Mechanism of Propene and Water Elimination from the Oxonium Ion $CH_3CH{=}O^+CH_2CH_2CH_3$

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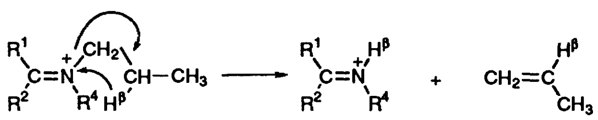
The site-selectivity in the hydrogen transfer step(s) which result in propene and water loss from metastable oxonium ions generated as $CH_3CH{=}O^+CH_2CH_2CH_3$ have been investigated by deuterium-labelling experiments. Propene elimination proceeds predominantly by transfer of a hydrogen atom from the initial propyl substituent to oxygen. However, the site-selectivity for this process is inconsistent with β-hydrogen transfer involving a four-centre transition state. The preference for apparent α- or γ-hydrogen transfer is interpreted by a mechanism in which the initial propyl cation accessible by stretching the appropriate bond in $CH_3CH{=}O^+CH_2CH_2CH_3$ isomerizes unidirectionally to an isopropyl cation, which then undergoes proton abstraction from either methyl group $\{CH_3CH{=}O^+CH_2CH_2CH_3 \longrightarrow CH_3CH{=}O\text{---}{}^+CH_2CH_2CH_3 \longrightarrow [CH_3CH{=}O\ {}^+CH(CH_3)_2] \longrightarrow [CH_3CH{=}OH^+\ CH_3CH{=}CH_2]\}$. This mechanism involving ion–neutral complexes can be elaborated to accommodate the minor contribution of expulsion of propene containing hydrogen atoms originally located on the two-carbon chain. Water elimination resembles propene loss insofar as there is a strong preference for selecting the hydrogen atoms from the α- and γ-positions of the initial propyl group. The bulk of water loss is explicable by an extension of the mechanism for propene loss, with the result that one hydrogen atom is eventually transferred to oxygen from each of the two methyl groups in the complex $[CH_3CH{=}O\ {}^+CH(CH_3)_2]$. This site-selectivity is strikingly different from that (almost random participation of the seven hydrogen atoms of the propyl substituent) encountered in the corresponding fragmentation of the lower homologue $CH_2{=}O^+CH_2CH_2CH_3$. This contrast is explained in terms of the differences in the relative energetics and associated rates of the cation rearrangement and hydrogen transfer steps.

The task of understanding the reactions of isolated ions continues to be a challenging theme in organic mass spectrometry. Much progress has been made during the past 20 years or so in providing mechanistically satisfying explanations for many isomerization and fragmentation processes. In particular, it has been demonstrated that great insight can be gained by examining the reactions of metastable ions. Metastable ions have relatively low internal energies and they eventually dissociate with excess energies in the transition states that are small and comparable to those found in solution chemistry.[1] Moreover, the lifetimes (typically *ca.* 10 μs) of metastable ions are generally too long to permit interference from isolated electronic states. As a result, it is often possible to describe the chemistry of metastable ions by means of a potential energy profile (PEP) model,[2] in which it is assumed that all possible rearrangements and dissociation steps occur from the ground state, with the relative rates of these competing processes being crucially dependent on the associated critical[3] energies.

Sometimes, the chemistry of metastable ions can be adequately explained by means of mechanisms involving only conventional ion structures (*i.e.* ones in which the atoms are connected by ordinary covalent links and the usual rules of valency hold good) and steps that are familiar in classical solution reactions. However, certain processes cannot be interpreted in this manner. In such systems, mechanisms in which ion–neutral complexes (INCs)[4–14] play important roles in permitting cation rearrangements, hydrogen transfers and skeletal rearrangements often offer a means of understanding previously inexplicable phenomena.

INC-mediated mechanisms have been of particular value in describing the chemistry of onium ions $R^1R^2C{=}Z^+R^3$ (Z = O, S, NR^4; R^1, R^2, R^3, R^4 = H, C_nH_{2n+1}) and related species.[15] Recent work on propene elimination from a propyl group attached to nitrogen in immonium ions $R^1R^2C{=}N(R^4)^+C_3H_7$ (R^4 = CH_3, C_2H_4, C_3H_7)[16,17] and protonated propylamines[18] has provided strong evidence that these processes proceed *via* INCs. An important point is that the site-selectivity in the hydrogen transfer step in propene elimination from these ions is inconsistent with the mechanism that has traditionally been offered to rationalise this ubiquitous process, [reaction (1)],



(1)

in which a β-hydrogen migrates to nitrogen in a four-membered ring transition state.[19] This traditional explanation requires that specific β-hydrogen transfer must accompany alkene expulsion, whereas the experimental data show a distinct preference for α- and γ-hydrogen transfer. However, the observed site-selectivity is accommodated by an INC-mediated mechanism because unidirectional rearrangement of the incipient propyl cation to the more stable isopropyl isomer converts the α-methylene group and one of the β-hydrogen atoms into a second methyl group. Abstraction of a proton from either of the two methyl groups of the resultant isopropyl cation then occurs, so that α-, β- and γ-hydrogen transfer from the original propyl group to nitrogen is found in the ratio 2 : 1 : 3, to a first approximation.[16,17]

A slightly earlier study[20] of the analogous metastable oxonium ions $CH_2{=}O^+CH_2CH_2CH_3$ and $CH_2{=}O^+CH(CH_3)_2$

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led to subtly different conclusions. These ions expel water and formaldehyde in closely similar ratios,[21] suggesting that they interconvert with one another and/or a common structure before dissociating. Furthermore, labelling experiments reveal that the hydrogen atoms of the eliminated molecule of water originate almost at random from the seven of the initial propyl substituent.[20] These findings were also interpreted in terms of an INC-mediated mechanism; however, unlike their analogues in the immonium ion and protonated propylamine systems, the cation rearrangement step was considered to be reversible. The interconversion of the isomeric propyl and isopropyl cations allows the seven hydrogen atoms within the propyl group to undergo extensive site-exchange before the hydrogen transfers to oxygen take place.

The divergent behaviour of the oxonium ions and the immonium ions or protonated propylamines suggests that the site-selectivity in the hydrogen transfer steps depends on the nature of the cation rearrangement. The distinctive selectivity found in the chemistry of the immonium ions and protonated propylamines appears to reflect a unidirectional isomerization of the incipient cation. If this hypothesis is correct, a similar selectivity should be observed in propene loss from oxonium ions in which the rearrangement is not reversible. Another explanation is that a different site-selectivity occurs when there is a more basic nitrogenous component in the INCs, because the proton transfer step is more exothermic and less likely to be reversible. If this view is correct, the site-selectivities in propene and water loss from oxonium ions may always differ from those found for the corresponding reactions of their immonium ion analogues. The second interpretation is less attractive than the first because it interprets the differences in the site-selectivities solely in terms of the presence or absence of a particular element, rather than the influence of energetic and kinetic factors on the mechanism of fragmentation. The two alternative explanations can be distinguished by examining the behaviour of $CH_3CH{=}O^+CH_2CH_2CH_3$,[22] which is known[23] to rearrange unidirectionally to $CH_3CH{=}O^+CH(CH_3)_2$ before dissociating.

Results and Discussion

The reactions of metastable oxonium ions generated as $CH_3CH{=}O^+CH_2CH_2CH_3$, **1**, and six of its specifically labelled analogues are reported in Table 1. These data give the relative abundance (*RA*, as measured from the area of the corresponding metastable peak and quoted as a percentage of the total) and kinetic energy (KE) release ($T_{\frac{1}{2}}$, as estimated from the width at half-height of the appropriate metastable peak) for each dissociation of the $C_5H_{11-n}D_nO^+$ ions.

The new data confirm and refine the earlier exploratory work[21–23] on **1**. Elimination of water and propene from metastable **1** occurs in approximately equal quantities. The hydrogen atoms of the expelled neutral species mainly originate from the propyl group. However, some minor discrepancies are found in the behaviour of labelled analogues of **1**. The older work[22] found that $CD_3CD{=}O^+CH_2CH_2CH_3$ lost specifically C_3H_6 and H_2O, thus leading to the conclusion that only the hydrogen (in this case protium) atoms from the propyl group of **1** are always selected in the neutral product. The new (and more extensive) labelling data reported in this work show that this conclusion is a slight oversimplification: the atoms of the eliminated water and propene molecules are indeed usually chosen from those of the propyl group, but the atoms of the two-carbon chain (particularly those of the methyl group) also participate to an appreciable extent.

Both water and propene elimination produce Gaussian metastable peaks. Neither the shape of the metastable peaks nor the associated KE releases ($T_{\frac{1}{2}} = 1.5 \pm 0.1$ kJ mol^{-1}) for water loss are significantly affected by deuteriation. Similarly, the KE releases for elimination of propene from the initial propyl group lie in the range 1.2–1.4 kJ mol^{-1}. However, for the minor signals for loss of propene molecules that are not derived simply by hydrogen abstraction from the intact propyl substituent, the $T_{\frac{1}{2}}$ values (1.0 ± 0.2 kJ mol^{-1}) appear to be slightly smaller. This trend is probably significant and it is discussed later. The invariance of the $T_{\frac{1}{2}}$ values associated with expulsion of water and most propene molecules is consistent with fragmentation *via* INC-mediated routes in which no bond to hydrogen is broken in the final dissociation step. Furthermore, the KE releases are typical of the small to moderate values that have been reported in analogous systems in which the chemistry has been interpreted in terms of INCs.

Even a cursory inspection of the new labelling data reveals that the site-selectivity in water loss from **1** is very different from that (almost random probability of transferring any two of the seven protium or deuterium atoms of the original propyl group) found for labelled analogues of $CH_2{=}O^+CH_2CH_2CH_3$. Similarly, the site-selectivity in propene loss is nowhere near that which would be anticipated on the basis of reaction (1); moreover, the observed site-selectivity differs significantly from that predicted by assuming that any one of the seven hydrogen atoms of the initial propyl group is transferred to oxygen during the reaction. However, propene loss from labelled analogues of **1** does show a clear resemblance to the corresponding reaction of the analogous immonium ions. Consequently, it appears that the chemistry of **1** involves a unidirectional rearrangement of the incipient propyl cation to its isopropyl isomer, followed by proton abstraction from either of the methyl groups. Detailed mechanisms for propene and water loss from **1** are best considered separately.

Table 1 Reactions of metastable $C_5H_{11-n}D_nO^+$ ions

	Neutral species lost[a,b]															
	H_2O		HOD		D_2O		C_3H_6		C_3H_5D		$C_3H_4D_2$		$C_3H_3D_3$		$C_3H_2D_4$	
Ion structure	*RA*	*T*	*RA*	*T*	*RA*	*T*	*RA*	*T*	*RA*	*T*	*RA*	*T*	*RA*	*T*	*RA*	*T*
$CH_3CH{=}O^+CH_2CH_2CH_3$	45.0	1.6					55.0	1.3								
$CH_3CH{=}O^+CHDCH_2CH_3$	32.1	1.5	9.4	1.6			15.2	1.2	43.2	1.2						
$CH_3CH{=}O^+CD_2CH_2CH_3$	21.6	1.6	18.6	1.4	≈0		3.3	~1	21.5	1.3	35.1	1.3				
$CH_3CH{=}O^+CH_2CD_2CH_3$	22.1	1.6	6.5	1.5	≈0		3.9	~1	17.1	1.3	50.4	1.4				
$CH_3CH{=}O^+CH_2CH_2CD_3$	8.7	1.5	28.2	1.4	<0.1		2.9	~1	<0.5		31.1	1.4	29.1	1.4		
$CH_3CD{=}O^+CH_2CH_2CH_3$	38.9	1.5	<0.2		≈0		54.5	1.3	6.6	1.0						
$CD_3CD{=}O^+CH_2CH_2CH_3$	31.2	1.6	8.9	1.6	≈0		52.4	1.3	0.7	~1.2	0.5	≈1	3.6	≈1	2.8	~0.9

[a] *RA* = Relative abundance, measured by metastable peak areas arising from dissociation of ions in the second field-free region of the VG Analytical ZAB-R mass spectrometer and normalized to a total of 100 units. Values are quoted to the first decimal place solely in order to avoid introducing rounding errors. [b] *T* = Kinetic energy release (in kJ mol^{-1}) estimated from the width at half-height of the associated metastable peak.

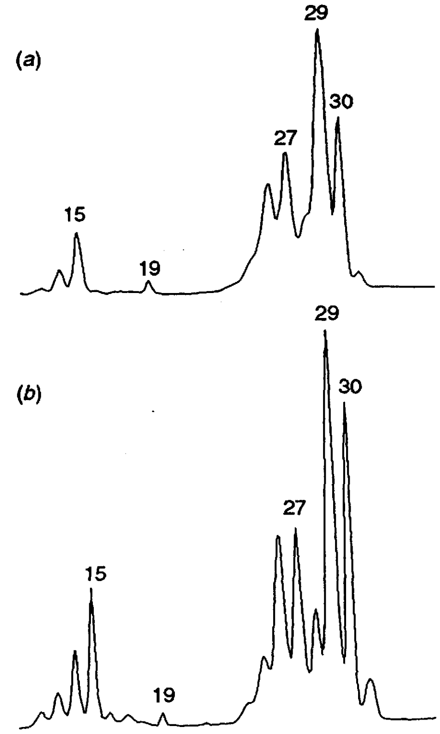


Fig. 1 Partial collisional activation mass spectra of $C_2H_5O^+$ ions derived (*a*) by loss of C_3H_6 from metastable $CH_3CH{=}O^+CH_2CH_2CH_3$ ions and (*b*) by loss of H˙ from metastable $CH_3CH_2OH^{\cdot+}$ radical cations

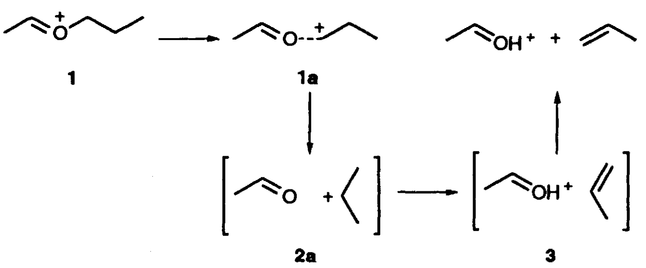
Elimination of Propene.—Earlier work interpreted propene loss from **1** in terms of an INC-mediated mechanism which resulted in production of the most stable isomer of $C_2H_5O^+$, $CH_3CH{=}OH^+$, as the fragment ion.[4,22] The four isomeric $C_2H_5O^+$ ions, $CH_3CH{=}OH^+$, $CH_2{=}O^+CH_3$, $CH_2{=}CHOH_2^+$ and $CH_2CH_2OH^+$ can be differentiated on the basis of their collisional activation (CA) spectra.[24–26] Fig. 1 shows the CA spectrum of the $C_2H_5O^+$ product ions formed by fragmentation of metastable $C_5H_{11}O^+$ ions generated as **1**. This spectrum is indistinguishable from that of $CH_3CH{=}OH^+$ reference ions produced from metastable $CH_3CH_2OH^{\cdot+}$ (by loss of H˙), thus confirming the earlier mechanistic deduction.

Table 2 gives the ratios of partially labelled propenes that are lost from labelled analogues of **1**, together with those expected on the basis of five models.

Model A assumes that specific β-hydrogen transfer occurs *via* reaction (1). This model is grossly in error: there is actually a strong discrimination *against* β-hydrogen transfer, as is shown most clearly by the loss of predominantly $C_3H_4D_2$ (71%) from $CH_3CH{=}O^+CH_2CD_2CH_3$, which is predicted by model A to lose only C_3H_5D. The inadequacy of reaction (1), which has been known for almost 30 years,[27] was recently underlined in definitive studies of propene loss from labelled analogues of $R^1R^2C{=}N(R^4)^+CH_2CH_2CH_3$ and $CH_3CH_2CH_2NH_3^+$.[16–18] However, despite this clear demonstration of its inaccuracy, reaction (1) is still widely held to be an adequate general explanation of this ubiquitous class of alkene elimination.

Model B corresponds to random transfer of any one of the seven protium or deuterium atoms from the original propyl group to oxygen in propene loss from labelled analogues of **1**. This model reproduces the experimental data far more accurately than model A does, but it cannot explain the appreciably different behaviour of $CH_3CH{=}O^+CD_2CH_2CH_3$ and $CH_3CH{=}O^+CH_2CD_2CH_3$. It underestimates the probability of α- and γ-hydrogen transfer while overestimating the likelihood of β-hydrogen transfer.

The ratios quoted for model C are derived from the mechanistic description of Scheme 1. After the requisite C–O bond in **1** has been sufficiently stretched, a 1,2-H shift occurs unidirectionally in the developing propyl cation in **1a**. Proton abstraction from either of the two methyl groups in the incipient isopropyl cation in the INC, **2a**, with equal probability and without interference from any isotope effects, then gives the second INC **3**, comprising $CH_3CH{=}OH^+$ and $CH_2{=}CHCH_3$. Separation of **3** into its components results in propene elimination. This model gives a good first approximation to the experimental data. In particular, it accounts for the discrimination against β-hydrogen transfer because only one of the two hydrogen atoms in the initial β-methylene group is moved by the 1,2-shift into a position (a new methyl group derived from the α-methylene residue and the migrating hydrogen atom) from which it can be transferred to oxygen. Thus, $CH_3CH{=}O^+CHDCH_2CH_3$ and $CH_3CH{=}O^+CH_2CD_2$-CH_3 undergo eventual H-transfer (resulting in C_3H_5D and $C_3H_4D_2$ loss, respectively) and D-transfer (resulting in C_3H_6 and C_3H_5D expulsion, respectively) in quite similar ratios because the isopropyl cation, from which proton or deuteron abstraction occurs, contains one CH_3 and one CH_2D group ($CH_3CH^+CH_2D$ and $CH_3CD^+CH_2D$, respectively).



Scheme 1

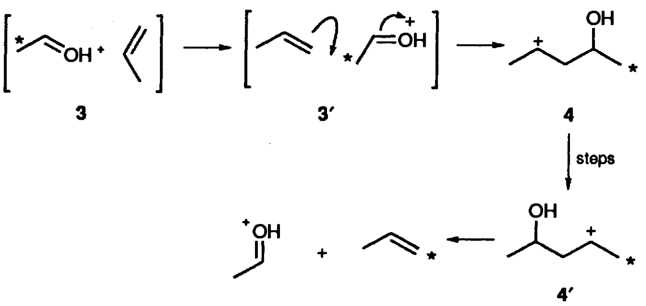
Although model C provides a reasonable first approximation to the observed ratios for $C_3H_{6-n}D_n$ loss from labelled analogues of **1**, it slightly underestimates the contribution from α- and β-hydrogen transfer. A refinement in the form of a preference factor, *p*, favouring hydrogen abstraction from the methyl group derived from the original α-methylene residue compensates for this deficiency. This preference factor arises because the components of the INC **3** do not enjoy complete rotational freedom; instead, there is a slightly increased probability of abstracting a proton from the methyl group derived from the α-methylene residue because the oxygen atom initially is located nearer to this methyl group than to the more distant γ-methyl group of the original propyl substituent. Similarly, the influence of a small inverse secondary isotope effect (k_H per deuterium atom) must be considered on the hydrogen transfer step. This isotope effect discriminates against transfer of a protium atom from a methyl group that does not contain any deuterium atoms. The origin of this unusual inverse isotope effect also lies in rotational effects. The rate of H-transfer from the CH_3 group in a $CH_3CH^+CHD_2$ cation will be reduced compared with that of H-transfer (or D-transfer) from the CHD_2 group because the centre of mass of the cation is shifted slightly away from the CH_3 group towards the CHD_2 group. Consequently, the atoms of the CH_3 group are marginally less likely to spend time in the near vicinity of the oxygen atom than are those of the CHD_2 group.

Model D corresponds to a system in which $p = 1.4$ and $k_H = 0.9$. Similar values for *p* and k_H have been found in propene loss from immonium ions containing propyl groups.[16] In some cases (*e.g.* $CH_3CH{=}O^+CD_2CH_2CH_3$), the effects induced by *p* and k_H reinforce each other (both favour hydrogen transfer from the methyl group derived from the α-methylene residue);

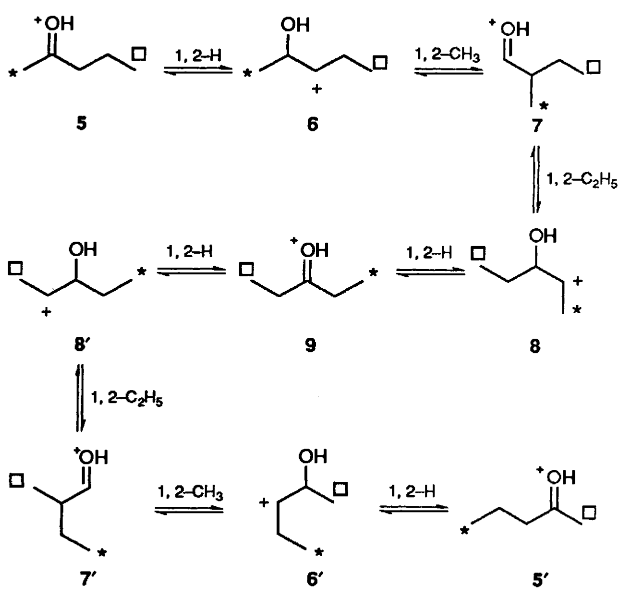
Table 2 Observed and calculated ratios of $C_3H_{6-n}D_n$ lost from labelled analogues of **1**

Ion structure	Neutral species lost	Obs.[a]	Expected from Model[a,b] A	B	C	D	E
$CH_3CH{=}O^+CHDCH_2CH_3$	C_3H_6	26	0	14	17	20	24–28 (26)
	C_3H_5D	74	100	86	83	80	72–76 (74)
$CH_3CH{=}O^+CD_2CH_2CH_3$	C_3H_6	5	0	0	0	0	4–8 (6)
	C_3H_5D	36	0	29	33	42	38–44 (40)
	$C_3H_4D_2$	59	100	71	67	58	52–54 (54)
$CH_3CH{=}O^+CH_2CD_2CH_3$	C_3H_6	5	0	0	0	0	0–6 (5)
	C_3H_5D	24	0	29	17	20	22–28 (22)
	$C_3H_4D_2$	71	100	71	83	80	72–74 (73)
$CH_3CH{=}O^+CH_2CH_2CD_3$	C_3H_6	5	0	0	0	0	0–6 (5)
	C_3H_5D	< 1	0	0	0	0	0–5 (1)
	$C_3H_4D_2$	49	0	43	50	50	45–50 (49)
	$C_3H_3D_3$	46	100	57	50	50	45 (45)
$CH_3CD{=}O^+CH_2CH_2CH_3$	C_3H_6	89	100	100	100	100	90–100 (92)
	C_3H_5D	11	0	0	0	0	5–10 (8)
$CD_3CD{=}O^+CH_2CH_2CH_3$	C_3H_6	87	100	100	100	100	90
	C_3H_5D	1	0	0	0	0	0
	$C_3H_4D_2$	< 1	0	0	0	0	0
	$C_3H_3D_3$	6	0	0	0	0	0–10 (5)
	$C_3H_2D_4$	5	0	0	0	0	0–10 (5)

[a] Values normalized to a total of 100 units for propene loss. [b] See text for details of models.



Scheme 2



Scheme 3

in others (*e.g.* $CH_3CH{=}O^+CH_2CH_2CD_3$), they oppose one another (*p* favours transfer from the substituent formed from the α-methylene residue, whereas k_H acts to the advantage of transfer from the original γ-methyl group). Model D reproduces the observed site-selectivity in the hydrogen transfer step from the original propyl substituent quite accurately.

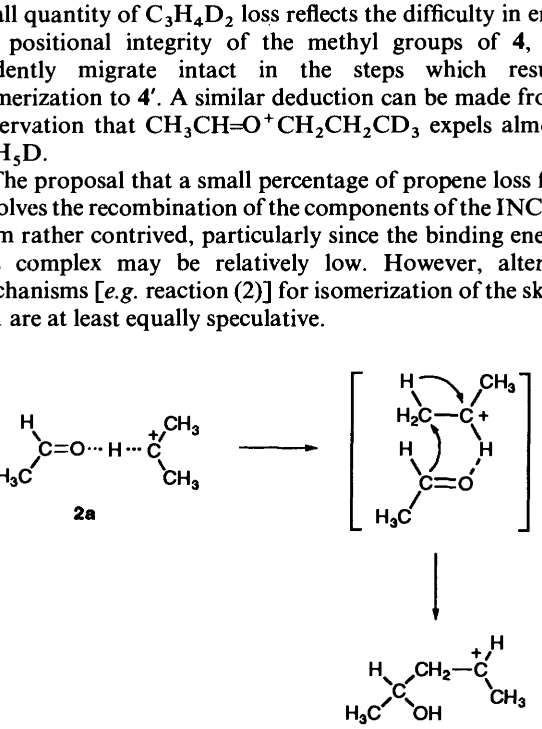
In order to account for the minor (but significant) contribution for hydrogen transfer from the isolated two-carbon unit of **1**, it is necessary to allow for the possibility of a skeletal rearrangement which destroys the positional integrity of the $CH_3CH{=}O$ entity. Such a skeletal isomerization could arise by recombination of the components of **3** to give the open-chain cation, $CH_3CHOHCH_2CH^+CH_3$, **4**, which then rearranges to $CH_3CH^+CH_2CHOHCH_3$, **4′**, before expelling propene, Scheme 2. Independent studies of the chemistry of the related oxonium ion, $CH_3CH_2CH_2C(CH_3){=}OH^+$, **5**, have shown that this isomer of **1** expels H_2O and C_3H_6 in slow dissociations.[28–30] Furthermore, although propene loss from labelled analogues of **5** proceeds with predominant retention of the γ-methyl group in the neutral fragment, there is a minor contribution (*ca.* 20%) from another route in which this substituent remains in the ionic fragment. This minor component can be explained by several mechanisms. Thus, open-chain cations such as $CH_3CHOHCH^+CH_2CH_3$, **6**, and **4**, are accessible to **5** *via* 1,2-H shifts; these species can then undergo ring-closure and ring-opening *via* either protonated oxiranes[28] or oxetanes,[29] thus allowing the hydroxy group to migrate from C(2) to C(4) of the five-carbon chain.

Alternatively, a series of 1,2-H and 1,2-alkyl shifts permits **5** to rearrange to **5′** *via* a sequence of steps that does not require rupture of the initial C–O bond (Scheme 3).[29,30] Attempts to distinguish between these mechanisms by examining the behaviour of ^{13}C-labelled variants of **5** [*e.g.* $CH_3CH_2CH_2{}^{13}C(CH_3){=}OH^+$] have not yet given conclusive results:[30] the carbon atom initially attached to oxygen is predominantly retained in the fragment ion (as would be expected from Scheme 3), but there appears to be a small contribution (*ca.* 10–20%) from a route in which the C–O bond is broken (as would be anticipated on the basis of the alternative routes involving protonated cyclic ethers). In the case of the lower homologue, $CH_3CH_2CH{=}OH^+$, the analogous reaction (ethene elimination) definitely proceeds without dislocation of the C–O bond, as is shown by the loss of C_2H_4 with high specificity from $CH_3CH_2{}^{13}CH{=}OH^+$.[31,32]

Fortunately, the residual doubt concerning the nature of the skeletal isomerization(s) which convert **5** into **5′** (or **4** into **4′**) creates only a minor uncertainty in estimating the ratios of $C_3H_{6-n}D_n$ that should be lost from labelled analogues of **1**. Model E corresponds to a situation in which the bulk (90%) of ions dissociate according to model D, but 10% of the INCs comprising protonated acetaldehyde and propene recombine to give **4** (or a labelled analogue) which undergoes further isomerization to **4′** before finally losing propene. The quoted range of values spans the maximum uncertainty in the ratios; the value in parentheses is the ratio considered to be most likely.

Model E clearly offers an excellent approximation to the experimental data: it accommodates the ratios of labelled propenes derived from the initial propyl substituent of **1** and also allows for the minor contribution for inclusion in the eliminated propene of some of the atoms of the two carbon entity. The behaviour of $CD_3CD{=}O^+CH_2CH_2CH_3$ is especially interesting. The CD_3 group tends to be incorporated intact when partially deuteriated propene is expelled: both $C_3H_2D_4$ and $C_3H_3D_3$ are lost in moderate abundance (*RA* = 6), but C_3H_5D and $C_3H_4D_2$ are very rarely eliminated. The negligibly small quantity of $C_3H_4D_2$ loss reflects the difficulty in eroding the positional integrity of the methyl groups of **4**, which evidently migrate intact in the steps which result in isomerization to **4′**. A similar deduction can be made from the observation that $CH_3CH{=}O^+CH_2CH_2CD_3$ expels almost no C_3H_5D.

The proposal that a small percentage of propene loss from **1** involves the recombination of the components of the INC **3** may seem rather contrived, particularly since the binding energy of this complex may be relatively low. However, alternative mechanisms [*e.g.* reaction (2)] for isomerization of the skeleton of **1** are at least equally speculative.



2a

(2)

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Some circumstantial evidence supporting the mechanism of Scheme 3 is found in the appreciably smaller KE releases accompanying propene losses which are considered to involve the recombination of the components of **3**. This trend appears to be significant and would be intelligible provided that the tendency of the dissociating ions to react in this manner increased as their average internal energy decreases. When these ions with a reduced average internal energy eventually expel propene, a smaller KE release should be observed. In contrast, the higher energy ions are more likely to fragment by eliminating propene directly, without undergoing the additional rearrangement entailed in recombination of **3** to **4**. Consequently, a somewhat greater excess energy is present in the transition state, thus slightly increasing the KE release.

In conclusion, propene elimination from **1** may be understood in some detail by means of an INC-mediated mechanism in which unidirectional rearrangement of a developing propyl cation to its more stable isopropyl isomer precedes hydrogen transfer from either of the methyl groups of the isomerized cation. This mechanism correctly accounts for the site-selectivity of hydrogen transfer from the propyl group to oxygen. Propene loss from **1** resembles the corresponding fragmentation of the analogous immonium ions[16,17] and protonated alkylamines[18] containing a propyl substituent. This finding indicates that the observed site-selectivity reflects the occurrence of a unidirectional rearrangement of the incipient cation from the unstable propyl structure to the stable isopropyl isomer, rather than the presence of nitrogen in the initial ion. A particularly interesting finding is the influence of an unusual inverse isotope effect on the rates of hydrogen transfer from the methyl groups of the isopropyl cation formed by this isomerization. An isotope effect of this kind was first documented in propene expulsion from the analogous immonium ions;[16] it appears that such isotope effects may be typical in these INC-mediated processes.

Elimination of Water.—Loss of H_2O from oxonium ions such as **1** in which the oxygen atom is flanked on both sides by carbons must involve extensive rearrangement. This process cannot be explained solely in terms of conventional intermediates. However, INC-mediated mechanisms have been applied successfully to give a detailed interpretation of water loss from $CH_2{=}O^+CH_2CH_2CH_3$, $CH_2{=}O^+CH(CH_3)_2$ and their labelled analogues.[20,33]

Table 3 gives the ratios of H_2O, HOD and D_2O that are lost from labelled analogues of **1**, together with the ratios expected on the basis of four models.

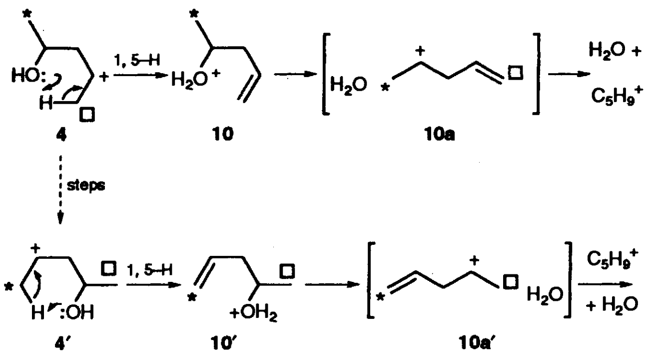
Model F corresponds to random selection of any two of the 11 protium or deuterium atoms from the $C_5H_{11-n}D_nO^+$ ion in the expelled molecule of water. Model G restricts the statistical selection to the seven protium or deuterium atoms in the initial propyl substituent. Neither of these models accounts for the experimental facts to even a first approximation. Both seriously overestimate the abundance of D_2O loss [as is particularly clear in the case of $CD_3CD{=}O^+CH_2CH_2CH_3$ (model F) and $CH_3CH{=}O^+CH_2CH_2CD_3$ (model G)]. Similarly, neither of these models can explain the different ratios of H_2O, HOD and D_2O which are eliminated from $CH_3CH{=}O^+CD_2CH_2CH_3$ and $CH_3CH{=}O^+CH_2CD_2CH_3$. The probabilities of incorporating the hydrogen atoms on the five distinct sites of **1** in the eliminated water are obviously not identical: those on the α- and γ-carbons of the propyl group are more readily transferred to oxygen than those on the β-carbon; moreover, the likelihood of transferring a hydrogen atom that was originally part of the isolated two-carbon entity of **1** to oxygen is smaller still. In addition, there is a strong discrimination against selecting two hydrogen atoms from the same carbon atom. Thus, $CH_3CH{=}O^+CH_2CH_2CD_3$, which would be expected to expel 5–14% of D_2O in water elimination, actually undergoes this reaction to a negligible extent (< 1%).

Model H attempts to allow for these trends by assuming that the transfer of the first hydrogen atom to oxygen is delayed until isomerization of the developing propyl cation has occurred. These steps correspond to those required in propene loss (Scheme 1). Once the first hydrogen transfer has taken place, recombination of the components of **3** gives **4**, which then undergoes a second hydrogen transfer from the more distant methyl group, *via* a favourable six-membered ring transition state, to yield the protonated homoallyl alcohol, **10**. Cleavage of the C–O bond (probably with rearrangement of the developing $C_5H_9^+$ cation) then results in expulsion of H_2O (Scheme 4). This mechanism explains why the two hydrogen atoms of the eliminated water are very rarely selected from the same carbon atom of the propyl group: the first hydrogen atom is abstracted from one of the methyl groups of the isopropyl cation in **3**; the other methyl group then becomes the more distant methyl substituent in **4**, from which the second hydrogen is abstracted in the rearrangement leading to **10**. Scheme 4 also accommodates the discrimination against selecting a hydrogen atom

Table 3 Observed and calculated ratios of $H_{2-n}D_nO$ lost from labelled analogues of **1**

Ion structure	Neutral species lost	Obs.[a]	Expected from Model[a,b] F	G	H	I
$CH_3CH{=}O^+CHDCH_2CH_3$	H_2O	77	82	71	67	70
	HOD	23	18	29	33	30
$CH_3CH{=}O^+CD_2CH_2CH_3$	H_2O	54	65	48	33	40
	HOD	46	32	48	67	60
	D_2O	0	2	4	0	0
$CH_3CH{=}O^+CH_2CD_2CH_3$	H_2O	77	65	48	67	70
	HOD	23	32	48	33	30
	D_2O	0	2	4	0	0
$CH_3CH{=}O^+CH_2CH_2CD_3$	H_2O	24	51	29	0	13
	HOD	76	44	57	100	87
	D_2O	< 1	5	14	0	0
$CH_3CD{=}O^+CH_2CH_2CH_3$	H_2O	> 99	82	100	100	100
	HOD	< 1	18	0	0	0
$CD_3CD{=}O^+CH_2CH_2CH_3$	H_2O	78	38	100	100	75
	HOD	22	51	0	0	25
	D_2O	0	10	0	0	0

[a] Values normalized to a total of 100 units for water loss. [b] See text for details of models.



Scheme 4

from the β-methylene residue in the eliminated water because only one of these two hydrogen atoms is moved to a site from which it may be subsequently transferred to oxygen in either of the appropriate steps (**2a**→**3** or **4**→**10**). Model H successfully accounts for the trends in the ratios of H_2O, HOD and D_2O which are lost from labelled analogues of **1**. In particular, it explains the divergent behaviour of $CH_3CH{=}O^+CD_2CH_2CH_3$ and $CH_3CH{=}O^+CH_2CD_2CH_3$ (the former expels a much greater proportion of HOD than the latter does); it also allows the absence of appreciable signals for D_2O elimination from any of the labelled analogues of **1** to be understood. However, the incorporation of a hydrogen atom from the methyl group of the two-carbon entity of **1** cannot be interpreted by Model H.

Model I allows for the possibility that 25% of ions formed as **4** undergo skeletal isomerization to **4′** prior to the second hydrogen transfer. This refinement opens a route for transfer of a hydrogen atom from the methyl group which was not originally part of the propyl substituent to oxygen. Model I provides a good approximation to the observed ratios of H_2O, HOD and D_2O that are lost from labelled analogues of **1**. Its only significant deficiency is that it slightly, but systematically, underestimates the proportion of H_2O elimination. This inaccuracy may arise merely because model I makes no allowance for the possibility of primary isotope effects discriminating against deuterium atom transfer to oxygen. Any such primary isotope effects should be small since the rate-limiting step in both H_2O and C_3H_6 loss from **1** is construed to be **1a**→**2a**.

The proportion of ions which participate in the steps which convert **4** into **4′** is greater (25%) for ions that lose water than that (10%) for those which eliminate propene. This apparent anomaly reflects two differences in the alternative fragmentations. First, both the skeletal rearrangement(s) and water loss should be favoured at lower internal energies; consequently, low energy ions which expel water also show an enhanced tendency to participate in isomerizations such as **4**→**4′**. Secondly, when **3** is formed from **1**, *via* **1a** and **2a**, any ions which eliminate water *must* undergo recombination to **4** before the second hydrogen transfer can occur. These ions *always* have the opportunity to rearrange to **4′**. In contrast, propene elimination need not (and probably normally does not) entail recombination of **3** to **4**. Therefore, most of the ions which expel propene do so by simple separation of the components of **3**, without ever isomerizing to **4**, thus reducing their tendency to participate in the process(es) which isomerize **4** to **4′**. As a result, **4**→**4′** occurs more often for the ions which eventually eliminate water.

Comparison of the Chemistry of $CH_3CH{=}O^+CH_2CH_2CH_3$ *and* $CH_2{=}O^+CH_2CH_2CH_3$.—The observed site-selectivities for the hydrogen transfer steps in the reactions of **1** differ markedly from those found in the fragmentation of its lower homologue, $CH_2{=}O^+CH_2CH_2CH_3$, **11**. The contrast in the reactivity of **1** and **11** is most clearly seen by considering how they lose H_2O. As was shown in the previous section, expulsion of water from labelled analogues of **1** mainly proceeds by selection of one hydrogen atom each from the α-methylene and γ-methyl group of the initial propyl substituent. On the other hand, loss of water from labelled analogues of **11** involves almost random participation of the seven hydrogen atoms of the corresponding propyl substituent. Whereas no labelled analogue of **1** eliminates D_2O to a significant extent, $CH_2{=}O^+CD_2CH_2CH_3$, $CH_2{=}O^+CH_2CD_2CH_3$ and $CH_2{=}O^+CH_2CH_2CD_3$ all lose appreciable (3, 3 and 10%, respectively) amounts of D_2O.[20] This contrast apparently reflects the nature of the rearrangement which converts the developing propyl cation into its stable isopropyl isomer. This step is unidirectional in the case of **1a**→**2a**. On the other hand, the corresponding step $\{CH_2{=}O\text{---}^+CH_2CH_2CH_3$, **11a**, $\rightarrow[CH_2{=}O\ ^+CH(CH_3)_2]$, **12a**$\}$ is at least partly reversible starting from **11**. Indeed, the reactions of **11a** and **12a** are explicable by INC-mediated mechanisms which allow **11a** and **12a** to interconvert with one another or rearrange to a common structure before dissociating.

However, this explanation poses another question: why should **1a**→**2a** be unidirectional when **11a**→**12a** is not? The stabilization energies of **1a**, **2a**, **11a** and **12a** should be fairly similar. In fact, **1a** and **2a** ought to be slightly more effectively stabilized than **11a** and **12a**, with respect to their separated components, by ion–dipole attractions and related forces because $CH_3CH{=}O$ has a greater dipole moment (μ) and is a larger and more polarizable molecule than $CH_2{=}O$ (μ = 2.7 and 2.7 D,[34] respectively). It would appear plausible on this basis to suppose that interconversion of **1a** and **2a** should be at least as facile as that of **11a** and **12a**.

This apparent difficulty is resolved when the energetic analysis is extended to include steps which occur after isomerization of the incipient cation. The stabilization energies of **1a**, **2a**, **11a** and **12a** certainly exert an important influence on the relative rates and reversibility of **1a**→**2a** and **11a**→**12a**, but the energetics of proton transfer between the components of **2a** and **12a** must also be considered. This step is energetically favourable for **2a** because the proton affinity E_{pa} of $CH_3CH{=}O$ exceeds that of $CH_3CH{=}CH_2$ by 30 kJ mol^{-1}.[35,36] In contrast, proton transfer between the components of **12a** is energetically unfavourable by 33 kJ mol^{-1}.[35,36] This possibility of exothermic proton transfer, which is open to **2a** but not **12a**, is much more significant than the marginally superior stabilization of **2a** compared with **12a**. In both systems, the magnitudes of the stabilization energies of **2a** and **12a** are comparable to or greater than the energy (65–80 kJ mol^{-1}) released by isomerization of $^+CH_2CH_2CH_3$ to $^+CH(CH_3)_2$.[37,38] However, reversion of **2a** to **1a** requires more energy than proton transfer followed by dissociation to give $CH_3CH{=}OH^+$ and C_3H_6; therefore, rearrangement of **2a** to **1a** is unidirectional. In contrast, the critical energy for reversion of **12a** to **11a** is lower than that for formation of $CH_2{=}OH^+$ and C_3H_6 *via* proton transfer between the components of **12a** and comparable to that for fragmentation to form $^+CH(CH_3)_2$ and CH_2O.

The contrasts between the reactions of **1** and **11** can be understood by comparing the relevant portions of the PEPs for isomerization and dissociation of these $C_4H_9O^+$ and $C_5H_{11}O^+$ ions, Fig. 2. These PEPs were constructed using known[35–42] and estimated[23,43–48] enthalpies of formation. There are some uncertainties concerning the enthalpies of certain intermediates or transition states and also the depth of the energy wells (if any) occupied by one or two species. Nevertheless, the following points deserve emphasis.

Firstly, the energies of the products of C_3H_6 and CH_2O or CH_3CHO loss are known with confidence.[35–37] There is no doubt about which combination of products is energetically preferable in each system. Moreover, there are good reasons for placing the estimated energies of **11a** and **12a** *ca.* 70 kJ mol^{-1} below the total energy of the separated products.[23] Similarly, **1a** and **2a** should lie *ca.* 80 kJ mol^{-1} lower than the total energy of CH_3CHO and the appropriate $C_3H_7^+$ cation.[23] Consequently, the view that isomerization of the developing cation in **1a** becomes rate-limiting because of the changes in the PEP induced by the possibility of exothermic proton transfer leading to C_3H_6 loss seems secure.

Secondly, there is more uncertainty about the geometries and energies of **3** and the analogous species $[CH_2{=}OH^+\ CH_3CH{=}CH_2]$, **13**. If assessed as INCs stabilized purely by ion–dipole attractions, these species would exist in very shallow energy wells *ca.* 10 kJ mol^{-1} deep because C_3H_6 has only a small permanent dipole moment (μ = 0.37 D). It is likely that the depth of these wells could be increased by ion-induced dipole attractions and other ionic forces, but it may be more accurate to regard these species as proton-bridged complexes in which C_3H_6 and CH_3CHO or CH_2O are coordinated to a common proton. This complication does not, however, affect the essential conclusion of the previous paragraph, provided that **3** and **13** are appreciably bound relative to the separated products, as is certainly the case. It is in fact not strictly necessary for **3** and **13** to lie in energy wells because it is the changes in the relative energies of **1a** or **11a** and the products of C_3H_6 loss that causes the isomerization of **1a** to be unidirectional and rate-limiting even though that of **11a** is not.

Thirdly, experimental values for the enthalpies of formation of **1**, **2**, **11** and **12** $\{CH_2{=}O^+CH(CH_3)_2\}$ are not known. The energies of these ions can be estimated from those[39] of their lower homologues either by means of a group equivalent approach[43,44] or from an algorithm[47] derived from trends in the enthalpies of formation of oxonium ions and the corresponding carbonium ions. Any errors in the estimated energies of **1**, **2**, **11** and **12** are of little consequence in the present context: there is no doubt that these oxonium ions are stable species existing in substantial energy wells.

The enthalpies of formation of the open-chain cations, $CH_3CH^+CH_2CHROH$, formed by recombination of the components of $[CH_3CH{=}CH_2\ RCH{=}OH^+]$, are estimated from known hydride abstraction energies.[40] It is necessary to include a correction of 10 kJ mol^{-1} to allow for the destabilizing influence of the electron-withdrawing γ-hydroxy group on the nearby cationic site.[45,46] Experimental values for the energies of **10** (R = CH_3) and **14** (R = H) are very difficult to obtain because formation of such species is usually pre-empted by ring-closure at threshold to give thermodynamically more stable structures. Despite the uncertainty surrounding the energies of **10** and **14**, it is clear that these species lie below the total enthalpies of formation of the products of C_3H_6 loss. As a result, it is plausible to suppose that formation of these intermediates or transition states will compete with C_3H_6 elimination in the dissociation of metastable ions. It is not necessary that **10** and **14** correspond to energy minima, but merely that they should lie at a lower energy level than those of the products of C_3H_6 elimination. In actual fact, there is strong evidence[49] that the open-chain cation, CH_3CH^+-$CH_2CH_2OCH_3$, corresponding to **14** does exist in an energy well, though this need not necessarily imply that the homologous ions containing a hydroxy group are also stable species.

Finally, the combined energies of the probable products of H_2O expulsion are still lower than those of **10** and **14**. Thus, the combined experimental enthalpies of formation of H_2O and the 1-methylallyl cation ($CH_3CH^+CH{=}CH_2$) (845[50] and −240[41,42] kJ mol^{-1}, respectively) formed from **11** and **12** amount to 605 kJ mol^{-1}. A mechanism for H_2O elimination from **1** and **2** involving direct cleavage of **10a** gives the 1-methylhomoallyl cation, $CH_3CH^+CH_2CH{=}CH_2$; the enthalpy of this species is estimated to be 800 kJ mol^{-1} on the assumption that the E_{pa} of penta-1,4-diene is *ca.* 830 kJ mol^{-1}, giving a total energy for these products of 560 kJ mol^{-1}. If, as is very likely, rearrangement of the developing $C_5H_9^+$ cation precedes H_2O loss, even more favourable products become accessible (*e.g.* the 1,3-dimethylallyl cation, $CH_3CH^+CH{=}CHCH_3$, having an enthalpy[51] of 765 kJ mol^{-1}). In the present context, details of the later stages of the mechanism for H_2O elimination from **11** and **12** or **1** and **2** are not of primary importance, but it is clear that recombination of the components of **11a** or **1a** to form $CH_3CH^+CH_2CHROH$ with eventual expulsion of H_2O is more favourable than C_3H_6 loss in either system (R = CH_3 or H, respectively). Therefore, the occurrence of H_2O elimination from both $RCH{=}O^+CH_2CH_2CH_3$ ions is explained, even though this process entails far more extensive rearrangement than $RCH{=}O$ or C_3H_6 expulsion. When R = CH_3, rate-limiting isomerization of **1a** to **2a** yields a dissociating population of $C_5H_{11}O^+$ ions with a higher average internal energy than is the case when **2a** is formed directly from **2**. The higher energy ions show an enhanced tendency to fragment *via* the channel involving the least rearrangement.[52] Consequently, the ratio of C_3H_6:H_2O loss from **1** exceeds that found for **2**;[22] indeed, **2** loses almost exclusively (97%) H_2O, whereas **1** expels H_2O and

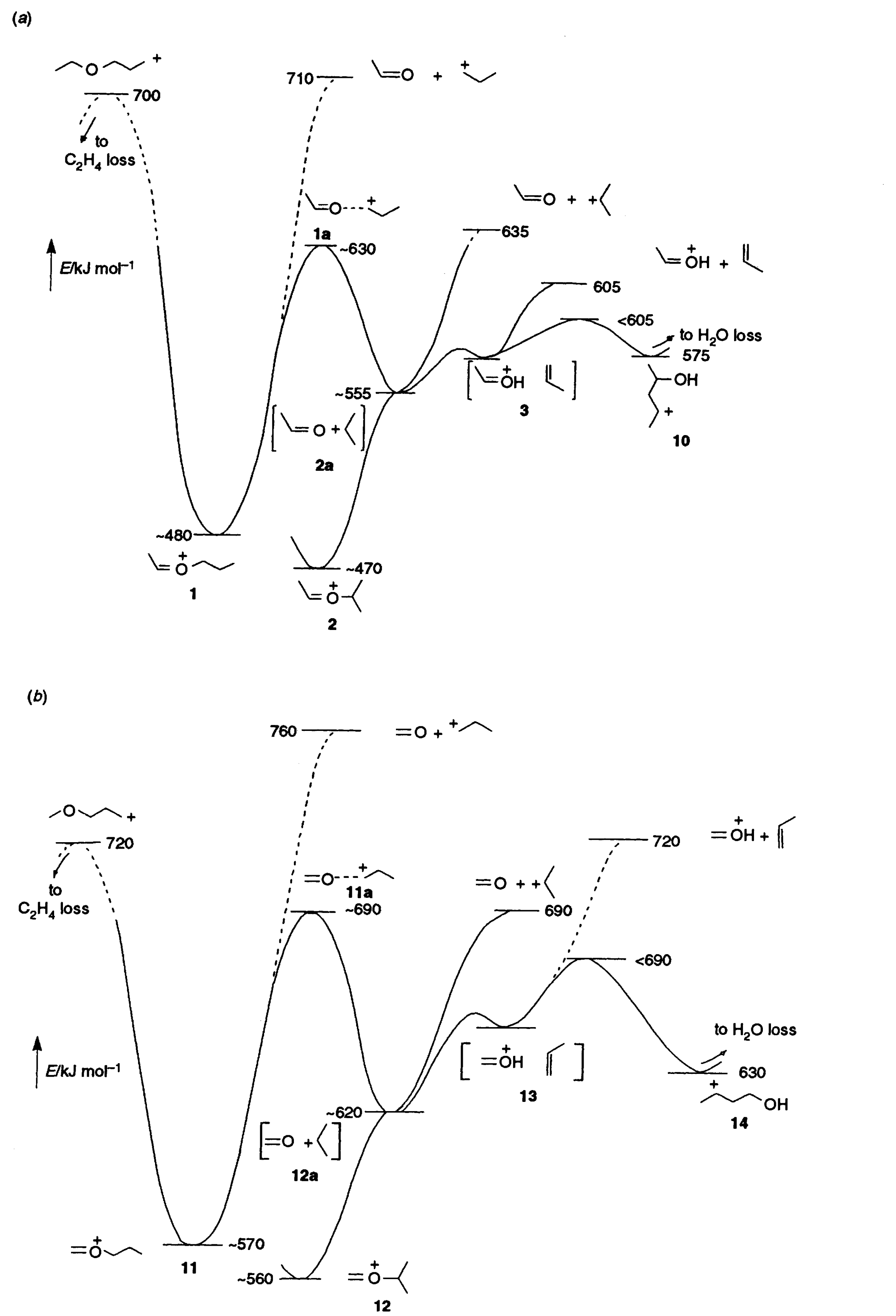


Fig. 2 Partial potential energy profiles for isomerization and dissociation of $CH_3CH{=}O^+CH_2CH_2CH_3$ and $CH_2{=}O^+CH_2CH_2CH_3$

C_3H_6 in comparable abundances (Table 1). Furthermore, the $T_{\frac{1}{2}}$ value for H_2O elimination from **1** exceeds that for **2**.[23] In contrast, no such rate-limiting isomerization occurs when R = H. Therefore, **11** and **12** eliminate CH_2O and H_2O in similar ratios,[21] with identical KE releases[23] and there is a common preference for H_2O loss.

Conclusions

The reactions of metastable oxonium ions generated as $CH_3CH{=}O^+CH_2CH_2CH_3$ are intelligible in detail by means of INC-mediated mechanisms. Both propene and water elimination occur after rate-limiting rearrangement of the incipient $^+CH_2CH_2CH_3$ cation to $^+CH(CH_3)_2$ has taken place. The site-selectivity in the hydrogen transfer step(s) reflects the unidirectional nature of the cation isomerization. The hydrogen transfer that precedes propene loss occurs predominantly from the α- and γ-positions of the initial propyl substituent. This dissociation of $CH_3CH{=}O^+CH_2CH_2CH_3$ shows many similarities with the corresponding fragmentation of immonium ions and protonated amines containing a propyl group. In particular, the hydrogen transfer is influenced by an unusual inverse isotope effect, as has been reported in analogous immonium ion systems. This isotope effect may be a diagnostic characteristic in INC-mediated alkene eliminations following rate-limiting cation isomerizations. Water loss from $CH_3CH{=}O^+CH_2CH_2CH_3$ exhibits a similar selectivity, with the additional preference for eventually transferring the second hydrogen from the methyl group of the incipient $^+CH(CH_3)_2$ which is not affected when $[CH_3CH{=}O\ ^+CH(CH_3)_2]$ rearranges to $[CH_3CH{=}OH^+\ CH_2{=}CHCH_3]$. This site-selectivity contrasts sharply with that found for water loss from $CH_2{=}O^+CH_2CH_2CH_3$. The selectivity in the hydrogen transfers that precede water expulsion from oxonium ions depends strongly on whether the cation rearrangement is reversible. The reversibility of this isomerization is influenced not only by the extent to which the $RCH{=}O{-}{-}{-}^+CH_2CH_2CH_3$ and $[RCH{=}O\ ^+CH(CH_3)_2]$ species are stabilized with respect to their separated components, but also the energetics of proton transfer to give $[RCH{=}OH^+\ CH_2{=}CHCH_3]$. When proton transfer is energetically favourable (*e.g.* $R = CH_3$), reversion of $[RCH{=}O\ ^+CH(CH_3)_2]$ to $RCH{=}O{-}{-}{-}^+CH_2CH_2CH_3$ can be pre-empted by dissociation, even when the species containing incipient propyl cations are extensively stabilized.

Experimental

All mass spectra were recorded on the VG Analytical ZAB-R mass spectrometer. Details of the geometry of this three-sector (BE_1QE_2) instrument have been reported elsewhere.[53] Data on the dissociation of metastable ions in the second field-free region were obtained by the MIKES technique.[1] The quoted spectra are integrated data, compiled from 2–5 individual scans. Typical operating conditions were 70 eV ionizing electron energy and 7910 V accelerating voltage. The KE releases were estimated from the width at half-height of the appropriate metastable peak, by means of the standard one-line equation,[1,54] after applying the usual correction[55] for the width at half-height of the main beam.

The structure of the $C_2H_5O^+$ ion generated from dissociation of metastable **1** in the second field-free region was probed by obtaining its collisional activation spectra in the third field-free region using oxygen as the collision gas and mass selected ions of 10 keV translational energy.

The ions studied in this work were generated by dissociative ionization of propyl isopropyl ethers. These ethers were prepared by condensation of the appropriate sodium propan-2-olate with a slight deficiency of the requisite propyl iodide in suspension/solution in triglyme [1,2-bis(2-methoxyethoxy)-ethane]. The synthetic routes are summarized in Scheme 5. Details of typical experimental procedures are illustrated by the following description of the preparation of $(CH_3)_2CHOCH_2CH_2CD_3$. Isotopically labelled starting materials [D_2O, $LiAlD_4$, CD_3CO_2D and $(CD_3)_2CDOD$] were obtained from Aldrich and were used without further purification. The estimated isotopic purity of the derived ethers was generally 96–99%; that for $(CH_3)_2CHOCH_2CD_2CH_3$ was 89%. These levels of incorporation of deuterium are amply sufficient given that the labelled oxonium ions of interest were specifically selected and transmitted for investigation in the MIKES experiments.

$$1\quad CH_3CH_2CH{=}O \xrightarrow{(i,ii)} CH_3CH_2CHDOH \xrightarrow{(iii)} CH_3CH_2CHDI$$

$$2\quad CH_3CH_2COCl \xrightarrow{(iv,ii)} CH_3CH_2CD_2OH \xrightarrow{(iii)} CH_3CH_2CD_2I$$

$$3\quad CH_3CH_2CH{=}O \xrightarrow{(v)} CH_3CD_2CH{=}O \xrightarrow{(vi,ii)} CH_3CD_2CH_2OH \xrightarrow{(iii)} CH_3CD_2CH_2I$$

$$4\quad CD_3CO_2D \xrightarrow{(vii)} CD_3COCl \xrightarrow{(viii,ii)} CD_3CH_2OH \xrightarrow{(iii)} CD_3CH_2I \xrightarrow{(ix,x)} CD_3CH_2CO_2H \xrightarrow{(vii)} CD_3CH_2COCl \xrightarrow{(viii,ii)} CD_3CH_2CH_2OH \xrightarrow{(iii)} CD_3CH_2CH_2I$$

$$5\quad (CH_3)_2C{=}O \xrightarrow{(i,ii)} (CH_3)_2CDOH$$

$$6\quad (CH_3)_2CHOH \xrightarrow{(xi,xii)} (CH_3)_2CHOCHDCH_2CH_3$$

$$7\quad (CH_3)_2CHOH \xrightarrow{(xi,xiii)} (CH_3)_2CHOCD_2CH_2CH_3$$

$$8\quad (CH_3)_2CHOH \xrightarrow{(xi,xiv)} (CH_3)_2CHOCH_2CD_2CH_3$$

$$9\quad (CH_3)_2CHOH \xrightarrow{(xi,xv)} (CH_3)_2CHOCH_2CH_2CD_3$$

$$10\quad (CH_3)_2CDOH \xrightarrow{(xi,xvi)} (CH_3)_2CDOCH_2CH_2CH_3$$

$$11\quad (CD_3)_2CDOD \xrightarrow{(xi,xvi)} (CD_3)_2CDOCH_2CH_2CH_3$$

Scheme 5 *Reagents and conditions:* (*i*) $LiAlD_4$ (0.3 mol), triglyme, stir 24 h; (*ii*) excess tetragol, distil.; (*iii*) I_2, red P; (*iv*) $LiAlD_4$ (0.6 mol), triglyme, stir 24 h; (*v*) D_2O, pyridine, reflux 24 h, repeat twice; (*vi*) $LiAlH_4$ (0.4 mol), triglyme, stir 24 h; (*vii*) excess PhCOCl, distil.; (*viii*) $LiAlH_4$ (0.8 mol), triglyme, stir 24 h; (*ix*) Mg, $(C_2H_5)_2O$; (*x*) excess CO_2, −78 °C; (*xi*) NaH (1.2 mol), triglyme; (*xii*) CH_3CH_2CHDI (0.9 mol), triglyme, stir overnight; (*xiii*) $CH_3CH_2CD_2I$ (0.9 mol), triglyme, stir overnight; (*xiv*) $CH_3CD_2CH_2I$ (0.9 mol), triglyme, stir overnight; (*xv*) $CD_3CH_2CH_2I$ (0.9 mol), triglyme, stir overnight; (*xvi*) $CH_3CH_2CH_2I$ (0.9 mol), triglyme, stir overnight

$(CH_3)_2CHOCH_2CH_2CD_3$. CD_3COCl.—[$^2H_4$]Acetic acid (24.8 g, 0.39 mol) was added cautiously to excess benzoyl chloride (85 g, 0.6 mol) and the mixture was carefully distilled through a 12 cm helix-packed column. [$^2H_3$]Acetyl chloride (26.1 g, 86%) was collected as the fraction distilling between 50 and 53 °C.

CD_3CH_2OH.—A suspension of lithium aluminium hydride (10.0 g, 0.26 mol) in triglyme (250 cm^3) was stirred magnetically under a nitrogen atmosphere. The temperature was kept between 30 and 50 °C by means of external cooling (ice–salt bath) during the dropwise addition over a period of 2 h of a solution of [$^2H_3$]acetyl chloride (26.1 g, 0.32 mol) in triglyme (50 cm^3). Stirring was continued overnight, after which tetragol

($HO[CH_2CH_2O]_3CH_2CH_2OH$) (80 cm^3) was added dropwise over 1 h. Careful distillation gave [2,2,2-$^2H_3$]ethanol (14.8 g, 94%) having b.p. 80–82 °C.

CD_3CH_2I.—A mixture of [2,2,2-$^2H_3$]ethanol (14.8 g, 0.30 mol) and purified red phosphorus (3.9 g, 0.126 mol) in a 50 cm^3 pear-shaped flask was heated gently until refluxing began. Resublimed iodine (39.0 g, 0.15 mol) was added in small portions (0.3–0.7 g) through the condenser at such a rate as to maintain gentle refluxing without causing an excessive development of iodine colouration in the vapour. After all the iodine had been added (1 h), the mixture was refluxed for a further 15 min by application of external heating (oil bath). Distillation gave crude [2,2,2-$^2H_3$]-1-iodoethane (36.7 g, 76%) having b.p. 60–75 °C. This material was washed with aqueous sodium metabisulfite solution (2 × 10 cm^3) and water (10 cm^3), dried with magnesium sulfate and distilled to give colourless [2,2,2-$^2H_3$]-1-iodoethane (30.6 g, 65%) having b.p. 70–72 °C.

$CD_3CH_2CO_2H$.—Magnesium turnings (6.0 g, 0.25 mol) were placed in a 1000 cm^3 three-necked round-bottomed flask equipped with an efficient condenser and a pressure equalizing addition funnel. The apparatus was flushed with dry nitrogen and sufficient redistilled dry diethyl ether (20 cm^3) to cover the magnesium was added. A small portion of [2,2,2-$^2H_3$]-1-iodoethane (0.5 g) and a single crystal of resublimed iodine was added. After initiation of the reaction had occurred, a solution of the remaining [2,2,2-$^2H_3$]-1-iodoethane (29.7 g; total 30.2 g, 0.19 mol) in dry diethyl ether (180 cm^3) was added dropwise during 45 min at a rate sufficient to maintain gentle refluxing. After the addition was completed, the mixture was stirred magnetically and warmed (water bath) to maintain gentle refluxing for a further 30 min. Solid carbon dioxide (*ca.* 50 g, 1.1 mol) was quickly crushed in a stout envelope and transferred to a 1000 cm^3 beaker; the ethereal solution was immediately poured in a continuous stream onto the contents of the beaker which were stirred manually with a glass rod. After the addition had been completed, manual stirring was continued for a further 15 min. The mixture was allowed to attain ambient temperature before being acidified with cold, moderately concentrated hydrochloric acid (50 cm^3). The ethereal phase was separated and the aqueous phase was extracted with diethyl ether (5 × 100 cm^3). The combined ethereal phases were dried with magnesium sulfate, filtered and evaporated at reduced pressure to give crude [3,3,3-$^2H_3$]propionic acid (14.8 g, 97%). This material was dissolved in diethyl ether (50 cm^3) and extracted with saturated sodium hydrogen carbonate solution (3 × 70 cm^3). The combined aqueous extracts were transferred to a 500 cm^3 conical flask surrounded by an ice-bath, covered with a layer of diethyl ether (50 cm^3) and stirred magnetically at a temperature between 5 and 10 °C during acidification by dropwise addition of ice-cold, moderately concentrated aqueous hydrochloric acid. The ethereal phase was separated and the aqueous phase was extracted with diethyl ether (3 × 50 cm^3). The combined ethereal phases were dried with magnesium sulfate, filtered and evaporated at reduced pressure to give colourless [3,3,3-$^2H_3$]propionic acid (9.35 g, 61%).

CD_3CH_2COCl.—[3,3,3-$^2H_3$]Propionic acid (9.35 g, 0.121 mol) was converted into [3,3,3-$^2H_3$]propionyl chloride (8.74 g, 75%) having b.p. 74–80 °C by treatment with excess benzoyl chloride (40 g, 0.28 mol) in the manner described above for preparing CD_3COCl.

$CD_3CH_2CH_2OH$.—[3,3,3-$^2H_3$]Propionyl chloride (8.74 g, 0.92 mol) dissolved in triglyme (10 cm^3) was reduced to [3,3,3-$^2H_3$]propan-2-ol (5.7 g, 99%) having b.p. 100–102 °C by addition to a stirred suspension of lithium aluminium hydride (3.2 g, 0.85 mol) in triglyme (80 cm^3) followed by addition of tetragol (30 cm^3) in the manner described above for preparing CD_3CH_2OH.

$CD_3CH_2CH_2I$.—[3,3,3-$^2H_3$]Propanol (5.27 g, 0.084 mol) was converted into [3,3,3-$^2H_3$]-1-iodopropane (9.1 g, 63%) having b.p. 98–100 °C by treatment with purified red phosphorus (1.3 g, 0.042 mol) and resublimed iodine (10.7 g, 0.042 mol) in the manner described above for preparing CD_3CH_2I.

$(CH_3)_2CHOCH_2CH_2CD_3$.—A solution of propan-2-ol (1.2 g, 0.020 mol) in triglyme (30 cm^3) was stirred magnetically under a nitrogen atmosphere; sodium hydride (1.2 g of 60% dispersion in mineral oil, 0.03 mol) was added in two portions. After evolution of hydrogen had ceased (20 min), a solution of [3,3,3-$^2H_3$]-1-iodopropane (1.4 g, 0.008 mol) in triglyme (5 cm^3) was added dropwise during 15 min. Initially, there was considerable frothing, but this subsided once the bulk of the iodopropane had been added (15 min). After stirring the mixture overnight, distillation gave isopropyl [3,3,3-$^2H_3$]propyl ether (0.57 g, 67%) having b.p. 79–81 °C.

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