The Mechanism of Water Loss from the Oxonium Ions $CH_3CH_2CH_2{}^+O{=}CH_2$ and $(CH_3)_2CH^+O{=}CH_2$

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Extensive new ^2H-labelling results are reported, which pertain to the mechanism of water expulsion from metastable $CH_3CH_2CH_2{}^+O{=}CH_2$ and $(CH_3)_2CH^+O{=}CH_2$ ions. Detailed mechanisms, involving ion–neutral complexes comprising incipient propyl cations coordinated to formaldehyde, propene attached to protonated formaldehyde, or propene and formaldehyde attached to a common proton, are discussed in the light of the labelling data. Loss of positional integrity of the hydrogen and deuterium atoms within the original propyl groups occurs; it is proposed that this takes place *via* interconversion of the ion–neutral complexes. The crucial step in water elimination appears to be irreversible reorganization of the proton-bound complex (or an ion–neutral complex of protonated formaldehyde and propene) to the open-chain carbonium ion $CH_3{}^+CHCH_2CH_2OH$.

The chemistry of isolated organic ions can be conveniently investigated by observing the behaviour of the appropriate metastable ions using a mass spectrometer.[1,2] Metastable ions are long-lived species, which typically have only just enough energy to dissociate within the 10–100 μs timeframe. Under these circumstances, the average internal energy in the transition state for decomposition is usually small and comparable to that found in solution experiments.[3] The critical[4] energy (corresponding in a conceptual sense to the activation energy in solution) associated with a particular process is normally a crucial parameter in influencing whether a given reaction of a metastable ion will occur.[5] This is illustrated by the frequent intervention of isotope effects in the reactions of metastable ions.[6] In addition, metastable ions show a pronounced tendency to undergo rearrangement reactions which lead to the formation of the energetically most favourable products, even when these processes must entail extensive isomerization of the original structure. Thus, for example, many $C_nH_{2n+1}O^+$ oxonium ions such as $C_2H_5{}^+O{=}CH_2$,[7–10] $C_3H_7{}^+O{=}CH_2$[11] and $C_4H_9{}^+O{=}CHCH_3$[12,13] eliminate H_2O in slow reactions.

It has been proposed that the mechanism by which oxonium ions of this general structure expel H_2O involves ion–neutral complexes (INCs).[13] These INCs were originally postulated in even-electron systems in order to interpret the rearrangement reactions that took place in metastable ions containing an incipient carbocation.[14] For instance, the isomeric $C_4H_9O^+$ ions $CH_3CH_2CH_2{}^+O{=}CH_2$ and $(CH_3)_2CH^+O{=}CH_2$ have very similar chemistries; this can be explained in terms of interconversion of these ions *via* $[C_3H_7{}^+ \text{ - - - } OCH_2]$, or related species, at energies below those required to promote dissociation.[15,16] Parallel mechanisms have been put forward in a wide variety of analogous systems, both for even- and odd-electron ions.[17–39] The general relevance of INCs has been emphasized in recent reviews,[40,41] and by the attention that these species are currently receiving. In particular, it has been shown that formation of protonated methanol from ^2H-labelled analogues of $CH_3O^+HC_3H_7$ is consistent with the involvement of INCs comprising a propyl cation attached to methanol, and of propene and methanol bound to a common proton.[42,43] In view of these developments, a detailed ^2H-labelling study of the mechanism of water loss from $C_3H_7{}^+O{=}CH_2$ ions is timely.

Results and Discussion

The relative abundances and kinetic energy release data for water losses from partly ^2H-labelled analogues of $CH_3CH_2CH_2{}^+O{=}CH_2$ (**1**) and $(CH_3)_2CH^+O{=}CH_2$ (**2**), generated by ionization and alkyl radical loss from suitably labelled ethers, are given in Table 1.

Besides eliminating water, these ions also undergo a minor amount (*ca.* 5–12%) of formaldehyde loss. In agreement with earlier work,[11] this subsidiary reaction was found to involve only the original formaldehyde entity of **1** and **2** and to proceed with a very small kinetic energy release ($T \lesssim 0.2$ kJ mol^{-1}).[16] The specificity of formaldehyde loss from ^2H-labelled analogues of **1** and **2** supports the interpretation that these oxonium ions are formed by direct cleavage of the ionized ethers. Any exchange of hydrogen and deuterium atoms before production of ^2H-labelled analogues of **1** and **2** would erode the positional integrity of the formaldehyde moiety of these ions in at least some cases. Similarly, the specific loss of the original formaldehyde entity of ^2H-labelled versions of **1** and **2** attests to the high level of deuterium incorporation in these species. Any significant contribution from ^{13}C-isotope satellite signals of peaks containing less than the desired level of deuterium incorporation (*e.g.*, $C_3{}^{13}CH_8DO^+$, instead of $C_4H_7D_2O^+$) would lead to an appreciable amount of $^{13}CH_2O$ elimination from the ions in which a ^{13}C atom was present. The quantity of $^{13}CH_2O$ lost from the oxonium ions studied in this work was too small to be detected. Moreover, the conventional electron ionization mass spectra of the ^2H-labelled ethers were consistent both with specific fragmentation to give the desired $C_4H_{9-n}D_nO^+$ ions and with an extremely high level (typically >95% D_3 for $C_4H_6D_3O^+$ precursors, with comparable or superior percentages for D_2 and D_1 species) of deuterium incorporation.

Neither the relative abundance of formaldehyde loss nor the associated kinetic energy release show more than a marginal variation upon deuteriation. All these results are in accord with the general mechanism that has previously been advanced for this reaction, Scheme 1.[14–16] Interconversion of **1** and **2**, *via* the INCs **1a** and **2a**, and/or the related proton-bound complex (PBC) **3**, allows ions generated as **1** and **2** to reach common

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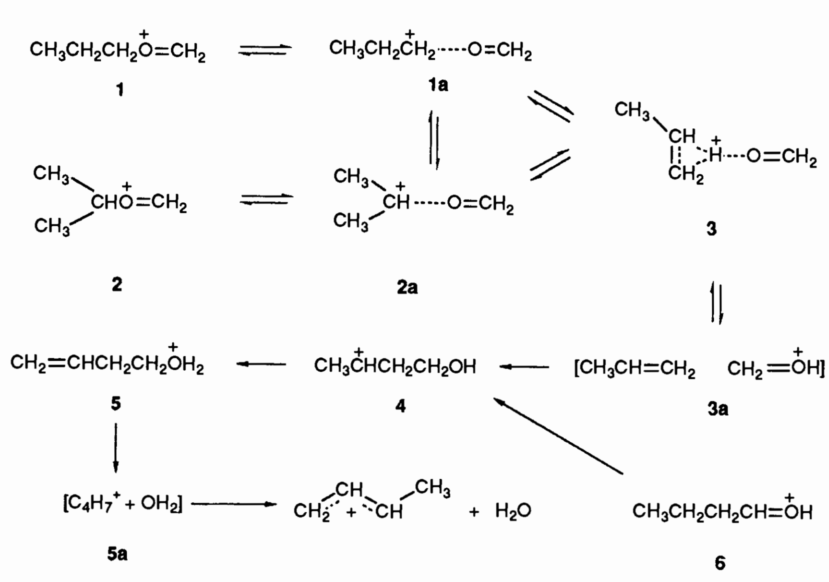
Table 1 Observed and expected water losses from ^2H-labelled analogues of **1** and **2**

			Relative abundance					
				Expected from model				
Ion	Neutral lost	$T_{\frac{1}{2}}$[a]	Found[b]	A	B	C	D	M
$CH_3CH_2CHD\overset{+}{O}{=}CH_2$	H_2O	1.63	72	78	71	67	67	75
	HOD	1.61	28	22	29	33	33	25
$CH_3CH_2CH_2\overset{+}{O}{=}CD_2$	H_2O		100[c]	58	100	100	100	100
	HOD		0[c]	39	0	0	0	0
	D_2O		0[c]	3	0	0	0	0
$CH_3CH_2CD_2\overset{+}{O}{=}CH_2$	H_2O	1.69	46	58	48	33	39	44
	HOD	1.60	51	39	48	67	55	53
	D_2O	1.63	3	3	4	0	6	3
$CH_3CD_2CH_2\overset{+}{O}{=}CH_2$	H_2O	1.71	53	58	48	67	67	53
	HOD	1.71	44	39	48	33	33	44
	D_2O	1.70	3	3	4	0	0	3
$CD_3CH_2CH_2\overset{+}{O}{=}CH_2$	H_2O	1.71	23	42	29	0	17	21
	HOD	1.65	67	50	57	100	67	68
	D_2O	1.70	10	8	14	0	17	11
$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CD\overset{+}{O}{=}CH_2$	H_2O	1.69	78	78	71	100	100	75
	HOD	1.73	22	22	29	0	0	25
$\genfrac{}{}{0pt}{}{CH_3}{CH_3}{>}CH\overset{+}{O}{=}CD_2$	H_2O		100[c]	58	100	100	100	100
	HOD		0[c]	39	0	0	0	0
	D_2O		0[c]	3	0	0	0	0
$\genfrac{}{}{0pt}{}{CH_3}{CD_3}{>}CH\overset{+}{O}{=}CH_2$	H_2O	1.64	23	42	29	0	17	21
	HOD	1.64	67	50	57	100	67	68
	D_2O	1.69	10	8	14	0	17	11
$\genfrac{}{}{0pt}{}{CD_3}{CD_3}{>}CH\overset{+}{O}{=}CH_2$	H_2O		0	8	0	0	0	0
	HOD	1.67	25	50	29	0	0	25
	D_2O	1.68	75	42	71	100	100	75
$\genfrac{}{}{0pt}{}{CD_3}{CD_3}{>}CD\overset{+}{O}{=}CH_2$	H_2O		0[c]	3	0	0	0	0
	HOD		0[c]	39	0	0	0	0
	D_2O		100[c]	58	100	100	100	100

[a] Kinetic energy release measured from the width at half-height of the associated metastable peak; values quoted in kJ mol^{-1}. [b] Relative abundances measured from metastable peak areas for ions dissociating in the second field-free region and normalized to a total metastable ion current of 100 units for water loss. [c] Data from ref. 11.



Scheme 1 (Model B)

transition states, whilst conserving the identity of the original formaldehyde moiety. The geometry of the PBC **3** may be such that this species closely resembles an INC comprising propene and protonated formaldehyde. Such a possibility does not, however, materially alter the mechanistic interpretation of the ^2H-labelling results.

The situation regarding water loss is somewhat more complicated. It is evident that extensive interchange of the hydrogen and deuterium atoms in the initial $C_4H_{9-n}D_nO^+$ ions must precede water elimination. Table 1 gives the ratios of H_2O, HOD and D_2O losses which would be expected to occur from ^2H-labelled analogues of **1** and **2** on the basis of four different models.

In model A the hydrogen and deuterium atoms are selected at random from any of the nine of those in the $C_4H_{9-n}D_nO^+$ ion. Model B assumes that only the seven hydrogens and deuteria in the propyl group participate randomly in water loss. This corresponds to rapid equilibration of **1**, **2** and **3**, followed by irreversible reorganization of **3** to **4**, *via* **3a**. Water loss then takes place by a [1,5]-H-shift (**4** ⟶ **5**) and cleavage of the resultant protonated alcohol. The final step must involve a [1,2]-H-shift in the developing homoallyl cation, possibly within an INC comprising $C_4H_7^+$ and H_2O. The third model, C, assumes that the steps **1** ⟶ **1a** ⟶ **3** and **2a** ⟶ **3** are essentially irreversible. Model D is a variant of C in which the step **4** ⟶ **5** is partially reversible and each ion **5** reverts once to **4** before returning to **5** and dissociating. Models C and D allow for varying degrees of exchange of the hydrogen and deuterium atoms to take place after the key isomerization step **3** ⟶ **3a** ⟶ **4** has occurred. It is important to consider these models because the behaviour of ^{2}H-labelled analogues of **6** reveals that water loss from these ions takes place after partial exchange of the hydroxylic hydrogen with those of the methyl group.[11] This indicates that when **4** is formed from **6**, the subsequent step **4** ⟶ **5** is not irreversible, presumably because the ions have low internal energies.

Comparisons of the expected and observed ratios of H_2O, HOD and D_2O losses reveals that model A is clearly inadequate: the hydrogens in the initial formaldehyde entity are not selected in the eliminated molecule of water. Similarly, models C and D cannot account for certain features of the data, especially the appreciable participation of the methine hydrogen in **2** in water expulsion. Thus, $(CH_3)_2CD^+O{=}CH_2$ loses 22% HOD and $(CD_3)_2CH^+O{=}CH_2$ eliminates 25% HOD. Similarly, models C and D cannot account for the small percentage of D_2O loss which occurs from $CH_3CD_2CH_2^+O{=}CH_2$. Model B, in contrast, does explain these facts and it also provides a reasonable approximation to the observed behaviour of all the ^{2}H-labelled analogues of **1** and **2**. It is likely, therefore, that the processes which result in exchange of the hydrogen and deuterium atoms occur before rearrangement of **3** to **4**.

The steps (**1a**/**2a** ⇌ **3**) which lead to loss of positional integrity of the hydrogens in the original propyl groups of **1** and **2** should occur relatively readily, since propene and formaldehyde have proton affinities that differ by only 25 kJ mol^{-1}.[44] In contrast, in systems in which the incipient neutral species in the PBC (or corresponding pairs of INCs) have proton affinities that differ by more than *ca.* 50 kJ mol^{-1}, little or no hydrogen exchange precedes fragmentation. Thus, $C_2H_5OH_2^+$ dissociates after considerable interchange of the carbon- and oxygen-bound hydrogen atoms, iso-$C_3H_7OH_2^+$ shows only a small amount of exchange, and protonated alkylamines undergo essentially no exchange.[33] Similarly, the nitrogen analogues of **1** and **2** [$CH_3CH_2CH_2^+NH{=}CH_2$ and $(CH_3)_2CH^+NH{=}CH_2$] eliminate C_3H_6 without exchanging the hydrogen atoms of the propyl group with that attached to nitrogen.[19] The variation in the degree of hydrogen interchange in these systems reflects changes in the proton affinities of the neutral species in the corresponding PBCs ([$CH_3CH{=}CH_2{\cdot}H^+{\cdot}X$], X = H_2O, CH_3OH, R^1R^2NH or $CH_2{=}NH$) or pairs of INCs.

Despite the overall success of model B, however, there remain some significant discrepancies between the expected ratios and those found by experiment. For ^{2}H-labelled analogues of **1**, there is a slight discrimination against selecting the β-hydrogen atoms in the eliminated water molecule. Thus, $CH_3CD_2CH_2^+O{=}CH_2$ loses somewhat less HOD and more H_2O than expected. Similarly, there is an apparent preference for picking one hydrogen from each of the two methyl groups in ^{2}H-labelled analogues of **2**. This is shown most clearly by the loss of significantly more HOD from $CH_3(CD_3)CH^+O{=}CH_2$ than is predicted by model B.

Since these trends sometimes involve preferential transfer of deuterium to oxygen, they are not readily rationalized by invoking isotope effects. The discrepancies can, however, be explained by a minor modification of model B in which about one quarter of the complexes **2a** rearrange to **4** *via* **3**, without undergoing hydrogen exchange *via* **2a** ⇌ **1a** ⇌ **3**. This fraction of the ions behave as predicted by model C. A combination of three quarters model B and one quarter model C yields a hybrid model, M, that provides a very close fit to the observed behaviour of the $C_4H_{9-n}D_nO^+$ ions. The average deviation of model M from experiment is less than one percent. One particularly compelling piece of evidence in favour of model M is the close similarity of the ratios of H_2O, HOD and D_2O lost from $CD_3CH_2CH_2^+O{=}CH_2$ and $CH_3(CD_3)CH^+O{=}CH_2$. This is naturally accommodated in terms of isomerization of both ions to the same INC [$CH_3(CD_3)CH^+ \cdots O{=}CH_2$]; consequently, they show very similar deviations from model B.

In actual fact, the distinction between ions which undergo complete hydrogen and deuterium exchange *via* **1a** ⇌ **3** ⇌ **2a**, and those for which **3** ⟶ **4** occurs directly, will not be so clear cut as is depicted by the idealized concept corresponding to model M. Many ions will undergo extensive or complete hydrogen exchange within the propyl group prior to rearrangement to **4**; others will show only limited exchange; a few will isomerize without undergoing the steps that lead to statistical distribution of the hydrogen and deuterium atoms. The net result is an average behaviour which is closely mimicked by model M.

A related model, in which it is assumed that the direct interconversion of **1a** and **2a** takes place relatively slowly compared to the (rapid) rate at which **3** (and possibly **2a**) interconverts with **3a**, does not explain the ^{2}H-labelling data so accurately as is possible using model M. The steps **3** ⇌ **3a** and **2a** ⇌ **3** exchange the hydrogen atoms on the terminal carbon atoms of the C_3H_6 or C_3H_7 moiety. However, the hydrogen atom on the central carbon atom of the C_3H_6 or C_3H_7 unit retains its identity; moreover, this hydrogen cannot become preferentially associated with the oxygen atom of **3** or **3a**. Consequently, this model predicts that $(CH_3)_2CD^+O{=}CH_2$ should eventually isomerize to $CH_3CD^+CH_2CH_2OH$, and therefore expel H_2O with little or no contribution from HOD elimination. This is inconsistent with experiment: $(CH_3)_2CD^+O{=}CH_2$ actually expels HOD (22%) as well as the expected H_2O (78%). Similarly, $(CD_3)_2CH^+O{=}CH_2$, which would be predicted to eliminate solely D_2O on the basis of this model, also loses a significant proportion of HOD (25%). Parallel arguments apply in the case of ^{2}H-labelled analogues of **1**. For example, $CH_3CD_2CH_2^+O{=}CH_2$ should isomerize to [$CH_3(CH_2D)CD^+ \cdots O{=}CH_2$], in which a deuteron is bound to the central carbon atom of the $C_3H_5D_2^+$ ion; therefore, no elimination of D_2O would be anticipated to occur from this ion, but H_2O and HOD losses would be expected in the ratio 67:33. In actual fact, however, $CH_3CD_2CH_2^+O{=}CH_2$ eliminates H_2O, HOD and D_2O in the ratios 53:44:3, respectively.

The inadequacy of this model indicates that at least a sizeable proportion of the ions generated as **1** and **2** must undergo the rearrangement steps **1a** ⇌ **2a**, which leads to loss of positional integrity of the hydrogen atom(s) of the methine group of **2** and the β-methylene group of **1**. This step is an essential feature of the chemistry of **1** and **2**; it may take place directly, or *via* interconversion of **1a** and **2a** with **3** (or **3a**), or by a combination of these processes. Only by postulating interconversion of the incipient n- and iso-propyl cations with each other or a common structure (or structures) is it possible to explain the participation of the methine hydrogen of **2** and both the β-hydrogens of **1** in water elimination.

A final point concerns the kinetic energy release ($T_{\frac{1}{2}}$, measured from the width at half-height of the corresponding metastable peak) which accompanies water loss from **1** and **2**. Any variations in the $T_{\frac{1}{2}}$ values for H_2O, HOD and D_2O losses from a particular ion are so small that they are probably statistically insignificant. All the values lie in the range 1.60–1.73 kJ mol^{-1} with an estimated uncertainty of 0.05 kJ mol^{-1}. These

Route

1 $CH_3CH_2CHO \xrightarrow{\text{i, ii}} CH_3CH_2CHDOH$

2 $(CH_3CH_2CO)_2O \xrightarrow{\text{i, ii}} CH_3CH_2CD_2OH$

3 $CH_3CH_2CHO \xrightarrow{\text{iii}} CH_3CD_2CHO \xrightarrow{\text{iv, ii}} CH_3CD_2CH_2OH$

4 $CD_3I \xrightarrow{\text{v, vi, ii}} CD_3CH_2CH_2OH$

5 $(CH_3)_2CO \xrightarrow{\text{i, ii}} (CH_3)_2CDOH$

6 $(CD_3)_2CO \xrightarrow{\text{iv, ii}} (CD_3)_2CHOH$

7 $CD_3I \xrightarrow{\text{v, vii}} CH_3(CD_3)CHOH$

Scheme 2 *Reagents and conditions:* i, $LiAlD_4$, triglyme $[CH_3O(CH_2CH_2O)_3CH_3]$; ii, tetragol $[HO(CH_2CH_2O)_4H]$; iii, D_2O, pyridine, reflux 24 h, repeat twice; iv, $LiAlH_4$, triglyme; v, Mg, Bu_2O; vi, CH_2CH_2O; vii, $CH_3CH{=}O$

values are substantially greater than that[16] (0.5 kJ mol^{-1}) associated with water elimination from $CH_3CH_2CH_2CH{=}OH^+$. These data support the hypothesis that hydrogen exchange in ^2H-labelled analogues of **1** and **2** precedes rearrangement of **3** to **4** and that the steps **3** ⟶ **4** ⟶ **5** ⟶ products are predominantly irreversible. The rate-determining step in water loss from **1** and **2** is construed to be **3** ⟶ **4**. Consequently, ions of structure **4** formed by isomerization of **1** and **2** have a greater average internal energy than ions of the same structure produced from **6**. This results in a greater kinetic energy release for water loss from **1** and **2** than is found starting from **6**.[9a] Moreover, whereas the sequence of steps **5** $\rightleftharpoons$ **4** competes with water loss for low energy ions generated from **6**, there is insufficient time for these isomerization processes to occur for higher energy ions formed from **1** and **2**.

Conclusions

Elimination of H_2O, HOD and D_2O from ^2H-labelled analogues of $CH_3CH_2CH_2{}^+O{=}CH_2$ and $(CH_3)_2CH^+O{=}CH_2$ is logically interpreted in terms of INCs containing incipient propyl cations coordinated to a formaldehyde molecule or protonated formaldehyde attached to propene. Interconversion of these INCs with one another and with PBCs in which propene and formaldehyde are attached to a common proton (or deuteron) permits extensive exchange of the hydrogen and deuterium atoms within the initial propyl group. Reorganization of the PBC (or an INC comprising propene and protonated formaldehyde) to $CH_3{}^+CHCH_2CH_2OH$ then occurs irreversibly, followed by relatively fast expulsion of water.

Experimental

The $C_4H_{9-n}D_nO^+$ ions studied in this work were generated by dissociative ionization of suitable ^2H-labelled n-propyl or isopropyl alkyl ethers, using electrons having a nominal energy of 70 eV. The source pressure was 2–3.5 × 10^{-6} Torr* and accelerating voltage was 8065–8075 V. Synthesis of the required ethers was achieved by condensation of the appropriate sodium alkoxide with n-butyl, n-propyl or ethyl iodide in triglyme suspension. The ^2H-labelled propanols were prepared by routes 1–7, as shown in Scheme 2. Further details may be obtained from the authors on request. The reactions of the oxonium ions were investigated by the MIKES[3] technique using a research mass spectrometer ('MMM')[45] of unusually large dimensions. This allows the required $C_4H_{9-n}D_nO^+$ ion to be selected and transmitted, thus minimizing any complications caused by incomplete deuterium incorporation in the labelled species. Typical experiments involved the accumulation of ion signals over 100–200 scans. The relative abundances of H_2O, HOD and D_2O losses were measured from the areas of the associated metastable peaks; the ratios based on peak heights were the same within experimental error. Kinetic energy releases were estimated from the widths at half-height of the metastable peaks, using the one-line formula[46] after applying a correction for the width at half-height of the main beam $\{W_{\frac{1}{2}}(\mathrm{corr}) = [(W_{\frac{1}{2}}\, m^*)^2 - (W_{\frac{1}{2}}\, \mathrm{mb})^2]^{\frac{1}{2}}\}$.[47]

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* 1 Torr ≈ 133.322 Pa.

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