Rate-determining Isomerisation of Protonated Acetone Prior to Unimolecular Decomposition

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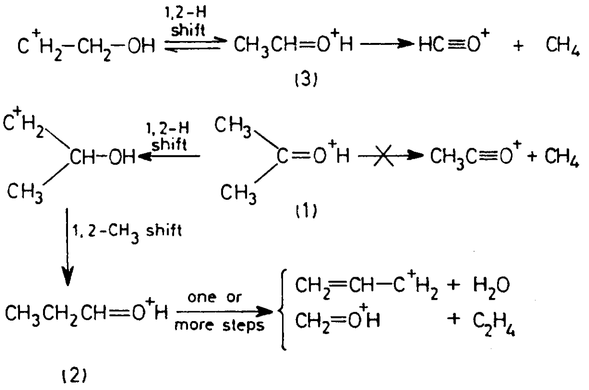
Summary It is shown that protonated acetone undergoes a rate-determining isomerisation onto the same potential surface as protonated propionaldehyde prior to unimolecular decomposition.

Protonated acetone (**1**) and protonated propionaldehyde (**2**) may be generated in the gas phase by fragmentation of the molecular ions of propan-2-ol and butan-2-ol, respectively. Both ions thus generated undergo, after some 10^8 vibrations, competitive decomposition to $CH_2{=}O^+H + C_2H_4$ and $C_3H_5^+ + H_2O$ (in metastable transitions). Starting from (**2**), the energy requirements for these reactions are 205 and 176 kJ mol^{-1} (Table 1); ccordingly, in slow reactions, loss of H_2O is dominant ver C_2H_4 loss (88:12 in terms of relative areas of metastable peaks observed in the second field-free region of an MS-902 mass spectrometer) but less so in reactions occurring at somewhat shorter times (68:32 in the first field-free region).

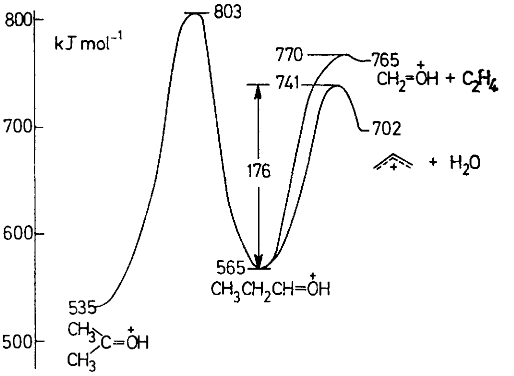
Table 1. Relevant heats of formation and activation energies (kJ mol^{-1}).

	$\Delta H_f(C_3H_7O^+)$[a]	$E°$ (H_2O loss)	$E°$ (C_2H_4 loss)
(**1**)	535	267[c]	269[c]
(**2**)	565[b]	176[c]	205[c]

[a] Values from photo-ionisation studies; K. M. A. Refaey and W. A. Chupka, *J. Chem. Phys.*, 1968, **48**, 5205. [b] This value is in close agreement with that (560 kJ mol^{-1}) from ion cyclotron resonance studies; J. L. Beauchamp and S. E. Butrill, *J. Chem. Phys.*, 1968, **48**, 1783. [c] Estimated accuracy ±20 kJ mol^{-1}.



Starting from (**1**), H_2O loss competes less effectively with C_2H_4 loss (31:69) for decompositions occurring in the second field-free region. This observation would be understandable if (**1**) isomerised over a high barrier to (**2**), so as to produce (**2**) with more energy than required to attain the transition states for eventual H_2O and C_2H_4 losses.[1] The ion (**2**) so produced would undergo an increased proportion of C_2H_4 loss provided that process could proceed through a less ordered transition state than H_2O loss (as might reasonably be the case).[1]



Figure

The consequences of the above postulate, which can be subjected to experimental test, are: (i) the barriers to C_2H_4 and H_2O losses starting from (**1**) should be the same [and correspond to the energy required to isomerise (**1**) to (**2**)], (ii) this isomerisation energy must be greater than the 176 kJ mol^{-1} quoted above (see also Figure), and (iii) the metastable peaks for the dissociations commencing from (**1**) should be slightly broader than those observed commencing from (**2**).[1] All these consequences are observed, and are summarised in Tables 1 and 2, and the Figure.

The difference in average kinetic energies released in the dissociations (Δ, Table 2) is a measure of the fraction of the excess energy ($803 - 741 = 62$ kJ mol^{-1} for H_2O loss; $803 - 770 = 33$ kJ mol^{-1} for C_2H_4 loss; Figure) which is partitioned into the reaction co-ordinate. On the assumption that the excess energy is classically partitioned into all the $3n - 6$ (27) vibrational degrees of freedom of the ion,[3] the excess energies in the reaction co-ordinates would be 2·3 (H_2O loss) and 1·2 (C_2H_4 loss) kJ mol^{-1}. The observed values are about one third of these amounts (Table 2).

Table 2. Average kinetic energies released[2] in the dissociations (kJ mol^{-1})[a]

	$-H_2O$	$-C_2H_4$
(**1**)	5·1	3·6
(**2**)	4·3	3·1
Δ	0·8	0·5
Calc.[b]	2·3	1·2

[a] Measurements made on an RMH-2 instrument. [b] Calculated on the basis of a statistical fluctuation of excess energy into the reaction co-ordinate (ref. 3).

The above conclusion is supported by the following arguments. One of two slow reactions observed for decomposition of protonated acetaldehyde (**3**) is by loss of CH_4,[4] requiring 305 ± 20 kJ mol^{-1}. If protonated acetone did not isomerise, then an analogous loss of methane might reasonably be expected to occur with a similar activation energy. In fact, methane loss from (**1**) is not a significant unimolecular metastable transition, this type of reaction being pre-empted by an isomerisation (**1**) $\rightarrow$ (**2**) which requires less energy (268 ± 20 kJ mol^{-1}).

A consequence of the above analysis is that the metastable peaks for unimolecular dissociation of protonated acetone will be due to relatively fast dissociations, the slow and rate-determining process being an isomerisation.[1]

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