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Fragmentation of 1- and 3-Methoxypropene Ions

Another Part of the $C_4H_8O^{+ \cdot}$ Potential Energy Surface

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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 $C_4H_8O^{+ \cdot}$ 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 $C_4H_8O^{+ \cdot}$ 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 $C_4H_8O^{+ \cdot}$ 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 $C_4H_8O^{+ \cdot}$ 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 $C_4H_8O^{+ \cdot}$ ion structures and their alkenyl ether isomers. To explore this aspect of $C_4H_8O^{+ \cdot}$ 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.

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

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 $CH_2CHCH_2OCH_3$ 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.

Results and Discussion

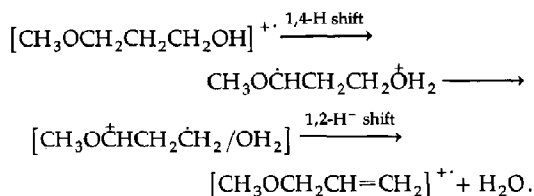
Allyl Methyl Ether

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

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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, CH_3^+ loss ($T_{0.5} = 443$ meV); and at m/z 42, CH_2O loss, ($T_{0.5} = 21.5$ meV). These dissociations are quite different from those of the keto/enol $C_4H_8O^{++}$ isomers [1, 2], all of which show major losses of CH_3^+ and $C_2H_5^+$ 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 $C_4H_8O^{++}$ 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 $\Delta H_f^\circ[CH_2CHCH_2OCH_3] = -105 \text{ kJ mol}^{-1}$ (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^+ , CH_3^+ , and CH_2O 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 H_2O 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 $\Delta H_f^\circ[C_4H_8O]^{++} = 800 \text{ kJ mol}^{-1}$ ($\Delta H_f^\circ[CH_3OCH_2CH_2CH_2OH] = -386 \text{ kJ mol}^{-1}$ [11], $\Delta H_f^\circ[H_2O] = -242 \text{ kJ mol}^{-1}$ [11]). The relatively large kinetic energy release for the above loss of H_2O , $T_{0.5} = 42$ meV, is in keeping with the ΔH_f° value of 800 kJ mol^{-1} , which is 15 kJ mol^{-1} above $\Delta H_f^\circ[1]^{++}$. A mechanism for this reaction is shown below



The deuterium-labeled precursors $CD_3OCH_2CH_2CH_2OH$ and $CH_3OCH_2CH_2CH_2OD$ lost only H_2O 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 $C_3H_5O^+$ ion produced by the CH_2O 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 $[C_3H_5O]^{++}$ 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 $C_4H_8O^{++}$ 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 $CH_3CH_2\dot{C}O$ and $\overline{CH_2CHCHOH}^+$ 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 $CH_3CH_2\dot{C}O$ ions is very narrow (Table 2) and corresponds only to the loss of CO from ions of structure $CH_3CH_2\dot{C}O$ [12]. The broadest metastable peak, that from the $C_3H_5O^+$ ion from $CH_2CHCH(OH)CH_3^+$, 7, has been shown to arise from loss of both CO and C_2H_4 from ions of structure $CH_3CH_2\dot{C}O$ and $\overline{CH_2CHCHOH}^+$, respectively [12, 13], with the latter as the major species present. The $C_3H_5O^+$ ions from 1, 2, and 10 have slightly lower $T_{0.5}$ values (Table 2) indicating a greater proportion of $CH_3CH_2\dot{C}O$ relative to that formed by 7. The kinetic energy release distribution for the metastable dissociation of $C_3H_5O^+$ ions from 1 is shown in Figure 2 and the presence of the two components is clearly visible, and discernable 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 C_2H_4 losses, showed that for these ion source generated species at least 95% of them must

have the $\overline{CH_2CHCHOH}^+$ 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 $C_3H_5O^+$ ions, small differences between the spectra are observable, compatible with a mixture of the two $C_3H_5O^+$ ions. Based on the low energy mass spectra

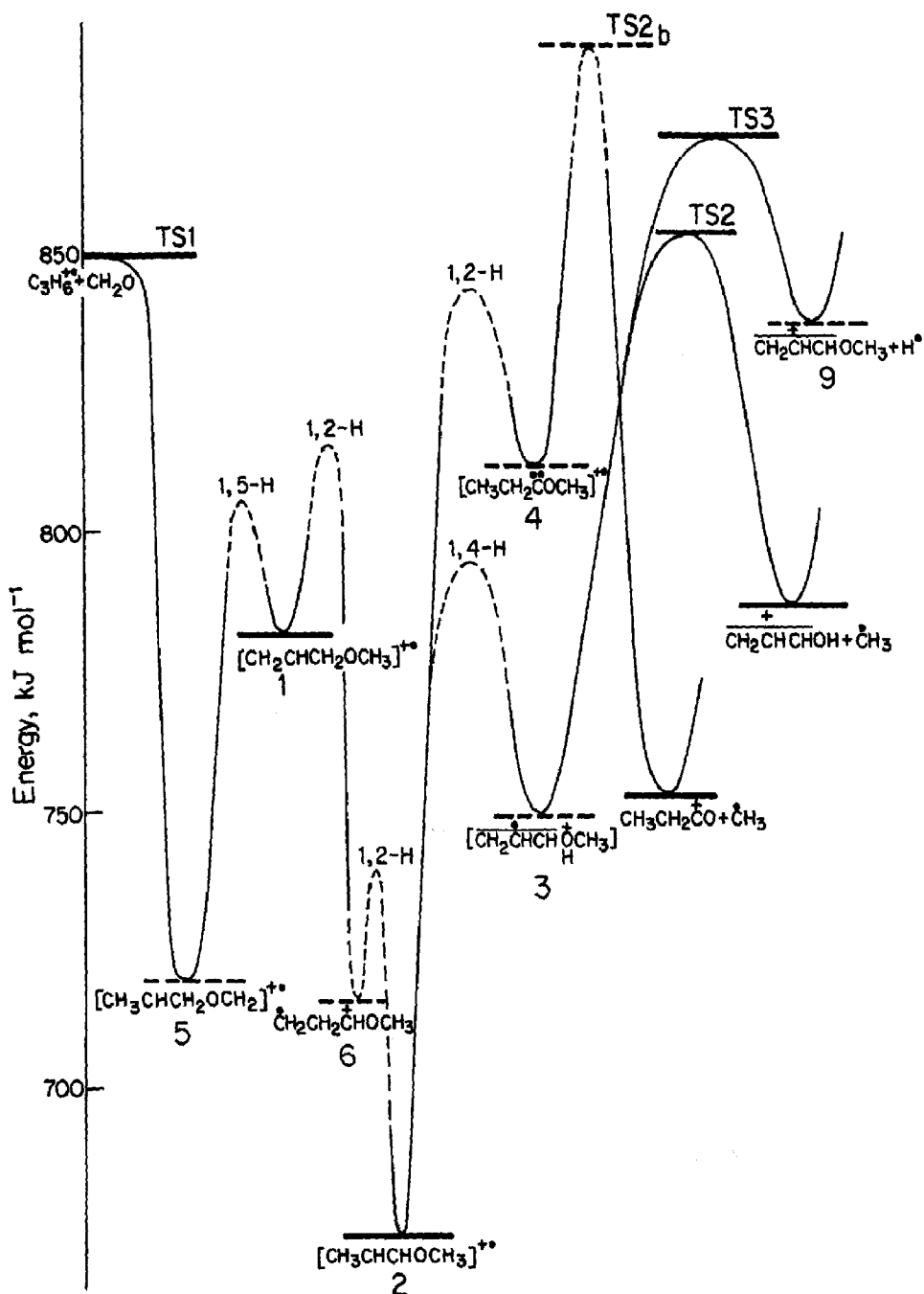


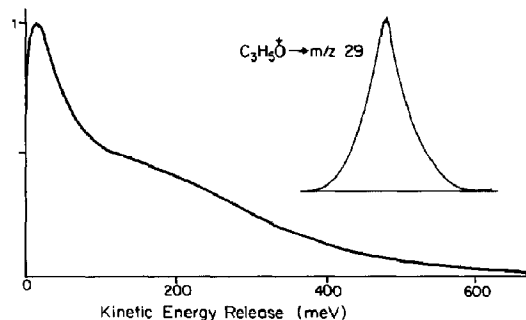
Figure 1. Potential energy surface for $C_4H_5O^+$ ions derived from 1- and 3-methoxypropene. Broken lines are for estimated energies, solid lines are from experimental measurements. The nature of the various H shifts is discussed in the text.

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
	$\downarrow -H$	$\downarrow -CH_3$	$\downarrow -CH_3$	$\downarrow -CH_3$	$\downarrow -OCH_3$
	$C_3H_5O^+$	$C_3H_5O^+$	$C_3H_5O^+$	$C_3H_5O^+$	CH_3CH_2CO
	$\downarrow -(C_2H_4 + CO)$	$\downarrow -(C_2H_4 + CO)$	$\downarrow -(C_2H_4 + CO)$	$\downarrow -(C_2H_4 + CO)$	$\downarrow -CO$
	m/z 29	m/z 29	m/z 29	m/z 29	m/z 29
$T_{0.5}$	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^+ , H_2O , CO/C_2H_4 , and H_2CO . 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 CH_3 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 CH_2O , CH_3 , 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

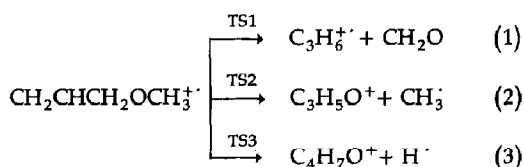
	CH_2CHCH_2OH S10 H^+	$CH_2CHCH_2OCH_3$ 1 H^+	$CH_2CHCH(OH)CH_3$ 7 CH_3	$CH_3CHCHOCH_3$ 2 CH_3	$CH_3CH_2C(O)OCH_3$ 8 CH_3OCH_3
Neutral lost m/z					
55	14	14	26	20	1.6
53	2.7	3.0	4.3	4.6	1.4
42	4.2	4.9	3.8	4.9	6.5
41	1.5	1.6	0.8	1.7	1.8
39	5.7	5.7	10	9.8	1.3
38	3.9	4.3	7.1	6.9	1.1
37	3.0	3.4	5.2	3.0	1.3
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 ₂ CHCH ₂ OCH ₃ 1 ↓ -H		CH ₂ CHCH ₂ OCD ₃ 1 ↓ -H		CH ₂ CH ₂ OCH(CH ₃)CH ₂ ↓ -CH ₃		CH ₂ CHC(CH ₃) ₂ OH ↓ -CH ₃	
	CH ₂ CHCHOCH ₃ ⁺		CH ₂ CHCHOCD ₃ ⁺		CH ₂ CH ₂ OCHCH ₂ ⁺		CH ₂ CHC(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						

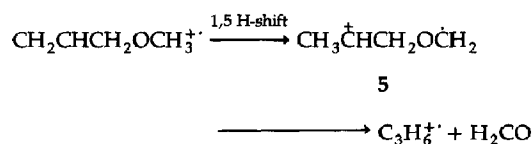
Fragmentation Mechanisms

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 $\text{CH}_2\text{CHCH}_2\text{O}^{13}\text{CH}_3$, 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.

$$\Delta H_f^\circ[\text{CH}_3\text{CH}_2\text{OCH}_2] = 594 \text{ kJ mol}^{-1} [10] \text{ and its}$$

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

m/z	CH ₂ CHCH ₂ OCH ₃ 1	CH ₂ CHCH ₂ O ¹³ CH ₃ 1*	CD ₂ CHCH ₂ OCH ₃ 1 _a	CH ₂ CHCD ₂ OCH ₃ 1 _b	CH ₂ CHCH ₂ OCD 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 ₂ O)			

homologue $[\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\dot{\text{C}}\text{H}_2]$ will have a ΔH_f° 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., $\text{CH}_3\dot{\text{C}}\text{HOCH}_3$, $\text{CH}_3\dot{\text{C}}\text{HOH}$, or $\text{CH}_3\dot{\text{C}}\text{HCH}_3$ [10]. The $[\text{C}-\text{H}]$ bond strength in $\text{CH}_3\text{CH}_2\text{CH}_2\text{O}\dot{\text{C}}\text{H}_2$ 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 $\Delta H_f^\circ[\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{OCH}_3] = 721 \pm 20 \text{ kJ mol}^{-1}$, 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 deuterated compounds, $\mathbf{1}_a$ and $\mathbf{1}_b$, (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 $\text{CH}_3\text{CHCH}_2\text{OCH}_2^+$ 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 $\dot{\text{C}}\text{H}_2\text{OH}$ 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 $\mathbf{1}^{++}$ 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 $\text{CH}_2\text{CHCHOH}^+$, as described above. The metastable peak for the loss of CH_3 from $\mathbf{1}^{++}$ is broad with a dishd 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 $\text{CH}_2\text{CHCHOH}^+$. The small yield of $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{O}$ 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 $\text{CH}_3\text{CH}_2\dot{\text{C}}(\text{OCH}_3)^+$, 4. Such ions show a large activation energy for $\text{O}-\text{CH}_3$ bond cleavage (e.g., 1.3 eV [19, 20] for $\text{CH}_3\dot{\text{C}}(\text{OCH}_3)^+ \rightarrow \text{CH}_3\text{CO}^+ + \text{CH}_3$). The ΔH_f° value for the ethyl methoxycarbene ion can be estimated as follows. The ΔH_f° value for $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOCH}_3$ will be $\sim 529 \text{ kJ mol}^{-1}$, $\sim 33 \text{ kJ mol}^{-1}$ below that of its homologue $\text{CH}_3\dot{\text{C}}\text{HOCH}_3$, 562 kJ mol^{-1} [10]. This difference can be estimated by comparing $\Delta H_f^\circ[\text{CH}_3\dot{\text{C}}\text{HOH}] = 583 \text{ kJ mol}^{-1}$ [10] with that of $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOH}$, 550 kJ mol^{-1} [10]. The $\text{C}-\text{H}$ bond strength in $\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HOCH}_3$ can be estimated by comparing those for the ions $\text{CH}_3\dot{\text{C}}\text{HOH}$ and $\text{CH}_3\text{O}\dot{\text{C}}\text{H}_2$, leading to $[\text{CH}_3\dot{\text{C}}(\text{OH})]^+$ and $[\text{CH}_3\text{O}\dot{\text{C}}\text{H}]^+$, respectively. The $D[\text{C}-\text{H}]$ 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 $\Delta H_f^\circ[\text{CH}_3\text{CH}_2\dot{\text{C}}(\text{OCH}_3)]^+ = 810 \text{ kJ mol}^{-1}$. 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 $\Delta H_f^\circ 2 = -140 \text{ kJ mol}^{-1}$ [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 $\mathbf{1}^{++}$ but with two important differences. Under single collision conditions, the MI peak intensities for the allyl methyl ether ion are barely effected

by collision gas; the collision-induced processes contribute only ~ 20% towards the combined CA and MI mass spectra. In contrast (see Table 1), the methoxypropene ion under the same experimental conditions shows an enhanced abundance of m/z 41 (see Table 1) and CA processes now dominate, contributing ~ 70% towards the combined mass spectra. A greater fraction of (ion source generated) allyl methyl ether ions are metastable (the combined metastable peak intensities are 8.1×10^{-3} of the m/z 72 ions' intensity) than for ion 2 (1.5×10^{-3}). We propose that 1^{+} isomerizes to 2^{+} by two consecutive 1,2-H⁻ shifts, passing through another intermediate, ion 6, which may or may not reside in a potential well. In any case, $\Delta H_f^\circ[6] = 715 \text{ kJ mol}^{-1}$, can be estimated using a [C—H] bond strength of ~ 406 kJ mol⁻¹ in $\text{CH}_2\text{HCH}_2\text{CHOCH}_3$ (see above). This energy for ion 6 is shown in Figure 1.

One more intermediate ion must be introduced, the (allylic) ylid ion $\text{CH}_2\text{CH}\dot{\text{C}}\text{H}(\text{H})\text{CH}_3$, 3. The heat of formation of this ion could not be measured but may be estimated in two ways. First, the effect of converting a conventional ether ion into its ylid counterpart leads to a small drop in ΔH_f° , e.g., $\text{CH}_3\text{OCH}_3^{+}$, by high level ab initio molecular orbital theory calculations [23] has $\Delta H_f^\circ = 783 \text{ kJ mol}^{-1}$ relative to $\dot{\text{C}}\text{H}_2\dot{\text{O}}(\text{H})\text{CH}_3$, $\Delta H_f^\circ = 774 \text{ kJ mol}^{-1}$ [24]. On this basis $\Delta H_f^\circ[3]$ would be expected to be close to, but below that of 1^{+} , at 785 kJ mol^{-1} . However, the ion 3 differs from $\dot{\text{C}}\text{H}_2\dot{\text{O}}(\text{H})\text{CH}_3$ in one important respect, namely that the formal radical site in 3 is at an allylic position and so further stabilization relative to 1^{+} must be entertained. A conservative estimate would use half the allylic stabilization energy, 25 kJ mol^{-1} , giving $\Delta H_f^\circ[3] \sim 750 \text{ kJ mol}^{-1}$.

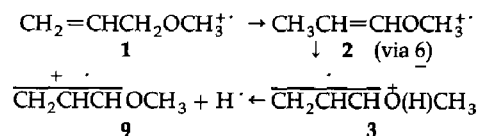
An alternative approach is to consider the bond strength $\text{D}[\dot{\text{C}}\text{H}_2\dot{\text{O}}(\text{CH}_3)\text{—H}]$ as being the same as $\text{D}[\dot{\text{C}}\text{H}_2\text{CH}\dot{\text{C}}\text{H}(\text{CH}_3)\text{—H}]$. The former is 101 kJ mol^{-1} , $\Delta H_f^\circ[\text{CH}_3\text{OCH}_2]^{+} = 657 \text{ kJ mol}^{-1}$ [10], $\Delta H_f^\circ[\text{H}^{\cdot}] = 218 \text{ kJ mol}^{-1}$ [10]. This leads to $\Delta H_f^\circ[3] = 738 \text{ kJ mol}^{-1}$. In either case $\Delta H_f^\circ[3]$ can with some confidence be placed below $\Delta H_f^\circ[1^{+}]$ and it is so shown in Figure 1.

The ion 3 dissociates by loss of CH_3^{\cdot} (TS2), or H^{\cdot} (TS3), each having an appreciable reverse energy barrier. Thus (see Figure 1), the O—H bond is slightly stronger than the O—C bond, and the kinetic energy releases, $T_{0.5} = 131 \text{ meV}$ for H^{\cdot} loss and $T_{0.5} = 443 \text{ meV}$ for CH_3^{\cdot} loss are in keeping with the reverse energy barriers of 0.35 and 0.70 eV, respectively, i.e., the heights of TS2 and TS3 above the product energies.

There remains the question as to the height of the barrier separating 3 and 2^{+} and which is governed by the energy requirement for the 1,4-H shift which converts 3 to 2^{+} . This barrier cannot be measured, nor can it confidently be stated that this intermediate ion 3^{+} exists in a potential well. Nevertheless, the

barrier shown in Figure 1 was chosen to be the same as that which separates $\text{CH}_2\text{CH}_2\text{CH}_2\text{OH}_2^{+}$ from $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}^{+}$; namely $\leq 43 \text{ kJ mol}^{-1}$ [8, 25].

The final mechanism is that for H^{\cdot} loss from 1^{+} . This difficult problem has been kept to the end, after other important intermediate ion structures had been described and justified. It is proposed that the ion generated by loss of H^{\cdot} is the 1-methoxyallyl cation. This could be achieved by a single C—H bond cleavage in the molecular ion of 1. However, the deuterium labeling results (Table 5) show that D loss from the ionized 1-d₂ analogue, 1_a^{+} , is the same, relative to H^{\cdot} loss, as for the 3-d₂ compound, 1_b^{+} , and therefore some H/D mixing must precede fragmentation. The proposed reaction sequence is shown below:



Note that D loss from 1_a^{+} (Table 5) is more facile (relative to methyl or formaldehyde loss) than for the other labeled compounds. Ion 9 was not considered in the investigation of Laderoute et al. [14] above, in spite of it being a methoxy substituted allyl cation and so, predictably a species of low heat of formation. We estimate $\Delta H_f^\circ[9]$ to be 621 kJ mol^{-1} by comparing $\Delta H_f^\circ[\text{CH}_3\dot{\text{C}}\text{HOH}] = 583 \text{ kJ mol}^{-1}$ with $\Delta H_f^\circ[\text{CH}_2\text{CH}\dot{\text{C}}\text{HOH}] = 642 \text{ kJ mol}^{-1}$, and the former with $\Delta H_f^\circ[\text{CH}_3\dot{\text{C}}\text{HOCH}_3] = 562 \text{ kJ mol}^{-1}$, showing the effects of replacing $\text{CH}_3\text{—}$ by $\text{CH}_2\text{CH—}$ and —OH with —OCH_3 in analogous small ions. This $\Delta H_f^\circ[9]$ agrees well with the estimate by Bouchoux et al. [15a], 630 kJ mol^{-1} , but the present MI and CA mass spectra do not agree very closely with their data [15b]. Nevertheless, in spite of the different relative abundances reported by them for the three MI processes, it is likely that the ion 9 is also produced by the fragmentation of a variety of ionized epoxides, as proposed by Bouchoux et al. [15a]. The sum of the product energies at 838 kJ mol^{-1} (see Figure 1) is in keeping with the height of TS3 above the products (0.35 eV) and the magnitude of the kinetic energy release associated with the metastable 3 ions (136 meV).

Additional support for the structure assignment of 9 is found in the CA mass spectra of the ¹³C and CD₂-labeled molecules, for the former m/z 15 is cleanly shifted to m/z 16 and for the latter the predominant ion in the low mass group is m/z 18 (CD₃) (see Table 6), indicating that the ion retains an —OCH_3 group.

It is useful briefly to discuss the major features of the dissociations of metastable ion 9. First, the loss of H_2CO always involves the methoxy carbon atom, as shown by ¹³C labeling and also the D₂CO loss from the —OCD_3 analogue (Table 6), and a $[\text{C}_3\text{H}_5\text{OCH}_2]^{+}$

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

<i>m/z</i>	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		

^a Collision 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)₂CHC⁺O for CO loss and CH₂CHC⁺(OH)CH₃ 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 CH₂CHC⁺(OH)CH₃ [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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