Unimolecular Reactions of Isolated $C_4H_8O^{+\cdot}$ Ions Derived From Unbranched Butenols

Richard D. Bowen *
Department of Chemistry, University of Warwick, Coventry CV4 7AL
Alex G. Harrison
Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1

The slow dissociations of $C_4H_8O^{+\cdot}$ radical cations produced by ionisation of $CH_2{=}CHCH_2CH_2OH$, $CH_3CH{=}CHCH_2OH$, $CH_2{=}CHCH(CH_3)OH$ and numerous ^2H-labelled analogues are reported and discussed. Each of these $C_4H_8O^{+\cdot}$ species undergoes three main reactions: loss of water, a methyl radical, and an ethyl radical. However, the labelling results reveal that the specificity of hydrogen selection is different for decomposition of each of the three ionised alkenols. Extensive exchange occurs between the hydroxylic and carbon-bound hydrogens of ionised homoallyl alcohol before decomposition takes place. In contrast, the hydroxylic hydrogen of ionised but-2-en-1-ol and but-3-en-2-ol participates with a high specificity in water and ethyl radical expulsion, but not in methyl radical loss. Moreover, there is only limited interchange of the carbon-bound hydrogens in the reactions of the ionised allylic alcohols. The results of these studies are compared with those of previous investigations of the $C_4H_8O^{+\cdot}$ system; in general, the agreement with earlier work is good.

The reactions of $C_nH_{2n}O^{+\cdot}$ radical cations have held the attention of mass spectroscopists and ion chemists for many years. Advances in characterising[1] and understanding the structures of radical cations, especially the recognition of the crucial role of distonic[2] species,[3] have facilitated the development of detailed descriptions of numerous ionic systems. Other novel structures include ion–neutral complexes,[4,5] which have recently been used to explain certain unusual reactions of ionised ketones.[6–8] A two-part definitive review[9] summarises the rich chemistry of various $C_nH_{2n}O^{+\cdot}$ ions.

Although considerable attention has been paid to the reactions of most $C_4H_8O^{+\cdot}$ and $C_5H_{10}O^{+\cdot}$ species containing a hydroxy function,[19–37] only limited work has been performed on the isomers derived from terminal linear alkenols. A study of the 12.1 eV 75 °C electron ionisation mass spectra of the terminal alkenols $CH_2{=}CH(CH_2)_mOH$ (m = 1–4) showed that the $[M - \text{methyl}]^+$ and $[M - \text{water}]^{+\cdot}$ peaks originated by processes involving different specificities of hydrogen atom selection for $m = 2$.[38] Consequently, a fuller investigation of the behaviour of $CH_2{=}CHCH_2CH_2OH^{+\cdot}$ is of interest.

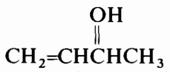
Results and Discussion

The reactions of metastable $C_4H_{8-n}D_nO^{+\cdot}$ (n = 0–4) radical cations generated by ionisation of but-3-en-1-ol (**1**), but-2-en-1-ol (**2**), but-3-en-2-ol (**3**), and selected ^2H-labelled analogues are given in Tables 1, 2, and 3. Where comparisons are possible, these data are in good qualitative agreement with those reported previously.

All three types of $C_4H_{8-n}D_nO^{+\cdot}$ species undergo predominantly methyl radical loss, together with smaller amounts of ethyl radical and water elimination. There is also a very minor quantity of ethylene loss. This behaviour appears to be general for $C_4H_8O^{+\cdot}$ radical cations which contain a hydroxyl group,[9,15,26] though there are exceptions.[15]

$CH_2{=}CHCH_2CH_2OH$
(**1**)

$CH_3CH{=}CHCH_2OH$
(**2**)



$CH_2{=}CH\overset{\overset{OH}{\|}}{C}HCH_3$

(**3**)

At first sight, the ratios of $CH_3^\cdot$, H_2O, and $C_2H_5^\cdot$ losses from $(\mathbf{1})^{+\cdot}$ and $(\mathbf{2})^{+\cdot}$ are so similar that it would seem likely that these ions interconvert prior to dissociation.[41] Similarly, although $(\mathbf{3})^{+\cdot}$ eliminates substantially less water than do $(\mathbf{1})^{+\cdot}$ and $(\mathbf{2})^{+\cdot}$, this difference could be ascribed to variations in the original internal energies of isomeric $C_4H_8O^{+\cdot}$ species which interconvert before decomposition.[42] The ^2H-labelling results, however, reveal that the resemblance between the reactions of $(\mathbf{1})^{+\cdot}$, $(\mathbf{2})^{+\cdot}$, and $(\mathbf{3})^{+\cdot}$ is coincidental. This is shown most clearly for $(\mathbf{1})^{+\cdot}$ and $(\mathbf{2})^{+\cdot}$ by the behaviour of the O-^2H analogues. [O-^2H]-(**2**) expels almost exclusively HOD in the water loss reaction; in contrast [O-^2H]-$(\mathbf{1})^{+\cdot}$ loses mainly H_2O. The specific loss of HOD from [O-^2H]-$(\mathbf{2})^{+\cdot}$ might have been expected, but the preference shown by [O-^2H]-$(\mathbf{1})^{+\cdot}$ for retaining the hydroxylic hydrogen in the hydrocarbon daughter ion is remarkable. The third isomer, [O-^2H]-$(\mathbf{3})^{+\cdot}$, retains the hydroxylic hydrogen in the expelled water molecule, but the preference for doing so is less pronounced than that exhibited by [O-^2H]-$(\mathbf{2})^{+\cdot}$. Variations in the specificities of hydrogen and deuterium selection are also evident in methyl and ethyl radical expulsions from [O-^2H]-$(\mathbf{1})^{+\cdot}$, [O-^2H]-$(\mathbf{2})^{+\cdot}$, and [O-^2H]-$(\mathbf{3})^{+\cdot}$. Starting from [O-^2H]-$(\mathbf{1})^{+\cdot}$, a considerable amount of exchange between the hydroxylic deuterium and the carbon-bound hydrogens precedes decomposition. This is shown by the abundant $CH_2D^\cdot$ and $C_2H_4D^\cdot$ losses from [O-^2H]-$(\mathbf{1})^{+\cdot}$. In contrast, [O-^2H]-$(\mathbf{2})^{+\cdot}$ and [O-^2H]-$(\mathbf{3})^{+\cdot}$ eliminate practically exclusively $CH_3^\cdot$ and $C_2H_4D^\cdot$. These observations prove that $(\mathbf{1})^{+\cdot}$ reacts over a different potential-energy profile from those involved in dissociation of $(\mathbf{2})^{+\cdot}$ and $(\mathbf{3})^{+\cdot}$. It is possible that $(\mathbf{1})^{+\cdot}$ may isomerise to $(\mathbf{2})^{+\cdot}$ and/or $(\mathbf{3})^{+\cdot}$ before decomposing; this rearrangement must be irreversible, since $(\mathbf{2})^{+\cdot}$ and $(\mathbf{3})^{+\cdot}$ do not show the mixing of the hydroxylic and carbon-bound hydrogens which is characteristic of $(\mathbf{1})^{+\cdot}$. A careful analysis of the fragmentation of C-deuteriated analogues of $(\mathbf{2})^{+\cdot}$ and $(\mathbf{3})^{+\cdot}$ reveals that these species do not equilibrate rapidly prior to dissociation. This view is consistent with the reported[26]

Table 1. Reactions of metastable $C_4H_{8-n}D_nO^{+\bullet}$ species derived from but-3-en-1-ols.

m/z of daughter ion	Parent structure and associated neutral species lost[a,b]			
	$CH_2{=}CHCH_2CH_2OH$ (**1**)	$CH_2{=}CHCH_2CH_2OD$ $[O\text{-}^2H]$-(**1**)	$CH_2{=}CHCH_2CD_2OH$ $[1,1\text{-}^2H_2]$-(**1**)	$CH_2{=}CHCH_2CD_2OD$ $[O,1,1\text{-}^2H_3]$-(**1**)
60				11.0 ($CH_3^{\bullet}$)
59			21.8 ($CH_3^{\bullet}$)	36.3 ($CH_2D^{\bullet}$)
58		39.5 ($CH_3^{\bullet}$)	37.4 ($CH_2D^{\bullet}$)	18.5 ($CHD_2^{\bullet}$)
57	64.1 ($CH_3^{\bullet}$)	25.6 ($CH_2D^{\bullet}$)	6.3 ($CHD_2^{\bullet}$)	7.0 ($CD_3^{\bullet}/H_2O^c$)
56			9.2 (H_2O)	3.5 (HOD)
55		10.0 (H_2O)	1.9 (HOD)	0.3 (D_2O)
54	12.4 (H_2O)	1.3 (HOD)		
47				0.3
46			0.4	1.3 ($C_2H_5^{\bullet}$)
45		0.6	3.5 ($C_2H_5^{\bullet}$)	7.9 ($C_2H_4D^{\bullet}$)
44	0.9	10.6 ($C_2H_5^{\bullet}$)	13.2 ($C_2H_4D^{\bullet}$)	11.3 ($C_2H_3D_2^{\bullet}$)
43	22.7 ($C_2H_5^{\bullet}$)	12.4 ($C_2H_4D^{\bullet}$)	6.3 ($C_2H_3D_2^{\bullet}$)	3.0 ($C_2H_2D_3^{\bullet}$)
Total methyl loss	64.1	65.1	65.5	65.8
Total water loss	12.4	11.3	11.1	10.8
Total ethyl loss	22.7	23.0	23.0	23.3

[a] Results were determined by MIKES technique (ref. 39) using a VG Analytical ZAB 2FQ mass spectrometer (ref. 40). [b] Abundances were normalised to a total metastable-ion current of 100 units; estimated uncertainty 0.5 units. [c] This is probably almost entirely H_2O.

Table 2. Reactions of metastable $C_4H_{8-n}D_nO^{+\bullet}$ species derived from but-2-en-1-ols.

m/z of daughter ion	Parent structure and associated neutral species lost[a,b]					
	$CH_3CH{=}CHCH_2OH$ (**2**)	$CH_3CH{=}CHCH_2OD$ $[O\text{-}^2H]$-(**2**)	$CH_3CH{=}CH$ $CHOOH$ $[1\text{-}^2H_1]$-(**2**)	$CH_3CH{=}CH$ $CHOOD$ $[O,1\text{-}^2H_2]$-(**2**)	$CH_3CH{=}CHCD_2OH$ $[1,1\text{-}^2H_2]$-(**2**)	$CH_3CH{=}CHCD_2OD$ $[O,1,1\text{-}^2H_3]$-(**2**)
60						34.5 ($CH_3^{\bullet}$)
59				43.3 ($CH_3^{\bullet}$)	30.8 ($CH_3^{\bullet}$)	20.1 ($CH_2D^{\bullet}$)
58		62.5 ($CH_3^{\bullet}$)	39.3 ($CH_3^{\bullet}$)	20.7 ($CH_2D^{\bullet}$)	20.0 ($CH_2D^{\bullet}$)	9.8 ($CHD_2^{\bullet}$)
57	59.9 ($CH_3^{\bullet}$)	0.8 ($CH_2D^{\bullet}$)	18.7 ($CH_2D^{\bullet}$)	0.4 ($CHD_2^{\bullet}$)	8.9 ($CHD_2^{\bullet}$)	2.1 ($CD_3^{\bullet}/H_2O^c$)
56				0.6 (H_2O)	12.9 (H_2O)	9.8 (HOD)
55		0.4 (H_2O)	14.4 (H_2O)	11.0 (HOD)	1.5 (HOD)	1.0 (D_2O)
54	16.0 (H_2O)	12.9 (HOD)	1.6 (HOD)	0.5 (D_2O)		
45					5.4 ($C_2H_5^{\bullet}$)	4.1 ($C_2H_4D^{\bullet}$)
44	0.4	0.5 ($C_2H_5^{\bullet}$)	9.8 ($C_2H_5^{\bullet}$)	8.1 ($C_2H_4D^{\bullet}$)	9.1 ($C_2H_4D^{\bullet}$)	6.9 ($C_2H_3D_2^{\bullet}$)
43	23.6 ($C_2H_5^{\bullet}$)	22.9 ($C_2H_4D^{\bullet}$)	16.0 ($C_2H_4D^{\bullet}$)	15.5 ($C_2H_3D_2^{\bullet}$)	11.4 ($C_2H_3D_2^{\bullet}$)	11.7 ($C_2H_2D_3^{\bullet}$)
Total methyl loss	59.9	63.3	58.0	64.4	59.7	66.1
Total water loss	16.0	13.3	16.0	12.1	14.4	11.3
Total ethyl loss	23.6	23.4	25.8	23.6	25.9	22.7

[a,b] These footnotes have the same significance as those in Table 1. [c] Estimated to be 1.7 $CD_3^{\bullet}$ and 0.5 H_2O.

collision-induced dissociation (CID) spectra of (**1**)$^{+\bullet}$, (**2**)$^{+\bullet}$, and (**3**)$^{+\bullet}$.

Before proceeding to a more detailed consideration of the behaviour of (**1**)$^{+\bullet}$, (**2**)$^{+\bullet}$, and (**3**)$^{+\bullet}$, it is worth mentioning the effect of deuteriation on the relative abundances of methyl, ethyl, and water losses. For (**1**)$^{+\bullet}$, deuteriation has just a marginal influence: the total amount of water loss is slightly suppressed, whilst there are small increases in the quantities of methyl and ethyl radical eliminations. In contrast, deuteriation of (**2**)$^{+\bullet}$ effects a sizeable diminution in the gross abundance of water expulsion and a corresponding increase in the amount of methyl radical loss. The effect is more pronounced for *O*-deuteriation, though a discernible change is produced by *C*-deuteriation. Only smaller changes occur in the abundance of ethyl radical expulsion. Deuteriation of (**3**)$^{+\bullet}$ results in quite different trends from those observed for (**1**)$^{+\bullet}$ and (**2**)$^{+\bullet}$. Methyl radical elimination is strongly suppressed, by either *O*- or *C*-deuteriation, whilst loss of an ethyl radical is strongly favoured. This effect is so marked that the ratio of methyl:ethyl expulsion is reduced from 2.2:1 for (**3**)$^{+\bullet}$ to only 1.2:1 for $[O,1,1,1\text{-}^2H_4]$-(**3**)$^{+\bullet}$. The minor percentage of water loss is not greatly affected by deuteriation. The disparate changes in the gross amounts of methyl, water, and ethyl losses brought about by deuteriation of (**1**)$^{+\bullet}$, (**2**)$^{+\bullet}$, and (**3**)$^{+\bullet}$ underline the subtle differences which exist between the reactions of these ions. In addition, these trends serve to emphasise the complexity of behaviour shown by $C_4H_8O^{+\bullet}$ radical cations.

The energetics of the products of decomposition of $C_4H_8O^{+\bullet}$ ions are well defined.[43–46] Table 4 summarises the relevant data for methyl, water, and ethyl loss from $C_4H_8O^{+\bullet}$; ethylene expulsion yields products having a total enthalpy of formation substantially (*ca.* 50–70[15] kJ mol^{-1}) above those involved in methyl, ethyl, and water loss. This accounts for the poor competition of ethylene elimination with the three main fragmentations of these $C_4H_8O^{+\bullet}$ ions.[15]

Table 3. Reactions of metastable $C_4H_{8-n}D_nO^{+\bullet}$ species derived from but-3-en-2-ols.

	Parent structure and associated neutral species lost[a,b]			
m/*z* of daughter ion	OH $CH_2{=}CHCHCH_3$ (**3**)	OD $CH_2{=}CHCHCH_3$ [*O*-^{2}H]-(**3**)	OH $CH_2{=}CHCHCD_3$ [1,1,1-^{2}H]-(**3**)	OD $CH_2{=}CHCHCD_3$ [*O*,1,1,1-$^2H_4$]-(**3**)
61				4.0 ($CH_3^\bullet$)
60			4.3 ($CH_3^\bullet$)	1.1 ($CH_2D^\bullet$)
59			1.2 ($CH_2D^\bullet$)	2.6 ($CHD_2^\bullet$)
58		59.9 ($CH_3^\bullet$)	2.7 ($CHD_2^\bullet$)	46.4 ($CD_3^\bullet/H_2O^c$)
57	66.6 ($CH_3^\bullet$)		53.0 ($CD_3^\bullet/H_2O^d$)	1.5 (HOD)
56			0.7 (HOD)	0.5 (D_2O)
55		0.4 (H_2O)		
54	2.6 (H_2O)	2.3 (HOD)		
47				0.5
46			34.9 ($C_2H_5^\bullet$)	40.3 ($C_2H_4D^\bullet$)
45			1.5 ($C_2H_4D^\bullet$)	1.5 ($C_2H_3D_2^\bullet$)
44			0.5 ($C_2H_3D_2^\bullet$)	0.5 ($C_2H_2D_3^\bullet$)
43	30.7 ($C_2H_5^\bullet$)	37.4 ($C_2H_4D^\bullet$)	1.3 ($C_2H_2D_3^\bullet$)	1.2 ($C_2HD_4^\bullet$)
Total methyl loss	66.6	59.9	59.5	53.8
Total water loss	2.6	2.7	2.4	2.3
Total ethyl loss	30.7	37.4	38.2	43.5

[a,b] These footnotes have the same significance as those in Table 1. [c] Almost entirely $CD_3^\bullet$ loss (estimated H_2O loss = 0.3). [d] Almost entirely $CD_3^\bullet$ loss (estimated H_2O loss = 1.7).

Table 4. Energy data relevant to dissociation of $C_4H_8O^{+\bullet}$ ions.

Products and ΔH_f[a]				$\Sigma\Delta H_f$[a]
$CH_2{=}CHCH{=}CH_2^{+\bullet}$	(983[b]) +	H_2O	(−242[c])	741
CH_3CO^+	(653[d]) +	$C_2H_5^\bullet$	(105[c])	758
$CH_3CH_2CO^+$	(602[b]) +	$CH_3^\bullet$	(138[c])	740
$CH_2{=}CHCH{=}OH^+$	(649[e]) +	$CH_3^\bullet$	(138[c])	787

[a] All values in kJ mol^{-1}; likely uncertainty limits = ±5. [b] Ref. 44. [c] Ref. 43. [d] Ref. 45. [e] Ref. 46.

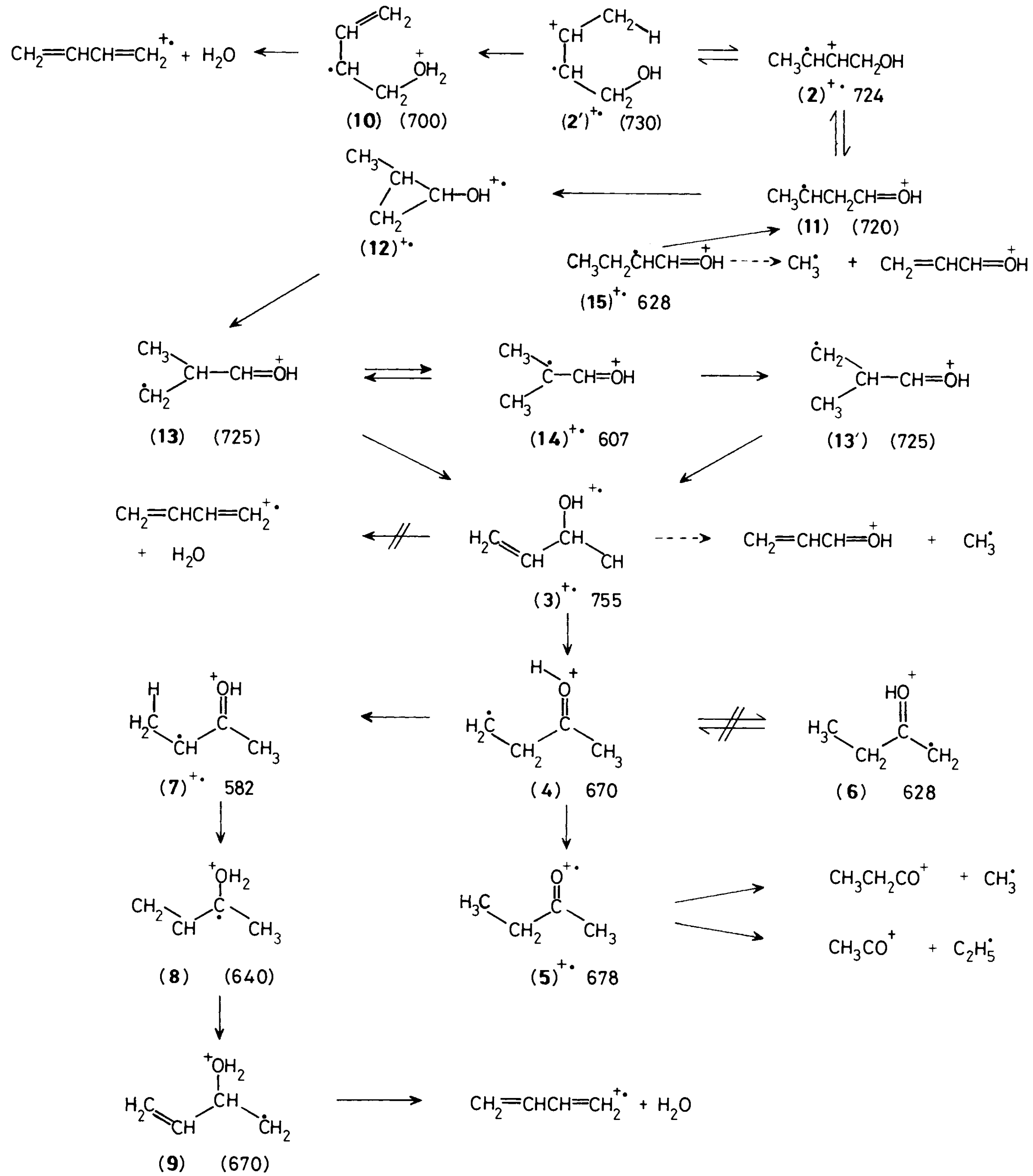
(a) *Reactions of* $CH_2{=}CH(CH_3)CHOH^{+\bullet}$.—(*i*) *Methyl radical loss.* Although it might appear attractive to rationalise $CH_3^\bullet$ loss from (**3**)$^{+\bullet}$ as a simple cleavage, earlier work[15,26] has established that the bulk of this reaction occurs after ketonisation to (**5**)$^{+\bullet}$. The modified mechanism[26] proposed for this process is contained in Scheme 1. A 1,2-hydrogen shift in (**3**)$^{+\bullet}$ leads to the distonic ion (**4**), which then undergoes ketonisation through a five-membered ring transition state. Methyl loss then takes place by fission of the bond connecting the methyl group to the carbonyl carbon atom in (**5**)$^{+\bullet}$. This explains the formation of $C_2H_5CO^+$ as the dominant daughter ion structure as demonstrated[26] by collision-induced decomposition of $C_3H_5O^+$ ions produced from (**3**)$^{+\bullet}$ and (**5**)$^{+\bullet}$. In addition, provided that the steps (**3**)$^{+\bullet} \longrightarrow$ (**4**) $\longrightarrow$ (**5**)$^{+\bullet}$ are largely irreversible, the ^{2}H-labelling results presented here and elsewhere[15] may be understood. Interconversion of (**4**) and (**6**) must be slow compared with the rate of methyl radical loss, as shown by the minimal loss of positional integrity of the original CD_3 group in [1,1,1-$^2H_3$]-(**3**)$^{+\bullet}$.

Simple cleavage of metastable (**3**)$^{+\bullet}$ occurs to only a slight extent. This reflects the higher enthalpy of formation of the associated daughter ion, protonated acrolein, compared with that of the acylium ion $C_2H_5CO^+$, Table 4. This emphasises the rigorous energy discrimination which operates against the formation of higher energy products. At higher energies, however, simple cleavage of (**3**)$^{+\bullet}$ dominates;[24] this energy dependence in the fragmentation of ionised secondary allylic alcohols is apparently quite a general phenomenon.[9,24,31,33]

(*ii*) *Ethyl radical loss.* This process is accounted for in the same way as the loss of methyl radical: ketonisation of (**3**)$^{+\bullet}$, *via* (**4**), followed by σ-cleavage in (**5**)$^{+\bullet}$ affords CH_3CO^+ and $C_2H_5^\bullet$. The retention of the deuterium of [*O*-^{2}H]-(**3**)$^{+\bullet}$ (Table 3) and [2-^{2}H]-(**3**)$^{+\bullet}$ (ref. 15) with high specificities in the expelled ethyl radical reveals that (**3**)$^{+\bullet} \longrightarrow$ (**4**) $\longrightarrow$ (**5**)$^{+\bullet}$ are predominantly irreversible steps. There is a minor participation of the intact methyl group originally present in (**3**)$^{+\bullet}$ in the eliminated ethyl radical. This follows from the greater abundance of $C_2H_2D_3^\bullet$ loss, compared with $C_2H_3D_2^\bullet$ elimination, from [1,1,1-$^2H_3$]-(**3**)$^{+\bullet}$ and [*O*,1,1,1-$^2H_4$]-(**3**)$^{+\bullet}$; the reverse would be expected on the basis of exchange of individual hydrogen and deuterium atoms. A plausible explanation is that a small percentage of (**3**)$^{+\bullet}$ ions rearrange to a structure containing two methyl groups [probably (**14**)$^{+\bullet}$, Scheme 1]; reversion to (**3**)$^{+\bullet}$ and ketonisation followed by dissociation then accounts for the $CD_3CH_2^\bullet$ loss from [1,1,1-$^2H_3$]-(**3**)$^+$ and [*O*,1,1,1-$^2H_4$]-(**3**)$^{+\bullet}$. A similar explanation can be offered for the minor amount of $CH_3^\bullet$ loss which also occurs from these ions. Indeed, the complementary behaviour seen in methyl and ethyl losses from ^{2}H-labelled analogues of (**2**)$^{+\bullet}$ and (**3**)$^{+\bullet}$ was one of the key factors in establishing that these ions underwent ketonisation prior to decomposition.[15]

(*iii*) *Water loss.* It is possible to make only tentative remarks about the mechanism of this reaction because it is of such low abundance. The hydroxylic hydrogen is lost in the expelled water molecule with about 85% specificity, but the second hydrogen originates mainly from the vinyl group. This suggests that water loss does not proceed predominantly *via* a 1,2-elimination since [*O*,1,1,1-$^2H_4$]-(**3**)$^{+\bullet}$ loses more HOD than D_2O. The sequence of steps (**3**)$^{+\bullet} \longrightarrow$ (**4**) $\longrightarrow$ (**7**)$^{+\bullet} \longrightarrow$ (**8**) $\longrightarrow$ (**9**) $\longrightarrow$ products is one explanation of these facts.

There is a limited amount of experimental thermochemical information concerning ionised C_4H_8O species.[37,43,44,47] These values are given in Scheme 1. Enthalpies for formation of the distonic ions can be estimated using known proton affinity data,[48] values for hydrogen-abstraction energies,[49] coupled with group equivalent[50] and isodesmic[51] substition procedures.[52] These estimated enthalpies of formation, rounded to the nearest 5 kJ mol^{-1}, are given in parentheses. Whilst these data are only approximate values, they do indicate that the routes proposed in Scheme 1 for dissociation of (**3**)$^{+\bullet}$ are energetically feasible. Indeed, the energy levels of the



Scheme 1.

intermediates involved in methyl and ethyl radical elimination differ only slightly from those given elsewhere.[9]

(b) *Reactions of* $CH_3CH{=}CHCH_2OH^{+\bullet}$.—(i) *Water loss.* This process involves expulsion of the hydroxylic hydrogen with high specificity (*ca.* 97%); furthermore, the loss of predominantly (*ca.* 90%)[15] HOD from [4,4,4-$^2H_3$]-(**2**)$^{+\bullet}$ indicates that a formal 1,4-elimination is involved. There is only minimal participation of the hydrogens attached to C_1 in water loss. These data are readily accommodated by a mechanism (Scheme 1) in which a 1,4-hydrogen shift in the *cis*-geometrical isomer of (**2′**)$^{+\bullet}$ leads to the distonic ion (**10**). Simple cleavage in (**10**) then yields ionised butadiene and water. Clearly, the step (**2′**)$^{+\bullet}$ ⟶ (**10**) must be irreversible. Water expulsion might be viewed as occurring by a concerted mechanism. This seems unlikely, however, in view of the apparent stability of (**10**), which is estimated to lie 40 kJ mol^{-1} below the threshold for water loss. There is also evidence that synchronously concerted mechanisms are the exception, rather than the rule, in the decomposition of isolated organic ions.[53,54]

(ii) *Methyl radical loss.* The results of this study confirm earlier findings[9,15,26] that the hydroxyl hydrogen does not participate significantly in the expelled methyl radical and that the hydrogen atoms are not selected randomly from the seven originally bound to carbon. There is a strong tendency for the original methyl group in (**2**)$^{+\bullet}$ to be lost as shown by the abundant $CD_3^\bullet$ elimination from [4,4,4-$^2H_3$]-(**2**)$^{+\bullet}$.[15] Rearrangement of (**2**)$^{+\bullet}$ to (**3**)$^{+\bullet}$, *via* a 1,3-hydroxyl shift has been exluded on the basis that [1-^{13}C]-(**2**)$^{+\bullet}$ dissociates in a manner compatible with retention of the initial ^{13}C–O bond.[34] This indicates that isomerisation of (**2**)$^{+\bullet}$ to (**3**)$^{+\bullet}$, and thence to (**5**)$^{+\bullet}$, must occur by another route.

Further analysis of the behaviour of ^{2}H-labelled analogues of (**2**)$^{+\bullet}$ sheds some light on this problem. Table 5 gives the

Table 5. Observed and calculated abundances of methyl radicals eliminated from $C_4H_{8-n}D_nO^{+\cdot}$ formed from but-2-en-1-ols.

Precursor structure	Neutral lost	Observed[a] This work	Observed[a] Ref. 26	Calculated[a,b] Model A	Calculated[a,b] Model B
[*O*-^{2}H]-(**2**)	$CH_3^{\cdot}$	99	99	100	100
	$CH_2D^{\cdot}$	1	1	0	0
[1-$^2H_1$]-(**2**)	$CH_3^{\cdot}$	68		57	67
	$CH_2D^{\cdot}$	32		43	33
[*O*,1-$^2H_2$]-(**2**)	$CH_3^{\cdot}$	67		57	67
	$CH_2D^{\cdot}$	32		43	33
	$CHD_2^{\cdot}$	1		0	0
[1,1-$^2H_2$]-(**2**)	$CH_3^{\cdot}$	52	55	29	50
	$CH_2D^{\cdot}$	33	30	57	33
	$CHD_2^{\cdot}$	15	15	14	17
[*O*,1,1-$^2H_3$]-(**2**)	$CH_3^{\cdot}$	52		29	50
	$CH_2D^{\cdot}$	30		57	33
	$CHD_2^{\cdot}$	15		14	17
	$CD_3^{\cdot}$	3		0	0
[4,4,4-$^2H_3$]-(**2**)	$CH_3^{\cdot}$		34	12	50
	$CH_2D^{\cdot}$		4	51	0
	$CHD_2^{\cdot}$		10	34	0
	$CD_3^{\cdot}$		52	3	50

[a] Abundances normalised to a total of 100 units for methyl loss. [b] See text for models.

observed and calculated abundances of partially deuteriated methyl radicals lost from ^{2}H-labelled analogues of (**2**)$^{+\cdot}$ as percentages of the total amount of methyl radical expulsion. Model A corresponds to random selection of any three of the seven carbon-bound hydrogens in the expelled methyl radical. Model B represents a situation in which half the original methyl radical loss proceeds by expulsion of the intact methyl group in (**2**)$^{+\cdot}$; the residual half is made up by selection of the hydrogen of the 3-position and any two of the three on carbons 1 and 2. Although there are discrepancies between the observed behaviour of ^{2}H-labelled analogues of (**2**)$^{+\cdot}$ and those predicted by model B, the general agreement is good. Model A clearly cannot explain the experimental facts.

One mechanism which would provide for the manner of hydrogen selection given by model B is shown in Scheme 1. Reversible 1,2-hydrogen shifts [(**2**)$^{+\cdot}\rightleftharpoons$(**11**)] render the hydrogens on carbons 1 and 2 equivalent. A formal 1,2-CHOH shift in (**11**) then affords (**13**). This process might be envisaged as occurring *via* ionised 2-methylcyclopropanol, (**12**)$^{+\cdot}$. A further 1,2-methyl shift leads to (**3**)$^{+\cdot}$, which then expels the original methyl group of (**2**)$^{+\cdot}$ after ketonisation to (**5**)$^{+\cdot}$. Rearrangement of (**13**) to (**14**)$^{+\cdot}$ would form a second methyl group containing the carbon atom originally at position 2 in (**2**)$^{+\cdot}$, together with two of the three hydrogens attached to carbons 1 and 2, with the final hydrogen specifically selected from position 3. This methyl group can then be lost by isomerisation of (**14**)$^{+\cdot}$ to (**13′**), followed by dissociation in the usual fashion [(**13′**) $\longrightarrow$ (**3**)$^{+\cdot}$ $\longrightarrow$ (**4**) $\longrightarrow$ (**5**)$^{+\cdot}$ $\longrightarrow$ products].

There is some evidence that 1,2-shifts in radicals involve energy barriers.[55] Nevertheless, there are clear examples of 1,2-hydrogen shifts at nominal radical sites in the reactions of isolated radical cations.[56–58] In such systems, the species undergoing these shifts are often the central intermediates in the mechanistic schemes. The shifts can be the slow and rate-determining steps in dissociation. This situation may well pertain for (**13**), (**14**)$^{+\cdot}$, and (**13′**). Rapid interconversion of these species would destroy the positional integrity of the methyl groups, but the labelling data can be explained if each ion undergoes on average one isomerisation (**13**) $\longrightarrow$ (**14**)$^{+\cdot}$, followed by reversion to (**13**) or (**13′**).

Although thermochemical arguments have been presented against the intermediacy of (**13**),[37] the labelling results are consistent with the mechanistic interpretation of Scheme 1. Additional relevant points are as follows. First, if the steps (**14**)$^{+\cdot}$ $\longrightarrow$ (**13**) and (**14**)$^{+\cdot}$ $\longrightarrow$ (**13′**) are relatively slow, there would be a preference for hydrogen rather than deuterium transfer from the methyl groups of $CD_3(CH_3)C^{\cdot}CH{=}OH^+$. This would enhance the proportion of CD_3, as opposed to CH_3, migration in (**13**)/(**13′**) $\longrightarrow$ (**3**)$^{+\cdot}$. Consequently, [4,4,4-$^2H_3$]-(**2**)$^{+\cdot}$ would expel rather more $CD_3^{\cdot}$ and less $CH_3^{\cdot}$ than predicted using model B. This is indeed the case.[15] A complementary argument leads to the conclusion that more $C_2H_5^{\cdot}$ and less $C_2H_2D_3^{\cdot}$ loss than expected on the basis of model B should be observed. Such a trend is found in ethyl loss from [4,4,4-$^2H_3$]-(**2**)$^{+\cdot}$. A related, though more involved, argument shows that $CHD_2^{\cdot}$ and $C_2H_4D^{\cdot}$ eliminations should be favoured over $CH_2D^{\cdot}$ and $C_2H_3D_2^{\cdot}$ losses in expulsion of mixed alkyl radicals from [4,4,4-$^2H_3$]-(**2**)$^{+\cdot}$. This reflects the greater resistance of CD_3 groups (deuterium shifts), compared with CH_3 groups (hydrogen shifts), to destruction of positional integrity. Both these trends are found[15] in the dissociations of [4,4,4-$^2H_3$]-(**2**)$^{+\cdot}$. Secondly, the behaviour of ^{13}C-labelled analogues of (**2**)$^{+\cdot}$ and the isomeric species, (**15**)$^{+\cdot}$, also is broadly consistent with Scheme 1. Thus, methyl expulsion from (**2**)$^{+\cdot}$ involves selection of carbon 2, {40% participation of $^{13}CH_3^{\cdot}$ loss from [2-^{13}C]-(**15**)$^{+\cdot}$} but not carbon 3.[34] This is accommodated on the basis of dissociation of (**15**)$^{+\cdot}$ *via* (**11**). Some direct decomposition of (**15**)$^{+\cdot}$ to $CH_3^{\cdot}$ and $CH_2{=}CHCH{=}OH^+$ may occur in this case; alternatively, preferential fragmentation of (**11**) $\longrightarrow$ (**13**) $\longrightarrow$ (**3**)$^{+\cdot}$ $\longrightarrow$ (**4**) $\longrightarrow$ (**5**)$^{+\cdot}$ $\longrightarrow$ products may account for the higher contribution of elimination of the carbon atom initially at position 4. A parallel argument explains why ethyl loss from (**15**)$^{+\cdot}$ always[34] involves position 3.

(iii) *Ethyl radical loss.* This process can be interpreted as the complement of methyl loss using Scheme 1. As indicated above, the bulk of available ^{13}C-labelling information can be understood in this way. Relevant data for loss of partially deuteriated ethyl radicals from ^{2}H-labelled analogues of (**2**)$^{+\cdot}$ are given in Table 6. Model A corresponds to incorporation of the hydroxylic hydrogen and any four of the seven attached to carbon in the expelled ethyl radical. This clearly is inadequate. Model B represents selection of the hydroxylic hydrogen and specifically the four not involved in methyl loss as constituent components of the eliminated ethyl radical. This gives a generally good fit to the experimental facts. The deviation from model B shown by [4,4,4-$^2H_3$]-(**2**)$^{+\cdot}$ in expelling more $C_2H_5^{\cdot}$ and less $C_2H_2D_3^{\cdot}$ than expected has been discussed above, as has the preference for $C_2H_4D^{\cdot}$ loss over $C_2H_3D_2^{\cdot}$ loss.

Thus, although the behaviour of (**2**)$^{+\cdot}$ is undoubtedly complex, much of the chemistry can be understood using the mechanism of Scheme 1.

(c) *Reactions of* $CH_2{=}CHCH_2CH_2OH^{+\cdot}$.—(i) *Water loss.* In contrast with (**2**)$^{+\cdot}$ and (**3**)$^{+\cdot}$ which retain the hydroxylic hydrogen in the expelled water molecule, (**1**)$^{+\cdot}$ shows preferential retention of the hydroxylic hydrogen in the ionised butadiene. This apparently extraordinary result reflects the relative ease of hydrogen transfer from oxygen to carbon in (**1**)$^{+\cdot}$, Scheme 2, through a six-membered ring transition state. However, even allowing for further reversible hydrogen

Table 6. Observed and calculated abundances of ethyl radicals eliminated from $C_4H_{8-n}D_nO^{+\bullet}$ formed from but-2-en-1-ols.

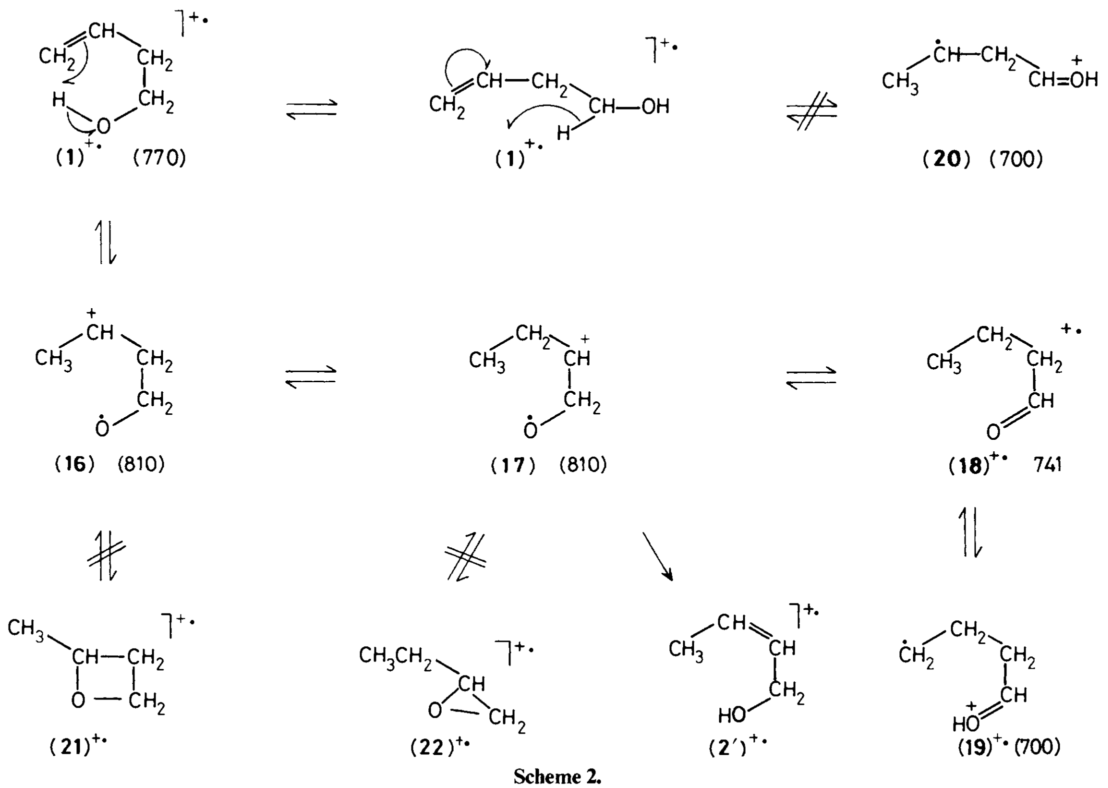
Precursor structure	Neutral lost	Observed[a] This work	Observed[a] Ref. 26	Calculated[a,b] Model A	Calculated[a,b] Model B
$[O\text{-}^2H]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$	2	2	0	0
	$C_2H_4D^\bullet$	98	98	100	100
$[1\text{-}^2H_1]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$	38		43	33
	$C_2H_4D^\bullet$	62		57	67
$[O,1\text{-}^2H_2]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$	0		0	0
	$C_2H_4D^\bullet$	34		43	33
	$C_2H_3D_2^\bullet$	66		57	67
$[1,1\text{-}^2H_2]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$	21	20	14	17
	$C_2H_4D^\bullet$	35	26	57	33
	$C_2H_3D_2^\bullet$	44	54	29	50
$[O,1,1\text{-}^2H_3]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$	0		0	0
	$C_2H_4D^\bullet$	18		14	17
	$C_2H_3D_2^\bullet$	30		57	33
	$C_2H_2D_3^\bullet$	52		29	50
$[4,4,4\text{-}^2H_3]\text{-}(\mathbf{2})$	$C_2H_5^\bullet$		66	3	50
	$C_2H_4D^\bullet$		9	34	0
	$C_2H_3D_2^\bullet$		4	51	0
	$C_2H_2D_3^\bullet$		21	12	50

[a] Abundances normalised to a total of 100 units for ethyl loss; the small contribution (*ca.* 1–3%) of ethylene losses is neglected. [b] See the text for models.

transfers and random distribution of the hydroxylic and carbon-bound hydrogens in $[O\text{-}^2H]\text{-}(\mathbf{1})^{+\bullet}$, there remains a substantial discrimination against HOD loss. Given random participation of hydrogen and deuterium atoms, the expected ratios of H_2O, HOD, and D_2O losses from $[O\text{-}^2H]\text{-}(\mathbf{1})^{+\bullet}$, $[1,1\text{-}^2H_2]\text{-}(\mathbf{1})^{+\bullet}$ and $[O,1,1\text{-}^2H_3]\text{-}(\mathbf{1})^{+\bullet}$ are 75:25:0, 54:43:3, and 36:54:10, respectively. The measured values are 88:12:0, 83:17:0, and 65:32:3, respectively. Assuming that isotope effects favour H_2O:HOD:D_2O expulsions by an overall factor of 9:3:1, the anticipated ratios of H_2O:HOD:D_2O losses from $[O\text{-}^2H]\text{-}(\mathbf{1})^{+\bullet}$, $[1,1\text{-}^2H_2]\text{-}(\mathbf{1})^{+\bullet}$, and $[O,1,1\text{-}^2H_3]\text{-}(\mathbf{1})^{+\bullet}$ with random selection of hydrogen and deuterium atoms are modified to 90:10;0, 78:21:1, and 65:33:2, respectively. Bearing in mind the simplicity of this model, the calculated ratios are in good agreement with the experimental facts.

One explanation of the discrimination against HOD loss from $[O\text{-}^2H]\text{-}(\mathbf{1})^{+\bullet}$ is that transfer of a hydrogen (or deuterium) atom back from carbon to oxygen is the rate-determining step in water loss from $(\mathbf{1})^{+\bullet}$. Thus for example, following a 1,5-hydrogen transfer $[(\mathbf{1})^{+} \longrightarrow (\mathbf{16})]$, further 1,2-shifts $[(\mathbf{16}) \rightleftharpoons (\mathbf{17}) \rightleftharpoons (\mathbf{18})^{+\bullet}]$ result in random hydrogen atom distribution; a 1,4-shift from carbon to oxygen in (**17**) yields $(\mathbf{2})^{+\bullet}$, from which water loss occurs. Support for this view stems from the closely similar behaviour observed for reactions of $(\mathbf{1})^{+\bullet}$ and $(\mathbf{18})^{+\bullet}$.[15] This similarity applies not only to the $C_4H_8O^{+\bullet}$ ions, but also to their ^2H-labelled analogues. For instance, $[2,2\text{-}^2H_2]\text{-}(\mathbf{18})^{+\bullet}$ expels H_2O, HOD, and D_2O in similar ratios (85:15:0)[15] to those reported here for $[1,1\text{-}^2H_2]\text{-}(\mathbf{1})^{+\bullet}$ (83:17:0). There is a difference in the ratios of H_2O:HOD:D_2O losses reported (54:40:6)[15] for $[4,4,4\text{-}^2H_3]\text{-}(\mathbf{18})^{+\bullet}$ and found in this work (65:32:3) for $[O,1,1\text{-}^2H_3]\text{-}(\mathbf{1})^{+\bullet}$. This discrepancy is not great, however, and it may merely reflect variations in abundances of reactions arising from different instruments and operating conditions. Alternatively, it is feasible that mixing of the hydroxylic and carbon-bound hydrogens it not quite complete in ions dissociating *via* water elimination.

It is somewhat difficult to obtain estimates of the enthalpies of formation of the distonic ions (**16**) and (**17**) on account of unknown influence of the radical site on oxygen on the nearby



Scheme 2.

Table 7. Observed and calculated abundances of methyl and ethyl radical losses from $C_4H_{8-n}D_nO^{+\bullet}$ ions formed from but-3-en-1-ols.

Precursor structure	Neutral lost	Observed[a] This work	Observed[a] Ref. 15	Calculated[a,b]
[*O*-^{2}H]-**(1)**	$CH_3^{\bullet}$	61	58	62
	$CH_2D^{\bullet}$	39	42	38
	$C_2H_5^{\bullet}$	46	44	38
	$C_2H_4D^{\bullet}$	54	56	62
[1,1-$^2H_2$]-**(1)**	$CH_3^{\bullet}$	33		36
	$CH_2D^{\bullet}$	57		53
	$CHD_2^{\bullet}$	10		11
	$C_2H_5^{\bullet}$	15		11
	$C_2H_4D^{\bullet}$	57		53
	$C_2H_3D_2^{\bullet}$	28		36
[*O*,1,1-$^2H_3$]-**(1)**	$CH_3^{\bullet}$	17		18
	$CH_2D^{\bullet}$	55		53
	$CHD_2^{\bullet}$	28		27
	$CD_3^{\bullet}$	<1[c]		2
	$C_2H_5^{\bullet}$	6		2
	$C_2H_4D^{\bullet}$	33		27
	$C_2H_3D_2^{\bullet}$	48		53
	$C_2H_2D_3^{\bullet}$	13		18

[a] Values normalised to a total of 100 units for methyl and ethyl loss. [b] Random selection of H and D. [c] CD_3 loss overlaps with D_2O loss.

cationic centre. Assuming that no stabilisation is conferred by interaction between the notional cationic and radical sites, the enthalpies of formation of **(16)** and **(17)** should be *ca.* 810 kJ mol^{-1}.[48–52] This is high enough to make the postulated rearrangement of **(17)** $\longrightarrow$ **(2)**$'^{+\bullet}$ irreversible, but not so high that **(17)** and **(18)**$^{+\bullet}$ would be energetically inaccessible to **(1)**$^{+\bullet}$.

Whilst there remains some uncertainty concerning the mechanism whereby **(1)**$^{+\bullet}$ and **(18)**$^{+\bullet}$ expel water, definite conclusions can be made about rearrangements that do not take place for metastable ions. Thus a 1,4-shift in **(1)**$^{+\bullet}$, leading to **(20)**, does not occur. This follows because **(20)** is known to lose water primarily by a mechanism involving retention of the hydroxylic hydrogen in the water. Consequently interchange of the hydrogens on C_1 and C_4 cannot occur by this mechanism. Similar arguments prove that ring closure of **(16)** [to ionised 2-methyloxetane, **(21)**$^{+\bullet}$] or **(17)** [to ionised 1-ethyloxirane, **(22)**$^{+\bullet}$] does not occur on a reversible basis. Ionised 2-methyloxetane eliminates a methyl radical (10%), ethylene (3%) and an ethyl radical (87%) but no water; **(22)**$^{+\bullet}$ has been reported[15] to undergo a negligible amount of water loss. These observations suggest that **(21)**$^{+\bullet}$ and **(22)**$^{+\bullet}$ decompose by routes involving initial steps other than C–O bond cleavage. Detailed studies on ionised oxiranes support this view.[59,60]

(*ii*) *Methyl and ethyl radical loss.* These fragmentations proceed with nearly statistical selection of the hydrogen atoms, Table 7. It is not possible to give a detailed mechanism for these processes, but it is logical to interpret the behaviour of **(1)**$^{+\bullet}$ as involving extensive hydrogen shifts between the various sites, followed by rearrangement to structures related to **(2′)**$^{+\bullet}$ or **(2)**$^{+\bullet}$ Eventually, ketonisation to **(5)**$^{+\bullet}$ occurs, followed by ethyl or methyl expulsion. A minor proportion of methyl loss probably proceeds with formation of $CH_2{=}CHCH{=}OH^+$ by a different route.

It is noteworthy that **(18)**$^{+\bullet}$ also shows extensive exchange of hydrogens between the various sites prior to methyl and ethyl radical elimination. Thus, [2,2-$^2H_2$]-**(18)**$^{+\bullet}$ loses $CH_3^{\bullet}$, $CH_2D^{\bullet}$, and $CHD_2^{\bullet}$, and $C_2H_5^{\bullet}$, $C_2H_4D^{\bullet}$, and $C_2H_3D_2^{\bullet}$ in the ratios 46:41:13, and 20:40:40, respectively.[15] The corresponding ratios for $CH_3^{\bullet}$, $CH_2D^{\bullet}$, $CHD_2^{\bullet}$, and $CD_3^{\bullet}$, and $C_2H_5^{\bullet}$, $C_2H_4D^{\bullet}$, $C_2H_3D_2^{\bullet}$, and $C_2H_2D_3^{\bullet}$ losses from [4,4,4-$^2H_3$]-**(18)**$^{+\bullet}$ are 15:44:34:7, and 0:40:47:13, respectively.[15] These values differ appreciably from those found for the isomeric species [1,1-$^2H_2$]-**(1)**$^{+\bullet}$ and [*O*-1,1-$^2H_3$]-**(1)**$^{+\bullet}$. A logical explanation is that the hydrogen and deuterium distributions in ^{2}H-labelled analogues of **(1)**$^{+\bullet}$ and **(18)**$^{+\bullet}$ do not become completely the same, but that each approaches to a statistical distribution. In contrast, **(20)** shows much more specific selection of hydrogens in ethyl and methyl loss: the hydroxylic hydrogen is predominantly lost in the expelled ethyl radical, but not in the methyl radical, and the carbon-bound hydrogens do not participate randomly in these processes. This confirms that the rate of interconversion of **(1)**$^{+\bullet}$ and **(20)** is slow compared with that of decomposition of either.

A final point concerning **(1)**$^{+\bullet}$ is that the reactions undergone in metastable transitions are quite different from those seen in the low-energy low-temperature mass spectra.[38] The most striking change is the absence of CH_2O loss from metastable **(1)**$^{+\bullet}$, whereas $[M - 30]^{+\bullet}$ is the base peak in the low-energy spectrum. This reveals that **(16)**, when formed from metastable **(1)**$^{+\bullet}$, has insufficient energy to undergo σ-cleavage to CH_2O and $C_3H_6^{+\bullet}$. This in turn shows that transition states of energy of approximately 830[43,44] kJ mol^{-1} or more are energetically inacessible when **(1)**$^{+\bullet}$ dissociates in metastable transitions. A prominent peak at *m*/*z* 42 is evident, however, in the CID spectrum of **(1)**$^{+\bullet}$.[26] This emphasises the strong energy dependence, even quite near to threshold, shown by the decomposition channels of **(1)**$^{+\bullet}$.

In contrast with **(1)**$^{+\bullet}$, ionised 1,2-dimethyloxirane and ionised 1-ethyloxirane both lose a neutral of mass 30 units (presumably CH_2O) in metastable transitions.[15] This shows that these ions are higher-energy species than **(1)**$^{+\bullet}$.

Conclusions

The chemistry of **(1)**$^{+\bullet}$, **(2)**$^{+\bullet}$, and **(3)**$^{+\bullet}$ is complex and multifaceted. There are differences in the behaviour of **(2)**$^{+\bullet}$ and **(3)**$^{+\bullet}$, compared with **(1)**$^{+\bullet}$, which become apparent on examination of ^{2}H-labelled analogues. 1,4-Hydrogen shifts from oxygen to carbon are slow for the ionised allylic alcohols, thus allowing the hydroxylic hydrogen to play a specific role in the dissociation of labelled forms of **(2)**$^{+\bullet}$ and **(3)**$^{+\bullet}$. For ionised homoallylic alcohol, however, a 1,5-hydrogen shift from oxygen to carbon destroys the positional integrity of the hydroxylic hydrogen. Distonic ions play an important role in the reactions of **(1)**$^{+\bullet}$, **(2)**$^{+\bullet}$, and **(3)**$^{+\bullet}$. The results of this study are in good qualitative agreement with those of earlier investigations, though the differences between the behaviour of **(1)**$^{+\bullet}$ and those of **(2)**$^{+\bullet}$ and **(3)**$^{+\bullet}$ may be more significant than was previously realised.

Experimental

The MIKES[39] scans were performed using a VG Micromass ZAB-2FQ mass spectrometer[40] operating in the e.i. mode. The ion source was operated at *ca.* 200 °C, with 70 eV electrons; the ion accelerating voltage was 8 kV. Samples were introduced by injection of the liquid compounds into the inlet line using a microlitre syringe.

The *O*-deuteriated alcohols were obtained *in situ* by admission of D_2O and the unlabelled alcohol simultaneously, thus allowing exchange of the hydroxylic hydrogen to occur. The *C*-deuteriated alcohols were prepared using the routes shown in Scheme 3.

$$CH_2CHCH_2COCl \xrightarrow[Et_2O]{LiAlD_4} CH_2{=}CHCH_2CD_2OH$$

$$CH_3CH{=}CHCOCl \xrightarrow[Et_2O\ -20\,^{\circ}C]{LiAlD_4} CH_3CH{=}CHCD_2OH$$

$$CH_3CH{=}CHCHO \xrightarrow[EtO,\ -20\,^{\circ}C]{LiAlD_4} CH_3CH{=}CHDOH$$

$$CD_3MgI \xrightarrow[Et_2O\ -60\,^{\circ}C]{CH_2{=}CHCHO} CH_2{=}CH(CD_3)CHOH$$

Scheme 3.

Acknowledgements

Financial support from the SERC (an Advanced Fellowship to R. D. B.), NSERC (Canada) (operating and equipment grants to A. G. H.) and Canada Council (Killam Fellowship to A. G. H.) is gratefully acknowledged. Special thanks are due to Mrs. M. Callaway for her care in preparing the typescript.

References

1 For a general review, see: J. L. Holmes, *Org. Mass. Spectrom.*, 1985, **20**, 169.
2 B. F. Yates, W. J. Bouma, and L. Radom, *J. Am. Chem. Soc.*, 1984, **106**, 5805.
3 For a review, see: S. Hammerum, *Mass. Spectrom. Rev.*, 1988, **7**, 123.
4 For an early review, see: T. H. Morton, *Tetrahedron*, 1982, **38**, 3195.
5 For a discussion of the bonding in these species, see: D. J. McAdoo, *Mass Spectrom. Rev.*, 1988, **7**, 363.
6 G. Bouchoux, J. Tortajada, J. Dagant, and J. Fillaux, *Org. Mass Spectrom.*, 1987, **22**, 451; G. Bouchoux, F. Bidault, F. Djazi, B. Nicod, and J. Tortajada, *ibid.*, 1987, **22**, 748.
7 M. Masur, A. Spafke, and H.-F. Grutzmacher, *Org. Mass Spectrom.*, 1987, **22**, 307.
8 J. C. Traeger, C. E. Hudson, and D. J. McAdoo, *Int. J. Mass Spectrom. Ion Proc.*, 1988, **82**, 101.
9 G. Bouchoux, *Mass Spectrom Rev.*, (*a*) 1988, **7**, 1; (*b*) 1988, **7**, 203.
10 B. Willhalm and A. F. Thomas, *Org. Mass Spectrom.*, 1968, **1**, 627.
11 D. J. McAdoo, F. W. McLafferty, and T. E. Parks, *J. Am. Chem. Soc.*, 1972, **94**, 1601.
12 J. L. Holmes and R. T. B. Rye, *Can. J. Chem.*, 1973, **51**, 2342.
13 D. G. I. Kingston and H. T. Tannenbaum, *Org. Mass Spectrom.*, 1975, **10**, 263.
14 R. Krenmayr, *Monatsh. Chem.*, 1975, **106**, 925.
15 D. J. McAdoo, C. E. Hudson, and D. N. Witiak, *Org. Mass Spectrom.*, 1979, **14**, 350.
16 D. J. McAdoo, W. Farr, and C. E. Hudson, *J. Am. Chem. Soc.*, 1980, **102**, 5165.
17 J. L. Holmes, M. Dakabu, and R. T. B. Rye, *Adv. Mass Spectrom.*, 1980, **8**, 847.
18 J. L. Holmes, M. Dakabu, and R. T. B. Rye, *Org. Mass Spectrom.*, 1981, **16**, 1.
19 J. J. Zwinselman, N. M. M. Nibbering, N. E. Middlemiss, J. H. Vajda, and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.*, 1981, **38**, 163.
20 D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.*, 1981, **16**, 294.
21 G. Depke and H. Schwarz, *Org. Mass Spectrom.*, 1981, **16**, 421.
22 D. J. Burinsky, G. L. Glish, R. G. Cooks, J. J. Zwinselman, and N. M. M. Nibbering, *J. Am. Chem. Soc.*, 1981, **103**, 465.
23 D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.*, 1983, **18**, 159.
24 G. Bouchoux, Y. Hoppilliard, R. Flammang, A. Maquestiau, and P. Meyrant, *Org. Mass Spectrom.*, 1983, **18**, 340.
25 G. Bouchoux, J. P. Flament, and Y. Hoppilliard, *Nouv. J. Chim.*, 1983, **7**, 385.
26 D. J. McAdoo and C. E. Hudson, *Org. Mass Spectrom.*, 1983, **18**, 466.
27 C. E. Hudson and D. J. McAdoo, *Org. Mass Spectrom.*, 1984, **19**, 1.
28 G. Bouchoux, Y. Hoppilliard, R. Flammang, A. Maquestiau, and P. Meyrant, *Can. J. Chem.*, 1984, **62**, 1740.
29 D. J. McAdoo, C. E. Hudson, F. W. McLafferty, and T. E. Parks, *Org. Mass Spectrom.*, 1984, **19**, 353.
30 J. J. Zwinselman and A. G. Harrison, *Int. J. Mass Spectrom. Ion Proc.*, 1984, **62**, 187.
31 J. J. Zwinselman and A. G. Harrison, *Org. Mass Spectrom.*, 1984, **19**, 573.
32 M. Bertranne and G. Bouchoux, *Tetrahedron Lett.*, 1984, **25**, 211.
33 K. R. Laderoute, J. J. Zwinselman, and A. G. Harrison, *Org. Mass Spectrom.*, 1985, **20**, 25.
34 C. E. Hudson and D. J. McAdoo, *Org. Mass Spectrom.*, 1985, **20**, 402.
35 A. Maccoll and M. Mruzek, *Org. Mass Spectrom.*, 1985, **21**, 251.
36 G. Bouchoux and F. Djazi, presented at the 5th Congrès de Spectrométrie de Masse, Grenoble, France, 1986.
37 J. C. Traeger and D. J. McAdoo, *Int. J. Mass Spectrom. Ion Proc.*, 1986, **68**, 35.
38 R. D. Bowen and A. Maccoll, *J. Chem. Soc., Perkin Trans. 2*, 1987, 1019.
39 R. G. Cooks, J. H. Beynon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.
40 A. G. Harrison, R. S. Mercer, E. J. Reiner, A. B. Young, R. K. Boyd, R. E. March, and C. J. Porter, *Int. J. Mass Spectrom. Ion Proc.*, 1986, **74**, 13.
41 T. W. Shannon and F. W. McLafferty, *J. Am. Chem. Soc.*, 1966, **88**, 5021.
42 A. N. H. Yeo and D. H. Williams, *J. Am. Chem. Soc.*, 1971, **93**, 395.
43 J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' NBS, Washington DC, 1969.
44 H. M. Rosenstock, K. Draxl, B. W. Steiner, and J. T. Herron, *J. Phys. Chem. Ref. Data, Suppl. 1*, 1977, 6.
45 J. C. Traeger, R. G. McLoughlin, and A. J. C. Nicholson, *J. Am. Chem. Soc.*, 1985, **20**, 223.
46 J. H. Vajda and A. G. Harrison, *Int. J. Mass Spectrom. Ion Phys.*, 1979, **30**, 293.
47 J. L. Holmes and F. P. Lossing, *J. Am. Chem. Soc.*, 1980, **102**, 1591.
48 S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, 1984, **13**, 695.
49 F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 6917.
50 J. L. Franklin, *Ind. Eng. Chem.*, 1949, **41**, 1070; *J. Chem. Phys.*, 1953, **21**, 2029; see also ref. 43.
51 L. Radom, J. A. Pople, and P. v. R. Schleyer, *J. Am. Chem. Soc.*, 1972, **94**, 5935.
52 R. D. Bowen and D. H. Williams, *Org. Mass Spectrom.*, 1977, **12**, 475.
53 R. D. Bowen, *J. Chem. Soc., Perkin Trans. 2*, (*a*) 1980, 1219; (*b*) 1982, 409.
54 D. J. McAdoo and C. E. Hudson, *Int. J. Mass Spectrom. Ion Proc.*, 1984, **62**, 269.
55 S. Hammerum, *Acta Chem. Scand., Ser. B*, 1984, **38**, 707; see also L. L. Griffin, K. Holden, C. E. Hudson, and D. J. McAdoo, *Org. Mass. Spectrom.*, 1985, **21**, 175.
56 H. Schwarz, T. Weiske, K. Levsen, A. Maquestiau, and R. Flammang, *Int. J. Mass Spectrom. Ion Phys.*, 1982, **45**, 367.
57 T. Weiske and H. Schwarz, *Chem. Ber.*, 1983, **116**, 323.
58 T. Weiske, H. Halim, and H. Schwarz, *Chem. Ber.*, 1985, **118**, 495.
59 G. Bouchoux, Y. Hoppilliard, and P. Jaudon, *Org. Mass Spectrom.*, 1987, **22**, 98.
60 G. Bouchoux, F. Djazi, Y. Hoppilliard, P. Jaudon, and N. Nouts, *Org. Mass Spectrom.*, 1988, **23**, 33.

Received 9th *November* 1988; *Paper* 8/04479A