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OMS Letters

Dear Sir,

Ion/Radical and Ion/Molecule Complexes: Experimental Demonstration of their Participation in the Fragmentation of Ionized Neopentanol.

The role of ion-molecule and ion-radical complexes in the fragmentation of odd electron ions is a topic of considerable current interest. Morton[1] has defined these species as "non-covalently bonded aggregates of an ion with one (or more) neutral molecules in which one of the partners rotates freely (or nearly so) in all directions." A good, well established example of an ion-molecule complex is the ethene ion-water molecule pair which has been thoroughly described by theory and experiment[2]. The second type of complex is well represented in the fragmentation behaviour of the alkyl phenyl ethers[3,4]. Both systems have been demonstrated by experimental investigations to fall within the above definition.

In general, it is not easy by experiment alone to obtain unequivocal evidence for the participation of such complexes in ion fragmentations. A detailed recent study by ourselves[5] failed to provide a satisfactory complete mechanism for the principal fragmentation of metastable ionized neopentanol, 1: namely, loss of CH_3OH. In D-labelled neopentanol, the fragment ion abundances were not in random statistical ratios but nevertheless indicated a major loss of positional identity of H and D. It was concluded however, in partial agreement with the earlier proposal of Hammerum and Audier[6], that the final reacting configuration is best described as an ion/molecule complex between ionized methylpropene and methanol. The suggested involvement[6] of an ion/radical complex between the t-butyl cation and a $^{\bullet}CH_2OH$ radical was considered unproven and the loss of positional identity among H and D atoms was ascribed to the participation of distonic and ylid ions[5]. A complete reaction mechanism for the system proved elusive and in particular, observations of the deuterium labelled distonic $[C_5H_{12}O]^{+\bullet}$ion, $[(CH_3)_2C^{\bullet}CH_2O^{+}(H)CD_3]$ 4, (the numbering here is that used in ref. 5) and its relationship with ionized neopentanol remained unexplained.

We report here the behaviour of another $[C_5H_{12}O]^{+\bullet}$ ion, generated by the loss of CH_2O from ionized 2-t-butoxyethanol, 6, which enables us to present a satisfactory overall mechanism for the behaviour of the neopentanol molecular ion, and also ion 4. This new mechanism includes the t-butyl cation/hydroxymethyl radical complex originally proposed by Hammerum and Audier[6], but for which direct experimental evidence was lacking.

Results and Discussion

The electron impact (EI) mass spectrum of $(CH_3)_3COCH_2CH_2OH$ contains small peaks at m/z 87 $[C_5H_{11}O]^+$ and m/z 88 $[C_5H_{12}O]^{+\bullet}$, of abundance 8% and 2% of the base peak m/z 57, $[C_4H_9]^+$. The $[C_5H_{12}O]^{+\bullet}$ ion is formed by loss of CH_2O from the molecular ion. The peaks m/z 87 and m/z 88 are shifted to m/z 89 and 90 and are at m/z 87 and m/z 89 in the mass spectra of $(CH_3)_3COCD_2CD_2OH$ and $(CH_3)_3COCH_2CH_2OD$ respectively. The m/z 88 ion $[C_5H_{12}O]^{+\bullet}$, is assigned the structure 5 as shown below

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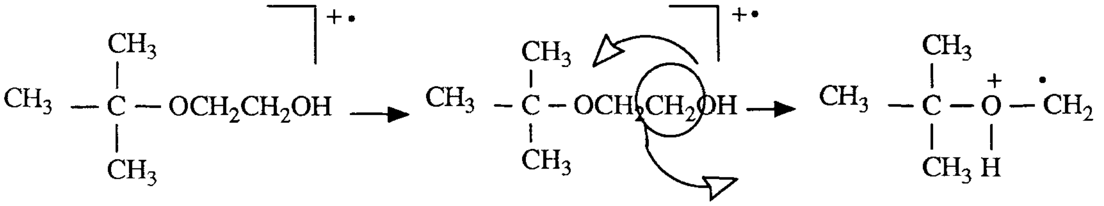
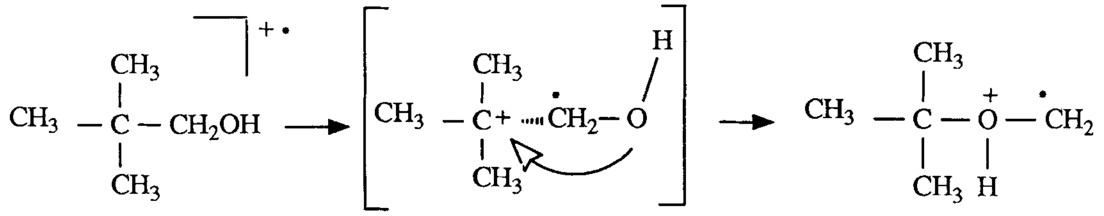


(6) (5)

The metastable ion (MI) mass spectrum of 5 displays three peaks, m/z 56, m/z 57 and m/z 58 in a 100:5:20 ratio. The latter two represent the statistical contributions from $^{13}CH_2O$ and CH_2O loss respectively from $^{13}CC_4H_{11}O^+$, m/z 57 being the only peak in the MI mass spectrum of m/z 87. Note that m/z 87 generated from 1, produces an intense metastable peak at m/z 69, corresponding to loss of H_2O. Thus the $[C_5H_{11}O]^+$ ions from 5 and 1 clearly have different structures. The kinetic energy release calculated from the half height width of the m/z 56 peak ($T_{0.5}$) was 1.5 ± 0.1 meV, in very close agreement with that for neopentanol molecular ions, 1, 1.4 ± 0.1 meV, time-scale ca 10 μs[5]. The metastable deuterium labelled 5 ions, referred to above, decompose with the same label retention and loss and $T_{0.5}$ values observed for α-D_2 and O-D neopentanol - see Table 1, showing that they have common fragmentation routes. Thus we conclude that the molecular ion of neopentanol undergoes a rearrangement formally described as a partial separation of a t-butyl cation and a $^{\bullet}CH_2OH$ radical in which, once a critical extension has been exceeded, the radical can rotate, presenting its electronegative O atom to the $[C_4H_9]^+$ core and so yielding the ylidion 5. These results provide the first direct experimental support for the original proposal of Hammerum and Audier[6] and the reaction has similarities with the rearrangement of alkyl phenyl ether ions.[3,4]

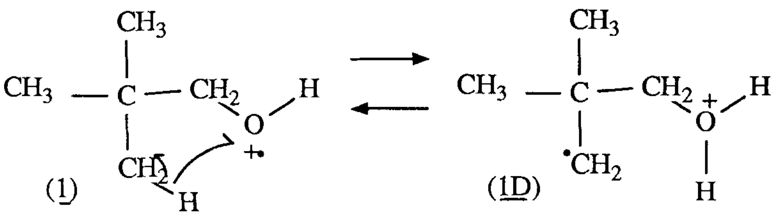


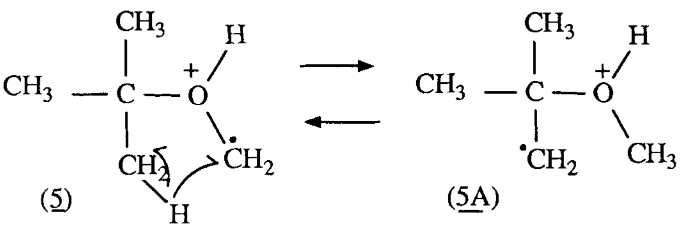
(1) (5)

Table 1 H/D distribution (%) among $[C_4H_8]^{+\bullet}$ ions produced from D-labelled metastable $[C_5H_{12}O]^{+\bullet}$ isomers. Numbers in parentheses are the random statistical ratios.

ION	LABEL	C_4H_8	C_4H_7D	$C_4H_6D_2$	$C_4H_5D_3$
$(CH_3)_3CCH_2OH^{+\bullet}$(1)	-OD	56(*33*)	44(*67*)		
	$-CD_2OH$	28(*9*)	56(*48*)	16(*43*)	
	$-CD_2OD$	12(2)	43(22)	37(*51*)	8(*25*)
	$-CH_2D$	55	45		
$(CH_3)_2C(CH_2D)CD_2OH^{+\bullet}$(1)		16	42	34	8
$(CH_3)_2C^{\bullet}CH_2O^+(H)CH_3$(4)	-OD	58	42		
	$-OCD_3$	14	43	37	6
$(CH_3)_3CO^+(H)CH_2^{\bullet}$(5)	-OD	56	44		
	$-CD_2$	29	53	18	

Exchange between the hydroxyl H and those in the methyl groups in 1 and between the methylene hydrogens and methyl group hydrogens in 5 can be accomplished as shown below, both processes involving 1,4 H shifts.





Note that deuterium labelled t-butyl methyl ether ions showed no H/D mixing[5] and therefore their fragmentation cannot involve distonic or ylid ions such as 5 or 5A.

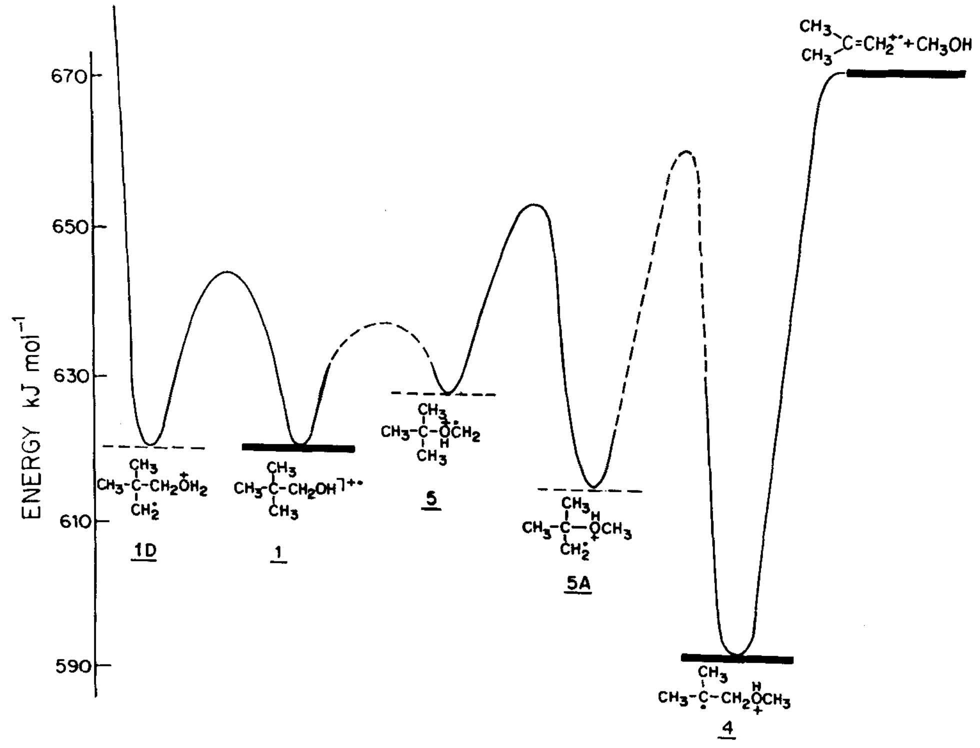


Figure 1 Energy diagram showing estimated energies (broken lines) and measured energies for isomeric $[C_5H_{12}O]^{+\bullet}$ ions.

The energy diagram, Fig 1, shows the relative energies of ions 1, 1D, 4, 5, 5A and the decomposition products. The heats of formation, ΔH_f, have only been experimentally measured for ions 1 and 4.[5] Earlier estimates[5] for ΔH_f 4 and ΔH_f 1D have been slightly revised; ΔH_f values for ions 5 and 5A were estimated using $\Delta H_f[(CH_3)_3CO^+(H)CH_3]$=402 kJ mol^{-1} [7] and with D[-CH_2-H] values of 444 and 431 kJ mol^{-1} respectively. Choice of the latter values is uncertain to within perhaps ± 15 kJ mol^{-1} but C-H bond strengths in such protonated ions are stronger than those in the neutral (unprotonated) species[8]. The transition state energy for the 1,4-H shifts has been set at 25 kJ mol^{-1}, slightly below that which has been measured for the 1,4-H transfer in the propanol molecular ion, 33 kJ mol^{-1} [9]. The other transition state energies are not known and so are of only qualitative significance.

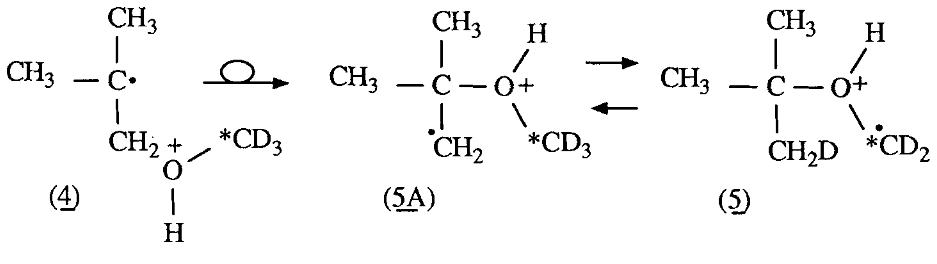
Ion 4, as described previously[5], showed exclusive loss of the methoxy carbon (starred below) in the eliminated methanol, showing that the formally simple methyl migration from oxygen to the radical site to yield ionized neopentanol does not take place. A simple solution is provided by the mechanism shown below, in which 4 rearranges to 5A and hence to ions 1 and 5. This proposal is strongly supported by the behaviour of the ion $(CH_3)_2C(CH_2D)CD_2OH^{+\bullet}$ (see Table 1), which produces labelled $[C_4H_8]^{+\bullet}$ fragment ions with the same relative abundances as the labelled (-OCD_3) ion 4. Thus the distribution of H and D in the fragmentation products is, within experimental error, independant of their initial positions in the precursor ions-see Table 1. Moreover, loss of label in the methylpropene ions is clearly favoured over retention and the labelled methanol produced showed a preference for deuterium to be attached to oxygen[5]. Qualitatively these results can be explained as follows:

(i)Positional identity of H and D in all these $[C_5H_{12}O]^{+\bullet}$ ions is randomly lost prior to their metastable decomposition.

(ii) The final reacting configuration is the methylpropene ion/methanol complex, with the kinetics of their metastable decomposition being governed by an isotope effect.

(iii) this isotope effect, which gives rise to the observed non-random distribution of labelled products, arises from a weaker binding between -OD and the olefin ion than for the -OH analogue.

Thus, within the time window for metastable decompositions, the variously labelled ion-molecule complexes dissociate with different rates. Finally, these proposals require that at shorter MI observation times (i.e. for ions of higher internal energy), the labelled product abundance ratios should be closer to random, as smaller isotope effects come into play. Experiments confirm this; these latter results and the magnitude of the isotope effects will be described elsewhere.



Experimental

Mass spectrometry experiments were performed as described earlier[5]. The 2-t-butoxyethanol was synthesized by refluxing t-butyl chloride with an equimolar amount of sodium (dissolved in an excess of ethylene glycol) for a period of 15 hours; the same reaction with ethylene-d_4 glycol produced $(CH_3)_3COCD_2CD_2OH$. The -OD alcohol was produced by exchange with D_2O. The $(CH_3)_2C(CH_2D)CD_2OH$ was made by reducing methyl (3-bromo-2,2-dimethyl) propionate with $LiAlD_4$ and $(CH_3)_2C(CH_2D)CH_2OH$ by a similar reduction with 3-bromo-2,2-dimethyl propanol.

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Yours,

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