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The chemistry of some low energy $C_5H_9O^+$ oxonium ions

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Abstract

The reactions of the low energy oxonium ions $CH_3CH{=}CH{-}C^+(H)OCH_3$, $\mathbf{b_1}^+$, $CH_2{=}CH{-}C^+(CH_3)OCH_3$, $\mathbf{b_2}^+$, and $CH_2{=}C(CH_3){-}C^+(H)OCH_3$, $\mathbf{b_3}^+$, are reported and compared with those of their 1,3-H shift isomers $CH_3CH{=}CHCH_2OCH_2^+$, $\mathbf{b_4}^+$, $CH_2{=}CHCH(CH_3)OCH_2^+$, $\mathbf{b_5}^+$, and $CH_2{=}C(CH_3)CH_2OCH_2^+$, $\mathbf{b_6}^+$. The metastable ion (MI) spectrum of the $C_4H_6OCH_3^+$ ions $\mathbf{b_1}^+$– $\mathbf{b_3}^+$ is dominated by loss of CH_2O. Elimination of C_3H_6, which is associated with a composite metastable peak, is also significant from $\mathbf{b_2}^+$ and $\mathbf{b_3}^+$. From (multiple) collision experiments and analysis of D- and ^{13}C-labeled isotopologues, it follows that $\mathbf{b_1}^+$–$\mathbf{b_3}^+$ do not readily interconvert. Loss of CH_2O is proposed to involve a 1,5-H shift followed by a (dipole-assisted) 1,3-H shift into an energy-rich ion-neutral complex (INC) $[C_4H_7^+/CH_2{=}O]$. Loss of CH_2O from $\mathbf{b_4}^+$–$\mathbf{b_6}^+$ may also occur via an INC. This reaction is associated with a very small kinetic energy release, indicating that it generates the most stable $C_4H_7^+$ ion, $CH_2{=}CHC^+(H)CH_3$, at the thermochemical threshold. However, this process is only prominent for ions $\mathbf{b_5}^+$, which also undergo a facile loss of H_2O, via rearrangement in the INC $[C_4H_7^+/CH_2{=}O]$, to yield $C_5H_7^+$ (most probably the cyclopentenyl cation). Loss of C_3H_6 and CO dominates the MI spectra of $\mathbf{b_4}^+$ and $\mathbf{b_6}^+$ and these reactions, which also occur from $\mathbf{b_5}^+$, are proposed to take place from 1,2-H shift isomers of the cyclic counterparts of $\mathbf{b_4}^+$–$\mathbf{b_6}^+$. The behavior of $\mathbf{b_1}^+$–$\mathbf{b_3}^+$ and $\mathbf{b_4}^+$–$\mathbf{b_6}^+$ differs considerably from their $C_4H_7O^+$ homologues, $CH_2{=}CH{-}C^+(H)OCH_3$, $\mathbf{a_1}^+$, and $CH_2{=}CHCH_2OCH_2^+$, $\mathbf{a_2}^+$. Differences in the dissociation characteristics of the $C_nH_{2n-2}OCH_3^+$ species ($n = 3$–5) are discussed in terms of the energetics of the products that may be formed. ΔH_f (298 K) values for the key ions in this study were obtained from CBS-QB3 calculations and thermochemical estimates. (Int J Mass Spectrom 209 (2001) 153–169) © 2001 Elsevier Science B.V.

Keywords: Rearrangement; Ion-neutral complex; Deuterium and ^{13}C-labeling; Kinetic energy release; Neutralization-reionization mass spectrometry; CBS-QB3 computations

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1. Introduction

The chemistry of $C_nH_{2n+1}O^+$ oxonium ions has been intensively studied, particularly for $n = 1$–5 [1]. In contrast, $C_nH_{2n-1}O^+$ oxonium ions have been given relatively little attention [2–7]. In the dissociation of the $C_4H_7O^+$ metastable ions $CH_2{=}CH{-}C^+(H)OCH_3$, $\mathbf{a_1}^+$, and $CH_2{=}CHCH_2OCH_2^+$, $\mathbf{a_2}^+$, double or triple H-transfer reactions feature prominently [7]. Both these ions lose CO in high abundance, but this reaction is rarely, if ever, observed from $C_nH_{2n+1}O^+$ oxonium ions. The associated composite metastable peak indicates the presence of competing reaction channels, one of which is characterized by a large kinetic energy release (KER) [8].

Whereas metastable ions $\mathbf{a_2}^+$ expel essentially only CO, ions $\mathbf{a_1}^+$ eliminate CO and CH_2O at similar

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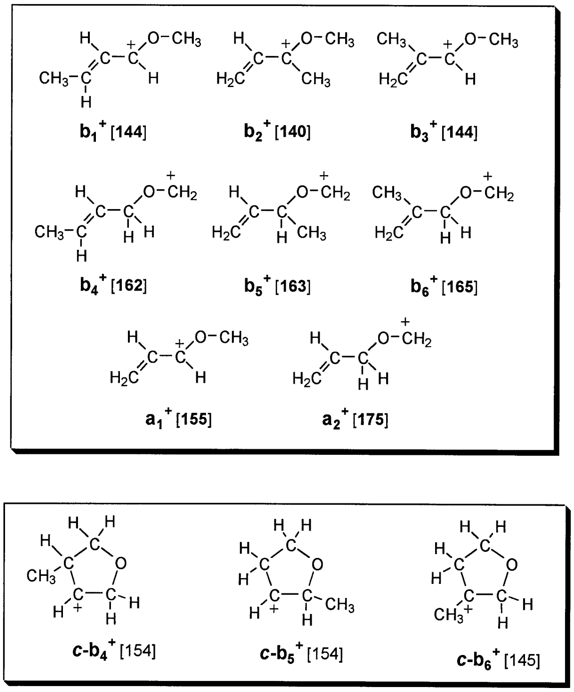
rates. Moreover, the ratio of CH_2O to CO loss from $\mathbf{a_1}^+$ decreases as the average internal energy of the dissociating ions increases. In addition, H_2O loss also occurs, though much less readily than CO expulsion.

From D- and ^{13}C-labeling experiments, it follows that the C atom of the CH_3O group is included in the CH_2O lost from $\mathbf{a_1}^+$, but there is some exchange of the H atoms of this substituent prior to dissociation. On the other hand, the C atom of the OCH_3 group is not always retained in the eliminated CO: both CO and ^{13}CO are lost from metastable $\mathbf{a_1}^+$ [$O^{13}CH_3$]; furthermore, the metastable peaks for CO and ^{13}CO loss are both composite. Consequently, CO loss from $\mathbf{a_1}^+$ proceeds via more than one mechanism. The minor route involves expulsion of CO derived from the OCH_3 group by a formal triple H-transfer; but the major channel entails a skeletal rearrangement and cleavage of the OCH_3 bond.

In view of this intriguing reactivity of $\mathbf{a_1}^+$ and $\mathbf{a_2}^+$, a study of the chemistry of the next higher homologues of these $C_4H_7O^+$ ions seemed worthwhile. This paper reports the reactions of six $C_5H_9O^+$ ions: $\mathbf{b_1}^+$– $\mathbf{b_3}^+$, homologues of $\mathbf{a_1}^+$, as well as $\mathbf{b_4}^+$–$\mathbf{b_6}^+$, homologues of $\mathbf{a_2}^+$, scheme 1, and compares their chemistry with that of other $C_nH_{2n-1}O^+$ oxonium ions. The numbers in square parentheses in scheme 1 refer to 298 K enthalpy values in kcal/mol. They were obtained from computational chemistry (numbers in bold) and/or by estimation, as discussed in Sec. 2.

2. Experimental and theoretical

All mass spectrometric experiments were performed on the VG Analytical ZAB-R mass spectrometer. Details of the geometry of this three-sector instrument have been reported elsewhere [9]. Data on the dissociation of metastable ions in the second field-free region (ffr) were obtained from MI spectra [8]. The quoted spectra are integrated data, compiled from 2-5 individual scans. Typical operating conditions were 70 eV ionizing electron energy and 8 or 10 kV accelerating voltage. The KERs were estimated from the width at half-height of the appropriate metastable peak, by means of the standard one-line equation after applying the usual correction for the width at half-height of the main beam [8].



Scheme 1.

The CID spectra of the $C_5H_9O^+$ ions of Fig. 1 were obtained in the 2ffr with oxygen as the collision gas. The CID spectra of the $C_2H_3O^+$ ions generated from dissociation of metastable ions $\mathbf{a_2}^+$, $\mathbf{b_2}^+$ and $\mathbf{b_3}^+$ in the 2ffr were obtained in the 3ffr using O_2 as the collision gas and mass selected ions of 10 keV translational energy. The neutralization-reionization mass spectra were obtained in the 2ffr, using N,N-dimethylaniline as the reducing agent and oxygen gas for reionization. All spectra were recorded using a small PC-based data system developed by Mommers Technologies Inc. (Ottawa).

The oxonium ions studied in this work were generated by dissociative ionization of the appropriate alkenyl methyl ethers. Illustrative examples of the synthesis of these ethers have been described in detail [10].

The (298 K) enthalpy values for ions $\mathbf{a_1}^+$, $\mathbf{a_2}^+$, $\mathbf{b_1}^+$ - $\mathbf{b_6}^+$, see Scheme 1, and $\mathbf{b_7}^+$ - $\mathbf{b_9}^+$, were obtained from computations involving standard CBS-QB3

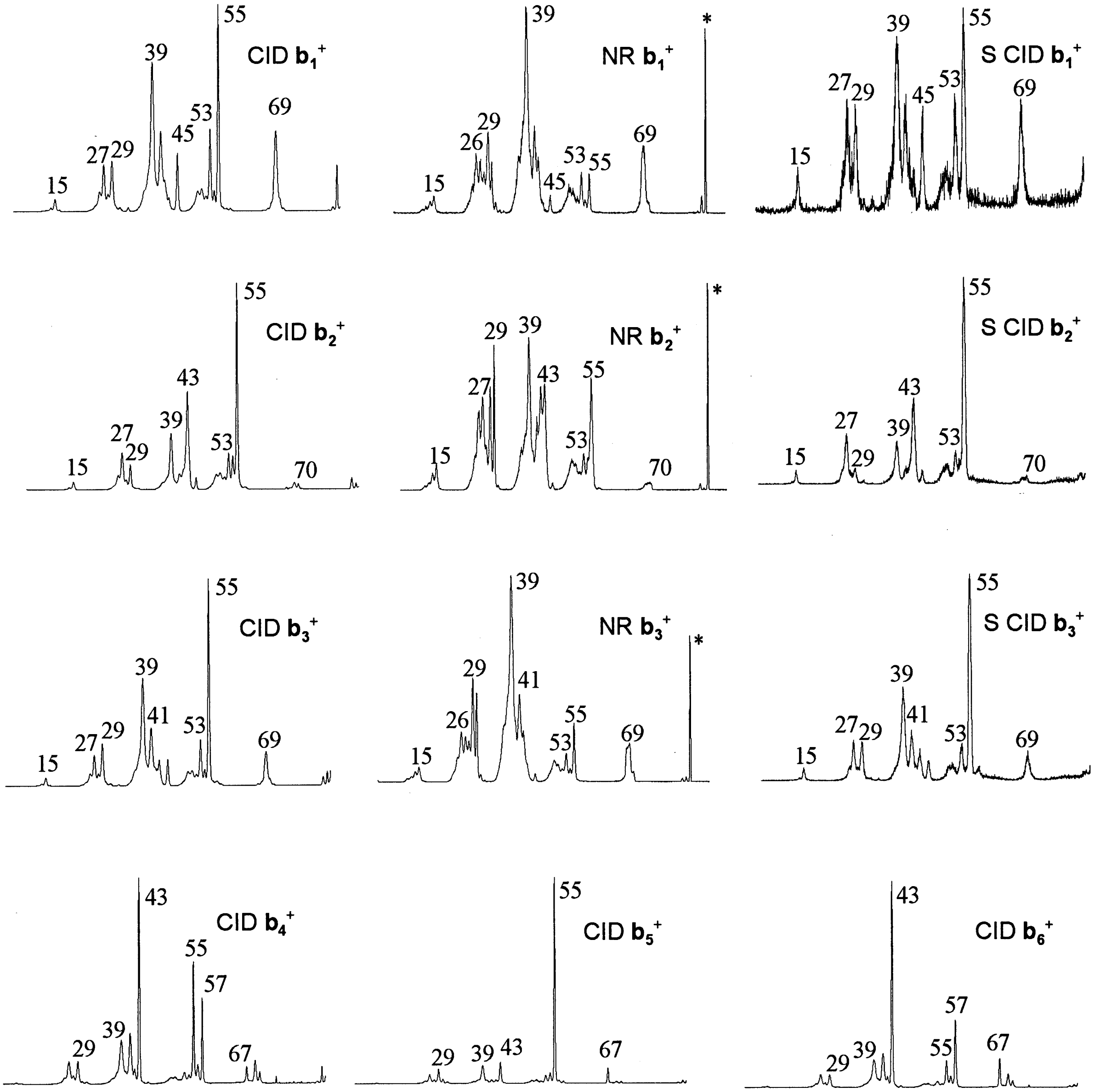


Fig. 1. CID, NR and survivor CID (S CID) spectra of the $C_4H_6OCH_3^+$ ions $b_1^+ - b_3^+$. The survivor signal at *m/z* 85 in the NR spectra is denoted with an asterisk. CID spectra of the isomeric $C_4H_7OCH_2^+$ ions $b_4 - b_6^+$ are displayed on the fourth row.

model chemistry [11] with the GAUSSIAN 98 suite of programs [12]. The detailed geometries of the various species are available upon request. Frequency calculations gave the correct number of negative eigenvalues for all minima. ΔH_f values for **c-b$_4$**$^+$ and **c-b$_6$**$^+$ were estimated from the enthalpies of the 2-and 1-methyl-cyclopentyl cations, 179 and 170 kcal/mol, respectively [13, 14], and the effect of O substitution at a noncharge-bearing group, −25 kcal/mol, as given by $\Delta(\Delta H_f)$ cyclopentane and tetrahydrofuran. ΔH_f [**c**-b$_5$$^+$] is expected to be close to that of the **c-b$_4$**$^+$ isomer.

Table 1
Relative abundances[a] and kinetic energy releases[b] for the main dissociations of metastable $C_5H_9O^+$ ions

Precursor molecule		Ion	Loss → CH_2O	C_3H_6	H_2O	CO
$CH_3CH{=}CHCH(C_2H_5)OCH_3$	**1a**	$\mathbf{b_1}^+$	100 [33]	2 [20/380]*	2 [47]	1[c]
$(CH_3)_2C{=}CHCH_2OCH_3$	**1b**	$\mathbf{b_1}^+$	100 [32]	3 (3:1)	1	2
$CH_2{=}C(CH_3)CH_2CH_2OCH_3$	**1c**	$\mathbf{b_1}^+$	100 [33]	5	2	3
$CH_2{=}CHC(CH_3)_2OCH_3$	**2a**	$\mathbf{b_2}^+$	100 [19]	25 [20/380]*	1 [41]	1[c]
$CH_2{=}CHC(CH_3)(C_2H_5)OCH_3$	**2b**	$\mathbf{b_2}^+$	100 [19]	30 (1:1)	1 [34]	1
$CH_2{=}C(CH_3)CH(C_2H_5)OCH_3$	**3a**	$\mathbf{b_3}^+$	100 [25]	20 [20/380]*	3 [37]	10[c]
$CH_3CH_2CH{=}CHCH_2OCH_3$	**3b**	$\mathbf{b_3}^+$	100 [29]	10 (1:1)	1	6
$CH_3CH{=}C(CH_3)CH_2OCH_3$	**3c**	$\mathbf{b_3}^+$	100 [27]	10	1	5
$CH_3CH{=}CHCH_2OCH_2CH(CH_3)_2$	**4**	$\mathbf{b_4}^+$	8 [1]	45 [17]	10 [27]	100 [17]
$CH_2{=}CHCH(CH_3)OCH_2C_2H_5$	**5**	$\mathbf{b_5}^+$	80 [1]	25 [22]	100 [24]	10 [30]
$CH_2{=}C(CH_3)CH_2OCH_2CH(CH_3)_2$	**6**	$\mathbf{b_6}^+$	2 [2]	100 [21]	25 [36]	45 [18]

[a] Relative abundance measured by peak height and normalized to a value of 100 units for the base peak in the metastable ion spectrum of ions dissociating in the second field-free region. The MI spectra of $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$ also contain weak signals for the loss of CH_3OH, C_3H_4 and CH_3CHO, see text and Figure 2.

[b] Numbers in square brackets represent kinetic energy releases, $T_{0.5}$, in meV as obtained from the width at half height of the peak. An asterisk indicates that the peak is composite; the approximate $T_{0.5}$ values for the narrow/broad component and their intensity ratio (in round brackets) are quoted.

[c] Composite metastable peaks dominated by a broad component whose $T_{0.5}$ values are estimated as ~370, ~460 and ~310 meV for $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$, respectively.

For **c**-$b_{\mathbf{5a}}^+$ and **c**-$b_{\mathbf{6a}}^+$, enthalpy values were derived from the PA of 5- and 4-methyl-2,3-dihydrofuran, 207.6 and 217.6 kcal/mol, respectively [14], and the closely similar ΔH_f values of the corresponding neutral molecules, −30 kcal/mol, as obtained from the Benson additivity method [15]. ΔH_f [**c**-$b_{\mathbf{4a}}^+$] can reasonably be expected to be close to that of the **c**-$b_{\mathbf{6a}}^+$ isomer.

3. Results and discussion

The reactions of the metastable ions $\mathbf{b_1}^+$ - $\mathbf{b_6}^+$, are summarized in Table 1.

Generation of $\mathbf{b_2}^+$ is readily achieved by ionization and alkyl radical loss from the tertiary alkenyl methyl ethers $CH_2 = CHCR(CH_3)OCH_3$ (R = CH_3, C_2H_5). The production of $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$ is not so straightforward, because isomerization of ionized primary and secondary alkenyl methyl ethers sometimes precedes $CH_3^{\cdot}$ expulsion. However, $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$ may be obtained by $C_2H_5^{\cdot}$ loss from ionized $CH_3CH = CHCH(C_2H_5)OCH_3$ and $CH_2 = C(CH_3)CH(C_2H_5)OCH_3$ [16].

Earlier research [16a,b] has shown that $\mathbf{b_1}^+$ is produced by $CH_3^{\cdot}$ elimination from $(CH_3)_2C{=}CHCH_2OCH_3^{\cdot\,+}$ or $CH_2{=}C(CH_3)CH_2CH_2OCH_3^{\cdot\,+}$; $\mathbf{b_3}^+$ is similarly formed from $C_2H_5CH{=}CH(CH_3)OCH_3^{\cdot+}$ or $CH_3CH{=}CH(CH_3)CH_2OCH_3^{\cdot+}$. Moreover, $CH_3^{\cdot}$ loss from $CH_2{=}CHCH(C_2H_5)OCH_3^{\cdot+}$ and $CH_2{=}C(C_2H_5)CH_2OCH_3^{\cdot+}$ also affords $\mathbf{b_3}^+$. These specific fragmentations allow $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$ to be generated from several precursors, see Table 1.

The isomeric species, $\mathbf{b_4}^+$, $\mathbf{b_5}^+$ and $\mathbf{b_6}^+$, in which the $-CH_2OCH_2^+$ subunit replaces the $-C^+(H)OCH_3$ entity, may be generated by simple bond cleavage of $CH_3CH{=}CHCH_2OCH_2CH(CH_3)_2^{\cdot\,+}$ and $CH_2{=}C(CH_3)CH_2OCH_2CH(CH_3)_2^{\cdot\,+}$, which yield $\mathbf{b_4}^+$ and $\mathbf{b_6}^+$, via loss of iso-$C_3H_7^{\cdot}$, and $CH_2{=}CHCH(CH_3)OCH_2C_2H_5^{\cdot\,+}$, which yields $\mathbf{b_5}^+$, via loss of $C_2H_5^{\cdot}$. However, the incipient ions $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$may well cyclize to their more stable counterparts **c**-b_4^+ - **c**-b_4^+. Alternatively, these cyclic ions may be generated directly from their precursor ions, by a displacement type reaction.

Each of the oxonium ions containing the $-C^+(H)OCH_3$ entity has a distinctive collision-induced dissociation (CID) spectrum [16a,b], thus indicating that $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ are stable species existing in appreciable potential energy wells. This deduction is supported by the CID, neutralization-reionization (NR) [17]) and survivor CID [18] spectra presented in Fig. 1. All three isomeric ions yield NR spectra with an intense survivor signal at *m/z* 85 (denoted by an asterisk in Fig.1). The CID spectra of these survivor ions (denoted by S-CID in Fig. 1) are very close to those of the corresponding ions, i.e. the conventional CID spectra of the (source-generated) ions. This attests to the isomeric purity of $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ and confirms that the intensity difference in the conventional CID spectra for peaks of structure diagnostic value, viz. *m/z* 69, 45, 43, and 41, reflects distinct ion structures rather than (internal energy dependent) mixtures of the isomeric species. Thus, when a mixture of ions $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ is generated from a given precursor molecule, see 16c, its composition can easily and reliably be quantified on the basis of its CID spectrum.

Also presented in Fig. 1 are the CID spectra of ions of putative structures $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$. It is seen that these $C_4H_7OCH_2^+$ ions yield distinct spectra. We further note that loss of CH_2O by direct bond cleavage is only prominent for $\mathbf{b_5}^+$. For $\mathbf{b_4}^+$ and $\mathbf{b_6}^+$ the major collision-induced dissociation yields *m/z* 43 ions, which, as will be shown below, involves loss of C_3H_6 to give CH_3CO^+ ions.

3.1. Overview of the reactions of low energy $C_5H_9O^+$ oxonium ions

The behavior of metastable $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$, each of which expels predominantly CH_2O, differs from that of the lower homologue, $\mathbf{a_1}^+$, which loses CO and CH_2O in comparable amounts. Indeed, CO elimination, which is the most abundant fragmentation of $\mathbf{a_1}^+$, is of only minor significance in the dissociation of $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$. Similarly, expulsion of H_2O is reduced in importance from 6%–8% for $\mathbf{a_1}^+$ to 1%–3% for $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$. However, C_3H_6 loss, which is barely noticeable in the dissociation of $\mathbf{a_1}^+$, is significant for $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$, and particularly so for $\mathbf{b_2}^+$. For all three ions, this process is associated with a composite metastable peak. This is illustrated in Fig. 2, which also shows that ions $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$ display signals at *m/z* 53, 45, and 41 for the minor losses of CH_3OH, C_3H_4, and CH_3CHO, respectively.

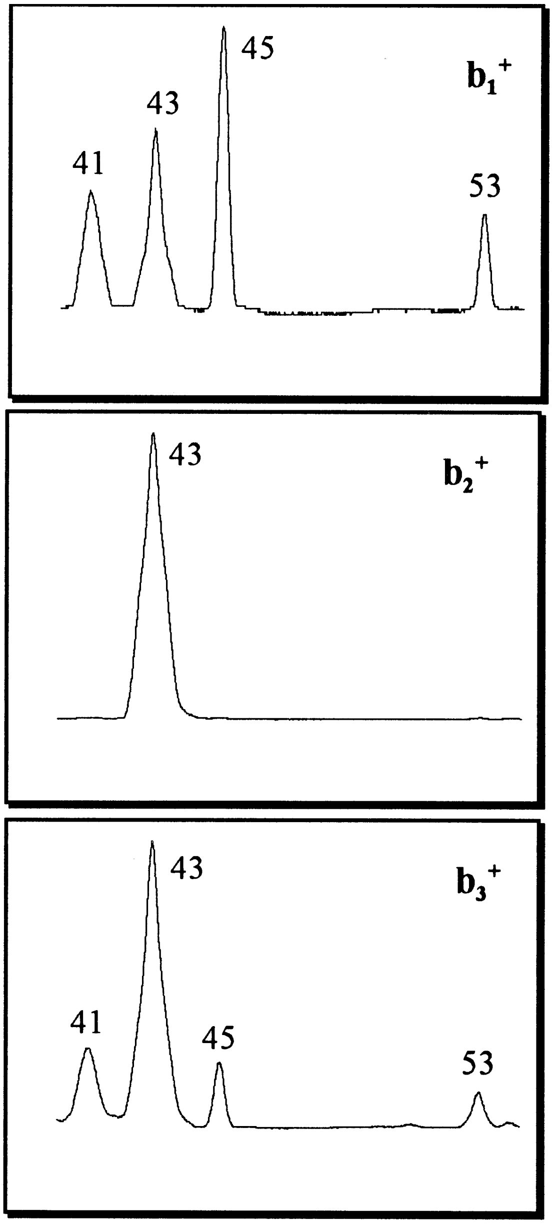


Fig 2. The *m/z* 40–54 region of the MI spectra of the $C_4H_6OCH_3^+$ ions $b_1^+ - b_3^+$.

The combined [product ion + neutral] enthalpy for loss of C_3H_4 as either propyne or allene to give $CH_3OCH_2^+$ is 202 kcal/mol, while loss of CH_3CHO to give $CH_2{=}CH\text{-}CH_2^+$ or $CH_3\text{-}C^+{=}CH_2$ yields values

Table 2
Product enthalpies, $\Sigma\Delta H_f$ in kcal/mol, for possible dissociation reactions of $C_nH_{2n-1}O^+$ ions[a]

Ion	Products	$\Sigma\Delta H_f$
$C_4H_7O^+$	$(CH_3)_2C^+(H) + CO$	165
	$CH_2{=}CHCH_2^+ + CH_2{=}O$	200
	$CH_3C{=}O^+ + C_2H_4$	169
	$HC{=}O^+ + CH_3CH{=}CH_2$	202
	$C_4H_5^{+b} + H_2O$	179
	$C_3H_3^{+c} + CH_3OH$	209
$C_5H_9O^+$	$(CH_3)_2C^+(CH_3)^d + CO$	139
	$(C_2H_5)C^+(H)CH_3 + CO$	157
	$CH_2{=}CHC^+(H)CH_3 + CH_2{=}O$	176
	$CH_2{=}C(CH_3)CH_2^+ + CH_2{=}O$	185
	$CH_3C{=}O^+ + CH_3CH{=}CH_2$	161
	$C_5H_7^{+e} + H_2O$	141
	$C_4H_5^{+b} + CH_3OH$	189
$C_6H_{11}O^+$	$(CH_3)_2C^+(C_2H_5) + CO$	132
	$(C_3H_7)C^+(H)CH_3 + CO$	149
	$CH_2{=}CHC^+(CH_3)_2 + CH_2{=}O$	157
	$CH_3C{=}O^+ + C_4H_8$	152
	$C_6H_9^{+f} + H_2O$	132
	$C_5H_7^{+e} + CH_3OH$	151

[a] Values from [14], rounded to the nearest kcal/mol.
[b] Most stable isomer, methylcyclopropenium cation.
[c] Most stable isomer, cyclopropenium cation.
[d] $\Sigma\Delta H_f$ = 143 kcal/mol if the revised ΔH_f value of tert-$C_4H_9^+$, 169.9 kcal/mol, is used, see [14].
[e] Most stable isomer, cyclopentenyl cation.
[f] Most stable isomer, 2-methylcyclopentenyl cation.

of 186 and 191 kcal/mol, respectively [13]. The corresponding value for loss of CH_2O to yield $CH_2{=}CHC^+(H)CH_3$, 176 kcal/mol (Table 2), is much lower. This thermochemical analysis indicates that the dissociation of these oxonium ions occurs at an energy level considerably above the thermochemical threshold, at least for metastable ions $\mathbf{b_1}^+$ and $\mathbf{b_3}^+$.

Comparison of the behavior of the isomeric pairs of oxonium ions $\mathbf{b_1}^+/\mathbf{b_4}^+$, $\mathbf{b_2}^+/\mathbf{b_5}^+$, and $\mathbf{b_3}^+/\mathbf{b_6}^+$, in which -$C^+(H)OCH_3$ is replaced by -$CH_2OCH_2^+$, reveals that some trends observed for the archetypal $C_4H_7O^+$ species, $\mathbf{a_1}^+$ and $\mathbf{a}_2^+$, persist for their higher homologues. Thus, see Table 1, the proportion of $\mathbf{b_4}^+$ -$\mathbf{b_6}^+$, which lose CO is greater than that for $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$. However, the stark contrast between $\mathbf{a_1}^+$ – which loses CH_2O, CO and a little H_2O – and ion $\mathbf{a_2}^+$ – which loses essentially only CO – no longer holds. Similarly, CH_2O is lost less readily, see Table 1, from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ than from $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$, but this reaction is not entirely superseded by CO loss as is the case for $\mathbf{a_2}^+$. On the other hand, H_2O elimination occurs to a greater extent from metastable $\mathbf{b_4}^+$ -$\mathbf{b_6}^+$ than from $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$. This reversal of the situation found for metastable ions $\mathbf{a_1}^+$and $\mathbf{a_2}^+$ is especially pronounced for$\mathbf{b_5}^+$, which loses mainly H_2O.

The apparent discrimination against CH_2O elimination from $\mathbf{a_2}^+$ and $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$, each of which contains an intact formaldehyde unit, is at first sight very surprising, especially since $\mathbf{a_1}^+$ and $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$, which do not contain this structural feature, expel CH_2O exclusively or predominantly. A logical explanation is that this reaction is favored at higher internal energies and that it occurs preferentially after $\mathbf{a_1}^+$ and $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ have undergone rate-limiting isomerization to form their $\mathbf{a_2}^+$ and $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ counterparts with internal energies higher than is needed to cause dissociation. Support for this interpretation is found in the $T_{0.5}$ values (the KER estimated from the width at half-height of the associated metastable peaks [8]) for CH_2O loss from $\mathbf{a_1}^+$ and $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$, which are consistently greater than those for the isomeric counterparts $\mathbf{a_2}^+$ and $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$.

This reaction from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ occurs with a very small KER: the metastable peaks are barely wider than the main beam of parent ions ($T_{0.5}$ = 1–2 meV). These values are consistent with CH_2O loss from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ essentially without reverse critical energy. In contrast, CH_2O loss from $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ produces broader metastable peaks with $T_{0.5}$ values of 33, 19, and 27 meV, respectively. The increased $T_{0.5}$ values reflect the excess energy in the transition state when ions formed as $\mathbf{b_1}^+$, $\mathbf{b_2}^+$ and $\mathbf{b_3}^+$ eventually lose CH_2O.

Parallel trends are found for other common reactions of $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$, and $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$. Thus, CO loss from $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ yields a very broad metastable peak, with $T_{0.5}$ in the range 310–465 meV, see Table 1, but the analogous fragmentation of $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$ is characterized by narrow peaks of Gaussian profile with $T_{0.5}$ values of 17, 30, and 18 meV, respectively.

All these data are consistent with the view that the CH_2O elimination from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ has a higher critical energy than loss of C_3H_6, CO or H_2O. However, CH_2O expulsion may occur by simple C–O cleavage from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$, whereas CO or H_2O loss entail

H-transfers and, at least in the latter case, skeletal isomerization. At the low internal energies appropriate to the dissociation of metastable ions [8] generated as $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$, the fragmentations with the lower critical energies are favored; consequently, CH_2O expulsion competes comparatively poorly with loss of C_3H_6, CO and H_2O. On the other hand, at the relatively high internal energies appropriate to the dissociation of ions formed by rate-limiting isomerization of $\mathbf{b_1}^+$- $\mathbf{b_3}^+$ to their counterparts $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$, CH_2O loss is favored because it may occur by simple bond cleavage, without further rearrangement.

Parallel behavior was found in a seminal study [19] of CH_3-C^+(H)OCH_3, and $CH_3CH_2OCH_2^+$, and in later work [20] on several isomers of $C_4H_9O^+$. Consequently, the tendency of oxonium ions containing the -C^+(H)OCH_3 entity to lose CH_2O, even though their isomers with the -$CH_2OCH_2^+$ subunit do not, appears to be general in both the $C_nH_{2n+1}O^+$ and $C_nH_{2n\text{-}1}O^+$ series.

Details of the rate-limiting isomerization(s) of $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ to $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ cannot be established from the current data. It is possible that $\mathbf{b_1}^+$ isomerizes to $\mathbf{b_4}^+$, $\mathbf{b_2}^+$ to $\mathbf{b_5}^+$ and $\mathbf{b_3}^+$ to $\mathbf{b_6}^+$ by a 1,3-hydride shift in each case. Such a shift was initially suggested in experimental studies [19] of $C_3H_7O^+$ and subsequently was supported by high-level ab initio calculations [21,22]. However, other mechanisms are possible, in particular a 1,5-H shift followed by a (dipole assisted) 1,3-H shift to form an ion-neutral complex (INC) [23], see Sec. 3.2.

The metastable ion characteristics of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ are superficially similar, but there are sufficient differences to suggest that these isomeric oxonium ions do not interconvert before fragmenting. Thus, $\mathbf{b_1}^+$ and $\mathbf{b}_3^+$ both lose CH_3OH, C_3H_4, and CH_3CHO, see Fig. 2, whereas $\mathbf{b_2}^+$ does not. Moreover, $\mathbf{b_1}^+$ shows a less pronounced loss of C_3H_6 than either $\mathbf{b_2}^+$ or $\mathbf{b_3}^+$ and the importance of CO loss is greatest from $\mathbf{b_3}^+$. The competition between possible fragmentation routes of metastable ions can be influenced by variations in the internal energy of the dissociating population of ions, as is the KER associated with each reaction [23]. Such an effect has already been noted in the comparative importance of CO and CH_2O loss from $\mathbf{a_1}^+$ [7a]. However, the variations in the ratios of CO, CH_3OH, C_3H_4 and, especially, C_3H_6 elimination from $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ seem too large to be explained solely in terms of changes in the internal energy of the fragmenting ions. Similarly, the $T_{0.5}$ values for CH_2O expulsion from $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$, 33, 19, and 27 meV, respectively, also vary substantially. Some reactions of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$, particularly CH_2O loss, may involve closely related intermediates or transition states, but in agreement with the CID data of Fig. 1, $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ do not easily interconvert prior to dissociation.

Similarly, the disparate behavior of $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$ suggests that the barriers towards interconversion of these oxonium ions are fairly high and that isomerization to a common structure occurs at a relatively late stage in their dissociation, if it occurs at all.

This deduction is confirmed for $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ by the behavior of labeled analogues, see Tables 3 and 4. Elimination of formaldehyde from $\mathbf{b_1}^+$ occurs only after fairly extensive exchange of the H atoms of the OCH_3 group.

Thus, see Table 3, $\mathbf{b_1}^+$[OCD_3], expels CD_2O and CHDO in approximately equal amounts; a little CH_2O loss is also observed. In contrast, $\mathbf{b_3}^+$[OCD_3], and particularly $\mathbf{b_2}^+$[OCD_3], show a much greater preference for losing formaldehyde as CD_2O derived from the intact OCD_3 group. Differences are also evident in the site selectivities of propene/cyclopropane loss from $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$: ions $\mathbf{b_2}^+$[OCD_3] lose $C_3H_4D_2$ and $C_3H_3D_3$ in roughly equal abundance, but C_3H_5D and C_3H_6 expulsion are negligible; $\mathbf{b_3}^+$[OCD_3] behaves similarly, with a slight tendency to expel C_3H_5D and C_3H_6. The weak and partially overlapping signals for this reaction from $\mathbf{b_1}^+$[OCD_3] are more equally divided between the $C_3H_{6\text{-}n}D_n$ (n = 0–3) species. This trend persists for the ^{13}C-labeled analogues: $\mathbf{b_2}^+$[$O^{13}CH_3$] and $\mathbf{b_3}^+$[$O^{13}CH_3$] lose $^{13}CC_2H_6$ with high selectivity, but $\mathbf{b_1}^+$[$O^{13}CH_3$], shows weak signals for elimination of C_3H_6 and $^{13}CC_2H_6$.

3.2. Elimination of formaldehyde

This fragmentation typically accounts for 75% of the total metastable ion current. It is characterized by

Table 3
Relative abundances[a] and kinetic energy releases[b] for the main dissociations of metastable $C_5H_6D_3O^+$ ions

Precursor	Ion → Loss	CH_2O	CHDO	CD_2O	C_3H_6	C_3H_5D	$C_3H_4D_2$	$C_3H_3D_3$
1a[OCD$_3$]	$\mathbf{b_1}^+$[OCD$_3$]	9 [31]	100 [31]	88 [30]				
1b[OCD$_3$]	$\mathbf{b_1}^+$[OCD$_3$]	11 [37]	76 [34]	100 [31]				
1c[OCD$_3$]	$\mathbf{b_1}^+$[OCD$_3$]	12 [36]	83 [31]	100 [31]				
2a[OCD$_3$]	$\mathbf{b_2}^+$[OCD$_3$]	. . .	4 [30]	100 [23]	. . .	. . .	7	6
2a[1-(CD$_3$)$_2$]	$\mathbf{b_2}^+$[1-CD$_3$]	100 [20]	1 [26]	. . .	14	. . .	. . .	10
2c[1-CD$_3$]	$\mathbf{b_2}^+$[1-CD$_3$]	100 [20]	2 [25]	. . .	10	. . .	. . .	6
2d[1-CD$_3$]	$\mathbf{b_2}^+$[1-CD$_3$]	100 [20]	2 [29]	. . .	8	. . .	. . .	6
3a[OCD$_3$]	$\mathbf{b_3}^+$[OCD$_3$]	. . .	20 [30]	100 [23]	1	1	9	9
3b[OCD$_3$]	$\mathbf{b_3}^+$[OCD$_3$]	7	44 [31]	100 [34]	1	1	5	5

[a] Relative abundance measured by peak height normalised to a value of 100 units for the base peak in the MI spectrum for ions dissociating in the second field-free region.

[b] Numbers in square brackets represent kinetic energy releases, $T_{0.5}$, in meV as obtained from the width at half height of the peak.

[c] Compound **2c** is CH_2=C(CH$_3$)CH(CD$_3$)OCH$_3$; **2d** is CH$_3$CH=CHCH(CD$_3$)OCH$_3$.

a Gaussian metastable peak; the associated KER increases in the order $\mathbf{b_2}^+ < \mathbf{b_3}^+ < \mathbf{b_1}^+$. All three [O^{13}CH$_3$] labeled analogues expel $^{13}CH_2O$ with selectivities of at least 99%, thus establishing that the carbon atom of the expelled formaldehyde originates from the OCH$_3$ group. Similarly, $\mathbf{a_1}^+$[O^{13}CH$_3$] does not lose a measurable amount of CH_2O [7]. These data suggest that formaldehyde loss occurs after H-transfer from the OCH$_3$ group to the C_4H_6 entity in $C_4H_6OCH_3^+$. Such an H-transfer should be more favorable than for the analogous $C_4H_8OCH_3^+$ ions because the C=C double bond permits a 1,5-H shift via a six-membered ring transition state, see Scheme 2a.

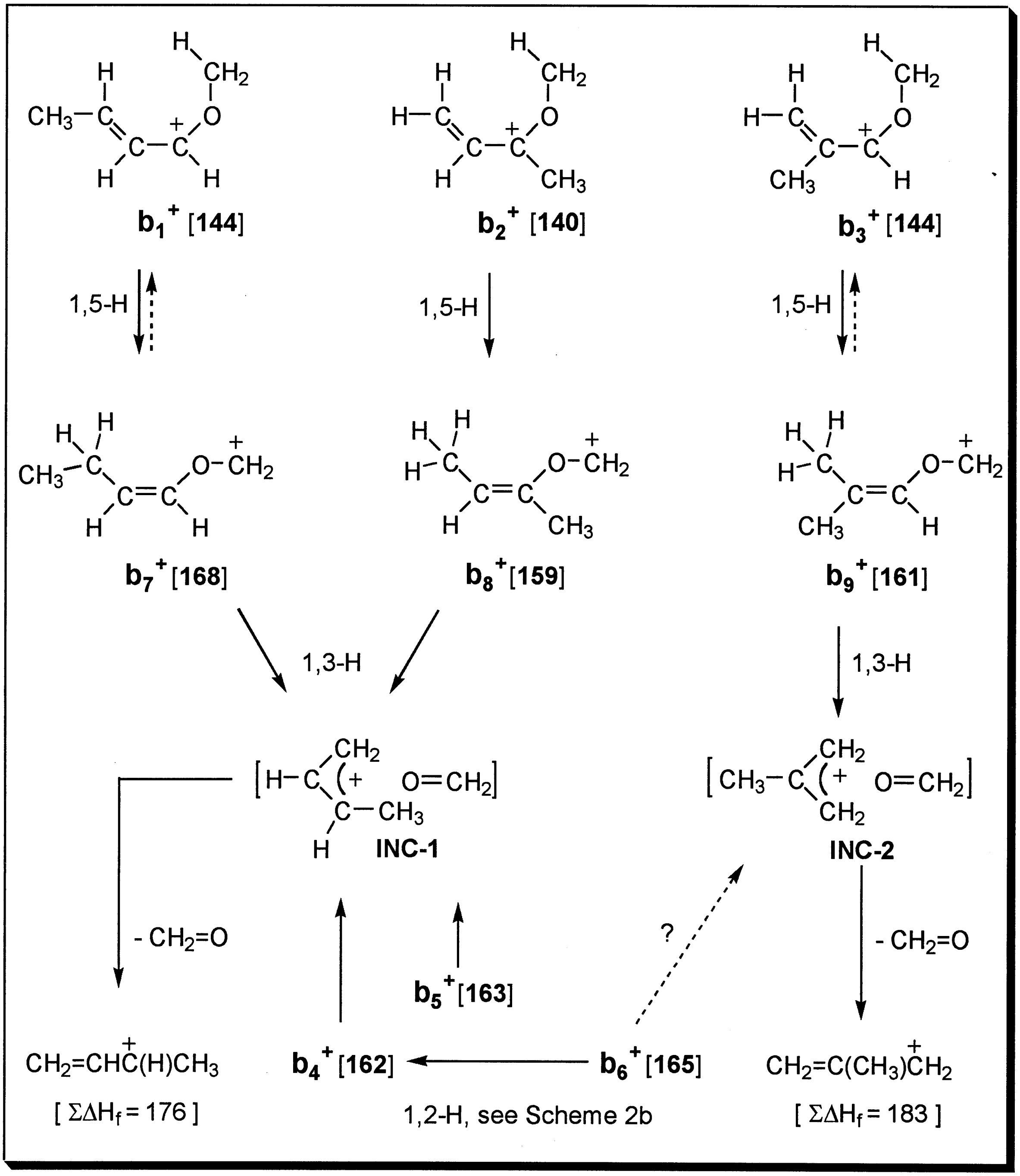
The D-labeling data of Table 3 reveal that the 1,5-H transfer is essentially unidirectional for $\mathbf{b_2}^+$: thus, $\mathbf{b_2}^+$[OCD$_3$] loses CD_2O with ~95% selectivity. The KERs for the minor elimination of formaldehyde containing 'exchanged' H atoms are greater than those for loss of the formaldehyde obtained by simple hydrogen abstraction from the initial OCH$_3$ group of $\mathbf{b_2}^+$. This trend applies regardless of whether an H or D atom is incorporated as 'exchanged' hydrogen. Consequently, it appears that the higher energy ions show an increased propensity for undergoing the steps that result in exchange of H atoms of the OCH$_3$ group with those of the four-carbon chain.

Rather more exchange is observed for $\mathbf{b_1}^+$[OCD$_3$] and $\mathbf{b_3}^+$[OCD$_3$], which expel CHDO in high and moderate abundance. Moreover, in the case of $\mathbf{b_3}^+$[OCD$_3$], the extent to which this exchange occurs depends on how the ions were formed. When the ion is generated by direct α-cleavage of CH_2=C(CH$_3$)CH(C$_2$H$_5$)OCD$_3^{\cdot +}$, **3a**[OCD$_3$] in Table 3, the preference for CD_2O loss is greater than when it is formed by rearrangement and γ-cleavage of C$_2$H$_5$CH=CHCH$_2$OCD$_3^{\cdot +}$, **3b**[OCD$_3$]. This trend is intelligible if $\mathbf{b_3}^+$[OCD$_3$] has more internal energy when generated by rearrangement via the enol ion (C$_2$H$_5$)(CH$_3$)C=C(H)OCD$_3^{\cdot +}$ followed by γ-cleavage than by direct α-cleavage of **3a**[OCD$_3$], provided that the higher energy ions have an enhanced tendency to

Table 4
Relative abundances[a] for the main dissociations of metastable $^{13}CC_4H_9O^+$ ions

Precursor	Ion/Loss →	CH_2)	$^{13}CH_2O$	C_3H_6	$^{13}C_3H_6$	CO	^{13}CO
1c[O^{13}CH$_3$]	$\mathbf{b_1}^+$[O^{13}CH$_3$]	<0.5	100	~1	~2	2	<0.1
2a[O^{13}CH$_3$]	$\mathbf{b_2}^+$[O^{13}CH$_3$]	<0.4	100	<0.1	30	3	<0.1
3a[O^{13}CH$_3$]	$\mathbf{b_3}^+$[O^{13}CH$_3$]	<0.4	100	1	19	12	<0.4

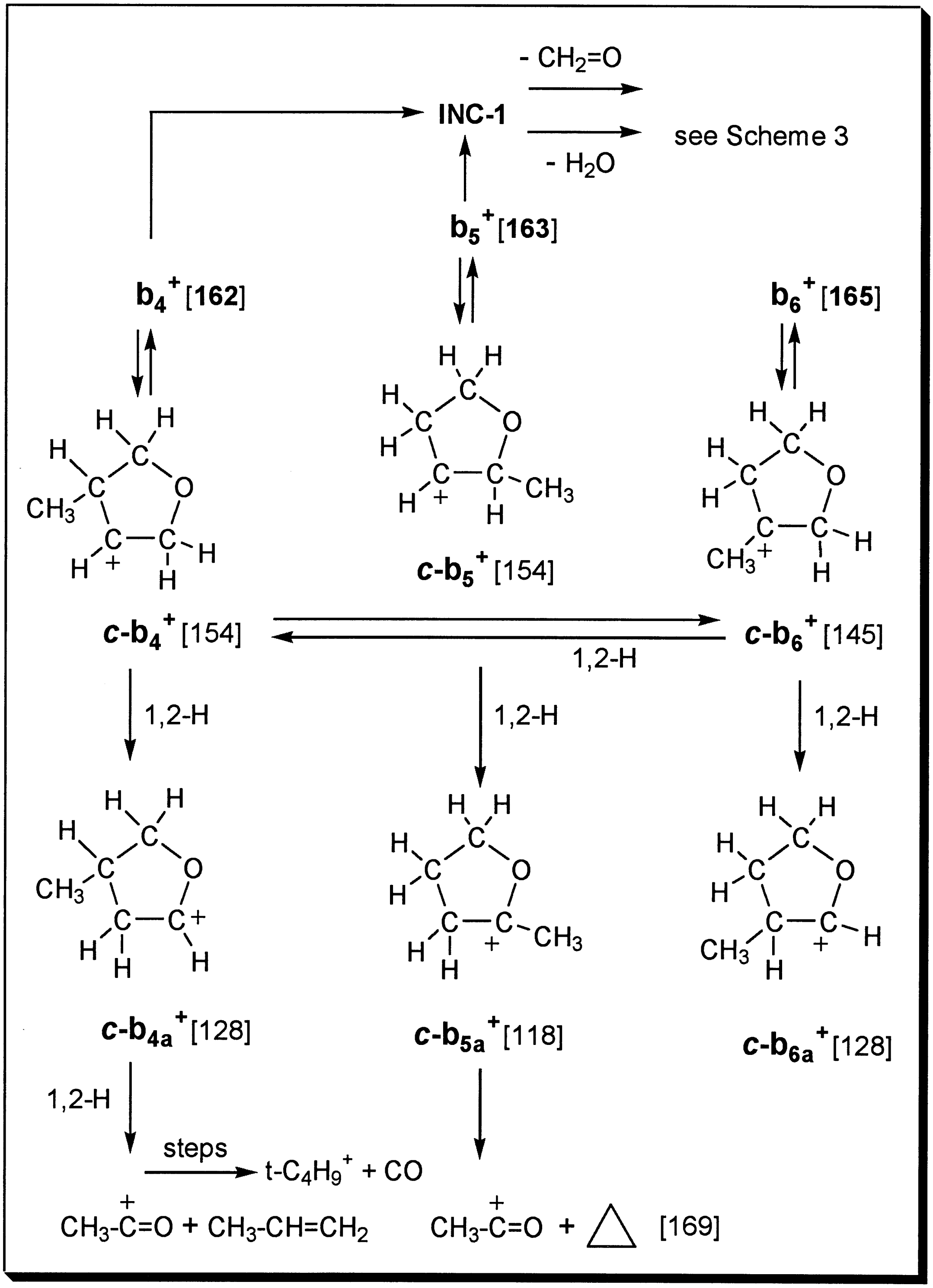
[a] Relative abundance measured by peak height normalized to a value of 100 units for the base peak in the MI spectrum of ions dissociating in the second field-free region.



Scheme 2a.

undergo the H-transfer steps. This possibility is supported by the significantly greater KER values for CD_2O/CHDO loss from $\mathbf{b_3}^+[OCD_3]$ formed from **3b**$[OCD_3]$ than from **3a**$[OCD_3]$.

The order of increasing KERs for formaldehyde expulsion: $\mathbf{b_1}^+[OCD_3] > \mathbf{b_3}^+[OCD_3] > \mathbf{b_2}^+[OCD_3]$ is the same as that for increasing incorporation of exchanged hydrogen in the eliminated formaldehyde.


- CH2=O
INC-1
- H2O
see Scheme 3
b5+ [163]
b4+ [162]
b6+ [165]
c-b5+ [154]
c-b4+ [154]
c-b6+ [145]
1,2-H
c-b4a+ [128]
c-b5a+ [118]
c-b6a+ [128]
steps
t-C4H9+ + CO
CH3-C=O + CH3-CH=CH2
CH3-C=O + [169]

Scheme 2b.

Both these trends are consistent with the view that formaldehyde loss and the exchange of the H atoms of the methoxy group are favored at higher internal energies. If the 1,5-H/D shift in $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ were reversible, this step would result in exchange of the H atoms of the methoxy group. According to this interpretation, the tendency of $\mathbf{b_7}^+$, $\mathbf{b_8}^+$, and $\mathbf{b_9}^+$ to revert to their original structures would vary: $\mathbf{b_8}^+$ rarely returns to $\mathbf{b_2}^+$; $\mathbf{b_9}^+$ occasionally reverts to $\mathbf{b_3}^+$; and $\mathbf{b_7}^+$ rearranges back to $\mathbf{b_1}^+$ rather more rapidly than it expels CH_2O, see scheme 2a. If $\mathbf{b_1}^+$ reverted to $\mathbf{b_7}^+$ on average once before losing CH_2O, the ratio of CD_2O : CHDO elimination from $\mathbf{b_1}^+[OCD_3]$ would be 2:1 in the absence of isotope effects.

An alternative to the 1,5-H shift proposed to initiate the isomerization of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ is a 1,3-H shift, which would lead directly to $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$, respectively. This possibility has several features which make it superficially attractive: there are fewer constraints on the geometry of the transition state, the need to invoke the involvement of $\mathbf{b_7}^+$, $\mathbf{b_8}^+$, and $\mathbf{b_9}^+$ is removed and CH_2O loss may occur by simple C–O cleavage of $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$. Moreover, there is precedence for a 1,3-H shift in the reactions of the analogous oxonium ions which do not contain the C=C bond that is present in $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$. However, mechanisms involving a direct 1,3-H shift in closed-shell systems have serious disadvantages and it is known from both experimental [19,20] and computational [21,22] studies of $C_nH_{2n+1}O^+$ that these processes have very high critical energies and are usually irreversible. Thus, $CH_3C^+(H)OCD_3$ and $CH_3CH_2C^+(H)OCD_3$ lose CD_2O, but not CHDO or CH_2O [19, 20]. In contrast, 1,5-H shifts in oxonium ions are often partially reversible. Consequently, if $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ rearranged via a 1,3-H shift to $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$, respectively, that step would probably be rate limiting and CH_2O loss would be expected to occur rapidly by C–O cleavage before H/D-exchange could occur. In actual fact, some H/D-exchange is observed, especially for $\mathbf{b_1}^+[OCD_3]$ and $\mathbf{b_3}^+[OCD_3]$. Furthermore, the amount of exchange increases as the internal energy of the dissociating ions increases. The opposite trend would be expected if a 1,3-H shift led directly from $\mathbf{b_1}^+[OCD_3]$, $\mathbf{b_2}^+[OCD_3]$ and $\mathbf{b_3}^+[OCD_3]$ to $\mathbf{b_4}^+[OCD_2]$, $\mathbf{b_5}^+[OCD_2]$ and $\mathbf{b_6}^+[OCD_2]$ because the higher energy ions would show an increased tendency to expel CD_2O rather than undergo any processes that resulted in H/D-exchange. In contrast, the possibility of a 1,5-H shift offers a natural route to explain the H/D-exchange that precedes formaldehyde loss from $\mathbf{b_1}^+[OCD_3]$, $\mathbf{b_3}^+[OCD_3]$ and, to a lesser extent, $\mathbf{b_2}^+[OCD_3]$. This possibility is not open to $CH_3C^+(H)OCD_3$ and $CH_3CH_2C^+(H)OCD_3$, thus accounting for the absence of H/D-exchange when formaldehyde is lost from oxonium ions in which there is no C=C bond to facilitate the 1,5-H shift. Nevertheless, the possibility of a 1,3-H shift cannot be entirely excluded on the basis of the current data, particularly for $\mathbf{b_2}^+[OCD_3]$, in which relatively little H/D-exchange is observed.

Further rearrangement after the 1,5-H shift must precede or accompany CH_2O elimination because it is most unlikely that the final product will be a vinyl type cation, like $CH_3CH_2CH{=}C^+H$, resulting from direct fission of $\mathbf{b_7}^+$. Formation of such energetically unfavorable species would be expected to be pre-empted by isomerization of the developing cation, perhaps via a dipole-assisted 1,3-H transfer within an INC [23] comprising $C_4H_7^+$ coordinated to CH_2O. This mechanism would permit the production of a more stable conjugated allylic cation, i.e. $CH_2{=}CHC^+(H)CH_3$ from $\mathbf{b_1}^+$ and $\mathbf{b_2}^+$ or $CH_2{=}C(CH_3)CH_2^+$ from $\mathbf{b_3}^+$. The likelihood of this further rearrangement is an important difference between $C_5H_9O^+$ ions of the type $C_4H_7OCH_2^+$ and $C_5H_{11}O^+$ ions of the type $C_4H_9OCH_2^+$ formed by isomerization of $C_4H_6OCH_3^+$ and $C_4H_8OCH_3^+$, respectively.

The secondary cation, $CH_2{=}CHC^+(H)CH_3$, is 9 kcal/mol [13] more stable than the primary isomer $CH_2{=}C(CH_3)CH_2^+$. However, the energy barriers to interconversion of the 1- and 2-methallyl cations are less than those towards decomposition (~60 kcal/mol). Consequently, the reactions of metastable $[C_4H_7]^+$ ions are not significantly dependent on the origin of the ion [24]. In line with this, we found that the CID spectra (not shown) of ions of putative structure $CH_2{=}CHC^+(H)CH_3$ and $CH_2{=}C(CH_3)CH_2^+$ (generated by loss of $Cl^\cdot$ from 3-chloro-1-butene and 3-chloro-2-methyl propene, respectively) are virtually identical. Thus, it is not possible to determine which of the allylic $C_4H_7^+$ isomers is generated in the loss of CH_2O from the oxonium ions studied.

Considering the very small KERs, it seems probable that $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ lose CH_2O via an INC and we propose that all three ions dissociate via INC-1 of Scheme 2a, to generate the most stable $C_4H_7^+$ isomer, the 1-methallyl cation. For $\mathbf{b_4}^+$ and $\mathbf{b_5}^+$, see Scheme 2a, this reaction entails a simple bond cleavage. Direct bond cleavage in $\mathbf{b_6}^+$ would yield the less favorable 2-methallyl cation, via INC-2. However, $\mathbf{b_6}^+$ and $\mathbf{b_4}^+$ may interconvert via a 1,2-H shift in their cyclic counterparts **c-b**$_6^+$ and **c-b**$_4^+$ prior to the loss of CH_2O from $\mathbf{b_6}^+$, see Scheme 2b.

Finally, we note that the average internal energies of any ions with a common structure generally depend on their origin. This caveat is necessary to explain the divergent site-selectivites and KERs for formaldehyde loss from $\mathbf{b_1}^+[OCD_3]$, $\mathbf{b_2}^+[OCD_3]$, and $\mathbf{b_3}^+[OCD_3]$ and also generic differences in the reactions of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ compared to $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$. Any common intermediate in CH_2O loss is likely to lie at a relatively late stage of the route when the reacting species is beginning to resemble $[C_4H_7^+/CH_2{=}O]$.

3.3. Elimination of C_3H_6 (propene or cyclopropane)

Loss of C_3H_6 involves either propene or cyclopropane. The latter isomer is 8 kcal/mol less stable but its (co)generation should be feasible since the minimum energy requirement for dissociation to CH_3CO^+ + c-C_3H_6 [$\Sigma\Delta H_f$ (products) = 169 kcal/mol] remains below the calculated threshold for the competing CH_2O loss, 176 kcal/mol, see Scheme 2a.

For $\mathbf{a_1}^+$, loss of C_3H_6 is negligible and only a slight increase is found on progressing to $\mathbf{b_1}^+$. However, for $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$, this reaction competes quite well with CH_2O loss, see Table 1. Similarly, loss of C_3H_6 plays no role in the dissociation of $\mathbf{a_2}^+$ [7a], but it does occur to an appreciable extent from $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$.

The eliminated neutral of mass 42 units is clearly C_3H_6 and not C_2H_2O (ketene) : inspection of the (3ffr) CID spectra (not shown) of the metastably generated *m/z* 43 product ions leaves no doubt that CH_3CO^+ [25], rather than $C_3H_7^+$, is produced by the dissociation of metastable ions $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ and $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$.

For ions $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$, this dissociation is characterized by a composite metastable peak consisting of a (conceivably common) narrow and broad component, see Table 1. However, the proportion of the components in $\mathbf{b_2}^+$ and $\mathbf{b_3}^+$(1 : 1) differs from that for $\mathbf{b_1}^+$ (3 : 1).

The behavior of $\mathbf{b_2}^+[O^{13}CH_3]$, which loses $^{13}CC_2H_6$ but not C_3H_6, reveals that the carbon atom of the OCH_3 group is always incorporated in the expelled neutral. However, $C_3H_3D_3$ and $C_3H_4D_2$ are eliminated at approximately equal rates from both $\mathbf{b_2}^+[OCD_3]$ and $\mathbf{b_3}^+[OCD_3]$; this finding indicates that up to one H atom from the OCH_3 substituent can become part of the ionic fragment. The third isomer, $\mathbf{b_1}^+[OCD_3]$, may behave similarly, but the low intensities of the partially overlapping signals prevent a meaningful analysis.

The elimination of comparable amounts of $C_3H_3D_3$ and C_3H_6 but no $C_3H_4D_2$ or C_3H_5D from $\mathbf{b_2}^+[1\text{-}CD_3]$ shows that all the atoms of the intact carbon-bound methyl group of $\mathbf{b_2}^+$ are included in either the ionic or neutral product. However, upon collisional activation, $\mathbf{b_2}^+[1\text{-}CD_3]$ yields a prominent peak at *m/z* 46 (CD_3CO^+) whereas that at *m/z* 43 (CH_3CO^+) is of only minor importance. This result indicates that the rearrangement reaction of metastable ions $\mathbf{b_2}^+[1\text{-}CD_3]$ that leads to dissociation to CH_3CO^+ + $C_3H_3D_3$ is a slow process, possibly because one of the steps involves a methyl migration. The dissociation to CD_3CO^+ + C_3H_6 seems to be more straightforward and one possibility to rationalize this pathway involves the route : $\mathbf{b_2}^+ \rightarrow \mathbf{b_5}^+$, either via $\mathbf{b_8}^+$ or else via a direct 1,3-H shift, followed by the steps : $\mathbf{b_5}^+ \rightarrow$ **c-b**$_5^+ \rightarrow$ **c-b**$_{5a}^+ \rightarrow CD_3CO^+$ + c-C_3H_6, as outlined in scheme 2b.

We note that this proposal accounts for the specific loss of $^{13}CC_2H_6$ from $\mathbf{b_2}^+[O^{13}CH_3]$, but want to stress that the complete picture is more complex because both the $C_3H_3D_3$ loss and the C_3H_6 loss from $\mathbf{b_2}^+[1\text{-}CD_3]$ are still associated with composite metastable peaks.

3.4. Elimination of Carbon Monoxide

Loss of CO from the isomeric $\mathbf{b}^+$-type oxonium ions yields $C_4H_9^+$ product ions. Of the four isomeric butyl cations that could conceivably be formed, only the tert-$C_4H_9^+$ and the sec-$C_4H_9^+$ isomers are likely candidates. Loss of CO obviously involves extensive rearrangement and for this reaction to compete with CH_2O loss—which for $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ involves a direct bond cleavage at the thermochemical threshold—its minimum energy requirement must be considerably lower than that for loss of CH_2O. This condition is satisfied for the production of either the tert- or the sec-butyl cation [$\Sigma\Delta H_f$ (products) = 139 and 157 kcal/mol, respectively], but not for the other two isomers. Unfortunately, isomeric $C_4H_9^+$ species cannot be distinguished on the basis of CID experiments.

Loss of CO is the major reaction of $\mathbf{a_1}^+$, but it is of only minor importance for $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$. The eliminated neutral must be mainly or wholly CO, rather than C_2H_4, because no D-labeled analogue of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ expels C_2H_3D in measurable abundance. If ethylene loss did occur, either $\mathbf{b_2}^+$[OCD_3] or CH_2=$CHC^+(CD_3)OCH_3$, $\mathbf{b_2}^+$[1-CD_3], would eliminate C_2H_3D.

The absence of ^{13}CO elimination from $\mathbf{b_1}^+$[$O^{13}CH_3$], $\mathbf{b_2}^+$[$O^{13}CH_3$], and $\mathbf{b_3}^+$[$O^{13}CH_3$], indicates that these ions do not expel carbon monoxide by double H-transfer between the components of any intermediate INC [$C_4H_7^+$/$^{13}CH_2$=O] en route to $^{13}CH_2O$ expulsion. Instead, skeletal rearrangement and cleavage of the C–O bond of the OCH_3 group occurs.

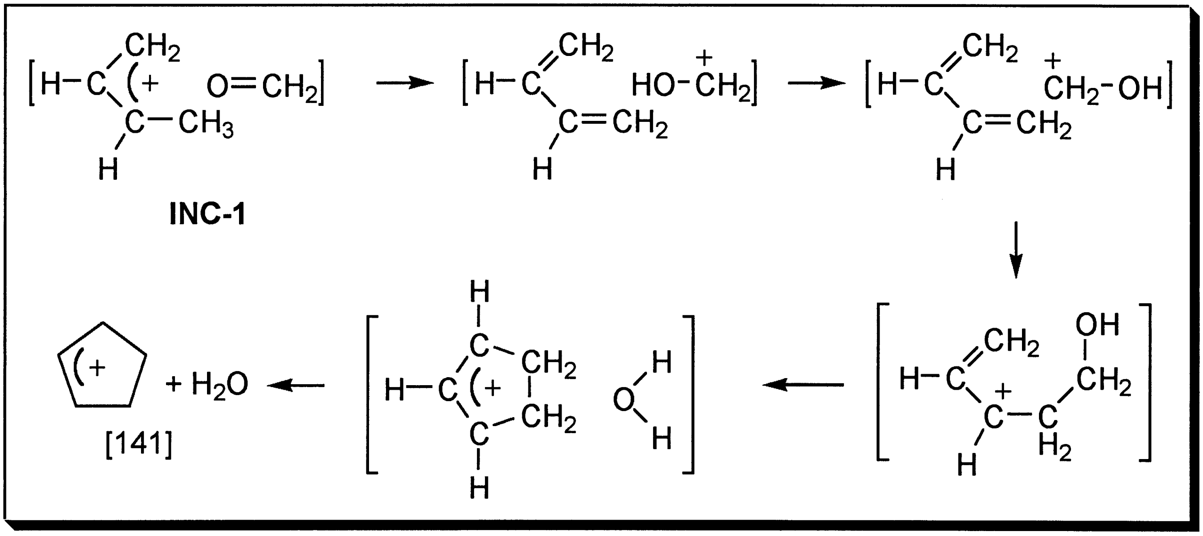
The signal for CO loss from $\mathbf{b_3}^+$ is appreciably stronger than that starting from $\mathbf{b_1}^+$ or $\mathbf{b_2}^+$. The metastable peak is very broad and the associated $T_{0.5}$ value (~300 meV) is very large. This value is even greater than that for CO elimination from $\mathbf{a_1}^+$. However, in contrast to $\mathbf{a_1}^+$[$O^{13}CH_3$], which loses both CO and ^{13}CO, with the former predominating, the [$O^{13}CH_3$] isotopologues of the higher homologues $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ all lose CO with high selectivity, possibly via rearrangement to the stable cyclic intermediates of the $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ manifold of ions.

All of these ions, particularly $\mathbf{b_4}^+$ and $\mathbf{b_5}^+$, expel an appreciably greater percentage of CO than the corresponding isomer containing a methoxy group. This trend in the relative abundance of CO loss is parallel to but less pronounced than that found for $\mathbf{a_1}^+$ and $\mathbf{a_2}^+$. However, in contrast to the situation found for $\mathbf{a_2}^+$, which expels CO by two routes one of which has a large KER [7], the metastable peaks for CO loss from $\mathbf{b_4}^+$, $\mathbf{b_5}^+$, and $\mathbf{b_6}^+$ have a noncomposite Gaussian shape; moreover, the associated $T_{0.5}$ values (17, 30, and 18 meV, respectively) are small.

This contrast must reflect a profound change in the mechanism for CO loss on progressing from $\mathbf{a_2}^+$ to the $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ system of ions. In both systems a cyclization reaction may occur but an important difference is that for the $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ system energetically very favorable tertiary alkyl cations could be formed as the product ion. For example, $\mathbf{b_4}^+$, see Table 1, readily loses CO in competition with C_3H_6. This reaction may well take place from the very stable cyclic intermediate c-$\mathbf{b_{4a}}^+$ of Scheme 2b. A 1,2-H shift in this ion yields a reactive intermediate from which both CH_3–CH=CH_2 and CO could be lost by direct bond cleavages. However, loss of CO by direct bond cleavage to form iso-$C_4H_9^+$ cannot compete with propene loss: $\Sigma\Delta H_f$ [CH_3CO^+ + $CH_3CH{=}CH_2$], 161 kcal/mol, is much lower than $\Sigma\Delta H_f$ [iso-$C_4H_9^+$ + CO], 173 kcal/mol [13]. On the other hand, en route to the loss of CO from the (INC type) reactive intermediate, rearrangement of the incipient primary carbenium ion $(CH_3)_2CHCH_2^+$ to the tert-butyl cation $(CH_3)_3C^+$ may occur. This would allow CO loss to compete with propene elimination, particularly for long-lived low energy ions. In support of this proposal, we note that the MI spectrum of *m/z* 85 $\mathbf{b_4}^+$ ions generated from *metastable* precursor ions displays only one signal, at *m/z* 57. The same peak dominates the CID spectrum of these ions. Thus, for these long-lived low energy ions $\mathbf{b_4}^+$, loss of CO prevails.

3.5. Elimination of Water

Ions $\mathbf{b_2}^+$[OCD_3] lose water as H_2O, whereas significant amounts of H_2O and HOD are lost from $\mathbf{b_3}^+$[OCD_3] and $\mathbf{b_1}^+$[OCD_3]. Since the reaction is of only minor importance, a detailed analysis is not possible. The metastable peaks are Gaussian in shape and the associated KERs are only moderately large ($T_{0.5}$ = 30–50 meV). This behavior resembles that of $\mathbf{a_1}^+$, which expels H_2O rather more readily.



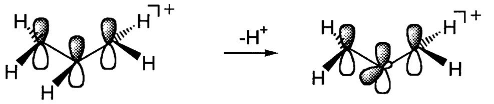
Scheme 3.

Elimination of H_2O is much more important starting from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ and particularly from $\mathbf{b_5}^+$. This trend is the reverse of that found for $\mathbf{a_1}^+$ and $\mathbf{a_2}^+$. The enhanced competition of H_2O expulsion with CO loss from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$, compared to $\mathbf{a_2}^+$, may reflect the presence of a four-carbon chain in these $C_5H_9O^+$ isomers.

Loss of H_2O is a remarkable process in which two C–O connections must be broken with the formation of two O–H bonds and one new C–C bond. It often occurs for the analogous metastable $C_nH_{2n+1}O^+$ ions with a nonterminal oxygen atom and it has been interpreted in terms of isomerization involving INCs [26, 27]. A similar mechanism Scheme 3, offers a means of interpreting H_2O loss from $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$ in terms of the previously proposed INC-1 associated with the loss of CH_2O from these ions. In this context, we note that the CID spectrum (not shown) of the $\mathbf{b_5}^+$ type ions generated from *metastable* (low energy) precursor ions differs from that presented in Fig. 1 for the high energy (source generated) ions: the former spectrum is dominated by a peak at *m/z* 43 (CH_3CO^+), while the losses of CH_2O (to give *m/z* 55) and H_2O (to give *m/z* 67) are barely present. This strongly suggests that long-lived, low energy ions $\mathbf{b_5}^+$ have adopted cyclic structures, see Fig. 2, from which losses of both CH_2O and H_2O are not favored. This reinforces our proposal that these two reactions take place from noncyclic ions, which have sufficient internal energy to adopt the INC-1 configuration.

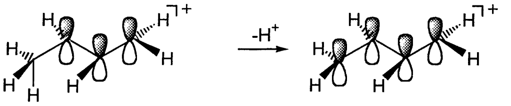
The crucial steps in this route are probably the initial proton transfer from the $C_4H_7^+$ cation to CH_2O and the subsequent recombination of C_4H_6 with $[CH_2OH]^+$ to form $[C_4H_6CH_2OH]^+$. Although the proton affinity (PA) of butadiene is 17 kcal/mol greater than that of formaldehyde [14], the proton-transfer may be feasible given the ability of butadiene to stabilize CH_2OH^+ by π-donation. Subsequent H-transfer and rearrangement of the developing $C_5H_7^+$ cyclopentenyl cation may then lead to a combination of products that is energetically very favorable, see Table 2.

Several factors may favor H_2O loss on progressing from $\mathbf{a_2}^+$ to $\mathbf{b_4}^+$, $\mathbf{b_5}^+$ and $\mathbf{b_6}^+$. First, the extra CH_2 unit makes possible the formation of a stable cyclic ionic product, namely the cyclopentenyl cation. Secondly, the initial proton-transfer from $C_4H_7^+$ to CH_2O should be easier than the analogous process from $C_3H_5^+$, especially for stable allylic species. Deprotonation of the allyl cation on the central carbon atom leads to an unfavorable geometry of allene in which the p-orbitals from which the developing new C=C bond is formed are orthogonal



(1)

No such unfavorable factors operate in the deprotonation of the 1-methallyl cation, which may lead smoothly to butadiene



(2)

Thirdly, the stabilization conferred on the INC $[CH_2OH^+/C_3H_4]$ is likely to be much less than the corresponding stabilization of $[CH_2OH^+/C_4H_6]$ because the possibility of donating electron density from both π-bonds is geometrically feasible only for a conjugated diene.

3.6. Trends in the reactions of $C_nH_{2n-2}OCH_3^+$ ions for n = 3–5

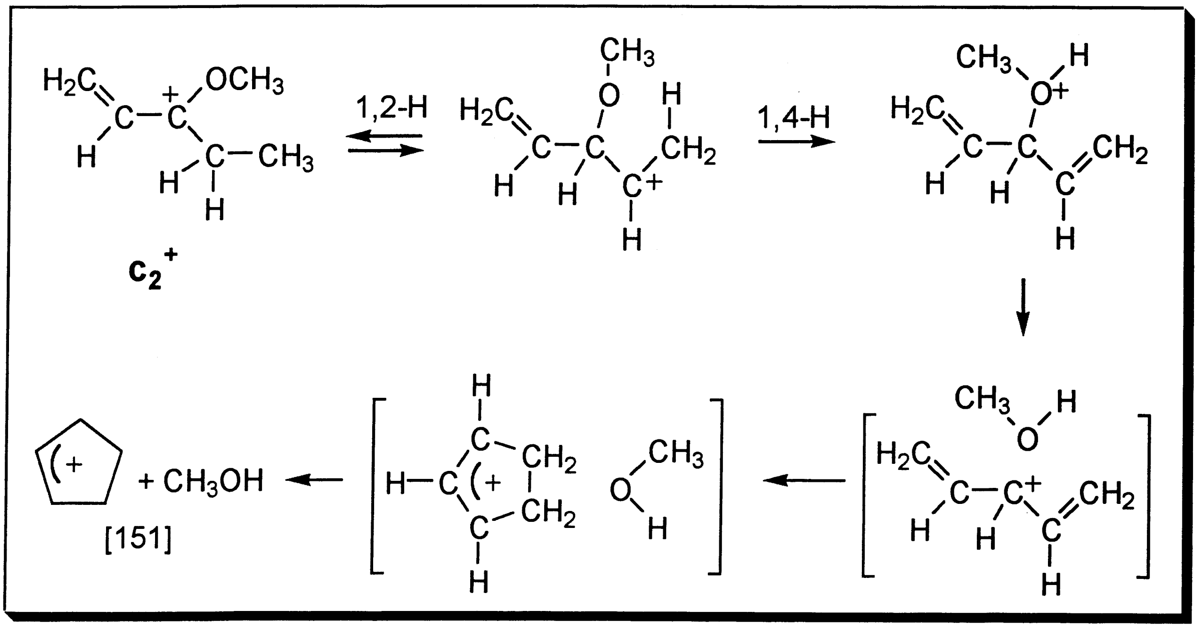
Homologation of $\mathbf{a_1}^+$ to $\mathbf{b_1}^+$, $\mathbf{b_2}^+$ or $\mathbf{b_3}^+$ induces strong changes in the reactions of metastable $C_nH_{2n-2}OCH_3^+$ ions. Some of these variations persist for metastable ions $CH_2{=}CHC^+(C_2H_5)OCH_3$, $\mathbf{c_1}^+$, which resemble $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ in expelling mainly CH_2O (67%) but very little CO (~3%). However, $\mathbf{c_1}^+$ differs from $\mathbf{b_1}^+$ - $\mathbf{b_3}^+$ in losing a substantial amount of CH_3OH (27%).

These trends may be understood in terms of the energies of the possible products, Table 2. Despite uncertainties about the structure of several of the ionic products and the magnitude of reverse critical energies associated with reactions that entail skeletal rearrangements, the following points can be made.

First, CO loss may always give more favorable products than CH_2O elimination, but the difference between the energies of the products decreases on ascending the homologous series of ions if the products of CO loss are assumed to be secondary or tertiary alkyl cations. The product enthalpy differential favoring CO elimination to give a secondary cation is 35, 19, and 8 kcal/mol, respectively for $n = 3$–5. This differential is so great for $\mathbf{a_1}^+$ that CO loss competes effectively with CH_2O expulsion, even though it involves more rearrangement and a sizeable reverse critical energy. In contrast, for $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{c_1}^+$, the advantages of the lower energy products given by CO loss are insufficient to offset the disadvantages of more extensive isomerization and the larger reverse critical energy for the final step compared to CH_2O elimination. It may not be coincidental that of the three $C_4H_6OCH_3^+$ ions, only $\mathbf{b_3}^+$, which contains a branched hydrocarbon chain from which a tertiary cation may be formed without skeletal isomerization, expels CO in more than very minor abundance.

Secondly, CH_3OH loss becomes important only for $\mathbf{c_1}^+$. This trend reflects the enthalpies of formation of the unsaturated $C_{n-1}H_{2n-5}^+$ carbocations, which diminish rapidly when $n \geq 6$ because it becomes possible to accommodate an allylic system within a five-membered ring, whereas smaller cycloalkenyl cations are much less stable. Another factor favoring methanol elimination from $\mathbf{c_1}^+$ is the greater facility of the larger oxonium ions for isomerizing to suitable intermediates (e.g. protonated dienyl methyl ethers) from which CH_3OH may be expelled. Thus, Scheme 4 gives a mechanistic proposal for the CH_3OH loss from $\mathbf{c_1}^+$ in which, via consecutive 1,2- and 1,4-H shifts, an INC is formed consisting of a 1,4-pentadienyl cation and a CH_3OH molecule. This species may further rearrange into an INC comprising cyclopentenyl cation and CH_3OH, which may dissociate to give favorable products. The cyclopentenyl cation is considerably more stable than its acyclic 1,4-pentadienyl counterpart, by 21 kcal/mol [13]. No analogous routes leading to such favorable products exist for the lower homologues.

Parallel trends to those found for CH_3OH expulsion could be considered to operate for H_2O loss. Such considerations would suggest that H_2O elimination should become more important once $n \geq 5$. However, a major difference between these two frag-



Scheme 4.

mentations is the need to disrupt the C–O bond of the OCH_3 group in order to permit expulsion of H_2O. If this process entails extensive reorientation in an INC involving the CH_2O molecule or CH_2OH^+ ion, as proposed in Scheme 3, a delicate internal energy balance may determine the degree of competition between the loss of CH_2O and H_2O from the metastable ions.

4. Conclusions

The reactions of $CH_3CH{=}CHC^+(H)OCH_3$, $\mathbf{b_1}^+$, $CH_2{=}CHC^+(CH_3)OCH_3$, $\mathbf{b_2}^+$, and $CH_2{=}CH(CH_3)$-$C^+(H)OCH_3$, $\mathbf{b_3}^+$, show some resemblance to those of the lower homologue $CH_2{=}CH\text{-}C^+(H)OCH_3$, but there are appreciable differences and CO loss ceases to be of much importance for the $C_4H_6OCH_3^+$ ions. Although the chemistries of $\mathbf{b_1}^+$, $\mathbf{b_2}^+$, and $\mathbf{b_3}^+$ are closely related, they are not identical and the distinctions become clearer when labeled analogues are examined. Elimination of CH_2O is by far the most important fragmentation of the $C_4H_6OCH_3^+$ ions. The first step of the reaction is proposed to involve a 1,5-H shift, from the OCH_3 group to the hydrocarbon chain. This H-transfer is usually unidirectional, especially for $\mathbf{b_2}^+$, but it is partly reversible for $\mathbf{b_3}^+$ and particularly $\mathbf{b_1}^+$. The second step may entail a (dipole-assisted) 1,3-H shift to give energy-rich ion-neutral complexes (INCs) of 1- or 2-methallyl cations and neutral CH_2O, which dissociate.

The strong preference of these $C_5H_9O^+$ ions for expelling CH_2O persists for the higher homologue, $CH_2{=}CH\text{-}C^+(C_2H_5)OCH_3$. Consequently, CH_2O loss is the major and characteristic reaction of these unsaturated oxonium ions containing the $\text{-}C(H)OCH_3^+$ entity.

Loss of CH_2O from $\mathbf{b_4}^+$- $\mathbf{b_6}^+$ may also occur via an INC. This reaction is associated with a very small kinetic energy release, suggesting that it generates the most stable $C_4H_7^+$ ion, 1-methallyl cation, at the thermochemical threshold. However, this process is only prominent for ions $\mathbf{b_5}^+$, which also undergo a facile loss of H_2O, via rearrangement in the INC $[C_4H_7^+/CH_2{=}O]$ to yield $C_5H_7^+$ (cyclopentenyl cations). Loss of C_3H_6 and CO dominates the MI spectra of $\mathbf{b_4}^+$ and $\mathbf{b_6}^+$ and these reactions, which also occur from $\mathbf{b_5}^+$, are proposed to take place from 1,2-H shift isomers of the cyclic counterparts of $\mathbf{b_4}^+$ - $\mathbf{b_6}^+$.

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