Hydrogen Transfer Reactions in the Decomposition of Isolated 'Onium' ions containing an Incipient Allyl Cation

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Decomposition of metastable $CH_2{=}CHCH_2O^+{=}CH_2$ ions by loss of a neutral of mass 28 daltons, rather than by simple cleavage to $C_3H_5^+$ and $O{=}CH_2$, is explained using a mechanism involving intermediates stabilised by ion–dipole attractions.

Recent work has shown that intermediates comprising an incipient cation co-ordinated to a neutral species are of importance in the slow unimolecular reactions of isolated organic ions.[1,2] Extensive ion–dipole stabilisation (50—90 kJ mol^{-1}) of these intermediates is possible, relative to the separated products, in systems containing a neutral species having a sizeable permanent electric dipole moment (1.5—2.5 D).[3] Rearrangement of the incipient cations and hydrogen transfers between the developing products are thus facilitated at energies lower than those needed to promote direct dissociation.

The chemistry of incipient allyl and prop-2-enyl cations can be investigated by studying the reactions of the oxonium ions (**1**) and (**2**). Good yields of (**1**) were obtained by ionisation and fragmentation of allyl alkyl ethers; however, the analogous process was unsatisfactory for the corresponding ionised propenyl alkyl ethers, which decomposed *via* a *retro* 'ene' reaction. Moreover, (**1**) did not expel the expected $CH_2{=}O$ molecule in slow reactions, but eliminated a neutral of mass 28 daltons.

$$CH_2{=}CHCH_2O^+{=}CH_2$$

(**1**)

$$CH_2{=}C(CH_3)O^+{=}CH_2$$

(**2**)

On the assumption that this process produces $(CH_3)_2CH^+$ and CO, the behaviour of (**1**) can be explained using the mechanism depicted in Scheme 1.

The C–O σ-bond in (**1**) is stretched, but before dissociation to allyl cation and CO is complete, a hydrogen transfer occurs to form a complex, (**3**), of HCO^+ and $CH_3CH{=}CH_2$. This process should be especially facile because it may proceed through a six-membered ring transition state; breakdown of (**3**) would give rise to single hydrogen transfer (SHT).

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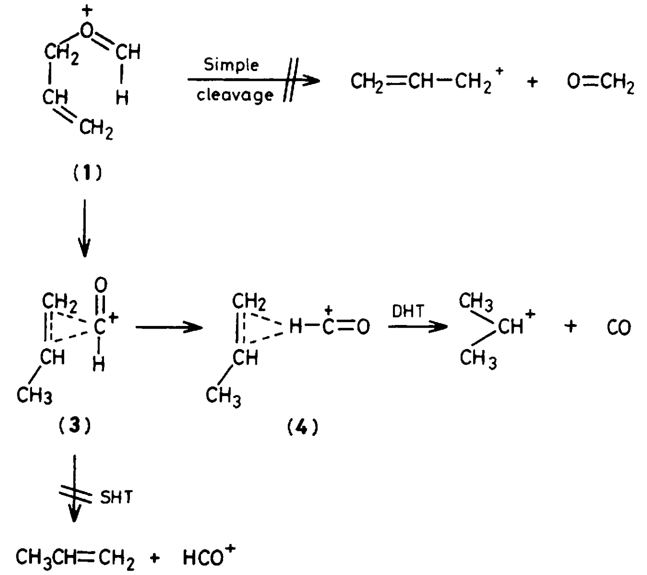
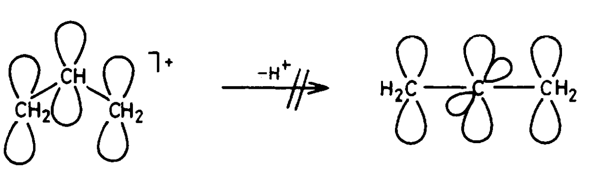
Reorganisation of (**3**) to (**4**) (or related species), followed by capture of the common proton by the incipient propene, provides a route for CO loss; this corresponds, overall, to double hydrogen transfer (DHT).

Reference to the appropriate energetics, Table 1, reveals that simple cleavage of (**1**) and SHT yields products of similar total energy; however, DHT gives products which are energetically far more favourable. The complexes (**3**) and (**4**) ought to be accessible starting from (**1**) at energies appreciably lower than those needed to induce simple cleavage in (**1**). Consequently, the unusual behaviour of (**1**) at low internal energies (metastable ions) is explained.

An alternative product combination, CH_3CO^+ and C_2H_4, would also be energetically feasible; but this possibility is mechanistically less likely.



Scheme 1



(1)

The nitrogen analogue of (**1**), (**5**), also undergoes DHT: (**5**) eliminates HCN (3 parts), together with C_3H_6 (1 part). The divergent behaviour of (**1**) and (**5**) reflects changes in the underlying energetics, Table 1: SHT and DHT starting from (**5**) yield product combinations of similar total energies, each of which is substantially lower than the energy of the products formed by simple cleavage. However, it is interesting that an 'inverse' SHT, to give C_3H_4 loss, does not compete with elimination of HCN and C_3H_6 from (**5**), even though C_3H_4 loss produces low energy products. In contrast, the saturated analogue, (**6**), does exhibit such an 'inverse' SHT, in that (**6**) eliminates C_3H_6 to form $CH_2{=}NH_2^+$.[12] A likely explanation for the non-occurrence of C_3H_4 loss from (**5**) is that deprotonation of the incipient allyl cation would lead to an unfavourable geometry of the developing $CH_2{=}C{=}CH_2$ orbitals (equation 1). This is consistent with earlier studies on the protonation of $CH_2{=}C{=}CH_2$ and $CH_3C{\equiv}CH$, which demonstrate that the prop-2-enyl cation is the usual daughter ion, and that a substantial barrier must be surmounted before the allyl cation can be formed.[17]

$CH_2{=}CHCH_2N^+H{=}CH_2$
(**5**)

$CH_3CH_2CH_2N^+H{=}CH_2$
(**6**)

$CH_2{=}CHCH_2O^+{=}CHCH_3$
(**7**)

The higher homologue of (**1**), (**7**), also does not undergo simple cleavage at low internal energies: loss of a neutral of mass 42 daltons is preferred. This may be formulated either as SHT (C_3H_6 elimination) or as DHT ($CH_2{=}C{=}O$ loss); SHT is more probable, since it is energetically preferable to simple cleavage or DHT. Again, no 'inverse' SHT (C_3H_4 loss) occurs from (**7**), although the saturated analogue of (**7**) ($CH_3CH_2CH_2O^+{=}CHCH_3$) does show such a reaction (C_3H_6 loss).[3]

Finally, it is significant that neither (**5**) nor (**7**) eliminate a neutral of mass 28 daltons in metastable transitions, even though C_2H_4 loss would lead to energetically favourable products in each case, Table 1. These observations support the view that C_2H_4 loss from (**1**) [and (**5**) and (**7**)] is mechanistically implausible.

Table 1. Energy data relevant to decomposition of (**1**), (**5**), and (**7**).

Ion	Products and ΔH_f (kJ mol^{-1})					$\Sigma\Delta H_f$ (kJ mol^{-1})
(**1**)	$CH_2{=}C{=}CH_2$	(190^4)	+	$CH_2{=}OH^+$	(705^5)	895
	$CH_2{=}CHCH_2^+$	($945^{6,7}$)	+	$CH_2{=}O$	(-115^4)	830
	$CH_3CH{=}CH_2$	(20^4)	+	HCO^+	(820^8)	840
	$(CH_3)_2CH^+$	($805^{7,9}$)	+	CO	(-110^4)	695
	CH_3CO^+	(650^{10})	+	$CH_2{=}CH_2$	(50^4)	700
(**5**)	$CH_2{=}C{=}CH_2$	(190^4)	+	$CH_2{=}NH_2^+$	(745^{11})	935
	$CH_2{=}CHCH_2^+$	($945^{6,7}$)	+	$HN{=}CH_2$	(55^a)	1000
	$CH_3CH{=}CH_2$	(20^4)	+	$HC{\equiv}NH^+$	(935^{13})	955
	$(CH_3)_2CH^+$	($805^{7,9}$)	+	$N{\equiv}CH$	(130^4)	935
	$CH_3C{\equiv}NH^+$	(840^{13})	+	$CH_2{=}CH_2$	(50^4)	890
(**7**)	$CH_3CH{=}OH^+$	(580^5)	+	$CH_2{=}C{=}CH_2$	(190^4)	770
	$CH_3CH{=}O$	(-165^4)	+	$CH_2{=}CHCH_2^+$	($945^{7,9}$)	780
	CH_3CO^+	(650^{11})	+	$CH_3CH{=}CH_2$	(20^4)	670
	$CH_2{=}C{=}O$	($-50^{14,15}$)	+	$(CH_3)_2CH^+$	($805^{7,9}$)	755
	$CH_3CH_2CO^+$	(600^{16})	+	$CH_2{=}CH_2$	(50^4)	650

[a] Estimated value; loss of C_4H_8, rather than $CH_2{=}NH$, from metastable $(CH_3)_3CN^+H{=}CH_2$ ions establishes a lower limit of 35 kJ mol^{-1} for $\Delta H_f(CH_2NH)$, ref. 12.

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