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Reactions of ionised methyl pent-4-enyl ether, $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$

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Abstract

The reactions of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$ are reported and discussed, with particular emphasis on the behaviour of the metastable ions. The main reactions of the low energy title ions are elimination of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, and CH_3OH, each occurring at similar rates; but loss of H_2O, $H^{\cdot}$ and, to a lesser degree, C_2H_4, also occurs. The mechanisms of these reactions have been probed by examining collision-induced dissociation spectra and by extensive D-labeling experiments. The site selectivity for the three main reactions and water elimination varies considerably. Thus, metastable $CH_2{=}CH(CH_2)_3OCD_3^{\cdot}$ expels almost exclusively $CH_3^{\cdot}$ (>97% selectivity) and mainly $C_2H_5^{\cdot}$ and CD_3OH (~90% selectivity); but H_2O (~37%), HOD (~53%), and even D_2O (~10%) all occur in water loss. Tentative mechanisms are proposed for these processes, several of which must entail extensive hydrogen transfers and skeletal isomerisations. Loss of $C_2H_5^{\cdot}$ and $CH_3^{\cdot}$ appear to involve rearrangements to species accessible to ionised cyclopentyl methyl ether, but expulsion of CH_3OH and H_2O do not. (Int J Mass Spectrom 210/211 (2001) 447–457) © 2001 Elsevier Science B.V.

Keywords: Distonic ions; Ion–neutral complexes; Deuterium labeling; Rearrangement

1. Introduction

The chemistry of $C_nH_{2n}O^{\cdot+}$ radical cations is one of the continuing themes of organic mass spectrometry [1–8]. Many of these species undergo hydrogen transfer prior to dissociation and as a result fragmentations that cannot be explained in terms of simple cleavage in the original structure are quite common. Distonic ions [9,10] often are involved in these hydrogen transfer and rearrangement steps [1]. Ion–neutral complexes [11–17] also have been postulated as intermediates in the skeletal rearrangements of some $C_nH_{2n}O^{\cdot+}$ species. Thus, the closely similar reactions of isomeric pairs of metastable ionised aldehydes and ketones are interpretable on the basis of isomerisation to a common ion–neutral complex by way of distonic ions [18,19].

Apart from a pioneering study by the Nibbering group [20] on ionised hex-5-enyl methyl ether, $CH_2{=}CH(CH_2)_4OCH_3^{\cdot+}$, and later studies on allyl and butenyl methyl ethers [21–23], ionised alkenyl methyl

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Dedicated to Professor Nico Nibbering on the occasion of his imminent retirement in recognition of his outstanding contributions to gas-phase ion chemistry.

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ethers are one of the few classes of $C_nH_{2n}O^{\cdot+}$ species to receive comparatively little scrutiny. However, the limited work that has been published suggests that their chemistry, like that of many other $C_nH_{2n}O^{\cdot+}$ radical cations, is far more interesting than might have been supposed from their apparently simple structures. Thus, $C_2H_5^{\cdot}$ elimination from $CH_2{=}CH(CH_2)_4OCH_3^{\cdot+}$ occurs by at least two mechanisms, one of which involves rearrangement to structures accessible to ionised cyclohexyl methyl ether [20]. A survey of the 70 and 12 eV electron impact ionisation mass spectra of a range of alkenyl methyl ethers $C_mH_{2m-1}OCH_3^{\cdot+}$ (m = 3–6) showed that several mechanisms operate for alkyl radical elimination from these $C_nH_{2n}O^{\cdot+}$ species [24]. Analysis of collision-induced dissociation (CID) mass spectra of the $[M\text{–alkyl}]^+$ ions formed from many $C_mH_{2m-1}OCH_3^{\cdot+}$ species clarified the mechanisms of these reactions at high internal energies and yielded conclusions relevant to the fragmentation of $C_nH_{2n}O^{\cdot+}$ ions formed from larger molecules of biological significance [25,26]. Thus, the suggestion [27] that alkyl radical loss from ionised methyl phytyl ether takes place after an allylic rearrangement was refuted by further CID work [28]. Instead, a mechanism involving hydrogen transfers and distonic ions, followed by γ cleavage, was established to be general for a range of $R^1R^2C{=}CHCH_2OCH_3^{\cdot+}$ species [29,30].

Extension of these studies to $C_5H_9OCH_3^{\cdot+}$ radical cations revealed that most of the isomeric ionised methyl pentenyl ethers derived from stable pentenols have distinct chemistries. For only three of the thir teen isomers, viz. $C_2H_5CH{=}CHCH_2OCH_3^{\cdot+}$, $CH_2{=}CHCH(C_2H_5)OCH_3^{\cdot+}$, and $CH_2{=}C(C_2H_5)CH_2OCH_3^{\cdot+}$, the dissociation reactions are sufficiently similar to suggest a common chemistry [31]. In view of this diversity of behaviour and the earlier work on $C_2H_5^{\cdot}$ loss from ionised hex-5-enyl methyl ether [20], a more detailed investigation was initiated on the reactions of the ionised methyl pent-4-enyl homologue, $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, **1**$^{\cdot+}$.

2. Experimental

The ethers used in this work were prepared by methylating the alkoxide of the corresponding pentenol with a slight deficiency of CH_3I. The alkoxides were made by treatment of the alcohols with a slight excess of a NaH dispersion in triethylene glycol dimethyl ether (triglyme). In the methylation procedure, after stirring for 24–72 h at ambient temperature, the ether was carefully distilled from the reaction flask, washed with water, dried with $MgSO_4$ and redistilled. Methylation with CD_3I under the same conditions gave the analogous $C_5H_9OCD_3$ ether. The labeled pent-4-enols were prepared by the routes summarised in Scheme 6. Details of representative examples of these procedures have been described elsewhere [32].

All 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 reported elsewhere [33]. Data on the dissociation of metastable ions in the second field-free region (ffr) were obtained by the matrix-assisted ion kinetic energy spectrometry technique [34]. The quoted spectra are integrated data, compiled from 2 to 5 individual scans. Typical operating conditions were 70 eV ionising electron energy and 8 kV accelerating voltage. The kinetic energy releases were obtained from the width at half-height of the appropriate metastable peak, by means of the standard one-line equation; no correction was applied for the width at half-height of the main beam [34].

The CID [35] spectra of the $C_4H_7O^+$ and $C_5H_9O^+$ product ions were obtained with O_2 as the collision gas in the 2ffr on ions generated by loss of $C_2H_5^{\cdot}$ or $CH_3^{\cdot}$, respectively, from the appropriate ionised ether in the ion source. Essentially the same spectra were obtained when the $C_4H_7O^+$ and $C_5H_9O^+$ product ions formed by dissociation of metastable ions **1**$^{\cdot+}$–**3**$^{\cdot+}$ in the 2ffr were subjected to CID in the 3ffr.

3. Results and discussion

The reactions of low energy ions $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, **1**$^{\cdot+}$, are summarised in Table 1. Three main processes, loss of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$ and elimination of CH_3OH occur at comparable rates and account for ~85% of the total metastable ion current for dissoci-

Table 1
Relative abundances[a] and kinetic energy releases[b] for the main dissociations of metastable $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$; $CH_3CH{=}CH(CH_2)_2OCH_3^{\cdot+}$, $\mathbf{2}^{\cdot+}$; and c-$C_5H_9OCH_3^{\cdot+}$, $\mathbf{3}^{\cdot+}$

Precursor	Species lost				
Ion	$H^{\cdot}$	$CH_3^{\cdot}$	H_2O	$C_2H_5^{\cdot}$	CH_3OH
$\mathbf{1}^{\cdot+}$	15[c]	90 [2.1]	20 [2.8]	100 [1.9]	70 [0.4]
$\mathbf{2}^{\cdot+}$	45[c]	7 [2.9]	100 [2.1]	95 [1.3]	95 [0.2]
$\mathbf{3}^{\cdot+}$	<4[c]	60 [2.1]	<1 [c]	100 [1.9]	35 [1.7]

[a] Relative abundance measured by peak height and normalised to 100 units for the base peak.

[b] Numbers in square brackets represent kinetic energy releases, $T_{1/2}$, in kJ/mol and obtained from the width at half height of the peak.

[c] KER could not be estimated because of overlap with the tail of the parent ion signal or because of the weakness of the metastable peak.

ation of $\mathbf{1}^{\cdot+}$. Expulsion of H_2O and $H^{\cdot}$ are also significant. Minor signals for loss of C_2H_4, C_3H_6, and $CH_2{=}O$ are also present but not reported in Table 1.

The loss of an alkyl radical or a CH_3OH molecule is hardly surprising, especially considering the frequent occurrence of these losses from other ionised alkenyl methyl ethers [24–30]; however, H_2O elimination is rather unusual. For the purpose of comparison, the reactions of the metastable ions of the isomers $CH_3CH{=}CH(CH_2)_2OCH_3^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and c-$C_5H_9OCH_3^{\cdot+}$, $\mathbf{3}^{\cdot+}$, are also included in Table 1. There are many similarities in the reactions of these isomeric ether ions, but also important differences, especially the (near) absence of H_2O loss and the much larger kinetic energy release associated with CH_3OH elimination from $\mathbf{3}^{\cdot+}$.

The CID spectra of the m/z 85 $C_5H_9O^+$ oxonium ions formed by $CH_3^{\cdot}$ loss from the three isomers were obtained and found to be closely similar. A representative spectrum is presented in Fig. 1(c). Earlier CID work [25,26] on the oxonium ions $CH_3CH{=}CHC(H)OCH_3^+$, $\mathbf{b}_1^+$, $CH_2{=}CHC(CH_3)OCH_3^+$, $\mathbf{b}_2^+$, and $CH_2{=}C(CH_3)C(H)OCH_3^+$, $\mathbf{b}_3^+$, has established that $\mathbf{b}_1^+$ and its branched isomer $\mathbf{b}_3^+$ are cleanly generated from the alkenyl methyl ethers $\mathbf{4}^{\cdot+}$ and $\mathbf{5}^{\cdot+}$, respectively, as depicted in Scheme 2. Comparison with these reference CID spectra, see Fig. 1(a) and (b), leaves little doubt that most of the oxonium ions generated from $\mathbf{1}^{\cdot+}$ to $\mathbf{3}^{\cdot+}$ have the structure of the branched isomer $\mathbf{b}_3^+$. This remarkable observation shows that skeletal isomerisation of the linear carbon atom chain must precede $CH_3^{\cdot}$ elimination. In this context, $C_2H_5^{\cdot}$ loss from $CH_2{=}CH(CH_2)_4OCH_3^{\cdot+}$ also yields $\mathbf{b}_3^+$ [20]. Consequently, the tendency of $CH_2{=}CH(CH_2)_mOCH_3^{\cdot+}$ species to expel an alkyl radical

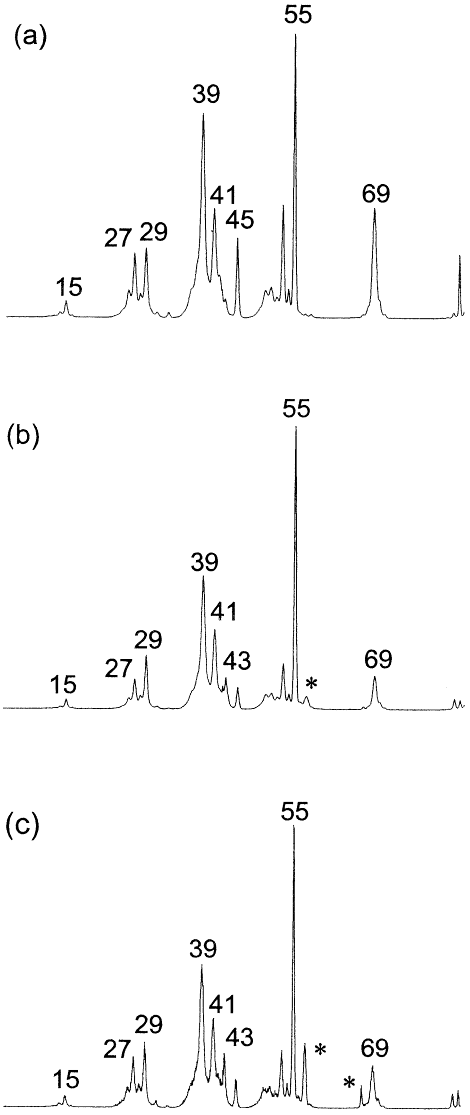


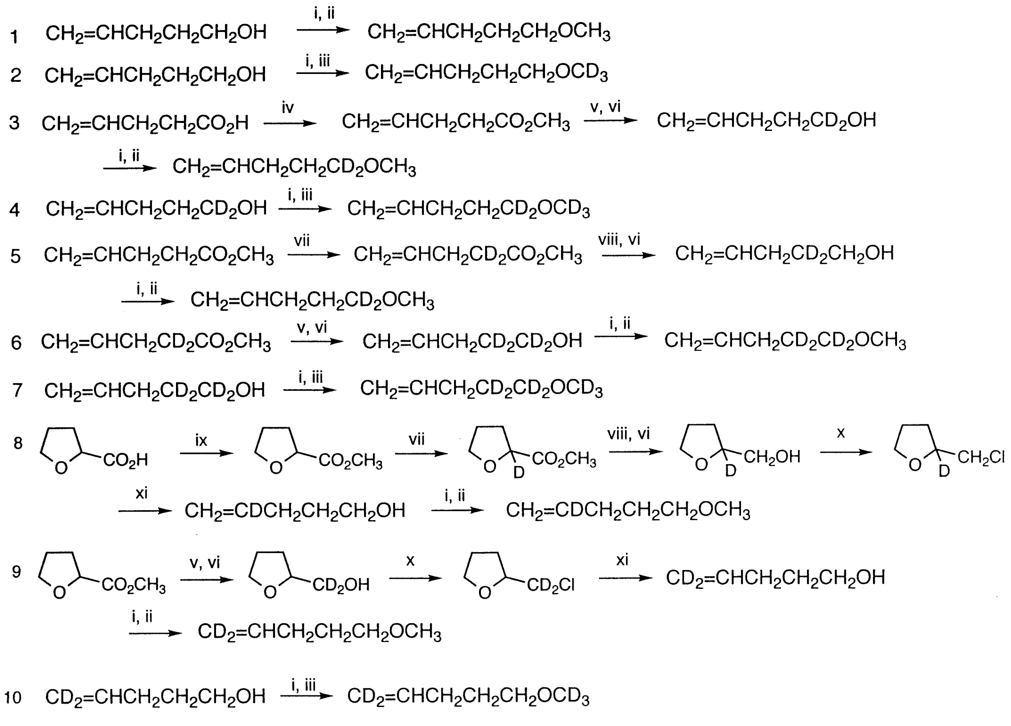
Fig. 1. Collision-induced dissociation (CID) mass spectra of m/z 85 ions $C_5H_9O^+$. (a) Ions $CH_3CH{=}CHC(H)OC_3^+$, $\mathbf{b}_1^+$; (b) ions $CH_2{=}C(CH_3)C(H)OCH_3^+$, $\mathbf{b}_3^+$; (c) ions generated from ionised methyl pent-4-enyl ether, $\mathbf{1}^{\cdot+}$. Peaks denoted with an asterisk, at m/z 57 and m/z 67, result from the dissociation of metastable ions rather than CID of stable ions.

after skeletal isomerisation to give $\mathbf{b}_3^+$ appears to be general for *m* = 3 and 4.

In addition, the structure of the *m/z* 71 $C_4H_7O^+$ oxonium ions formed by $C_2H_5^{\cdot}$ loss from $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{3}^{\cdot+}$ has been shown to be $CH_2{=}CHC(H)OCH_3^+$ by similar CID experiments. In this case, however, only one conjugated oxonium ion is possible, ion $\mathbf{a}_1^+$ in Scheme 1.

Unfortunately, the structures of the products formed by CH_3OH and H_2O loss from $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{3}^{\cdot+}$ could not be determined reliably because the CID spectra of isomeric $C_5H_8^{\cdot+}$ and $C_6H_{10}^{\cdot+}$ ions are closely similar. In principle, this problem could be overcome by examining the corresponding charge-stripping spectra; however, the large number of possible isomeric products made this task impractical, particularly for the ions of low abundance formed by expulsion of H_2O.

Further information on $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, CH_3OH, and H_2O losses from metastable $\mathbf{1}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$ is provided by the labeling data of Tables 3–6, respectively. It is not easy to interpret all these data, which are complicated by uncertainties concerning some signals (e.g. $CD_3^{\cdot}$ and H_2O losses overlap, as do $C_2H_2D_3^{\cdot}$ and CH_3OH eliminations). Nevertheless, it is clear that the site selectivities of the four processes differ. Thus, see



Reagents and conditions:

i, 1.5 moles NaH, $CH_3O(CH_2CH_2O)_3CH_3$; ii, 0.9 moles CH_3I, stir 24-72 hr; iii, 0.9 moles CD_3I, stir 24-72 hr; iv,1.1 moles CH_2N_2, $(C_2H_5)_2O$; v, addition to 0.7 moles $LiAlD_4$, $(C_2H_5)_2O$; vi, $H_2O/NaOH$; vii, CH_3OD, CH_3ONa, reflux 72 hr; repeat twice; viii, addition to 0.9 moles $LiAlH_4$, $(C_2H_5)_2O$; ix, CH_3OH/HCl, reflux 12 hr; x, $SOCl_2$, pyridine (cat.) Δ; xi, addition to 2.1 moles Na under $(C_2H_5)_2O$, 0°C; xii, H_2O.

Scheme 1.

Table 2
Relative abundance[a] for the methyl radical loss from various D labeled isotopologues of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$ and c-$C_5H_9OCD_3^{\cdot+}$, $\mathbf{3}^{\cdot+}$

Precursor ion		Species lost			
		$CD_3^{\cdot}$	$CHD_2^{\cdot}$	$CH_2D^{\cdot}$	$CH_3^{\cdot}$
$CH_2{=}CH(CH_2)_3OCD_3^{\cdot+}$	**1**-$OCD_3^{\cdot+}$	<3[b]	. . .	. . .	100
$CH_2{=}CH(CH_2)_2CD_2OCH_3^{\cdot+}$	**1**-1,1-$D_2^{\cdot+}$	. . .	7	35	100
$CH_2{=}CHCH_2CD_2CH_2OCH_3^{\cdot+}$	**1**-2,2-$D_2^{\cdot+}$	. . .	85	100	90
$CH_2{=}CD(CH_2)_3OCH_3^{\cdot+}$	**1**-4-$D^{\cdot+}$	. . .	. . .	25	100
$CD_2{=}CH(CH_2)_3OCH_3^{\cdot+}$	**1**-5,5-$D_2^{\cdot+}$	. . .	85	97	100
$CH_2{=}CHCH_2(CD_2)_2OCH_3^{\cdot+}$	**1**-1,1,2,2-$D_4^{\cdot+}$	50[c]	55	100	10
c-$C_5H_9OCD_3^{\cdot+}$	**3**-$OCD_3^{\cdot+}$	. . .	. . .	. . .	100

[a] Relative abundance measured by peak height and normalised to a total of 100 units for the methyl radical isotopologue lost in greatest abundance.

[b] All of this signal probably represents the loss of a H_2O molecule.

[c] Part of the abundance of this signal comes from the loss of a H_2O molecule.

Table 2, the probability of including a deuterium atom from the OCD_3 group of $CH_2{=}CH(CH_2)_3OCD_3^{\cdot+}$, **1**–$OCD_3^{\cdot+}$, in the expelled methyl radical is almost negligible (<3%). A similar, but somewhat less pronounced trend is found in ethyl radical loss from **1**–$OCD_3^{\cdot+}$, in which ~10% of the neutral species contain one or more deuterium atoms, see Table 3. In contrast, **1**–$OCD_3^{\cdot+}$ eliminates CD_3OH with a selectivity (90%) which complements that found for the loss of $C_2H_5^{\cdot}$. Perhaps the most surprising site selectivity is observed for H_2O loss: **1**–$OCD_3^{\cdot+}$ loses H_2O, HOD and D_2O in the ratio 70:100:19.

Rapid and reversible interconversion of ions $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{3}^{\cdot+}$ does not occur prior to dissociation; however, some reactions of these species probably involve common intermediates and transition states. Thus, relative to ions $\mathbf{1}^{\cdot+}$ and $\mathbf{3}^{\cdot+}$, ions $\mathbf{2}^{\cdot+}$ show a markedly reduced tendency to lose $CH_3^{\cdot}$ and a greatly enhanced tendency to expel H_2O, see Table 1. Moreover, metastable ions $\mathbf{3}^{\cdot+}$ differ from $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ in not eliminating H_2O. In addition, CH_3OH expulsion from $\mathbf{3}^{\cdot+}$ is characterised by a significantly larger kinetic energy release than that for the corresponding reaction of $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$; consequently, a different mechanism must operate for CH_3OH loss from $\mathbf{3}^{\cdot+}$. Finally, **3**–$OCD_3^{\cdot+}$ expels $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, and CD_3OH essentially exclusively, whereas for **1**–$OCD_3^{\cdot+}$ limited exchange occurs in all three reactions. All these facts

Table 3
Relative abundance[a] for the ethyl radical loss from various metastable D-labeled isotopologues of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$, and c-$C_5H_9OCD_3^{\cdot+}$, $\mathbf{3}^{\cdot+}$

Precursor	Species lost					
	$C_2D_5^{\cdot}$	$C_2HD_4^{\cdot}$	$C_2H_2D_3^{\cdot}$	$C_2H_3D_2^{\cdot}$	$C_2H_4D^{\cdot}$	$C_2H_5^{\cdot}$
1-$OCD_3^{\cdot+}$	. . .	. . .	1	8	2	100
1-1,1-$D_2^{\cdot+}$	. . .	. . .	. . .	15	95	100
1-2,2-$D_2^{\cdot+}$	. . .	. . .	. . .	100	100	30
1-4-$D^{\cdot+}$	. . .	. . .	. . .	. . .	80	100
1-5,5-$D_2^{\cdot+}$	. . .	. . .	. . .	100	90	12
1-1,1,2,2-$D_4^{\cdot+}$	. . .	7	100[b]	75	25	15
1-1,1,2,2-D_4-$OCD_3^{\cdot+}$	17	3	18	100	25	5
3-$OCD_3^{\cdot+}$	. . .	. . .	. . .	. . .	. . .	100

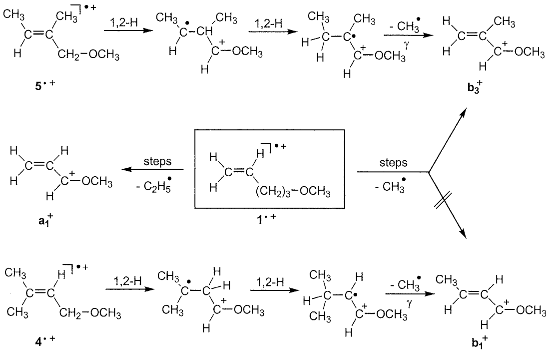
[a] Relative abundance measured by peak height and normalised to a total of 100 units for the ethyl radical isotopologue lost in greatest abundance.

[b] Analysis of the peak shape indicates that a substantial part of this signal represents the loss of a CH_3OH molecule.

point to differences, some of which are subtle, in the chemistry of $\mathbf{1}^{\cdot+}$, $\mathbf{2}^{\cdot+}$, and $\mathbf{3}^{\cdot+}$.

3.1. Loss of $C_2H_5^{\cdot}$

The data of Table 3 show that the hydrogen atoms of positions 2 and 5 appear in the expelled $C_2H_5^{\cdot}$ with higher probability than those on positions 1 and 4. Thus, $\mathbf{1}$–2,2-$D_2^{\cdot+}$ and $\mathbf{1}$–5,5-$D_2^{\cdot+}$ eliminate ~50% $C_2H_3D_2^{\cdot}$. On the other hand, $\mathbf{1}$–1,1-$D_2^{\cdot+}$ loses only 7%$C_2H_3D_2^{\cdot}$ and $\mathbf{1}$–4-$D_1^{\cdot+}$ expels $C_2H_3D_2^{\cdot}$ and $C_2H_4D^{\cdot}$ in approximately equal amounts. These data may be interpreted by the mechanism of Scheme 2, in which at least limited isomerisation to $\mathbf{3}^{\cdot+}$ generates two equivalent pairs of methylene groups, derived from C-2 and C-5, and C-3, and C-4 in $\mathbf{1}^{\cdot+}$. Ethyl radical loss eventually occurs by γ-cleavage of the ionised enol ether, $\mathbf{6}^{\cdot+}$, to give the required oxonium ion, $\mathbf{a}_1^{+}$. Since one or both of the 1,4-H transfer steps in this route are likely to be partially reversible, some exchange of the hydrogen atoms in the various positions in $\mathbf{1}^{\cdot+}$ may occur. However, $C_2H_5^{\cdot}$ loss should involve selection of a methylene group from position 2 or 3, with a carbon atom from position 4 or 1; there should also be approximately a 50% probability of selecting the lone hydrogen atom attached to position 4, and one of the two hydrogen atoms from position 1 in the expelled neutral fragment. Consequently, this mechanism also explains why $\mathbf{1}$–1,1-2,2-$D_4^{\cdot+}$ and $\mathbf{1}$–1,1-2,2-D_4–$OCD_3^{\cdot+}$ lose predominantly $C_2H_3D_2^{\cdot}$.

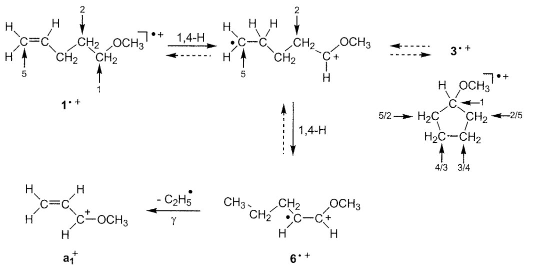


Scheme 2.

3.2. Loss of $CH_3^{\cdot}$

The data of Table 2 indicate that the site selectivity in $CH_3^{\cdot}$ loss from $\mathbf{1}^{\cdot+}$ has features in common with that for $C_2H_5^{\cdot}$ loss. The similar behaviour of $\mathbf{1}$–2,2-$D_2^{\cdot+}$ and $\mathbf{1}$–5,5-$D_2^{\cdot+}$, both of which eliminate ~30% $CHD_2^{\cdot}$, ~35% $CH_2D^{\cdot}$and ~35% $CH_3^{\cdot}$, points to a mechanism involving isomerisation to $\mathbf{3}^{\cdot+}$ or species accessible to $\mathbf{3}^{\cdot+}$. One plausible route for the later steps in the methyl radical loss proceeds by way of a sequence of 1,4- and 1,5-H shifts to produce an ionised cyclopropane, which opens to give an isomerised carbon skeleton; a 1,2-H shift to the radical site of this distonic ion then forms an ionised enol ether, $\mathbf{10}^{\cdot+}$, which may fragment by γ cleavage to give $\mathbf{b}_3^{+}$, as depicted in Scheme 3. This route entails more hydrogen transfers than that for $C_2H_5^{\cdot}$ loss, thus explaining the greater degree of hydrogen exchange which appears to precede $CH_3^{\cdot}$ loss.

There is ample precedence in the reactions of ionised alkenyl methyl ethers and other radical cations for the H transfer, skeletal isomerisation and γ-cleavage steps postulated in Schemes 2 and 3. Thus, although 1,2-H shifts to purely radical sites usually entail substantial energy barriers [36,37], the migration terminus for the 1,2-H shifts that initiate $CH_3^{\cdot}$ or $C_2H_5^{\cdot}$ elimination from $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ is a carbon atom that is part of a π system from which an electron may be considered to have been removed. This partial cationic character facilitates the initial 1,2-H shift. Similarly, although few examples, if any, of 1,3-H shifts to a radical centre have been reported, H transfers through larger ring transition states occur readily, in both simple radicals [36] and radical cations [10,38,39]. In addition, skeletal isomerisa-



Scheme 3.

Table 4
Relative abundance[a] for methanol loss from various metastable D-labeled isotopologues of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$, and $c\text{-}C_5H_9OCD_3^{\cdot+}$, $\mathbf{3}^{\cdot+}$

	Species lost				
Precursor	CD_3OD	CD_3OH	CHD_2OH[b]	CH_3OD	CH_3OH
1-$OCD_3^{\cdot+}$	...	100	11	...	...
1-1,1-$D_2^{\cdot+}$	...	...	<1	4	100
1-2,2-$D_2^{\cdot+}$	...	...	...	7	100
1-4-$D^{\cdot+}$	...	...	...	6	100
1-5,5-$D_2^{\cdot+}$	...	...	2	100	85
1-1,1,2,2-$D_4^{\cdot+}$	...	...	<1	7	100[c]
1-1,1,2,2-D_4-$OCD_3^{\cdot+}$	7	100	17[d]	3	17[e]
3-$OCD_3^{\cdot+}$	...	100	...	...	...

[a] Relative abundance measured by peak height and normalised to a total of 100 units for the methanol isotopologue lost in greatest abundance.

[b] Possibly CH_2DOD loss, in some cases.

[c] Part of this signal is possibly $C_2H_2D_3^{\cdot}$ loss.

[d] Part of this signal is possibly C_2D_5 loss.

[e] Analysis of the peak shape indicates that all or most of this signal is probably $C_2H_2D_3^{\cdot}$ loss.

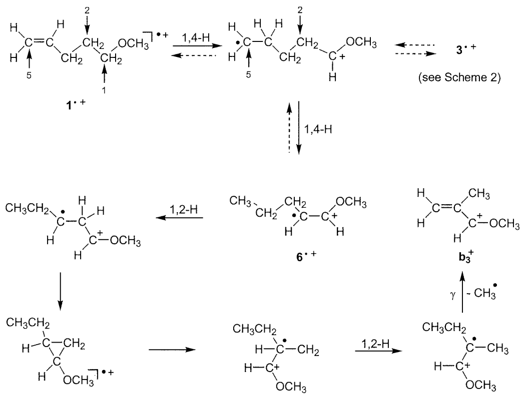
tions, which may be formulated in terms of ionised cyclopropanes, have been postulated for many distonic ions, including those derived from ionised carboxylic acids [40,41] and alkenols [42]. Moreover, rate-limiting 1,2-H shifts to the radical site of distonic ions, followed by γ cleavage of the resultant ionised enol ether, have been shown to explain the fragmentation of ionised carboxylic acids [40,41].

3.3. Loss of CH_3OH

In contrast to the loss of $C_2H_5^{\cdot}$ or $CH_3^{\cdot}$, CH_3OH elimination mainly involves retention of the OCH_3 group in the expelled neutral. Moreover, see Table 4, the H atoms on C-1, C-2 and C-4 of $\mathbf{1}^{\cdot+}$ are rarely transferred to oxygen to become part of the eliminated methanol. The strong preference (≥50%) for selecting the fourth hydrogen atom from C-5, together with the negligible probability of transferring this hydrogen atom from C-2 (≤7%), seems to exclude cyclisation of $\mathbf{1}^{\cdot+}$–$\mathbf{3}^{\cdot+}$ prior to CH_3OH loss. This interpretation is consistent with the much larger kinetic energy release associated with the loss of CH_3OH from $\mathbf{3}^{\cdot+}$.

Some progress in unraveling the mechanism of this reaction may be made by postulating that the reaction begins with a hydrogen transfer to oxygen. Isomerisation of $\mathbf{1}^{\cdot+}$ to $\mathbf{2}^{\cdot+}$ by way of the allylic distonic ion depicted in Scheme 4 by consecutive 1,4- and 1,6-H transfers creates a terminal CH_3 group in which one of the hydrogen atoms originates from C-3 whereas the other two come from the terminal CH_2 group. Elimination of CH_3OH by slow cyclisation of this distonic ion to give ionised cyclopentene as the $C_5H_8^{\cdot+}$ product ion would account for the observed preferential transfer to oxygen of a hydrogen atom initially attached to C-5. There would, however, be some participation of the hydrogen atoms originally bound to C-3, which appears to occur, see Table 4.

The results in Table 4 further show that H transfer from C-1, C-2, or C-4 is not significant and H transfer



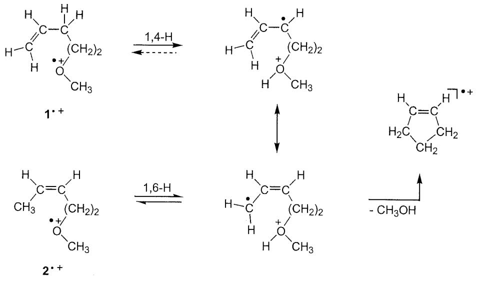
Scheme 4.

Table 5
Relative abundance[a] for water loss from various metastable D-labeled isotopologues of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$, and $CH_3CH{=}CH(CH_2)_2OCH_3^{\cdot+}$, $\mathbf{2}^{\cdot+}$

Precursor		Species lost		
		D_2O	HOD	H_2O
$CH_2{=}CH(CH_2)_3OCD_3^{\cdot+}$	**1**-$OCD_3^{\cdot+}$	19	100	70
$CH_2{=}CH(CH_2)_2CD_2OCH_3^{\cdot+}$	**1**-1,1-$D_2^{\cdot+}$	. . .	4	100
$CH_2{=}CHCH_2CD_2CH_2OCH_3^{\cdot+}$	**1**-2,2-$D_2^{\cdot+}$	. . .	5	100
$CH_2{=}CD(CH_2)_3OCH_3^{\cdot+}$	**1**-4-$D^{\cdot+}$	. . .	35	100
$CD_2{=}CH(CH_2)_3OCH_3^{\cdot+}$	**1**-5,5-$D_2^{\cdot+}$	6	55	100
$CH_2{=}CHCH_2CD_2CD_2OCH_3^{\cdot+}$	**1**-1,1,2,2-$D_4^{\cdot+}$	. . .	7	100[b]
$CH_2{=}CHCH_2CD_2CD_2OCD_3^{\cdot+}$	**1**-1,1,2,2-D_4-$OCD_3^{\cdot+}$	60	100	60[b]
$CH_3CH{=}CH(CH_2)_2OCD_3^{\cdot+}$	**2**-$OCD_3^{\cdot+}$	18	100	85
$CH_3CH{=}CHCH_2CD_2OCH_3^{\cdot+}$	**2**-1,1-$D_2^{\cdot+}$	<1	4	100
$CH_3CH{=}CHCH_2CD_2OCD_3^{\cdot+}$	**2**-1,1-D_2-$OCD_3^{\cdot+}$	20	100	65

[a] Relative abundance measured by peak height and normalised to a total of 100 units for the water isotopologue lost in greatest abundance.
[b] Part of this signal is probably $CD_3^{\cdot}$ loss.

from C-5 alone does not take place with a sufficiently high selectivity to be the sole route for CH_3OH loss. If the steps depicted in Scheme 4 were fast and reversible, hydrogen transfer from C-3 and C-5 would occur with equal probability; but this possibility seems unlikely. More complex mechanisms may be envisaged, in which skeletal rearrangement occurs to give other isomers of $C_5H_8^{\cdot+}$. The main criterion for any such mechanistic proposal is that the route for CH_3OH loss must diverge at a very early stage from that for the losses of $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ because the labeling and kinetic energy release data exclude cyclisation to $\mathbf{3}^{\cdot+}$ prior to CH_3OH loss. The route proposed in Scheme 4 satisfies this criterion and it is also consistent with the behaviour of metastable $\mathbf{2}^{\cdot+}$, which loses CH_3OH more readily than any other ionised methyl pentenyl ether [31].



Scheme 5.

3.4. Loss of H_2O

The expulsion of H_2O from low energy $\mathbf{1}^{\cdot+}$ and $\mathbf{2}^{\cdot+}$ is quite remarkable: it entails cleavage of two C–O bonds and formation of two new O–H bonds. The labeling results in Table 5 indicate that this process differs from both CH_3OH and $CH_3^{\cdot}$ or $C_2H_5^{\cdot}$ elimination: one or both of the H atoms in the expelled H_2O molecule may originate from the OCH_3 group. Thus, in contrast to the CH_3OH loss, the positional integrity of the OCH_3 groups may be substantially eroded in the H_2O elimination. On the other hand, in common with the CH_3OH loss, the low probability of incorporating a H atom from C-1 or C-2 and the high probability of selecting one H atom from C-5 in the H_2O molecule excludes cyclisation to $\mathbf{3}^{\cdot+}$ prior to water loss. This deduction is consistent with the behaviour of metastable $\mathbf{3}^{\cdot+}$, which does not lose water. However, in contrast to the loss of CH_3OH, the lone H atom on C-4 is incorporated to a significant extent in the eliminated H_2O molecule. There may also be a reasonably high probability that one of the H atoms originates from C-3. Scheme 5 offers a tentative mechanism for this interesting dissociation and an explanation for why it differs from both the alkyl radical and the CH_3OH loss.

The first step is either a 1,6-H or 1,7-H transfer from the OCH_3 group to C-4 or C-5. These steps

Table 6
Observed (O) and calculated (models A and B) ratios of H_2O, HOD, and D_2O losses from various metastable D-labeled isotopologues of $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$, and $CH_3CH{=}CH(CH_2)_2OCH_3^{\cdot+}$, $\mathbf{2}^{\cdot+}$

	Species lost[a]								
	D_2O			HOD			H_2O		
Precursor	O	A	B	O	A	B	O	A	B
1-$OCD_3^{\cdot+}$	19	33	20	100	100	100	70	33	67
1-1,1-$D_2^{\cdot+}$	0	0	0	4	0	0	100	100	100
1-2,2-$D_2^{\cdot+}$	0	0	0	5	0	0	100	100	100
1-4-$D^{\cdot+}$	0	0	0	33	50	33	100	100	100
1-5,5-$D_2^{\cdot+}$	6	12	7	55	100	80	100	75	100
1-1,1,2,2-$D_4^{\cdot+}$	0	0	0	7	0	0	100	100	100
1-1,1,2,2-D_4-$OCD_3^{\cdot+}$	60	33	20	100	100	100	60	33	67
2-$OCD_3^{\cdot+}$	18	14	20	100	57	100	85	100	67
2-1,1-$D_2^{\cdot+}$	<1	0	0	4	0	0	100	100	100
2-1,1-D_2-$OCD_3^{\cdot+}$	20	14	20	100	57	100	65	100	67

[a] All values normalised to a total of 100 units for the water isotopologue lost in greatest abundance.

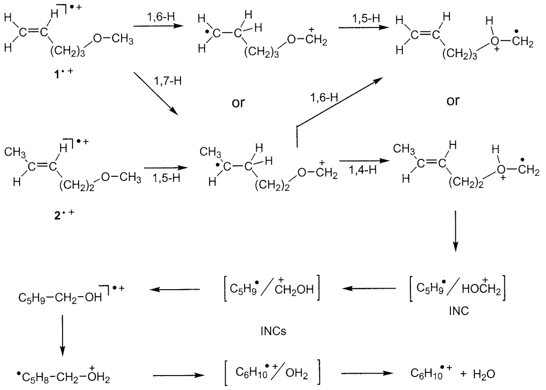
allow the H atoms of the OCH_3 group to exchange with those on C-4 and C-5; a related sequence of hydrogen transfers would allow the H atoms on C-3 to participate in these exchanges, with formation of $\mathbf{2}^{\cdot+}$. Transfer of a hydrogen atom from C-5 in one of these distonic ions to the O atom would then produce an ion containing a CH_2OH^+ entity and an unsaturated $C_5H_9^{\cdot}$ radical attached to the O atom. Cleavage of the C–O bond would then afford an ion–neutral complex, the components of which may undergo mutual rotation, followed by recombination to give an ionised alkenol. Further H transfer from carbon to oxygen then leads to a protonated alcohol which may lose H_2O with formation of $C_6H_{10}^{\cdot+}$. There is a precedent for the proposal of Scheme 5 in general mechanisms [25] proposed in experimental studies [43,44] and recent high-level theoretical investigations [45,46] for H_2O loss from $C_nH_{2n+1}O^+$ oxonium ions containing an internal oxygen atom.

Provided that the final H transfer occurs preferentially from one of the carbon atoms, which was originally C-5 or C-4 (or, possibly, C-3), the experimental observations can be rationalised, at least to a first approximation. Table 6 compares the observed abundances of H_2O, HOD, and D_2O loss from D-labeled analogues of $\mathbf{1}^{\cdot+}$ with those calculated on the basis of two models.

Model A allows for random selection of any two of the six H atoms on C-4, C-5, and the OCH_3 group; model B corresponds to statistical selection of any two of the eight H atoms on C-3, C-4, C-5, and the OCH_3 group. Both models assume that isotope effects can be neglected. Model B is the more attractive of the two as it reproduces the observed behaviour of labeled analogues of $\mathbf{1}^{\cdot+}$ reasonably well. However, this agreement does not mean that model B alone describes the real situation: a combination of the two models with contributions from other minor processes may well represent the actual mechanism for H_2O loss.

4. Conclusions

The three most important reactions of metastable $CH_2{=}CH(CH_2)_3OCH_3^{\cdot+}$, $\mathbf{1}^{\cdot+}$, viz. losses of $CH_3^{\cdot}$, $C_2H_5^{\cdot}$, and CH_3OH are preceded by extensive H transfers involving distonic ions. Interesting contrasts are found in the site selectivities of each of these three processes and the rather less facile expulsion of H_2O. The $CH_3^{\cdot}$ and $C_2H_5^{\cdot}$ losses may be rationalised in terms of rearrangements leading to cyclisation to ionised methyl cyclopentyl ether. Both these reactions begin with H transfers between carbon atoms of the pente-



Scheme 6.

nyl chain. In contrast, H_2O and CH_3OH loss appear to be initiated by H transfer between the pentenyl chain and the methoxy group. These reactions do not involve isomerisation to ionised cyclopentyl methyl ether. The mechanism of $CH_3^{\bullet}$ elimination from $\mathbf{1}^{\bullet+}$ may show some resemblance to that for $C_2H_5^{\bullet}$ loss from the higher homologue $CH_2{=}CH(CH_2)_4OCH_3^{\bullet+}$ [20].

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