O^{13}CH_3$, which contained signals only at m/z 42 and 57, respectively. The simplest mechanism for reaction (1) is shown below:



It involves the intermediacy of the distonic ion, 5. The ΔH_f° value for 5 can be estimated as follows.

$$\Delta H_f^\circ[CH_3CH_2O\overset{\ddagger}{C}H_2] = 594 \text{ kJ mol}^{-1} [10] \text{ and its}$$

Table 5. Metastable ion mass spectra of deuterium and ^{13}C -labeled allyl methyl ether ions

m/z	$CH_2CHCH_2OCH_3$ 1	$CH_2CHCH_2O^{13}CH_3$ 1*	$CD_2CHCH_2OCH_3$ 1 _a	$CH_2CHCD_2OCH_3$ 1 _b	$CH_2CHCH_2OCD_3$ 1 _c
74					(355) (-H)
73			(431) (-H)	(208) (-H)	21 (-D)
72		167 (-H)	39 (-D)	23 (-D)	
71	125 (-H)				
60					4 (-CH ₃)
59			100 (-CH ₃)	100 (-CH ₃)	33 (-CH ₂ D)
58			40 (-CH ₂ D)	46 (-CH ₂ D)	84 (-CHD ₂)
57	100 (-CH ₃)	100 (- $^{13}CH_3$)			100 (-CD ₃)
45					15 (-CH ₂ O)
44			75 (-CH ₂ O)	71 (-CH ₂ O)	38 (-CHDO)
43			18 (-CHDO)	18 (-CHDO)	48 (-CD ₂ O)
42	54 (-CH ₂ O)	47 (- $^{13}CH_2O$)			

homologue $[\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\overset{+}{\text{C}}\text{H}_2]$ will have a ΔH_f^\ddagger some 30 kJ mol^{-1} lower, by analogy with the effect of successive addition of CH_2 groups to several series of ions, e.g., $\text{CH}_3\overset{+}{\text{C}}\text{HOCH}_3$, $\text{CH}_3\overset{+}{\text{C}}\text{HOH}$, or $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_3$ [10]. The $[\text{C}-\text{H}]$ bond strength in $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\overset{+}{\text{C}}\text{H}_2$ will be weaker than a secondary $\text{C}-\text{H}$ bond in an alkane, $\sim 400 \text{ kJ mol}^{-1}$ [16], but not reduced so much as when the charge site is adjacent to the bond broken [17], $\sim 335 \text{ kJ mol}^{-1}$. Conservatively, we will adopt a bond strength of $375 \pm 20 \text{ kJ mol}^{-1}$. This gives $\Delta H_f^\ddagger[\text{CH}_3\overset{+}{\text{C}}\text{HCH}_2\text{OCH}_2] = 721 \pm 20 \text{ kJ mol}^{-1}$, an energy for ion 5 which is significantly lower than that of ionized allyl methyl ether (see Figure 1). It is noteworthy that for the dideuterated compounds, 1_a and 1_b , (Table 5), the relative losses of CH_2O and CHDO are the same. This could result from a facile migration of the methoxy group from end to end of an allyl ion, which in conjunction with the above reversible 1,5 H-shift provides a ready explanation for the observed H/D mixing, as well as preserving the identity of the C atom lost in CH_2O . Note that a cyclic intermediate ion such as $\text{CH}_3\overset{+}{\text{C}}\text{HCH}_2\text{OCH}_2^+$ can be ruled out because ^{13}C is *always* lost as $^{13}\text{CH}_2\text{O}$ (see Table 5) and the involvement of a cyclic ion would lead to equal losses of CH_2O and $^{13}\text{CH}_2\text{O}$.

The mechanism proposed by Bowen et al. [9] based only on low energy mass spectral data, involves a concerted 1,2-H shift together with loss of the methyl group. They use the loss of CH_3 from $(\text{CH}_3)_2\text{O}^+$ (to produce $\overset{+}{\text{C}}\text{H}_2\text{OH}$ ions) as a precedent [18] but this latter reaction is only a high energy, collision induced process and does not, as originally reported [P. C. Burgers, personal communication], involve metastable ions.

The final question concerns the height of the energy barrier for the 1,5 H-shift. This cannot be very small, because if 1^+ ions easily rearranged to 5, then the m/z 42 peak in the MI mass spectrum could be expected to be sensitive to collision gas, the reaction being only a simple bond cleavage for 5. The m/z 42 peak is not collision gas sensitive and so the allyl methyl ether ions themselves must lie in a potential well of significant depth. This energy barrier has been shown as 25 kJ mol^{-1} in Figure 1, i.e., lower than that for the 1,2-H⁻ shift which yields ion 6.

The dissociation channel which leads to loss of CH_3 will be considered next. In the ion source, loss of CH_3 produces a mixture of daughter ions, predominantly $\text{CH}_2\overset{+}{\text{C}}\text{HCHOH}$, as described above. The metastable peak for the loss of CH_3 from 1^+ is broad with a dish top, ($T_{0.5} = 443 \text{ meV}$) and with no sign of a discontinuity which would indicate the production of more than one $\text{C}_3\text{H}_5\text{O}^+$ fragment ion. In view of the conservative estimate that $> 90\%$ of the source generated ions have the hydroxyallyl ion structure (see above) we infer that the ethylcarbonyl cation is not produced in the μs (metastable ion) time frame. Therefore the measured AE for TS2 is proposed to

represent that for the production of $\text{CH}_2\overset{+}{\text{C}}\text{HCHOH}$. The small yield of $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{O}$ in the ion source could result from there being a barrier significantly higher than TS2, TS2b in Figure 1, for the fragmentation which produces them. The proposed route is shown in the energy diagram and involves the intermediacy of the carbene ion $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}(\text{OCH}_3)$, 4. Such ions show a large activation energy for $\text{O}-\text{CH}_3$ bond cleavage (e.g., 1.3 eV [19, 20] for $\text{CH}_3\overset{+}{\text{C}}(\text{OCH}_3) \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3$). The ΔH_f^\ddagger value for the ethyl methoxycarbene ion can be estimated as follows. The ΔH_f^\ddagger value for $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{HOCH}_3$ will be $\sim 529 \text{ kJ mol}^{-1}$, $\sim 33 \text{ kJ mol}^{-1}$ below that of its homologue $\text{CH}_3\overset{+}{\text{C}}\text{HOCH}_3$, 562 kJ mol^{-1} [10]. This difference can be estimated by comparing $\Delta H_f^\ddagger[\text{CH}_3\overset{+}{\text{C}}\text{HOH}] = 583 \text{ kJ mol}^{-1}$ [10] with that of $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{HOH}$, 550 kJ mol^{-1} [10]. The $[\text{C}-\text{H}]$ bond strength in $\text{CH}_3\text{CH}_2\overset{+}{\text{C}}\text{HOCH}_3$ can be estimated by comparing those for the ions $\text{CH}_3\overset{+}{\text{C}}\text{HOH}$ and $\text{CH}_3\text{O}\overset{+}{\text{C}}\text{H}_2$, leading to $[\text{CH}_3\overset{+}{\text{C}}(\text{OH})]^+$ and $[\text{CH}_3\text{O}\overset{+}{\text{C}}\text{H}]^+$, respectively. The $[\text{C}-\text{H}]$ values are 498 and 502 kJ mol^{-1} , respectively (energies from refs 10 and 21). A bond strength of 500 kJ mol^{-1} leads to $\Delta H_f^\ddagger[\text{CH}_3\text{CH}_2\overset{+}{\text{C}}(\text{OCH}_3)] = 810 \text{ kJ mol}^{-1}$. A relatively minor question which now arises is how the allyl methyl ether ion rearranges to the ionized carbene, 4. Symmetry forbidden 1,3 H-shifts require a large activation energy and so will be discarded. Two consecutive 1,2 H⁻ shifts followed by an energy demanding 1,2-H atom transfer to form the carbene ion are a possibility and would involve inter-alia the intermediacy of the 1-methoxypropene ion, 2^+ ; $[\text{CH}_3\text{CH}=\text{CHOCH}_3]^+$. (Such arrangements are known to involve an appreciable energy barrier; e.g., the CH_2CHOH^+ to CH_3COH^+ transformation requires $\leq 240 \text{ kJ mol}^{-1}$ [22].) As will be seen in the continuing discussion, this ion plays an important role on the potential energy surface shown in Figure 1, and so we will next describe the mass spectral characteristics of ionized 1-methoxypropene, 2.

The heat of formation of ionized 2 was measured to be 665 kJ mol^{-1} , based on its IE which was measured to be $8.34 \pm 0.05 \text{ eV}$ and $\Delta H_f^\ddagger 2 = -140 \text{ kJ mol}^{-1}$ [11]. Thus 2^+ is thermodynamically much more stable than 1^+ . The MI mass spectrum of 2^+ was closely similar to that of 1^+ ; see Table 1, both in regard to relative peak intensities and kinetic energy release values, 131 , 427 , and 24.7 meV , respectively, for the losses of H ; CH_3 ; and CH_2O . The respective AE values for the three metastable peaks were measured, 10.40 , 10.33 , and 10.34 eV , all $\pm 0.1 \text{ eV}$, giving transition state energies all within experimental error of TS1, TS2, and TS3. The energy barrier for 2^+ to rearrange to the carbene ion 4 is not known and so is shown as a broken line in Figure 1. Finally, the CA mass spectrum of $[\text{CH}_3\text{CHCHOCH}_3]^+$ was found to be similar to that for 1^+ but with two important differences. Under single collision conditions, the MI peak intensities for the allyl methyl ether ion are barely effected

Table 6. Metastable ion (MI) and major peaks in the collisional activation (CA)^a mass spectra of C₄(H, D)₇O⁺ ions

m/z	CH ₂ CHCH ₂ OCH ₃ ↓ -H C ₄ H ₇ O ⁺		CH ₃ CHCHOCH ₃ ↓ -H C ₄ H ₇ O ⁺		CH ₂ CHCD ₂ OCH ₃ ↓ -D C ₄ H ₆ DO ⁺		CH ₂ CHCD ₂ OCH ₃ ↓ -H C ₄ H ₅ D ₂ O ⁺		CH ₂ CHCH ₂ OCD ₃ ↓ -H C ₄ H ₄ D ₃ O ⁺	
	MI	CA	MI	CA	MI	CA	MI	CA	MI	CA
56									25	39
55							9	11	16	32
54					15	20	14	17.5		
53	22	26	22	30	8	13	1	2		
46									100	100
45							100	100	7	10
44					100	100	8	12	13	20
43	100	100	100	100	15	23	36	133	25	33
42					50	155		24	41	140
41	38	135	36	170		14		15		5
40						21		15		11
39		25		30		14		6		18
30						5		11		3
29		10		12		13		12		13
28		4		5		11		10		8
27		14		17		8		5		14
26		4		5		3		1		5
18										4
17										0.7
16						< 0.5		0.6		
15		5		4		3		3		

^aCollision gas, helium. Spectra were recorded at 10% beam reduction, uncorrected for contributions from the MI decompositions.

intermediate must be involved. The loss of 28 u from the unlabeled ion is complicated, with the metastable peak for the C₄H₇O⁺ ion from 1, being clearly composite in nature as also described by Bouchoux et al. [15a]. Deuterium labeling essentially separates the components into CO and ethene losses. Table 4 showed the kinetic energy release values for the dissociation of the OCD₃ analogue; T_{0.5} for CO loss is ≤ 88 meV and for the elimination of C₂H₃D and C₂H₂D₂ (the major ethene loss processes) T_{0.5} is ~ 400 meV. These observations can usefully be compared with those for C₄H₇O⁺ ions derived from 2-methyltetrahydrofuran and 3,3-dimethylprop-1-ene-3-ol (Table 4) where the metastable peaks for loss of 28 u are also composite. For the latter this is known [14] to result from the loss of CO (narrow component) and C₂H₄ (broad component). For the former the narrow component, assumed to be CO loss, is predominant. From the results of Laderoute et al. [14] we propose that the intermediates are (CH₃)₂CHCO⁺ for CO loss and $\overline{\text{CH}_2\text{CH}^+(\text{OH})\text{CH}_3}$ for C₂H₄ loss. Note that for the CO loss, ¹³C labeling showed that the methoxy carbon atom is retained in the C₃H₇⁺ ion. The elimination of H₂O also derives from the ion $\overline{\text{CH}_2\text{CH}^+(\text{OH})\text{CH}_3}$ [14].

Summary

The fragmentation behaviors of the ionized isomers 1- and 3-methoxypropene were shown to involve complex rearrangements requiring the introduction of four more C₄H₈O⁺ ions. None of these relate to the ions proposed to describe the behavior of hydroxy, keto, or enol type C₄H₈O⁺ ions. It is worth noting that these methyl alkenyl ethers have unique dissociation characteristics, which are not repeated when the methyl group is replaced by a larger alkyl substituent and where loss of an olefin from the molecular ion is the predominant reaction channel. This work will be described in a future publication.

Before closing this report a few remarks should be made concerning the third methoxy derivative, ionized 2-methoxypropene. It has loss of HCO as the major metastable process together with minor losses of CO and H₂CO, and so ion structures common to the 1- and 3-methoxypropenes are highly unlikely to be involved.

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