The Mechanism of Ethylene Elimination from the Oxonium Ions $CH_3CH_2CH{=}O^+CH_2CH_3$ and $(CH_3)_2C{=}O^+CH_2CH_3$

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The reactions of the metastable oxonium ions $CH_3CH_2CH{=}O^+CH_2CH_3$ and $(CH_3)_2C{=}O^+CH_2CH_3$ are reported and discussed. Various mechanisms for ethylene elimination, which is the principal dissociation route for these ions, are considered. It is shown by means of ^2H-labelling experiments and analysis of collision-induced dissociation spectra that routes involving ion–neutral complexes pre-empt 'conventional' mechanisms for these processes. In contrast, the behaviour of the lower homologues $CH_3CH_2CH{=}OR^+$ and $(CH_3)_2C{=}OR^+$ ($R = H, CH_3$) is consistent with the operation of 'conventional' mechanisms for ethylene expulsion. This contrast is interpreted in energetic terms. The significance of these results for the chemistry of homologous and analogous 'onium' ions containing a $Z^+–R$ function ($Z = O, S, NH, NCH_3$; $R = C_nH_{2n+1}, n \geq 2$) is explained.

Tremendous progress has been made during the last ten or fifteen years in understanding the mechanisms by which isolated organic ions dissociate.[1,2] It is well-established that the chemistry of ions can be documented by generating the species of interest in a mass spectrometer and observing the reactions of metastable ions.[1] There are many parallels between the behaviour of these long-lived, low-energy species and that of ions in solution. Thus, as a general rule, energetic parameters exercise an important influence on the relative rates of the various fragmentation routes that are open to a particular ion.[3,4] In addition, complications caused by the interference of isolated electronic states, which might intervene in the competition among alternative dissociation channels, arise only in exceptional cases.[5] A battery of techniques can be brought to bear in the gas phase so as to determine the structures of both the ionic[6–8] and neutral[9–11] products formed by a given reaction. One unique advantage of conducting the experiments in the absence of solvent molecules is that information on the kinetic energy (KE) released during decomposition is directly accessible from the shape and width of the associated metastable peak.[1,2,4] The KE releases are usually quoted as $T_{\frac{1}{2}}$ values ($T_{\frac{1}{2}}$ corresponds to the KE release evaluated from the width at half-height of the appropriate metastable peak).

Many ions react in the gas phase *via* mechanisms which can be formulated solely in terms of 'conventional' structures and steps (*e.g.*, 1,2-H and 1,2-alkyl shifts, and σ-cleavage of single bonds) that are familiar to organic chemists. However, 'unconventional' ion structures have also been shown to play prominent roles in the fragmentation of isolated ions. Ion–neutral complexes (INCs) constitute one important general class of 'unconventional' ions.[12–15] An INC consists of an ion and a neutral species held together by ion–dipole attractions and other ionic forces, but not connected by a normal covalent bond. 'Intramolecular' (*e.g.*, isomerisation of the incipient cation) and 'intermolecular' (*e.g.*, H-transfers between the ionic and neutral components) reactions can occur within the INC at energies below those needed to cause rapid separation to products. These possibilities offer a means of understanding many rearrangements that would be otherwise inexplicable.

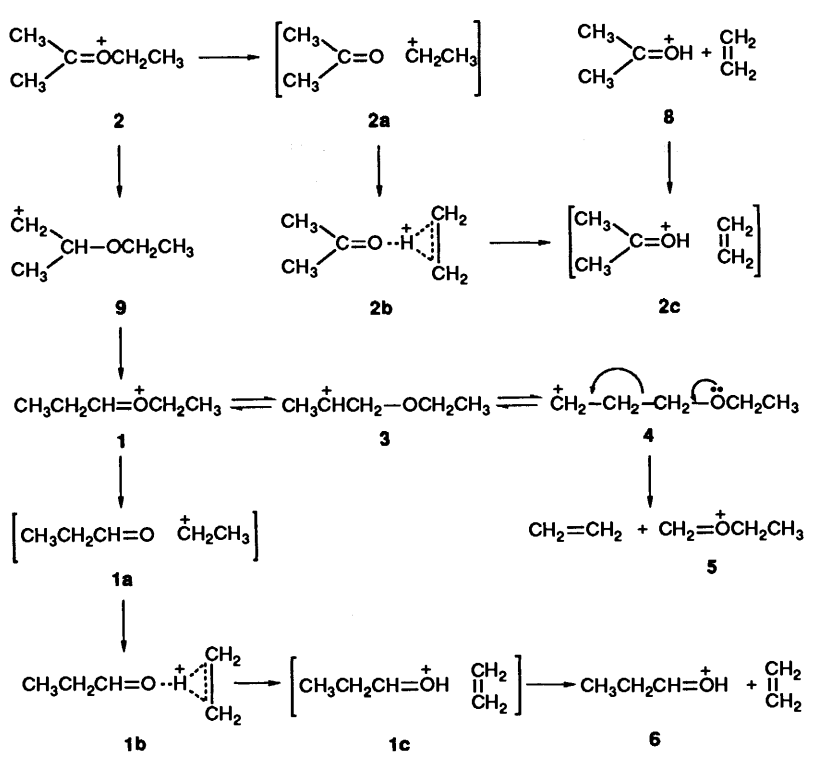
It is important to know the circumstances in which mechanisms involving INCs compete with and pre-empt alternative 'conventional' routes for the fragmentation of ions. Such knowledge is not only intrinsically significant, but it should also permit the analytical utility of mass spectrometry to be increased.

Results and Discussion

Reactions of $CH_3CH_2CH{=}O^+CH_2CH_3$ *and* $(CH_3)_2C{=}O^+CH_2CH_3$.—The distinction between mechanisms that may be formulated in 'conventional' terms and those in which INCs participate is illustrated by the behaviour of $CH_3CH_2CH{=}O^+CH_2CH_3$ (**1**) and $(CH_3)_2C{=}O^+CH_2CH_3$ (**2**). Each of these $C_5H_{11}O^+$ ions undergoes predominantly C_2H_4 expulsion in slow reactions, Table 1.

Several mechanisms for these processes can be devised by extrapolation from the routes that have been proposed for C_2H_4 elimination from lower homologues of **1** and **2**, Scheme 1. Thus, two consecutive 1,2-H shifts in **1** lead to **4** *via* **3**; σ-cleavage in **4** then yields C_2H_4 and $CH_2{=}O^+CH_2CH_3$, **5**. This 'conventional' route for C_2H_4 elimination has been postulated in the dissociation of $CH_3CH_2CH{=}OH^+$, **6**,[16,17] and $CH_3CH_2CH{=}O^+CH_3$, **7**.[17] Thus, the reactions of ^2H-labelled analogues of **6** and **7** reveal that the four hydrogen atoms of the expelled ethylene molecule are selected almost statistically from the six protium or deuterium atoms of the $C_3H_nD_{6-n}$ moiety, with minor[16] and negligible[18] participation, respectively, from the hydrogens of the hydroxy or methoxy groups. These data are consistent with extensive hydrogen exchange, *via* such reversible 1,2-H shifts, prior to ethylene expulsion. A second, 'unconventional', mechanism for C_2H_4 expulsion from **1** involves elongation of the C–O σ-bond to form the INC, **1a**, followed by hydrogen transfer between the developing products ($CH_3CH_2CH{=}O$ and $^+CH_2CH_3$) to yield $CH_3CH_2CH{=}OH^+$ and $CH_2{=}CH_2$. It has been proposed[12,16] that this route operates for C_2H_4 elimination from $CH_2{=}O^+CH_2CH_3$ and other 'onium' ions containing the $=Z^+–CH_2CH_3$ function ($Z = O, S, NH, NCH_3$). The INCs in Scheme 1 are represented by the ionic and neutral components enclosed in square brackets.

Similar alternatives are open to **2**. An exactly parallel 'unconventional' mechanism *via* the INC **2a** leads to $(CH_3)_2C{=}OH^+$, **8**, and $CH_2{=}CH_2$. Alternatively, a 1,2-H shift in **2** affords **9**, which then could undergo a 1,2-CH_3 shift to form **1**. The lower homologues, $(CH_3)_2C{=}OR^+$ ($R = H, CH_3$), are known to rearrange irreversibly in this manner to $CH_3CH_2CH{=}OR^+$



Scheme 1

Table 1 Reactions of metastable $C_5H_{11}O^+$ ions

	Neutral species lost					
	H_2O		C_2H_4		C_3H_6	
Ion structure	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]
$CH_3CH_2CH{=}O^+CH_2CH_3$	<1	2.1	>98	1.89	1	1.6
$(CH_3)_2C{=}O^+CH_2CH_3$	1	2.5	>98	1.88	<0.5	1.7

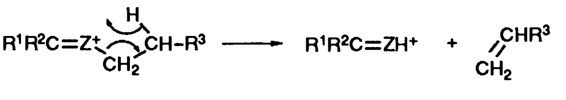
[a] RA = Relative Abundance, as measured by product ion counts (these data correspond to metastable peak areas) and normalised to a total metastable ion current of 100 units for ions dissociating in the second field-free region. [b] $T_{\frac{1}{2}}$ = kinetic energy release accompanying dissociation, quoted in kJ mol^{-1}, as estimated from the width at half-height of the appropriate metastable peak.

before elimination of C_2H_4 takes place.[18,19] In the case of **1** generated by unidirectional isomerisation of **2**, eventual loss of C_2H_4 could in principle then occur *via* either a 'conventional' or an 'unconventional' mechanism, resulting in $CH_2{=}O^+CH_2CH_3$, **5**, or $CH_3CH_2CH{=}OH^+$, **6**, respectively, as the product ion.

Structure of the $C_3H_7O^+$ *Ions Formed by* C_2H_4 *Loss from* **1** *and* **2**.—The three isomers of $C_3H_7O^+$ (**5**, **6** and **8**) which are produced by the various routes for C_2H_4 loss each have distinctive collision-induced dissociation (CID) spectra, Table 2. The clearest differences in the spectra of **5** and **6** are found in the increased relative intensities (RIs) of the signals at *m*/*z* 57, 43, 42, 27, 26 and 15 in the spectrum of **6**. The spectrum of **8** (base signal at *m*/*z* 43, rather than 27; enhanced RIs for 58 and 42; and diminished RIs for 30, 28, 27, 26 and especially 29) differs even more obviously from that of either **5** or **6**. Comparison of the spectra of authentic **5**, **6** and **8** with those of the $C_3H_7O^+$ ions generated by rapid C_2H_4 elimination from **1** and **2** reveals that these reactions give **6** and **8**, respectively, Table 2. Thus, the INC-mediated mechanisms are the dominant routes for C_2H_4 loss from **1** and **2** in fast reactions occurring in the ion source.

Reactions of ^{2}*H-Labelled Analogues of* **1** *and* **2**.—This conclusion is reinforced by ^{2}H-labelling experiments. Ethylene elimination from the $C_5H_nD_{11-n}O^+$ analogues involves the atoms of the *O*-ethyl group with at least 99% specificity, Table 3. Thus, $CH_3CD_2CD{=}O^+CH_2CH_3$ and $(CD_3)_2C{=}O^+CH_2CH_3$ expel essentially exclusively C_2H_4; the 'conventional' mechanism would require loss of partly or wholly deuteriated ethylenes, respectively, from these ions. Similarly, $CH_3CH_2CH{=}O^+CH_2CD_3$ and $(CH_3)_2C{=}O^+CH_2CD_3$ lose predominantly $C_2H_2D_2$ (β-deuterium transfer), together with a minor amount (8% and 5%, respectively) of C_2HD_3, but no C_2H_4. The 'conventional' mechanism predicts only C_2H_4 expulsion from these ions.

The strong preference for this β-hydrogen transfer in ethylene loss from ^{2}H-labelled analogues of **1** and **2** deserves comment. Alkene eliminations of this general type have often been rationalised in terms of a 'four-centre' mechanism, eqn. (1). This



$$R^1R^2C{=}Z^+\overset{H}{CH}{-}R^3\,(CH_2) \longrightarrow R^1R^2C{=}ZH^+ + CH_2{=}CHR^3 \quad (1)$$

[R^1, R^2, R^3 = H, alkyl; Z = O, S, NH, NCH_3]

'traditional' mechanism predicts that alkene losses of this kind should always proceed with specific β-hydrogen transfer from the intact alkyl group ($CH_2CH_2R^3$) to the heteroatom. The site selectivity (92–95% β-hydrogen transfer) observed in ethylene loss from ^{2}H-labelled analogues of **1** and **2** deviates only slightly from that expected on the basis of the traditional mechanism. However, the apparent success of the traditional mechanism is illusory: it reflects the special nature of the *O*-alkyl group, rather than an accurate general description of alkene expulsion from onium ions.

The inadequacy of the traditional mechanism is exposed most clearly by examining the behaviour of onium ions in which an n-alkyl group larger than ethyl is attached to the heteroatom. Such ions do not expel alkenes derived exclusively by β-hydrogen transfer from the alkyl group to the heteroatom.

Table 2 Collision-induced dissociation mass spectra of $C_3H_7O^+$ ions[a] (structure and/or origin of ion given at top of column)

m/z	$CH_3CH_2{}^+O{=}CH_2$ (**5**) from $CH_3CH_2OCH_2CH_3$ RI[b]	C_2H_4 loss from $CH_3CH_2CH{=}O^+CH_2CH_3$ RI[b]	$CH_3CH_2CH{=}OH^+$ (**6**) from $(CH_3CH_2)_2CHOH$ RI[b]	C_2H_4 loss from $(CH_3)_2C{=}O^+CH_2CH_3$ RI[b]	$(CH_3)_2C{=}OH^+$ (**8**) from $(CH_3)_3COH$ RI[b]
58	7.3	14	27	55	47
57	14	53	63	11	11
56	0.1	0.8	1.2	<0.1	<0.1
55	1.0	6.5	7.6	3.2	2.9
53	0.4	2.2	2.7	1.7	1.7
44	5.2	7.4	8.4	7.0	6.7
43	8.7	30	31	100	100
42	3.9	14	14	27	26
41	(290)	(193)	(333)	(80)	(129)
40	1.5	4.9	6.3	5.7	5.5
39	10.5	42	46	40	41
38	3.7	13	15	13	13
37	2.6	11	11	7.8	8.2
36	0.4	3.1	2.1	1.6	1.4
31	(480)	(386)	(403)	(123)	(219)
30	15	16	17	1.2	1.6
29	100	100	100	22	26
28	22	23	22	2.8	3.3
27	49	68	68	16	19
26	17	33	30	7.0	8.2
25	3.0	8.3	6.4	1.7	2.1
24	0.6	2.2	1.4	0.4	0.3
15	7.0	17	18	10	14
14	4.7	8.6	7.6	2.6	4.0
13	1.4	3.7	2.8	0.6	0.8
12	0.6	2.3	1.4	0.1	0.2

[a] Helium collision gas; 60% attenuation of initial $C_3H_7O^+$ ion signal. [b] RI = Relative Intensities; these values were normalised to a value of 100 units for the most intense peak containing no component arising from dissociation of parent ions which were not energised by collision; values in parentheses contain contributions from dissociation of ions which were not energised by collision.

Table 3 Ethylene losses from $C_5H_nD_{11-n}O^+$ ions

	Neutral species lost							
	C_2H_4		C_2H_3D		$C_2H_2D_2$		C_2HD_3	
Ion structure	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]
$CH_3CD_2CD{=}O^+CH_2CH_3$	>99	1.81	<0.2		<0.2			
$CH_3CH_2CH{=}O^+CH_2CD_3$			<0.2		92	2.0	8	1.97
$(CD_3)_2C{=}O^+CH_2CH_3$	>99	1.89	<0.1					
$(CH_3)_2C{=}O^+CH_2CD_3$			<0.2		95	1.89	5	1.88

[a] These RAs were normalised to a total metastable ion current of 100 units for ethylene losses; other reactions (water and propene losses) account for only 1–2% of the ion current arising from ethylene elimination. [b] See footnote to Table 1.

Substantial amounts of α-, γ-, δ- (and ε-) hydrogen transfer also accompany butene and pentene elimination from ions containing n-butyl or n-pentyl substituents.[21–23] This deviation from the site-specificity predicted by eqn. (1) occurs both for fast reactions in the ion source[21–22] and for the dissociation of metastable ions of long lifetimes and low internal energies.[23]

In contrast to the inadequacy of the traditional explanation for these alkene eliminations, a mechanism involving INCs can provide a unifying and general description of the site-selectivity in the hydrogen transfer step.[12d] In systems for which the hydrogen transfer is unidirectional, specific β-hydrogen transfer appears to be associated with INCs containing an incipient cation that is stable with respect to isomers accessible by 1,2-H or 1,2-alkyl shifts. For instance, $(CD_3)_2CH^+N(CH_3){=}CH_2$ expels exclusively (>99%) C_3HD_5 *via* β-deuterium transfer.[24] On the other hand, if the incipient cation is not stable to 1,2-H or 1,2-alkyl shifts, rearrangement of the cation occurs, followed by hydrogen transfer to the heteroatom from sites other than the initial β-position. Thus, $CH_3CH_2CD_2{}^+N(CH_3){=}CH_2$ and $CD_3CH_2CH_2{}^+N(CH_3){=}CH_2$ undergo sizeable amounts (36% and 41%, respectively) of apparent α- and γ-deuterium transfer.[24] These contributions can be interpreted given irreversible rearrangement of the original n-propyl cation to the thermodynamically more stable isopropyl isomer, followed by specific β-hydrogen transfer from the isomerised cation ($[CH_3CH^+CHD_2]$ from $[CH_3CH_2CD_2{}^+]$ or $[CD_3CH^+CH_3]$ from $[CD_3CH_2CH_2{}^+]$, respectively) within INCs.[15] The behaviour of $CH_3CD_2CH_2{}^+N(CH_3){=}CH_2$ is especially illuminating. According to the traditional explanation, specific C_3H_5D loss should be found in propene elimination from this ion. However, C_3H_5D expulsion (18%) is actually of much lower abundance than $C_3H_4D_2$ loss (82%).[24] This discrimination against β-deuterium transfer in $CH_3CD_2CH_2{}^+N(CH_3){=}CH_2$ is expected if the mechanism involving INCs operates because $[CH_3CD_2CH_2{}^+]$ should isomerise to $[CH_3CD^+CH_2D]$, from which β-protium transfer is *ca.* five times more probable than β-deuterium transfer.

Ethylene loss from an ethyl substituent is a special case since a classical ethyl cation is the only n-$C_nH_{2n+1}{}^+$ species ($n \geqslant 2$) that is stable with respect to any 1,2-H or 1,2-alkyl shifts. A 1,2-H shift in $CH_3CH_2{}^+$ results in a degenerate rearrangement

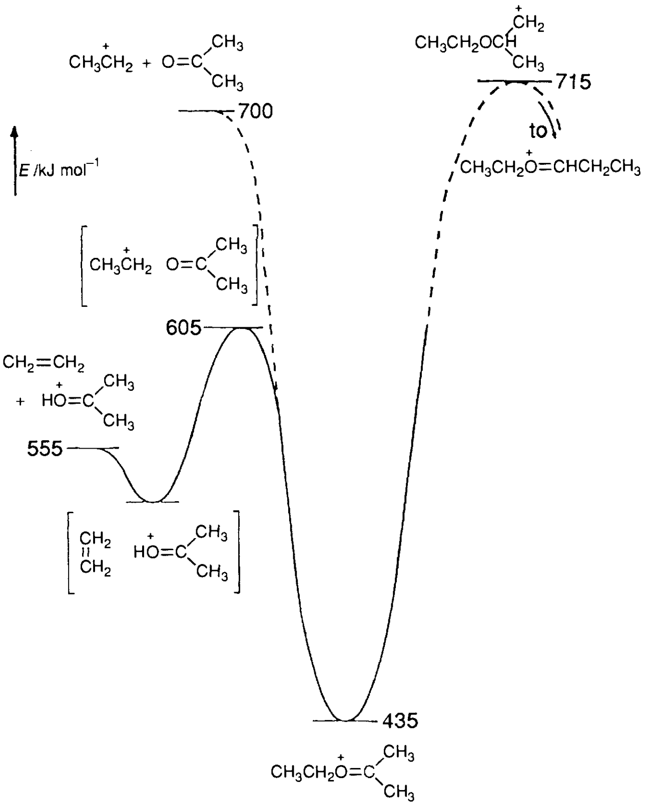


Fig. 2 Potential energy profile for isomerisation and dissociation of $(CH_3)_2C{=}O^+CH_2CH_3$

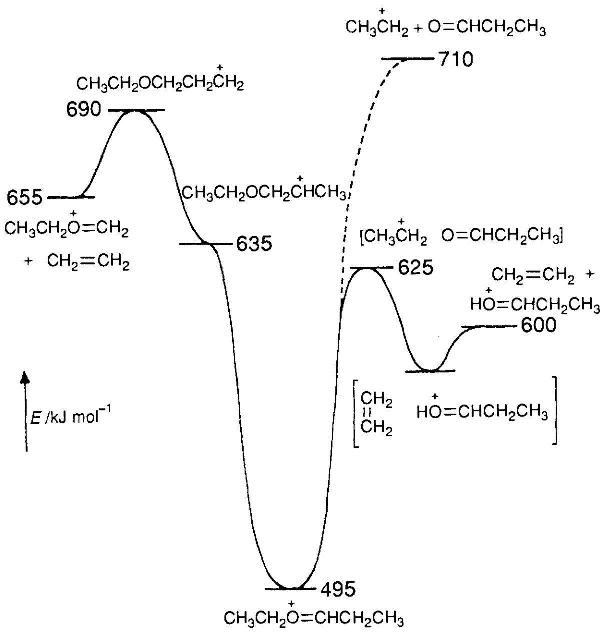


Fig. 1 Potential energy profile for isomerisation and dissociation of $CH_3CH_2CH{=}O^+CH_2CH_3$

to ${}^+CH_2CH_3$. According to MO calculations, these classical ethyl cations are marginally less stable than the bridged, non-classical structure $[\overline{CH_2CH_2\text{-}H}^+]$.[25] Therefore, in the case of $CH_3CH_2CH{=}O^+CH_2CD_3$ and $(CH_3)_2C{=}O^+CH_2CD_3$, the predominant β-D-transfer can be taken to reflect the ease of isomerisation of ${}^+CH_2CD_3$ to the slightly more stable species, $\overline{CH_2CD_2\text{-}D}^+$. The bridging deuteron originates from the β-position, and it is this deuteron that is ideally located for transfer to oxygen *via* the steps corresponding to **1** ⟶ **1a** ⟶ **1b** ⟶ **1c** ⟶ products. The small quantity of apparent α-protium transfer is explained by assuming that limited interconversion of classical and non-classical forms of $C_2H_2D_3^+$ precedes hydrogen transfer. Alternatively, the data can be interpreted by assuming that a classical ethyl cation (${}^+CH_2CD_3$) exists in the INC, and that specific β-hydrogen transfer takes place more rapidly than 1,2-hydride and deuteride shifts occur within the cation (${}^+CH_2CD_3 \rightleftharpoons CH_2DCD_2{}^+$, *etc.*).

In the main, though not quite exclusively, the reorganisation steps which result in hydrogen transfer in **1** and **2** are unidirectional. This phenomenon is not unexpected, given the much greater proton affinities (PAs) (793 and 823 kJ mol⁻¹, respectively)[26] of propionaldehyde and acetone, compared to that (680[26] kJ mol⁻¹) of ethylene.[27]

Reactions of $C_3H_mD_{7-m}O^+$ Ions Formed by Ethylene Losses from $C_5H_nD_{11-n}O^+$ Ions.—The slow dissociations of $C_3H_mD_{7-m}O^+$ ions produced by ethylene expulsion from ²H-labelled analogues of **1** and **2** are shown in Table 4. These data are very similar to those pertaining to the decomposition of the appropriately labelled analogues of protonated propionaldehyde and protonated acetone. Thus, the behaviour of $C_3H_4D_3O^+$ formed by C_2H_4 loss from $CH_3CD_2CD{=}O^+CH_2CH_3$ closely resembles that of $CH_3CD_2CD{=}OH^+$ generated directly from $(CH_3CD_2)_2CDOH$. The reactions of $C_3HD_6O^+$ formed from $(CD_3)_2C{=}O^+CH_2CH_3$ likewise show a strong resemblance to those of $(CD_3)_2C{=}OH^+$ produced from $(CD_3)_2C(C_2H_5)OH$. These results are further evidence that C_2H_4 elimination from **1** and **2** proceeds *via* INC-mediated routes.

There are slight discrepancies between the behaviour of $CH_3CD_2CD{=}OH^+$ (**6**-1,2,2-²H₃) generated directly or by C_2H_4 expulsion from $CH_3CD_2CD{=}O^+CH_2CH_3$. These deviations, which are certainly statistically significant (especially the variation in the $T_{\frac{1}{2}}$ values for loss of the partly deuteriated ethylenes), probably reflect minor differences in the energy distributions of the dissociating population of $C_3H_4D_3O^+$ ions.[28] It is known that elimination of C_2H_4 from **6** requires more energy than does expulsion of H_2O.[16] The energetic discrimination against C_2H_4 loss is shown by the progressive reduction in the relative abundance of this process as the average internal energy of the decomposing $C_3H_7O^+$ ions is diminished.[28] Therefore, the somewhat higher overall percentage of water [$\Sigma RA(H_nD_{2-n}O)$] expelled from $CH_3CD_2CD{=}OH^+$ generated directly, compared to that for $CH_3CD_2CD{=}OH^+$ formed by C_2H_4 elimination from $CH_3CD_2CD{=}O^+CH_2CH_3$, is explained by supposing that the former population of ions have a smaller average internal energy. Similarly, the diminished $T_{\frac{1}{2}}$ values for loss of partly deuteriated ethylenes from the former class of ions is also rationalised on the assumption that these ions have a lower energy, thus reducing the kinetic energy release accompanying dissociation. These $T_{\frac{1}{2}}$ values are usually particularly sensitive to the excess energy present in the final dissociation step.[4] The same trend (larger $T_{\frac{1}{2}}$ values for loss of the more heavily-deuteriated ethylenes, which require a greater number of isomerisation steps) is found for both classes of $C_3H_4D_3O^+$ ions. A similar effect, though in the opposite direction (larger $T_{\frac{1}{2}}$ value for C_2H_4 elimination, which here necessitates more rearrangement than C_2H_3D expulsion) is observed for ethylene loss from $CH_3CH_2CH{=}OD^+$ formed from $CH_3CH_2CH{=}O^+CH_2CD_3$ by $C_2H_2D_2$ elimination. Consequently, two distinct trends are discernible in these $T_{\frac{1}{2}}$ values. First, increased $T_{\frac{1}{2}}$ values accompany ethylene expulsion from $C_3H_mD_{7-m}O^+$ ions of slightly higher internal energy formed by initial ethylene loss from the ²H-labelled analogues of **1**. Secondly, regardless of the origin of the ion, larger $T_{\frac{1}{2}}$ values are found for ethylene losses from $C_3H_mD_{7-m}O^+$ ions in cases

Table 4 Reactions of metastable $C_3H_mD_{7-m}O^+$ (neutral species lost given at column head)

Ion structure and/or origin	H_2O		HOD		D_2O		$H_nD_{2-n}O$	C_2H_4		C_2H_3D		$C_2H_2D_2$		C_2HD_3		C_2D_4		$C_2H_nD_{4-n}$
	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	ΣRA[a,c]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	RA[a]	$T_{\frac{1}{2}}$[b]	ΣRA[a,d]
$CH_3CD_2CD{=}OH^+$ from $(CH_3CD_2)_2CDOH$	53.1	2.1	34.3	2.1	3.3	2.2	90.7	0.3	1.0	3.1	1.1	4.8	1.3	1.2	1.6			9.3
$C_3H_4D_3O^+$ from $CH_3CD_2CD{=}O^+CH_2CH_3$	52.0	2.1	33.0	2.1	2.9	2.1	87.9	0.3	1.1	3.7	1.3	6.4	1.7	1.7	2.1			12.1
$C_3H_6DO^+$ from $CH_3CH_2CH{=}O^+CH_2CD_3$	32.8	2.4	59.6	2.1			92.4	5.5	1.8	2.1	1.4							7.6
$(CD_3)_2C{=}OH^+$ from $(CD_3)_2C(C_2H_5)OH$			28.1	2.6	2.2	2.4	30.3							26.3	1.5	43.4	1.6	69.7
$C_3HD_6O^+$ from $(CD_3)_2C{=}O^+CH_2CH_3$			30.3	2.7	2.4	2.4	32.7							25.3	1.5	42.0	1.7	67.3
$C_3H_6DO^+$ from $(CD_3)_2C{=}O^+CH_2CH_3$	5.2	2.3	37.5	2.6			42.7	40.6	1.9	16.7	1.5							57.3

[a,b] See footnotes to Table 1. [c] Total relative abundance of water (H_2O, HOD and D_2O) losses. [d] Total relative abundances of ethylene (C_2H_4, C_2H_3D, $C_2H_2D_2$, C_2HD_3 and C_2D_4) losses.

in which extensive rearrangement is involved, especially if exchange of a deuterium atom originally attached to oxygen is required.

Parallel, but much less pronounced trends, are seen in the reactions of ^2H-labelled protonated acetones generated directly or *via* ethylene loss from labelled variants of **2**. This phenomenon is consistent with the previous hypothesis[19] that the rate-determining step in both H_2O and C_2H_4 eliminations from **8** is rearrangement to **6**, which then decomposes with increased excess energy in the transition states for the final steps. The effects induced by variations in the initial energy distributions of labelled analogues of **8** are, therefore, diminished. Moreover, the labelled analogues of **8** invariably expel far more ethylene [$\Sigma RA(C_2H_nD_{4-n})$] than is observed for the counterparts of **6**, as would be expected given that ethylene elimination from **6** is favoured for ions of higher internal energy.[28]

Potential Energy Profiles for C_2H_4 *Loss from* **1** *and* **2**.—The routes for C_2H_4 loss from **1** and **2** are summarised by the potential energy profiles (PEPs)[1] of Figs. 1 and 2, respectively. These PEPs are constructed from known[26,29–32] or estimated[33–36] enthalpies of formation of the reactants, intermediates and products. There remains some uncertainty (± 10–20 kJ mol^{-1}) about the values of several of the energy levels in these PEPs and also in the precise details of the geometries of the INCs **1a**, **2a**, **1c** and **2c**, and the related proton-bridged complexes (PBCs) **1b** and **2b**.

It is becoming recognised that a distinctive property of a true INC (*i.e.*, a genuine intermediate, as opposed to a transient species) is the ability of the constituent partners to undergo mutual rotation (the so-called Longevialle criterion).[37] Unfortunately, it is not always possible to demonstrate that this criterion is satisfied. In the present system, the hydrogen transfer steps (**1a** $\longrightarrow$ **1c** and **2a** $\longrightarrow$ **2c**) are almost certainly unidirectional because of the large differences between the PAs of ethylene and propionaldehyde or acetone. The exoergic nature of the hydrogen transfer step results in dissociation of **1c** and **2c** with an appreciable excess energy in the transition state for the final step.[38] In such circumstances, a moderate KE release accompanies fragmentation (the $T_{\frac{1}{2}}$ values of 1.8–2.0 kJ mol^{-1} found for ethylene loss from ions generated as **1** or **2** are typical of what would be expected in this situation). If **1a** and **1c** (or **2a** and **2c**) were of closely comparable energy, interconversion of the pair(s) of INCs would occur prior to fragmentation. In these circumstances, only a very small KE release ($T_{\frac{1}{2}} < 0.2$ kJ mol^{-1}) usually is associated with dissociation.

Similarly, although MO calculations suggest strongly that PBCs corresponding to **1b** and **2b** sometimes occupy distinct energy wells (*e.g.*, $C_2H_4{\cdot}H^+{\cdot}OH_2$ in the $CH_3CH_2OH_2^+$ system),[39] it is improbable that this possibility is realised in this case. The difference in the PAs of ethylene and propionaldehyde or acetone is so great that the proton is likely to be much more closely bound to the C_3H_6O component than to the C_2H_4 molecule. Thus, **1b** and **2b** are probably transition states for rearrangement of **1a** to **1c** and **2a** to **2c**, respectively.

Despite the uncertainty concerning the precise values of some of the energy levels in Fig. 1, there is no doubt that the critical[40] energies associated with INC-mediated elimination of C_2H_4 from **1** and **2** are appreciably lower (by *ca.* 65–110 kJ mol^{-1}, respectively) than those relating to the 'conventional' routes. In addition, substitution of a larger and more stable incipient alkyl cation for the $C_2H_5^+$ species in the initial INCs **1a** and **2a** should further reduce the height of the barrier to these INC-mediated processes. This homologation should, therefore, enhance the already substantial energetic factors that favour INC-mediated alkene losses from such onion ions.

Conclusions

Loss of C_2H_4 from **1** and **2** proceeds *via* INC-mediated mechanisms with formation of **6** and **8** as the respective product ions. 'Conventional' routes for C_2H_4 elimination from **1** and **2** are pre-empted by the energetically more favourable alternatives involving INCs. The contrast between the behaviour of $CH_3CH_2CH{=}OR^+$ and $(CH_3)_2C{=}OR^+$ (R = H, CH_3), all of which eliminate C_2H_4 *via* 'conventional' routes, and the chemistry of **1** and **2** is striking. This contrast reflects the ease of INC-mediated C_2H_4 loss from **1** and **2**; no such possibility is open to $CH_3CH_2CH{=}OR^+$ and $(CH_3)_2C{=}OR^+$ (R = H, CH_3).

The mechanistic and energetic considerations that favour the INC-mediated routes over their 'conventional' alternatives ought to be general in scope. Consequently, expulsion of C_2H_4 from 'onium' ions containing the $Z^+C_2H_5$ entity should normally dominate or preclude 'conventional' mechanisms for dissociation of these ubiquitous ions. Moreover, elimination of higher alkenes (C_nH_{2n}) from homologous ions containing a larger alkyl group (C_nH_{2n+1}, $n > 2$) than ethyl ought to be even more facile than C_2H_4 loss from an ethyl substituent. Thus, the 'conventional' routes for alkene elimination from 'onium' ions are likely to be pre-empted in most or all cases where an ethyl or larger C_nH_{2n+1} alkyl group is attached to the heteroatom.

Experimental

The alcohols and ethers required in this work were synthesised *via* standard procedures, as illustrated in Scheme 2; further details are available on request. The levels of deuterium incorporation of the specifically labelled compounds were typically 95–99%. The routes by which the desired oxonium ions were generated by ionisation and fragmentation of the appropriate compounds are shown in Scheme 3.

$$(C_2H_5)_2CHOH \xrightarrow{\text{i,ii}} (C_2H_5)_2CHOC_2H_5$$

$$(CH_3)_2C(C_2H_5)OH \xrightarrow{\text{i,ii}} (CH_3)_2C(C_2H_5)OC_2H_5$$

$$(C_2H_5)_2CO \xrightarrow{\text{iii}} (CH_3CD_2)_2CO \xrightarrow{\text{iv}} (CH_3CD_2)_2CDOH$$

$$\xrightarrow{\text{i,ii}} (CH_3CD_2)_2CDOC_2H_5$$

$$(CD_3)_2CO \xrightarrow{\text{v}} (CD_3)_2C(C_2H_5)OH \xrightarrow{\text{i,ii}} (CD_3)_2C(C_2H_5)OC_2H_5$$

$$CD_3CO_2D \xrightarrow{\text{vi}} CD_3COCl \xrightarrow{\text{vii,viii}} CD_3CH_2OH \xrightarrow{\text{ix}} CD_3CH_2I$$

$$(C_2H_5)_2CHOH \xrightarrow{\text{i,x}} (C_2H_5)_2CHOCH_2CD_3$$

$$(CH_3)_2C(C_2H_5)OH \xrightarrow{\text{i,x}} (CH_3)_2C(C_2H_5)OCH_2CD_3$$

Scheme 2 i, NaH, triglyme {triethylene glycol, dimethyl ether [$CH_3O(CH_2CH_2O)_3CH_3$]}; ii, C_2H_5I, stir 24–48 h; iii, 10% NaOD in D_2O, $(C_4H_9)_4N^+Br^-$; repeat four times; (iv) $LiAlD_4$, $(C_2H_5)_2O$; v, C_2H_5MgI, $(C_2H_5)_2O$; saturated aq. $NH_4{}^+Cl^-$; vi, C_6H_5COCl, distil.; vii, $LiAlH_4$, triglyme; viii, Tetragol, {tetraethylene glycol [$HO(CH_2CH_2O)_4H$]}, distil.; ix, Red P, I_2; x, CD_3CH_2I, stir 24–48 h

$$(C_2H_5)_2CHOH \xrightarrow{\text{i,ii}} CH_3CH_2CH{=}OH^+$$

$$(CH_3)_2C(C_2H_5)OH \xrightarrow{\text{i,ii}} (CH_3)_2C{=}OH^+$$

$$(CH_3CH_2)_2O \xrightarrow{\text{i,iii}} CH_3CH_2{}^+O{=}CH_2$$

$$(C_2H_5)_2CHOC_2H_5 \xrightarrow{\text{i,ii}} CH_3CH_2CH{=}O^+CH_2CH_3$$

$$(CH_3)_2C(C_2H_5)OC_2H_5 \xrightarrow{\text{i,ii}} (CH_3)_2C{=}O^+CH_2CH_3$$

$$(CH_3CD_2)_2CDOH \xrightarrow{\text{i,iv}} CH_3CD_2CD{=}OH^+$$

$$(CD_3)_2C(C_2H_5)OH \xrightarrow{\text{i,ii}} (CD_3)_2C{=}OH^+$$

$$(CH_3CD_2)_2CDOC_2H_5 \xrightarrow{\text{i,iv}} CH_3CD_2CD{=}O^+CH_2CH_3$$

$$(CD_3)_2C(C_2H_5)OC_2H_5 \xrightarrow{\text{i,ii}} (CD_3)_2C{=}O^+CH_2CH_3$$

$$(C_2H_5)_2CHOCH_2CD_3 \xrightarrow{\text{i,ii}} CH_3CH_2CH{=}O^+CH_2CD_3$$

$$(CH_3)_2C(C_2H_5)OCH_2CD_3 \xrightarrow{\text{i,ii}} (CH_3)_2C{=}O^+CH_2CD_3$$

Scheme 3 Ionisation and fragmentation i, $-e$; ii, $-C_2H_5{}^{\bullet}$; iii, $-CH_3{}^{\bullet}$; iv, $-CH_3CD_2{}^{\bullet}$

The mass spectra were recorded on a research mass spectrometer (MMM) of unusually large dimensions.[41] Typical parameters were: source pressure, 1–2 × 10^{-6} Torr; accelerating voltage, 8066–8075 V; ionising electron energy, 70 eV. The relative abundances of the fragmentations of the ions of interest were measured from the product ion counts in the MIKES[4,42] spectra of metastable ions that dissociated in the second field-free region. The MIKES spectra were acquired by repetitive microcomputer-controlled sweeping of the electric sector voltage over the range of voltages required to transmit the appropriate product ions. The quoted spectra represent the integrated data of 100–250 separate scans. Kinetic energy release data were estimated from the width at half-height of the requisite metastable peaks; a one line formula[4,42] was utilized in these calculations, after the usual correction for the width of the main beam had been applied.[43] The CID spectra were also acquired by means of the MIKES technique, after sufficient helium had been admitted to the collision cell to cause attenuation of the parent ion signal by 60% of its initial value. The CID spectra correspond to the integrated data of 20–50 individual scans.

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