Ion–Dipole Interactions in the Unimolecular Reactions of Isolated Organic Ions: Some Isomers of $C_nH_{2n+1}O^+$

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The slow, unimolecular dissociations of four isomers of $CH_3CH=\overset{+}{O}-C_4H_9$ and two isomers of $CH_3CH=\overset{+}{O}-C_5H_{11}$ are compared. The results are interpreted in terms of a general mechanism involving an intermediate in which the incipient carbonium ion, $C_4H_9^+$ or $C_5H_{11}^+$, is co-ordinated to acetaldehyde. Rearrangement of this intermediate can take place, to form a complex in which acetaldehyde and a potential olefin, C_4H_8 or C_5H_{10}, are bound to a common proton. Dissociation can then occur, the nascent neutral species having the greater proton affinity retaining the proton. In some cases, rate-determining isomerisation of the incipient carbonium ion takes place. The mechanism explains the observed competition between CH_3CHO and C_4H_8 (or C_5H_{10}) elimination and also the relative magnitude of the kinetic energy released upon decomposition of isomeric ions.

CONSIDERABLE progress has been made recently in understanding the slow unimolecular reactions of organic ions.[1] These reactions may be studied conveniently, using conventional magnetic-sector mass spectrometers, by generating the ions of interest by ionisation and fragmentation of suitable precursors.[2] Slow reactions can be detected readily by the appearance of metastable peaks in the mass spectrum. In the vast majority of cases, these metastable peaks arise from the dissociation of ions in their ground states, with small excess energies in the transition state(s) for decomposition.[3] A careful consideration of the shape of a metastable peak often yields valuable insight into the nature of the corresponding reaction.[1,2]

A general class of ions which have attracted much attention is the ' onium ' ions $[C_nH_{2n+1}Z]^+$ ($Z = O$, NH, S, *etc.*).[4-12] Intermediates appear to be involved, in the dissociation of these ions, where a carbonyl component is loosely co-ordinated to a carbonium ion.[13,14] Such intermediates can be extensively stabilised, by an ion–dipole attraction, especially if the carbonyl component has a large permanent dipole.[14] Isomerisation of the incipient carbonium ion may take place; alternatively, rearrangement can occur to form a species in which the carbonyl component and an olefin are bound to a common proton. This species may then dissociate, with the nascent neutral compound having the greater proton affinity retaining the proton.[13]

The observed slow reactions, and associated kinetic energy releases, for four isomeric oxonium ions $C_4H_9O^+{=}CHCH_3$ are given in Table 1. It is immediately apparent that elimination of C_4H_8 occurs to a significant extent, compared to CH_3CHO loss, only for those ions [(1) and (2)] containing a straight butyl chain. In contrast, for (3) and (4), which contain a branched butyl chain, C_4H_8 loss is insignificant, in comparison with CH_3CHO elimination. This apparently puzzling result may be understood in terms of the appropriate aldehyde–olefin complexes as shown in Schemes 1 and 2.

Starting from (1), stretching of the C–O σ-bond leads to (1a), a species in which CH_3CHO is co-ordinated to the n-butyl cation. A slight reorganisation of (1a) yields (5), an intermediate where CH_3CHO and but-1-ene are bound to a common proton.

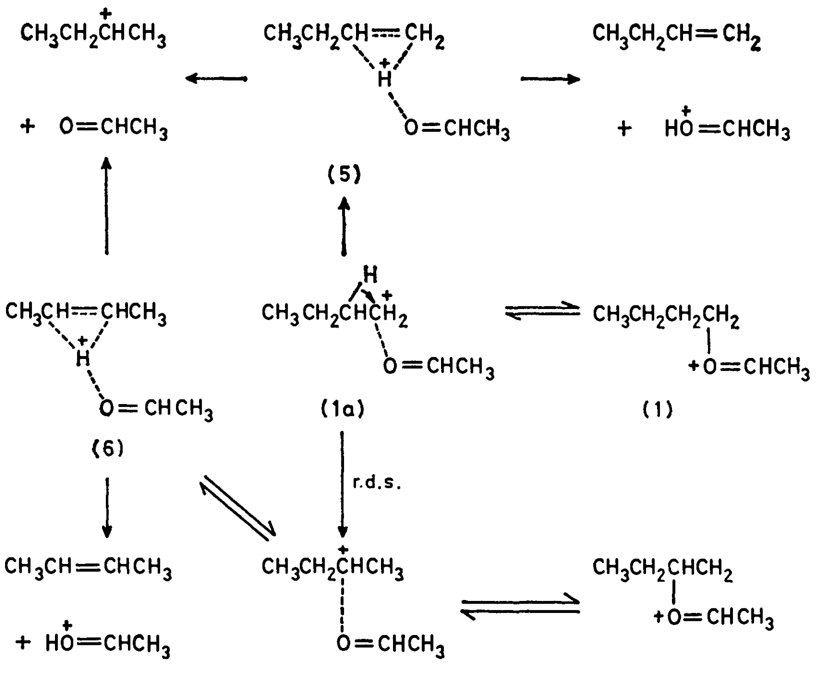
Alternatively, a 1,2-hydride shift in (1a) can lead to (2a), where the incipient carbonium ion is the thermodynamically more stable s-butyl cation. Rearrangement of (2a), which can also be produced by C–O σ-bond stretching in (2), yields another aldehyde–olefin complex (6) comprising CH_3CHO and but-2-ene bound to a common proton. Each of these complexes can break down, with a strong preference for proton retention by the incipient neutral compound (CH_3CHO or C_4H_8) with the greater proton affinity. The relevant proton affinities of but-1- and -2-enes (755—765 [16] kJ mol^{-1}) are comparable with that (775 [17] kJ mol^{-1}) of acetaldehyde. Consequently, loss of C_4H_8 and CH_3CHO occurs from (1) and (2). However, the analogous complex for (3) and (4) ought to comprise 2-methylpropene and acetaldehyde bound to a common proton (Scheme 2). The

TABLE 1

Unimolecular reactions of four oxonium ions $C_4H_9\overset{+}{O}=CHCH_3$

	Neutral lost and associated kinetic energy (k.e.) release					
	H_2O		CH_3CHO		C_4H_8	
Ion	Relative [a] abundance	K.e. [b] release	Relative [a] abundance	K.e. [b] release	Relative [a] abundance	K.e. [b] release
$CH_3CH_2CH_2CH_2\overset{+}{O}=CHCH_3$ (1) [c]	52	7.1 ± 0.5	8	5.9 ± 0.5	33	4.2 ± 0.7
$CH_3CH_2CH(CH_3)\overset{+}{O}=CHCH_3$ (2) [c]	80	5.9 ± 0.5	7	5.4 ± 0.5	8	3.7 ± 0.7
$(CH_3)_2CHCH_2\overset{+}{O}=CHCH_3$ (3)	22	8.8 ± 0.6	74	4.2 ± 0.7	4	*d*
$(CH_3)_3C\overset{+}{O}=CHCH_3$ (4)	54	4.2 ± 0.4	44	1.0 ± 0.2	2	*d*

[a] Values measured from second field-free region metastable peak areas and normalised to a total of 100 units. [b] Average [15] values in kJ mol^{-1}. [c] A small percentage of C_3H_6 loss is also observed from these ions. [d] Too weak to measure.

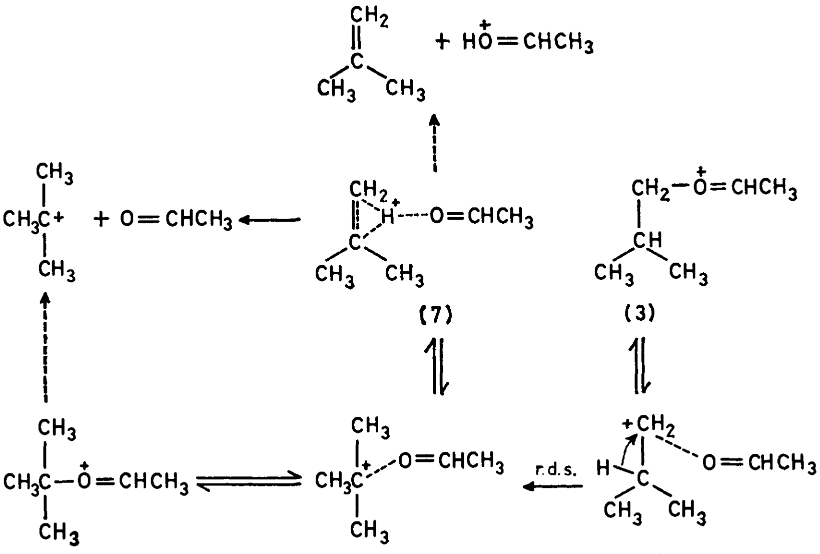


SCHEME 1

proton affinity of 2-methylpropene (815 [17] kJ mol^{-1}) is much greater than that of any linear butene (755—765 [16] kJ mol^{-1}) or acetaldehyde (775 [17] kJ mol^{-1}). Therefore, protonation of the olefin component, to give t-butyl cation, is preferred and CH_3CHO is lost, rather than C_4H_8.

It is now well established that rate-determining isomerisations of organic ions may take place prior to unimolecular dissociation.[1,2,11,13,14] After such rate-determining isomerisations have taken place, excess energy is present in the transition states for the subsequent steps. The presence of this excess energy causes a discrimination against any subsequent rearrangements with a stringent geometrical requirement.[11] This effect arises because these rearrangements are unable to proceed as rapidly as simple bond-cleavages, at relatively high internal energies. Moreover, part of the excess energy, present in ions that have undergone the rate-determining isomerisation, is partitioned into the bond which breaks in the final step, thus causing an increase in the kinetic energy release accompanying decomposition.[11]

In the system of interest, loss of H_2O must proceed *via* deep-seated rearrangement of the original structure



SCHEME 2

since three C–O bonds must be broken and two O–H bonds formed. This rearrangement probably has a stringent geometrical requirement. In contrast, elimination of C_4H_8 and CH_3CHO requires only at most a single hydrogen transfer from carbon to oxygen, in some cases followed by rearrangement of the incipient butyl cation. Therefore, these processes ought to be favoured, relative to H_2O loss, for ions of higher internal energy. A distinct trend in this direction is observed in the relative competition of H_2O and C_4H_8 losses from both (1) and (2). Thus, in 70 eV spectra (1) and (2) eliminate C_4H_8 and H_2O in the ratios 22 : 1 and 27 : 1, respectively. However, at low internal energies, corresponding to decompositions occurring in the first field-free region, these ratios fall to 2.4 : 1 and 0.18 : 1, respectively.[9] Furthermore, at even lower internal energies (Table 1), H_2O loss competes more effectively, against C_4H_8 and CH_3CHO loss, starting from (2) compared with (1). This suggests that (1) undergoes, at least to some extent, rate-determining isomerisation to (2), or structures accessible to (2). A postulate of this nature is involved in Scheme 1, where the 1,2-hydride shift, in (1a), leads irreversibly to (2a). In addition, the average kinetic energy releases, associated with each decomposition channel, are greater starting from (1) than (2). This is more evidence that (1) undergoes irreversible isomerisation to (2).

Similarly, a consideration of the relative abundances of H_2O and CH_3CHO losses, together with the associated kinetic energy releases, shows that (3) undergoes a rate-determining isomerisation to (4). It is interesting to note that a 1,2-hydride shift in the incipient isobutyl cation is preferred to a 1,2-methyl shift. This presumably reflects a preference, in these systems, for forming the most stable carbonium ion; in the present example, t-butyl, rather than s-butyl cation, is produced.

Similar trends are followed by the higher homologues (8) and (9) which undergo the unimolecular dissociations shown in Table 2. For ion (8), rearrangement of the incipient n-pentyl cation could occur when the C–O σ-bond is sufficiently stretched. This isomerisation ought to be rate-determining and would give a complex of the 1-methylbutyl cation loosely bound to acetaldehyde. Further 1,2-hydride shifts may occur, to give a mixture of equilibrating complexes, in which acetaldehyde is loosely co-ordinated to a secondary pentyl cation, with the cationic site at the β-, γ-, or δ-position. Any of these complexes may then be reorganised, to give an aldehyde–olefin complex, with acetaldehyde and either pent-2- or -3-ene bound to a common proton. Acetaldehyde and linear pentenes have similar proton affinities (755—775 kJ mol^{-1}); consequently, loss of both C_5H_{10} and CH_3CHO is observed from (8).

TABLE 2

Unimolecular reactions of two oxonium ions $C_5H_{11}\overset{+}{O}{=}CHCH_3$

Ion	Neutral lost [a]		
	H_2O	CH_3CHO	C_5H_{10}
$CH_3CH_2CH_2CH_2CH_2\overset{+}{O}{=}CHCH_3$ (8) [b]	37	60	2
$(CH_3)_2CHCH_2CH_2\overset{+}{O}{=}CHCH_3$ (9)	0	100	0

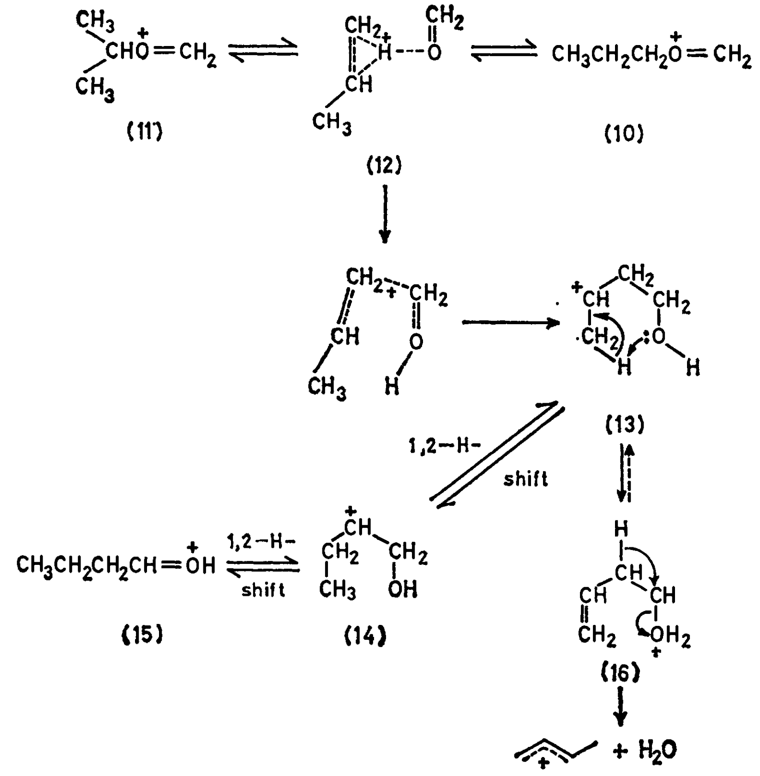
[a] Values measured from second field-free region metastable peak areas and normalised to a total of 100 units. [b] A small percentage of C_4H_8 loss is also observed from this ion.

In contrast, ion (9) loses exclusively CH_3CHO; this shows that the incipient isopentyl cation isomerises to t-pentyl cation prior to dissociation. Thus, as the C–O σ-bond in (9) is stretched, either a direct 1,3-hydride shift, or two consecutive 1,2-hydride shifts, leads to a complex of acetaldehyde co-ordinated to t-pentyl cation. Reorganisation of this complex may take place, to give an aldehyde–olefin complex in which acetaldehyde and 2-methylbut-2-ene (or 2-methylbut-1-ene) are bound to a common proton. Nevertheless since these olefins have much higher proton affinities (820—830 kJ mol^{-1}) than acetaldehyde (775 kJ mol^{-1}), dissociation always occurs to give t-pentyl cation and acetaldehyde.

A final point is that the proposed mechanism, for olefin and aldehyde loss from these oxonium ions, may be extended to explain how these ions eliminate H_2O. The postulated aldehyde–olefin complexes, for example (12) in Scheme 3, may or may not have enough internal energy to eliminate olefins or aldehydes. Alternatively, another isomerisation may take place, involving migration of the incipient olefin to the carbonyl carbon atom of the potential protonated aldehyde.[12,18] The open-chain carbonium ion, thus formed, for example (13) in Scheme 3, can then lose H_2O, *via* the route (13) $\longrightarrow$ (16) $\longrightarrow$ products, or undergo a series of 1,2-hydride shifts, (13) $\rightleftharpoons$ (14) $\rightleftharpoons$ (15), to produce a protonated aldehyde or ketone. This is supported by the observation that such protonated aldehydes and ketones lose H_2O in high abundance, in metastable transitions.[4,12,18] Moreover, ^2H-labelling studies on (10) and (11) reveal that both hydrogen atoms of the expelled water molecule originate from the propyl group. Thus, $(CD_3)_2CD\overset{+}{O}{=}CH_2$, $(CH_3)_2CH\overset{+}{O}{=}CD_2$, and $CH_3CH_2CH_2\overset{+}{O}{=}CD_2$ eliminate D_2O, H_2O, and H_2O, respectively, in the water loss reaction.[4] This is what would be expected on the basis of the mechanism postulated in Scheme 3. Similarly, $CD_3CD{=}\overset{+}{O}CH_2CH_2CH_2CH_3$ eliminates exclusively H_2O in the water loss reaction.[9]

The non-occurrence of NH_3 loss from nitrogen analogues of (10), (11), and related ions may also be understood. In the first instance, the nitrogen complex corresponding to (12) would normally prefer to break down, *via* olefin elimination, instead of isomerising to the analogue of (13). This reflects the higher proton affinity of imines, compared to aldehydes or olefins. Secondly, loss of NH_3 does not produce particularly stable products in any case. This is due to the higher heat of formation (−45 [19] kJ mol^{-1}) of NH_3 compared with that (−240 [19] kJ mol^{-1}) of H_2O.

Conclusions.—The unimolecular reactions of several oxonium ions are interpreted in terms of intermediates involving the co-ordination of a carbonyl compound to



SCHEME 3

an incipient cation. In some cases, rate-determining rearrangement of the incipient carbonium ion occurs, to give thermodynamically more stable isomers. Isomerisation also may take place to form other intermediates, in which the carbonyl compound and an olefin are bound to a common proton. These complexes can break down, with the elimination of either the carbonyl compound or the olefin; alternatively, further rearrangement is feasible, leading to eventual water loss.

EXPERIMENTAL

The required ethers were synthesised by conventional procedures. All mass spectra were obtained using an AEI MS902 double-focusing mass spectrometer, operating with an ionising electron beam energy of nominally 70 eV, at a source pressure of *ca.* 10^{-6} Torr. Samples were admitted into the source through the all-glass heated-inlet system.

The relative abundances of competing decay routes were obtained from the areas of the corresponding metastable peaks. Average kinetic energy release values were computed from the widths, at half-height, of these peaks; no correction was applied for the width of the main beam. In all cases where comparison was to be made, between the kinetic energy released upon decomposition of isomeric ions, the measurements were made consecutively, under identical operating conditions.

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