Reactions of low-energy pentenyl methyl ether radical cations $C_2H_5CH{=}CHCH_2OCH_3^{\bullet+}$, $CH_2{=}CHCH(C_2H_5)OCH_3^{\bullet+}$ and $CH_2{=}C(C_2H_5)CH_2OCH_3^{\bullet+}$

Richard D. Bowen [a,*], Lisa N. Heydorn [b], Johan K. Terlouw [b]

[a] *Department of Chemical and Forensic Sciences, University of Bradford, Bradford BD7 1DP, UK*
[b] *Department of Chemistry, McMaster University, Hamilton, Ont., Canada L8S 4M1*

Dedicated to the memory of Pierre Longevialle, in appreciation of his pioneering contribution to mass spectrometry in general and gas-phase ion chemistry in particular.

Abstract

The mechanisms for isomerisation and dissociation of the title ions have been probed by a combination of mass spectrometric techniques. In contrast to the other 10 ionised methyl pentenyl ethers, each of which has a unique and characteristic reactivity, these three isomers show many common features. Elimination of an ethyl radical, a methyl radical and a molecule of methanol occur at similar relative rates. Selective labelling experiments are broadly consistent with the conclusion that interconversion of these three $C_5H_9OCH_3^{\bullet+}$ radical cations competes effectively with dissociation. This enhanced rate of interconversion, compared to that for the other 10 ionised ethers, is explained in terms of facile 1,2-H and 1,2-C_2H_5 shifts and, in some instances, skeletal rearrangements involving ionised ethylmethoxycyclopropane. (Int J Mass Spectrom 217 (2002) 109–118) © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Rearrangement; Distonic ions; Deuterium labelling; Collision-induced dissociation

1. Introduction

Many $C_nH_{2n}O^{\bullet+}$ radical cations show intriguing reactions which cannot be explained solely by simple cleavage of the original structure [1]. Distonic ions [2,3] often play key roles in the hydrogen transfer and skeletal rearrangements that precede fragmentation of $C_nH_{2n}O^{\bullet+}$ species.

Although most classes of $C_nH_{2n}O^{\bullet+}$ radical cations have been intensively studied for several decades, ionised 5-hexenyl methyl ether [4] was until quite recently the only species of its kind to be investigated in detail. Later work has shown that ionised alkenyl methyl ethers have a rich and varied chemistry [5–15] despite their deceptively simple structures. Thus, each of the four isomers of $C_4H_7OCH_3^{\bullet+}$ formed by ionisation of the methyl ethers of stable butenols has a different chemistry, though the reactions of $CH_3CH{=}CHCH_2OCH_3^{\bullet+}$ and $CH_2{=}C(CH_3)CH_2OCH_3^{\bullet+}$ show some common features [10]. An overview [15] of the reactions of ionised methyl pentenyl ethers shows that this trend persists for higher homologues: 10 of the 13 isomeric $C_5H_9OCH_3^{\bullet+}$ radical cations have a unique and characteristic reactivity. However, in contrast to these isomers and their lower homologues,

* Corresponding author. E-mail: r.d.bowen@bradford.ac.uk

$C_2H_5CH{=}CHCH_2OCH_3^{\bullet+}$, $CH_2{=}CHCH(C_2H_5)$-$OCH_3^{\bullet+}$ and $CH_2{=}C(C_2H_5)CH_2OCH_3^{\bullet+}$ denoted as $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$, respectively,[1] react in closely similar ways. This paper presents a more detailed analysis of their reactions.

2. Results and discussion

2.1. Overview of the reactions of low energy ions
$C_2H_5CH{=}CHCH_2OCH_3^{\bullet+}$ ($3^{\bullet+}$),
$CH_2{=}CHCH(C_2H_5)OCH_3^{\bullet+}$ ($4^{\bullet+}$) and
$CH_2{=}C(C_2H_5)CH_2OCH_3^{\bullet+}$ ($13^{\bullet+}$)

The metastable ion (MI) spectra of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$ and selected labelled analogues are presented in Table 1. The spectra were obtained under carefully controlled experimental conditions and were found to be close to those reported in the overview [15]. The small intensity differences between the *cis*- and *trans*-geometrical isomers of $3^{\bullet+}$ reported in [15] appear not to be significant, thus indicating that the stereochemistry of the C=C bond in $3^{\bullet+}$ does not exert a tangible influence on their reactivity. This observation is not unexpected: facile *cis/trans* isomerisation is commonly observed for ionised alkenes and related species [16].

In common with most other isomers of $C_5H_9OCH_3^{\bullet+}$ [15], the principal reactions of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$ at low internal energies are elimination of $CH_3^{\bullet}$, $C_2H_5^{\bullet}$ and CH_3OH. Losses of C_2H_4 and C_3H_6 are the most pronounced of the minor processes, which also include loss of $H^{\bullet}$, H_2O and CH_2O. The relative abundances (RAs) of the ions formed by the three major dissociations lie in the range of 70–90, 100 and 30, respectively. Considering that RAs of competing processes may vary with the internal energy of the fragmenting metastable ions [17,18], the similarity of these ratios is strong evidence that these three isomers interconvert or react via the same transition states. In

support of this interpretation, the kinetic energy release associated with each of the major dissociations is the same within experimental error for all three isomers. Moreover, collision-induced dissociation (CID) and neutralisation–reionisation (NR) experiments [19] established that the loss of $CH_3^{\bullet}$ and $C_2H_5^{\bullet}$ from all three isomers yields the same $C_5H_9O^+$ and $C_4H_7O^+$ product ions, $CH_2{=}C(CH_3)–C^+(H)OCH_3^+$, b_3^+, and $CH_2{=}CH–C^+(H)OCH_3^+$, a_1^+. (These techniques did not permit structure analysis of the $C_5H_8^{\bullet+}$ ion generated by loss of CH_3OH.)

A more precise analysis of the competition between the three main reactions of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$ might be possible in terms of variation of the density of states of the reacting configurations with the origin of the fragmenting ions. However, a rigorous treatment of this kind is not feasible in the absence of a detailed potential energy diagram for the system. Such a diagram cannot be readily constructed owing to the absence of reliable thermochemical data for many of the reactants, intermediates and products formed in the reactions of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$. Indeed, in the case of methanol elimination, neither the product ion nor the reacting configuration can be unequivocally established by experimental methods. Although dissociation of ions in a mass spectrometer is in essence governed by kinetic factors, the relative rates of these reactions are strongly influenced by their critical energies, especially for low-energy metastable ions. Consequently, the discussion in this paper is confined to a more qualitative analysis, which nevertheless serves to illustrate how quite complex reactions may be understood by means of mechanistic concepts that are familiar in organic mass spectrometry.

As reported before [15], the NR and CID spectra of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$ are also closely similar. In the analysis of these CID spectra the relative intensities of the dominant peaks at $m/z = 85$ (loss of $CH_3^{\bullet}$), $m/z = 71$ (loss of $C_2H_5^{\bullet}$) and $m/z = 68$ (loss of CH_3OH) were not considered because the signals for these low energy dissociations contain a significant MI contribution of unknown magnitude. To probe these collision-induced dissociations, we have recorded partial CID spectra of ions $3^{\bullet+}$, $4^{\bullet+}$ and

---

[1] In order to maintain internal consistency and to facilitate comparison with other papers in this series, the numbers and letters assigned to ion structures in this paper are the same as those used in [15].

Table 1
Relative abundances[a] and kinetic energy releases[b] for the reactions of metastable ions $C_2H_5CH=CHCH_2OCH_3^{\bullet+}$, $\mathbf{3^{\bullet+}}$, $CH_2=CHCH(C_2H_5)OCH_3^{\bullet+}$, $\mathbf{4^{\bullet+}}$, and $CH_2=C(C_2H_5)CH_2OCH_3^{\bullet+}$, $\mathbf{13^{\bullet+}}$

Ion	Loss							
	$CH_3^{\bullet}$		$C_2H_5^{\bullet}$		CH_3OH		C_2H_4	C_3H_6
$\mathbf{3^{\bullet+}}$	80	[22]	100	[13]	30	[16]	2	2
$\mathbf{4^{\bullet+}}$	65	[23]	100	[14]	25	[17]	2	2
$\mathbf{13^{\bullet+}}$	100	[25]	100	[14]	30	[19]	2	2

[a]Measured by peak height and normalised to a total of 100 units for the base peak in the metastable ion spectrum for ions dissociating in the second field-free region.

[b]Numbers in square brackets represent kinetic energy releases, $T_{1/2}$, in meV as obtained from the width at half height of the Gaussian-shaped peaks.

$\mathbf{13^{\bullet+}}$ at a collision-gas cell potential of $-1\,kV$. These spectra are presented in Fig. 1. The negative potential on the cell causes a shift to lower energies of all peaks resulting from collision-induced dissociations in the cell. The position of peaks which result from unimolecular dissociations outside the cell—predominantly the spontaneous dissociations of the metastable ions—remains unchanged.

Several interesting conclusions follow from the results of Fig. 1. Firstly, the dominant reactions in the "pure" CID spectra of $\mathbf{3^{\bullet+}}$, $\mathbf{4^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$ are loss of $CH_3^{\bullet}$, $C_2H_5^{\bullet}$ and CH_3OH, as is found in their MI spectra. Other signals, including those outside the m/z range included in Fig. 1, in these CID spectra are inconsequential. Secondly, the three major processes occur in quite similar ratios in the CID spectra of $\mathbf{3^{\bullet+}}$, $\mathbf{4^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$, but the similarity is not so strong as is observed in their MI spectra. This distinction, which is evident on comparison of the peaks marked with an asterisk with those that are not, probably indicates that the reactions of $\mathbf{3^{\bullet+}}$, $\mathbf{4^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$, though closely connected, differ subtly from each other. Thirdly, the overall intensity of the CID component compared to the MI components is lowest for $\mathbf{4^{\bullet+}}$. Although this kind of comparison between CID and MI components must be made with caution, the relevant spectra were recorded consecutively under identical conditions and the differences were reproducible. Consequently, it is likely that $\mathbf{4^{\bullet+}}$ is less susceptible than $\mathbf{3^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$ to fragmentation when subjected to CID. This result is surprising because it might have been expected that an ionised ether with a secondary structure would frag-

ment more rapidly than its primary isomers, especially at the higher internal energies appropriate to CID spectra. In particular, elimination of $C_2H_5^{\bullet}$ from $\mathbf{4^{\bullet+}}$ may occur by simple cleavage to give a stable oxonium ion, but the signal for this process in the CID spectrum of $\mathbf{4^{\bullet+}}$ is weaker than those in the corresponding spectra of $\mathbf{3^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$. One explanation for this unexpected contrast is that an appreciable proportion of $\mathbf{4^{\bullet+}}$ may have rearranged to structures from which $C_2H_5^{\bullet}$ cannot be lost so readily. Finally, the signal for loss of CH_3OH is noticeably stronger in the CID spectrum of $\mathbf{3^{\bullet+}}$, from which it may occur by a process resembling a cycloreversion without prior rearrangement. On the other hand, CH_3OH loss from $\mathbf{4^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$ does entail isomerisation if energetically favourable product ions are to be formed. This slight, but significant, contrast probably indicates that certain reactions of $\mathbf{3^{\bullet+}}$, $\mathbf{4^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$ are preferentially associated with a particular structure.

2.2. Ethyl radical elimination

The structure of the $[M–C_2H_5]^+$ ion in each case is the allylic oxonium ion, $[CH_2=CH–C^+(H)OCH_3]^+$, $\mathbf{a_1}^+$, [7,15,19] as might have been anticipated since there are few alternative acyclic stable isomers of $C_4H_7O^+$. This reaction could be formulated as direct α-cleavage of $\mathbf{4^{\bullet+}}$, but at least limited isomerisation is necessary before $C_2H_5^{\bullet}$ may be expelled from $\mathbf{3^{\bullet+}}$ and $\mathbf{13^{\bullet+}}$. In the former case, a 1,2-H shift leads to the distonic ion $\mathbf{3^{\bullet+}}(\delta)$; a further 1,2-H shift then leads to an ionised enol ether, $\mathbf{15^{\bullet+}}$, from which $C_2H_5^{\bullet}$ may be
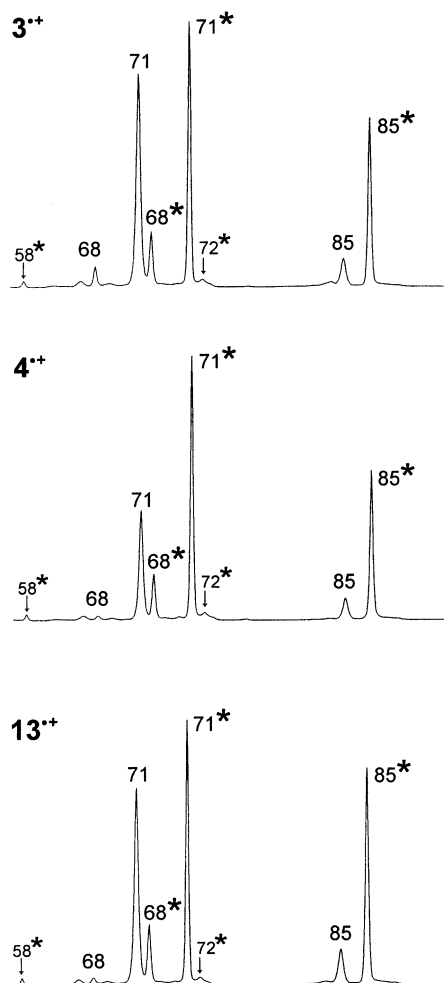
Fig. 1. Collision-induced dissociation mass spectra of 8 keV $m/z = 100$ ions $3^{\bullet+}$, $4^{\bullet+}$, $13^{\bullet+}$ recorded with a voltage of -1 kV on the collision-gas cell. Peaks denoted with an asterisk originate from the dissociation of metastable ions outside the cell. See Section 4 for further details.

lost by γ-cleavage, Scheme 1 [7,15]. The situation for $13^{\bullet+}$ is more complicated: at first sight, a 1,2-H shift to give the distonic ion $13^{\bullet+}(\delta)$, which could fragment by β-cleavage, offers a route for $C_2H_5^{\bullet}$ elimination. However, CID studies on the regioselectivity of alkyl radical loss from other ionised alkenyl methyl ethers indicate that β-cleavage entails a significant reverse critical energy and does not always lead to the correct

isomeric oxonium ion [7]. A more general explanation for loss of an alkyl group from the β-position is rearrangement of $13^{\bullet+}(\delta)$ to form $3^{\bullet+}(\delta)$, followed by a 1,2-H shift and γ-cleavage. This skeletal rearrangement can be formulated as ring closure of $13^{\bullet+}(\delta)$ to ionised 2-ethyl-1-methoxycyclopropane, $17^{\bullet+}$, which may open to give $3^{\bullet+}(\delta)$ [7,15]. There is ample precedent for these steps in the reactions of distonic ions derived from ionised carboxylic acids [20]. This skeletal isomerisation may also be described as a 1,2-shift of an incipient ionised carbene to a radical centre [21]. Species such as $17^{\bullet+}$, $18^{\bullet+}$ and $21^{\bullet+}$ in which there is a strained three-membered ring may be transition states, rather than genuine intermediates. However, they are included in Schemes 1–4 because they permit the rearrangement steps to be easily visualised.

There are two plausible routes for $C_2H_5^{\bullet}$ loss: direct α-cleavage of $4^{\bullet+}$ or isomerisation of $3^{\bullet+}$ and $13^{\bullet+}$ and subsequent γ-cleavage of $15^{\bullet+}$. Consequently, it is possible that rearrangement of $4^{\bullet+}$ to $3^{\bullet+}$ and $13^{\bullet+}$ is finely balanced with $C_2H_5^{\bullet}$ loss. The labelling results support this interpretation: $3^{\bullet+}[OCD_3]$ and $13^{\bullet+}[OCD_3]$ expel $C_2H_5^{\bullet}$ with ~97% selectivity; in contrast, the RAs for $C_2H_4D^{\bullet}$ and $C_2H_3D_2^{\bullet}$ loss from $4^{\bullet+}[OCD_3]$ are 9 and 5%, respectively, whereas little $C_2H_2D_3^{\bullet}$ elimination is observed. These results may be explained (see Scheme 2) if the formation of $19^{\bullet+}(\delta)$ by a 1,5-H shift between the methoxy and vinyl group in $4^{\bullet+}(\delta)$, which is readily accessible to $4^{\bullet+}$ via a 1,2-H-shift, competes to a limited extent with both rearrangement to $3^{\bullet+}$ and $13^{\bullet+}$ and α-cleavage to give a_1^{+}. This interpretation is supported by the reduced rate of $C_2H_5^{\bullet}$ loss from $4^{\bullet+}$ in the "pure" CID spectra shown in Fig. 1. This reduction of the rate of the direct cleavage permits more extensive exchange of the hydrogen atoms in the methoxy and pentenyl entities to take place. These exchange processes appear to be initiated by a 1,2-H shift in $4^{\bullet+}$, which may be more favourable than the corresponding step in $3^{\bullet+}$ or $13^{\bullet+}$, because the resultant distonic ion, $4^{\bullet+}(\delta)$, would be expected to be more stable than $3^{\bullet+}(\delta)$ or $13^{\bullet+}(\delta)$, in which the positive charge is located on a less substituted carbon atom.
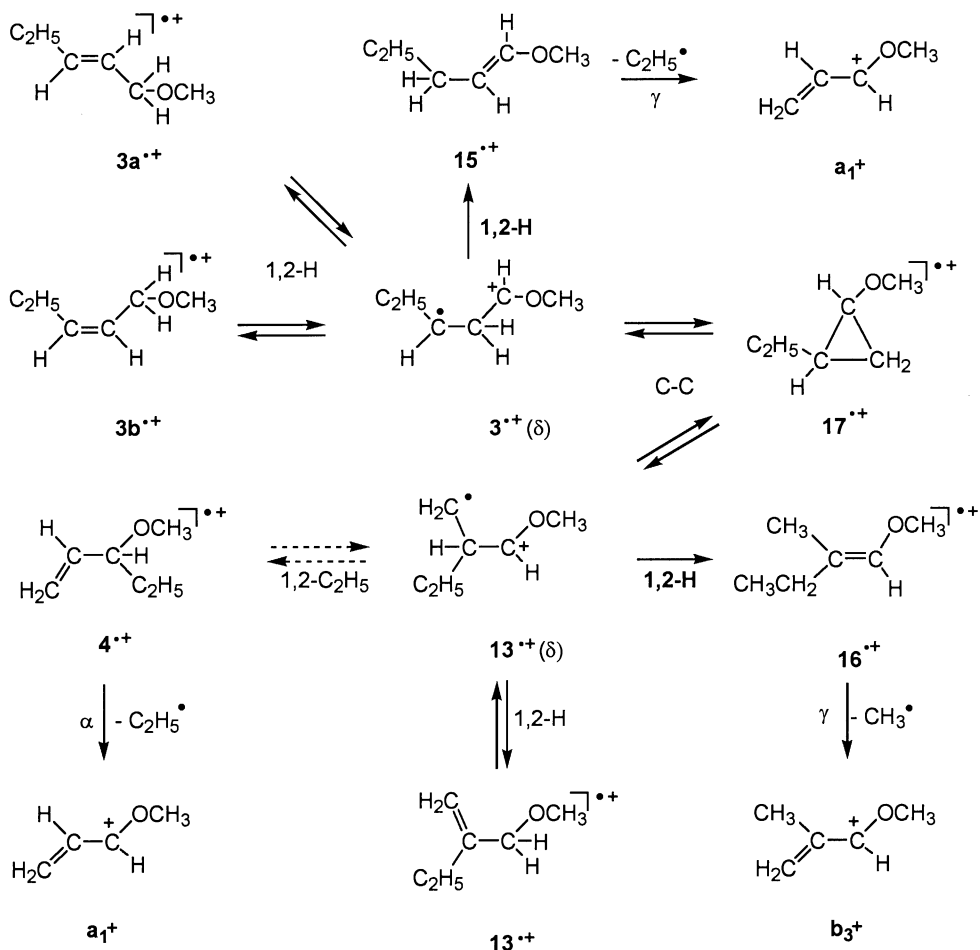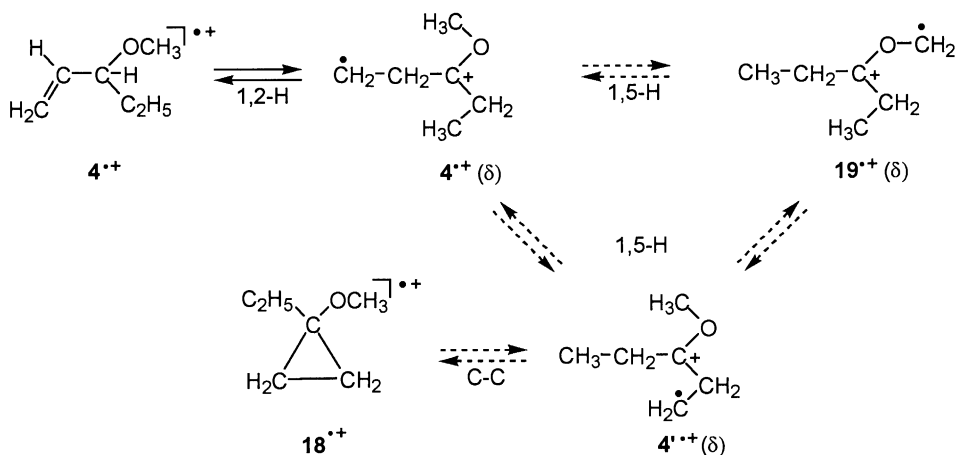
"δ" denotes a distonic ion. "1,2-H" and "1,2-C$_2$H$_5$" denote a shift to a formal cationic site;
"**1,2-H**" denotes a shift to a formal radical site; "C-C" denotes closure or opening.

Scheme 1.

Other rearrangements are necessary to explain why $4^{\bullet +}[4,4\text{-}D_2]$ and $4^{\bullet +}[5\text{-}CD_3]$ do not eliminate only $C_2H_3D_2^{\bullet}$ and $C_2H_2D_3^{\bullet}$, respectively. A degenerate 1,5-H shift between the ends of the alkyl chains in $4^{\bullet +}(\delta)$ or cyclisation to give $18^{\bullet +}$ are obvious possibilities, but more complex processes, including skeletal rearrangements, may also occur. Further analysis is hindered by the overlap between the signals for $C_2H_2D_3^{\bullet}$ and CH_3OH elimination from $4^{\bullet +}[5\text{-}CD_3]$.

Although some details of the $C_2H_5^{\bullet}$ loss from $4^{\bullet +}$ remain uncertain, it is clear that hydrogen

exchange precedes α-cleavage. Even more facile exchange precedes $CH_3^{\bullet}$ loss from the lower homologue of $4^{\bullet +}$, $CH_2=CHCH(CH_3)OCH_3^{\bullet +}$, especially at low internal energies [10]. Consequently, hydrogen transfers between the alkyl groups and the methoxy group are a general feature of the $CH_2=CHCH(CH_3)OCH_3^{\bullet +}$ species, even though direct α-cleavage is at first sight so favourable. In contrast, the methoxy group of $3^{\bullet +}$ and $13^{\bullet +}$ and their lower homologues, $CH_3CH=CHCH_2OCH_3^{\bullet +}$ and $CH_2=C(CH_3)CH_2OCH_3^{\bullet +}$, is retained in the product

$4^{\bullet+}$ $\xrightleftharpoons[\text{1,2-H}]{}$ $4^{\bullet+}(\delta)$ $\xrightleftharpoons[\text{1,5-H}]{}$ $19^{\bullet+}(\delta)$

1,5-H

$18^{\bullet+}$ $\xleftarrow{\text{C-C}}$ $4'^{\bullet+}(\delta)$

"1,5-H" denotes a shift to a formal radical site

Scheme 2.

ion with a selectivity of over 99% when the corresponding alkyl radical ($CH_3^\bullet$) is lost. Therefore, the subtle differences disclosed by labelling experiments between the chemistry of $CH_3CH=CHCH_2OCH_3^{\bullet+}$ and $CH_2=CHCH(CH_3)OCH_3^{\bullet+}$ or $CH_2=C(CH_3)CH_2OCH_3^{\bullet+}$ persist for $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$, though they are appreciably less pronounced for the higher homologues.

2.3. Methyl radical elimination

The formation of the branched oxonium ion, $[CH_2=C(CH_3)CHOCH_3]^+$, b_3^+, by $CH_3^\bullet$ loss is quite surprising, particularly for $3^{\bullet+}$ and $4^{\bullet+}$, which contain a linear pentenyl chain. This finding confirms that rearrangement to isomers containing a branched hydrocarbon chain must precede at least some fragmentations of $3^{\bullet+}$ and $4^{\bullet+}$. A likely mechanism starting from $13^{\bullet+}$ involves successive 1,2-H shifts to form $16^{\bullet+}$ via $13^{\bullet+}(\delta)$; $CH_3^\bullet$ may then be expelled by γ-cleavage of $16^{\bullet+}$ to give b_3^+. This route may be extended to encompass $CH_3^\bullet$ loss from $4^{\bullet+}$ because $13^{\bullet+}(\delta)$ is accessible to $4^{\bullet+}$ via a 1,2-C_2H_5 shift. Similarly, elimination of $CH_3^\bullet$ from $3^{\bullet+}$ may be explained by isomerisation of $3^{\bullet+}(\delta)$ to $13^{\bullet+}(\delta)$ via $17^{\bullet+}$.

In contrast to the variable degree of hydrogen exchange that precedes ethyl radical loss, the methoxy group of $3^{\bullet+}[OCD_3]$, $4^{\bullet+}[OCD_3]$ and $13^{\bullet+}[OCD_3]$ is retained in each case with over 99% selectivity in the cationic product in methyl radical elimination. Consequently, the hydrogen transfer steps involving the methoxy group which occur before $C_2H_5^\bullet$ is lost from $4^{\bullet+}$ do not compete with $CH_3^\bullet$ elimination. This distinction is underlined by the reactions of $4^{\bullet+}[4,4-D_2]$ and $4^{\bullet+}[5-CD_3]$, which reveal that the expelled radical is not always the methyl group from the end of the ethyl substituent. Thus, $4^{\bullet+}[5-CD_3]$ loses $CD_3^\bullet$ (from the initial CD_3CH_2 substituent) and $CH_3^\bullet$ in almost equal amounts, but comparatively little $CH_2D^\bullet$ or $CHD_2^\bullet$. Moreover, since $4^{\bullet+}[4,4-D_2]$ expels $CH_3^\bullet$, but almost no $CH_2D^\bullet$ or $CHD_2^\bullet$, the other methyl radical must originate from the vinyl group. Some circumstantial evidence supporting this aspect of Scheme 1 is found in the slightly stronger signal for $CH_3^\bullet$ loss in the CID spectrum of $13^{\bullet+}$, from which it may occur with less rearrangement than is required starting from $3^{\bullet+}$ or $4^{\bullet+}$.

One explanation for the contrast between $CH_3^\bullet$ and $C_2H_5^\bullet$ loss from $4^{\bullet+}$ is that the former is initiated by a 1,2-C_2H_5 shift to give $13^{\bullet+}(\delta)$, whereas the latter begins with a 1,2-H shift to form $4^{\bullet+}(\delta)$. The
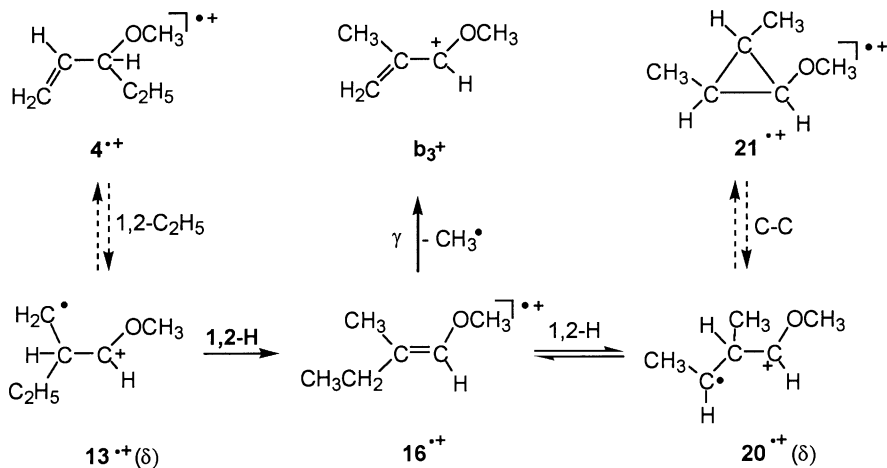
Scheme 3.

H-transfers that erode the positional integrity of the OCH$_3$ group are specifically associated with $\mathbf{4^{\bullet+}}(\delta)$. On the other hand, once $\mathbf{13^{\bullet+}}(\delta)$ has been formed, a different sequence of steps occurs, leading eventu-

ally to $\mathbf{16^{\bullet+}}$, which eliminates CH$_3^{\bullet}$ by γ-cleavage. If $\mathbf{16^{\bullet+}}$ were formed directly from $\mathbf{4^{\bullet+}}$ by a 1,2-C$_2$H$_5$ shift followed by a 1,2-H shift in $\mathbf{13^{\bullet+}}(\delta)$, only CD$_3^{\bullet}$ loss would be expected from $\mathbf{4^{\bullet+}}$[5-CD$_3$]. However,
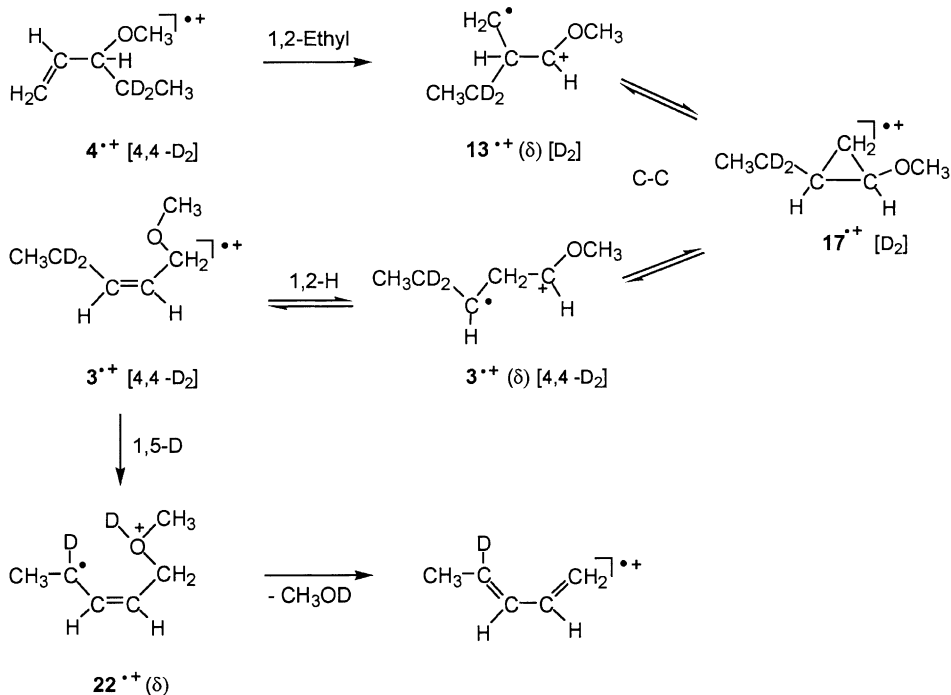
Scheme 4.

the expulsion of $CH_3^\bullet$ at a similar rate may be explained if a further 1,2-H shift in $16^{\bullet+}$ led to $20^{\bullet+}(\delta)$, which could then undergo a degenerate rearrangement that may be formulated in terms of ring closure to ionised 2,3-dimethyl-1-methoxycyclopropane, $21^{\bullet+}$, Scheme 3. There is a strong precedent for this isomerisation in the reactions of the distonic isomers of ionised 2-methylbutyric acid [20] and related species. An alternative description of the crucial degenerate rearrangement is a 1,2-shift of an incipient ionised carbene to a radical centre.

2.4. Methanol elimination

Far fewer conclusions may be made about CH_3OH loss from the three isomers because establishing the structure of the resultant $C_5H_{10}^{\bullet+}$ species by CID or NRMS techniques is impracticable and at least three products (ionised cyclopentene, isoprene and piperylene) are energetically feasible. The expulsion of CD_3OH with $\sim$98% specificity from $3^{\bullet+}[OCD_3]$, $4^{\bullet+}[OCD_3]$ and $13^{\bullet+}[OCD_3]$ suggests that methanol loss from $4^{\bullet+}$ starts with a 1,2-C_2H_5 shift to give $13^{\bullet+}(\delta)$. Hydrogen transfers involving the methoxy group would be expected to intervene if $4^{\bullet+}(\delta)$ were formed by a 1,2-H shift. A little more insight is given by the loss of almost no CH_3OD from $4^{\bullet+}[5\text{-}CD_3]$, which shows that D-transfer from the terminal methyl group is of minor importance. However, a sizeable amount of CH_3OD is lost from $4^{\bullet+}[4,4\text{-}D_2]$, thus establishing that D-transfer from the methylene group of the original ethyl substituent is significant. One tentative interpretation is that isomerisation of $4^{\bullet+}$ to $3^{\bullet+}$ occurs via the route shown in Scheme 1. These steps would convert $4^{\bullet+}[4,4\text{-}D_2]$ into $3^{\bullet+}[4,4\text{-}D_2]$. A 1,5-D transfer from the allylic δ-position to the oxygen atom would then yield a distonic ion, $22^{\bullet+}(\delta)$, which may then expel CH_3OD to give ionised piperylene $[4\text{-}D_1]$, Scheme 4.

However, the dominance of CH_3OH loss from $4^{\bullet+}[4,4\text{-}D_2]$ could be explained only if additional hydrogen shifts occurred during the isomerisation of $4^{\bullet+}$ to $3^{\bullet+}$, thus resulting in the presence of at least one H atom in the δ-position. The degenerate rearrangement

of $20^{\bullet+}(\delta)$ depicted in Scheme 3 may contribute to this process, but an isotope effect favouring H- over D-transfer would still be necessary to account for the strong preference of $4^{\bullet+}[4,4\text{-}D_2]$ for expelling CH_3OH instead of CH_3OD. Several other plausible routes for the loss of CH_3OH may be devised, but the proposal that CH_3OH loss is preferentially associated with $3^{\bullet+}$ is at least supported by the enhanced signal for this process in the CID spectrum of this isomer compared to the much weaker signals in the spectra of $4^{\bullet+}$ and $13^{\bullet+}$.

3. Conclusions

The reactions of low-energy $C_2H_5CH=CHCH_2O\text{-}CH_3^{\bullet+}$, $3^{\bullet+}$, $CH_2=CHCH(C_2H_5)OCH_3^{\bullet+}$, $4^{\bullet+}$, and $CH_2=C(C_2H_5)CH_2OCH_3^{\bullet+}$, $13^{\bullet+}$, show a much greater resemblance to one another than to those of any of the other 10 isomeric $C_5H_9OCH_3^{\bullet+}$ radical cations generated from ionised pentenyl methyl ethers. Although these similarities are even more pronounced than those found for the lower homologues, $CH_3CH=CHCH_2OCH_3^{\bullet+}$, $CH_2=CH(CH_3)CHOCH_3^{\bullet+}$ and $CH_2=(CH_3)CCH_2OCH_3^{\bullet+}$, deuterium labelling and CID experiments reveal that interconversion of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$ is not rapid and reversible prior to elimination of $C_2H_5^\bullet$, which probably occurs by two distinct, but related, routes. The first is α-cleavage of $4^{\bullet+}$, which is preceded by at least limited hydrogen exchange between the methoxy and alkyl groups and is favoured starting from $4^{\bullet+}$. The second, which probably operates preferentially for $3^{\bullet+}$ and $13^{\bullet+}$, involves rearrangement, followed by γ-cleavage of the ionised enol ether, $C_2H_5CH_2CH=CHOCH_3^{\bullet+}$, $15^{\bullet+}$. Both these routes lead to the oxonium ion a_1^+, $CH_2=CHC(H)OCH_3^+$. The $CH_3^\bullet$ elimination appears to involve isomerisation to another ionised enol ether, $C_2H_5C(CH_3)=CHOCH_3^{\bullet+}$, $16^{\bullet+}$, which undergoes γ-cleavage to give the branched oxonium ion b_3^+, $CH_2=C(CH_3)C(H)OCH_3^+$. Further rearrangements precede $CH_3^\bullet$ loss from $4^{\bullet+}$, which ironically is initiated by a 1,2-C_2H_5 shift. In contrast, $C_2H_5^\bullet$ elimination is preceded, at least on some occasions,

by a 1,2-H shift in $4^{\bullet+}$. The greater similarity in the behaviour of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$, compared to that of their lower homologues, is consistent with the view that 1,2-C_2H_5 shifts occur more readily in the former series than 1,2-CH_3 shifts do in the latter. Far fewer deductions may be made concerning the mechanism of CH_3OH loss because the structure of the $C_5H_{10}^{\bullet+}$ fragment cannot be established unequivocally. However, this reaction occurs more readily in the CID spectrum of $3^{\bullet+}$, from which it may take place by a process resembling a simple cycloreversion. Moreover, in common with $CH_3^{\bullet}$ elimination from $4^{\bullet+}$, CH_3OH loss from $4^{\bullet+}$ and $13^{\bullet+}$, probably involves skeletal rearrangement by 1,2-C_2H_5 shifts and the formation of ionised methoxycylcopropane. The complexity of the reactions of $3^{\bullet+}$, $4^{\bullet+}$ and $13^{\bullet+}$, together with the fine balance between isomerisation and fragmentation of these species, emphasises that the chemistry of ionised alkenyl methyl ethers belies their apparently simple structures.

4. Experimental

The ethers required for this work were prepared by classical routes, as has already been summarised [15]. Illustrative examples of the synthesis of labelled pentenyl methyl ethers have been described in detail [22].

All the mass spectrometric experiments were performed on the VG Analytical ZAB-R mass spectrometer. Details of the geometry of this three-sector (BEE) instrument have been published [23]. Data on the fragmentation of metastable ions in the second field-free region were obtained from MI spectra [18]; the data quoted in Table 2 were compiled from two to five individual scans. The typical operating conditions were 70 eV ionising electron energy and 8 kV accelerating voltage. Kinetic energy releases were estimated from the width at half-height of the appropriate metastable peak, using the usual one-line formula, with no correction for the width of the main beam [24].

The CID spectra of Fig. 1 were obtained in the second field-free region with oxygen as the collision gas, at an accelerating voltage V_a of 7900 V and a collision-gas cell voltage V_c of −1080 V. The position of the CID peaks originating from dissociation in the collision-gas cell is given by the expression $m_2/m_1 e(V_a + V_c) - eV_c$, where m_1 and m_2 are the mass numbers of the precursor and product ions, respectively.

Table 2
Relative abundances[a] for the losses of methyl, ethyl and methanol from selected labelled isotopomers of the ionised methyl pentenyl ethers **3**, **4** and **13**

Loss	Ion				
	$3^{\bullet+}$[OCD_3]	$4^{\bullet+}$[OCD_3]	$4^{\bullet+}$[4,4-D_2]	$4^{\bullet+}$[5-CD_3]	$13^{\bullet+}$[OCD_3]
$CH_3^{\bullet}$	100	100	100	100	100
$CH_2D^{\bullet}$	<0.5	<0.5	4	16	0.5
$CHD_2^{\bullet}$	–	–	5	19	–
$CD_3^{\bullet}$	–	–	–	85	–
$C_2H_5^{\bullet}$	100	100	80	16	100
$C_2H_4D^{\bullet}$	1	9	28	35	<0.5
$C_2H_3D_2^{\bullet}$	1	5	100	100	–
$C_2H_2D_3^{\bullet}$	0.5	1	–	100[b]	–
CH_3OH	–	–	100	100[c]	–
CH_3OD	–	–	30	10	–
CHD_2OH	<0.5	<0.5	–	–	<0.5
CD_3OH	100	100	–	–	100

[a]Measured by peak height and normalised to a total of 100 units for the most intense peak for each of the three losses in the MI spectrum. The KER values for these processes were unexceptional.

[b]After allowance for the contribution from CH_3OH loss, assuming that the ethyl loss does not suffer from an isotope effect.

[c]After allowance for the contribution from $C_2H_2D_3^{\bullet}$ loss.

All the spectra were recorded by means of a small PC-based data system developed by Mommers Technologies Inc. (Ottawa).

References

[1] G. Bouchoux, Mass Spectrom. Rev. 7 (1988) 1, 203.
[2] B.F. Yates, W.J. Bouma, L. Radom, J. Am. Chem. Soc. 106 (1984) 5805.
[3] S. Hammerum, Mass Spectrom. Rev. 7 (1988) 123.
[4] T.A. Molenaar-Langeveld, R.H. Fokken, N.M.M. Nibbering, Org. Mass Spectrom. 23 (1988) 364.
[5] R.D. Bowen, A.D. Wright, S.R. Thomas, K.R. Jennings, A. Maccoll, Org. Mass Spectrom. 26 (1991) 421.
[6] R.D. Bowen, A.D. Wright, J. Chem. Soc., Chem. Commun. (1991) 1055.
[7] R.D. Bowen, A.D. Wright, J. Chem. Soc., Chem. Commun. (1992) 96;
A.D. Wright, R.D. Bowen, Can. J. Chem. 71 (1993) 1073.
[8] J.R. Cao, M. George, J.L. Holmes, J. Am. Soc. Mass Spectrom. 3 (1992) 99.
[9] R.D. Bowen, A.D. Wright, P.J. Derrick, Org. Mass Spectrom. 27 (1992) 905.
[10] R.D. Bowen, A.D. Wright, A.W. Colburn, P.J. Derrick, Int. J. Mass Spectrom. Ion Processes 116 (1992) 193.
[11] J.-F. Rontani, Org. Mass Spectrom. 29 (1994) 808.
[12] R.D. Bowen, R.T. Gallagher, S. Meyerson, J. Am. Soc. Mass Spectrom. 7 (1996) 205.
[13] R.D. Bowen, P. Clifford, J.T. Francis, J.K. Terlouw, Int. J. Mass Spectrom. Ion Processes 165/166 (1997) 155.
[14] R.D. Bowen, S.J. Mandeville, M.A. Trikoupis, J.K. Terlouw, Int. J. Mass Spectrom. 210/211 (2001) 447.
[15] R.D. Bowen, M.A. Trikoupis, J.K. Terlouw, Eur. J. Mass Spectrom. 7 (2001) 225.
[16] (a) J.H. Beynon, R.A. Saunders, A.E. Williams, The Mass Spectra of Organic Molecules, Elsevier, Amsterdam, 1968;
(b) R.D. Bowen, D.H. Williams, Org. Mass Spectrom. 7 (1977) 453.
[17] A.N.H. Yeo, D.H. Williams, J. Am. Chem. Soc. 93 (1971) 395.
[18] R.G Cooks, J.H. Beynon, R.M. Caprioli, G.R. Lester, Metastable Ions, Elsevier, Amsterdam, 1973.
[19] R.D. Bowen, L.N. Heydorn, J.K. Terlouw, Int. J. Mass Spectrom. 209 (2001) 153.
[20] T. Weiske, H. Schwarz, Chem. Ber. 116 (1983) 323;
T. Weiske, H. Halim, H. Schwarz, Chem. Ber. 118 (1985) 495;
T. Weiske, H. Schwarz, Tetrahedron 42 (1986) 6245, and references therein.
[21] C.E. Hudson, D.J. McAdoo, Tetrahedron 46 (1986) 331, and references therein.
[22] R.D. Bowen, H.G.M. Edwards, D.W. Farwell, I. Rusike, D.M. Saunders, J. Chem. Res. (S) (1998) 426;
R.D. Bowen, H.G.M. Edwards, D.W. Farwell, I. Rusike, D.M. Saunders, J. Chem. Res. (M) (1998) 1901.
[23] H.F. van Garderen, P.J.A. Ruttink, P.C. Burgers, G.A. McGibbon, J.K. Terlouw, Int. J. Mass Spectrom. Ion. Processes 121 (1992) 159.
[24] J.L. Holmes, J.K. Terlouw, Org. Mass Spectrom. 15 (1980) 383.