Non-concerted Unimolecular Reactions of Ions in the Gas Phase: Isomerisation of Weakly Co-ordinated Carbonium Ions

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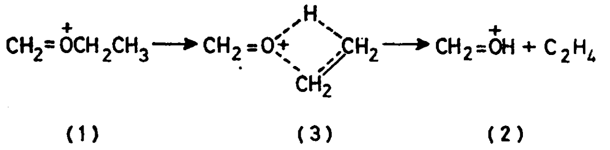
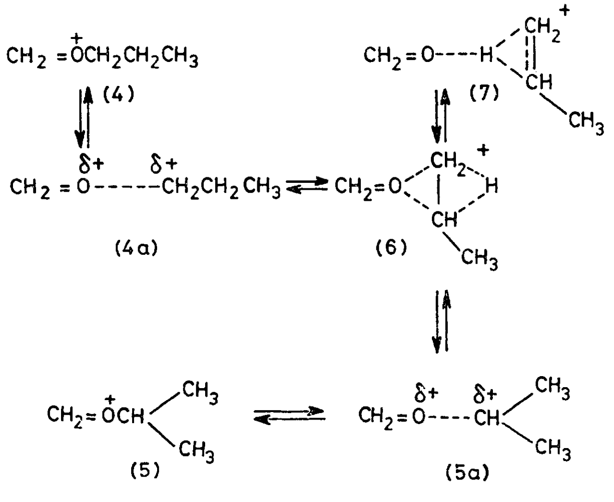
Summary Mass spectral evidence is presented to show that the dissociations of some simple oxonium ions in the gas phase occur by relatively non-concerted pathways.

We had long been fascinated by the fact that the oxonium ion (**1**) loses C_2H_4 to give protonated formaldehyde (**2**) in a reaction which occurs close to the thermochemical threshold.[1]



Although such reactions have in the past[2] been represented as concerted reactions (*e.g. via* **3**), in the present case this pathway must be excluded since this process would involve a symmetry-imposed barrier,[3] and be expected to occur with a relatively large release of kinetic energy.[4] In contrast, the average[5] kinetic energy release in slow reactions (metastable transitions) is only 1·7 kJ mol^{-1}.[1]

The possibility arises that such reactions are non-concerted, and we have therefore sought systems and criteria to test this hypothesis. We first examined the energetically most favoured unimolecular reactions of (**4**) and (**5**), both higher homologues of (**1**). In metastable transitions (excess energies in the transition state comparable to solution reactions[6]), both (**4**) and (**5**) lose H_2O and CH_2O in the ratio 5(±2) : 1.[7] This very similar channelling between reaction pathways indicates that (**4**) and (**5**) interconvert prior to unimolecular dissociation.[7,8] This constitutes evidence that the O–alkyl bonds of (**4**) and (**5**) are sufficiently stretched prior to dissociation that the weakly co-ordinated cations (**4a**) and (**5a**) are formed. A 1,2-hydride shift in (**4a**) can then lead exothermically to (**5a**); equilibration of (**4**) and (**5**) will occur if the energy required for isomerisation is less than that required for dissociation of either (**4**) or (**5**). If the above scheme is correct, then three consequences which can be subjected to experimental test follow.



(i) The prior equilibration of (**4**) and (**5**) demands that dissociation *via* CH_2O loss will occur only from (**5**) since the isopropyl cation is more stable than the n-propyl cation by *ca.* 65 kJ mol^{-1}.[9] Indeed, appearance potential measurements establish that (**4**) and (**5**) (which have almost identical heats of formation) both require 95 ± 10 kJ mol^{-1} for $CH_2{=}O$ loss. This value is close to that (90 kJ mol^{-1}) theoretically required to produce $(CH_3)_2CH^+$ together with $CH_2{=}O$ and insufficient to produce $CH_3CH_2CH_2^+$ together with CH_2O (requiring at least 155 kJ mol^{-1}).

(ii) Since both (**4**) and (**5**) dissociate *via* CH_2O loss from the complex (**5a**) [or (**6**) or (**7**), see later] dissociation of both should occur with the same kinetic energy release. This is the case, the average energy release being small (2·2 kJ mol^{-1}).

(iii) If the carbonium ion complex (**6**) which facilitates the 1,2-hydride shift is sufficiently loose so that rotation to (**7**) can occur, then CH_2O and a potential olefin can compete for a proton which is temporarily co-ordinated to both. The neutral species lost in dissociation should then be the molecule (CH_2O or olefin) with the lower proton affinity (this argument is identical to one stating that the product combination with the lowest sum of heats of formation will be observed). The proton affinities relevant to the present work are 670 (C_2H_4),[10] 730 (CH_2O),[11] and 750 ($CH_3CH{=}CH_2$)[10] kJ mol^{-1}. Thus, in the complex (**7**), the propene should 'win' the proton and formaldehyde be observed as the neutral species, as found experimentally. In contrast since the proton affinity of CH_2O is greater than that of C_2H_4, then (**1**) should lose C_2H_4 rather than CH_2O, again as observed.

Table

Proton affinities (P.a./kJ mol^{-1}) of some olefins and carbonyl compounds

Compound	P.a.	Compound	P.a.
CH_2O	730[11]	$CH_2{=}CH_2$	670[10]
CH_3CHO	775[11]	$CH_3CH{=}CH_2$	750[10]
$(CH_3)_2CO$	810[11]	$(CH_3)_2C{=}CH_2$	810[10,11]

Given the proton affinities of relevant olefins and carbonyl compounds (Table), it should therefore be possible to account for the observed reaction channels (olefin or carbonyl compound loss) of simple oxonium ions.

The ions (**8**)—(**13**) have therefore been generated by ionisation and fragmentation of suitable ethers. Reference to the data in the Table shows that, for the two reactions under consideration, (**8**), (**9**), (**11**), and (**13**) should decompose unimolecularly *via* loss of C_2H_4, C_3H_6, C_2H_4, and C_3H_6,

$CH_3CH{=}\overset{+}{O}CH_2CH_3$ **(8)**

$CH_3CH{=}\overset{+}{O}CH(CH_3)_2$ **(9)**

$CH_2{=}\overset{+}{O}C(CH_3)_3$ **(10)**

$(CH_3)_2C{=}\overset{+}{O}CH_2CH_3$ **(11)**

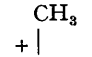
$CH_3CH{=}\overset{+}{O}C(CH_3)_3$ **(12)**

$(CH_3)_2C{=}\overset{+}{O}CH(CH_3)_2$ **(13)**

respectively, whereas (**10**) and (**12**) should lose CH_2O and CH_3CHO, respectively. Experimentally, these are the observed results in metastable transitions (ref. 12 and the present work).

We have also studied ions in which the isomerisation of weakly co-ordinated carbonium ions is rate-determining. For example, the isomeric oxonium ions (**14**)—(**16**) and (**10**) can be generated conveniently by ionisation and fragmentation of suitable ethers. In slow reactions (metastable

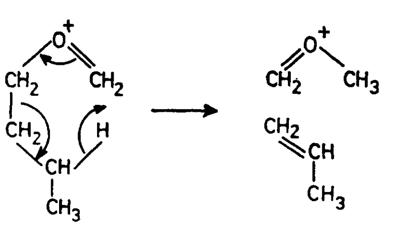
$CH_2{=}\overset{+}{O}CH_2CH_2CH_2CH_3$ **(14)**



$CH_2{=}\overset{+}{O}\underset{}{\overset{CH_3}{C}}HCH_2CH_3$ **(15)**

$CH_2{=}\overset{+}{O}CH_2CH(CH_3)_2$ **(16)**

transitions), (**15**), (**16**), and (**10**) lose almost exclusively CH_2O ($>97\%$) whereas (**14**) loses 95% CH_2O and 5% C_3H_6 (MS902 instrument, second field-free region). Appearance potential measurements establish that (**14**) and (**16**) do not dissociate to ($CH_3CH_2CH_2CH_2^+ + CH_2O$) and [$(CH_3)_2CHCH_2^+ + CH_2O$], respectively, since the internal energies required for dissociation are only *ca.* 80 kJ mol^{-1} (from **14**) and 65 kJ mol^{-1} (from **16**). In each case, these figures are some 70 kJ mol^{-1} less than those required to produce the relatively unstable primary cations.[9] These measurements, though approximate only, are consistent with the minimum internal energy of (**14**) (85 kJ mol^{-1}) which would be required to give the products of equation (1) (observed as a minor slow reaction which may or may not be concerted.)



(1)

The C_4 alkyl chains of (**14**) and (**16**) must therefore isomerise before or during dissociation. If such isomerisation (to a more stable secondary or tertiary butyl cation) is rate-determining, then potential energy which is released following isomerisation can appear as kinetic energy release accompanying the dissociation to more stable products. This is observed (Figure); the average kinetic energy[5] released when (**10**) dissociates to the t-butyl cation and CH_2O is small (0·8 kJ mol^{-1}), but that released upon dissociation of (**14**), (**15**), and (**16**) is much larger (4, 5, and 5 kJ mol^{-1}, respectively). The data are in accord with the following sequence of events: CH_2O is partially removed from (**14**) so that $CH_3CH_2CH_2CH_2^+$ can isomerise to $CH_3CH_2\overset{+}{C}HCH_3$. The internal energy required for this (*ca.* 75 kJ mol^{-1}) is sufficient to dissociate relatively few cations (**14**) to $CH_3CH_2\overset{+}{C}HCH_3$ and CH_2O; most pass to vibrationally excited (**15**). Similarly (**15**), when generated directly, undergoes C–O bond stretching and then isomerises to (**16**). In turn, vibrationally excited (**16**) undergoes a 1,2-hydride shift to produce (**10**), which is formed with excess energy (since its dissociation *via* CH_2O loss requires only *ca.* 15 kJ mol^{-1}). The ion (**10**) therefore undergoes dissociation with a relatively large average kinetic energy release (Figure; a, b, c).[1] This is in contrast to the behaviour of directly generated (**10**) (Figure; d). On the basis of the above scheme, the slightly smaller kinetic energy release from (**14**) relative to (**15**) and (**16**) (see above)

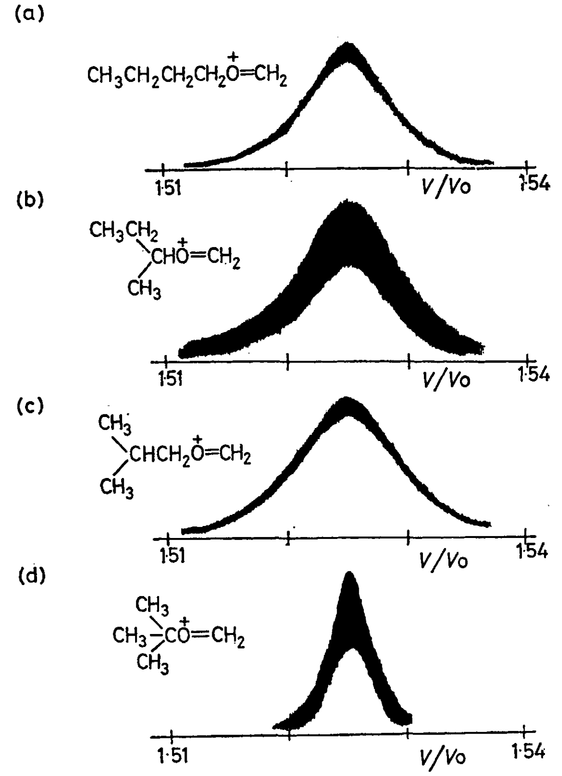


FIGURE. Metastable peaks (MS902 instrument, first field-free region) for $H_2C{=}O$ loss from (**14**), (**15**), (**16**), and (**10**). The abscissae are in units of V/V_0 where V_0 is the accelerating voltage used to transmit the main beam, and V the corresponding voltage required to transmit butyl cations formed in the first field-free region.

is due to the minor dissociation route (**14**)→(**15**)→*sec.*-$C_4H_9^+$, which occurs with less excess energy in the transition state.

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