Products of Low Potential Energy in Mass Spectra as a Consequence of Ion–Dipole Attractions: Some Neopentyl Compounds

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The 12.0 eV mass spectra of five neopentyl derivatives [$(CH_3)_3CCH_2Z$; Z = OH, OCH_3, NH_2, $NHCH_3$, and $N(CH_3)_2$] are reported. The competition between simple α-cleavage, single, and double hydrogen transfer reactions is discussed in mechanistic and energetic terms. Double hydrogen transfer occurs for Z = OCH_3 and NH_2, giving rise to the unusual daughter ions $(CH_3)_2OH^+$ and $CH_3NH_3^+$, respectively. The behaviour of the ionised neopentyl compounds is compared with that of the homologous isobutyl species, for which similar rearrangements have been previously reported.

Ion–dipole attractions have recently been shown to play an important role in the unimolecular reactions of isolated organic ions.[1,2] These attractions facilitate isomerisation of incipient carbonium ions and permit hydrogen transfers between the incipient products. A striking example is ionised isobutyl alcohol, which decomposes *via* a double hydrogen transfer, to give protonated methanol and allyl radical, instead of undergoing simple α-cleavage to protonated formaldehyde and isopropyl radical. However, dissociation of ionised isobutylamine proceeds by simple α-cleavage; this contrast must reflect the high energy of the intermediates involved en route to protonated methylamine and allyl radical, because this product combination is energetically the most favourable.[3]

Other novel rearrangements have been observed in the low-energy mass spectra of ethers and amines.[4,5] In the course of a systematic search for such reactions, an ion at *m/z* 32 ($CH_3NH_3^+$) was detected in the 12.0 eV mass spectrum of neopentylamine. This reaction is analogous to that found for ionised isobutyl alcohol and corresponds to the elimination of a methylallyl radical. Table 1 summarises the 12.0 eV mass spectra of five neopentyl derivatives. It is clear from these data that the occurrence of the double hydrogen transfer reaction is not general; moreover, the trend found is the opposite of that seen in the isobutyl analogues. These differences may be understood by reference to the probable mechanism (Scheme) and energetics (Table 2) of the reactions.

Three general classes of decomposition routes can be envisaged. First, simple α-cleavage, with retention of charge by either fragment [(1) ⟶ (2) ⟶ products]. Secondly, hydrogen transfer in the complex (2), to form (3), followed by separation to products in which $C_4H_8^{+\cdot}$ is the daughter ion. Thirdly, two successive hydrogen transfers [(1) ⟶ (2) ⟶ (3) ⟶ (4) ⟶ products]. Each of the complexes (2)—(4) can be substantially stabilised, relative to the corresponding separated products, by ion–dipole attractions. The magnitude of these stabilisations depends on the size of the dipole moment of the incipient neutral species. In the homologous system, $(CH_3)_2CHCH_2OCH_3^{+\cdot}$, a minimum value of *ca.* 40 kJ mol^{-1} was found for the stabilisation conferred upon ionised propene by a co-ordinated molecule of methanol.[3] Comparable and greater values have been reported in similar cases.[2]

For ionised neopentyl alcohol (1a) no significant peak appears at *m/z* 33 ($CH_3OH_2^+$, if formed by double hydrogen transfer). Large peaks are found at *m/z* 57 and 56; these arise by simple α-cleavage or by single hydrogen transfer, with the hydrocarbon fragment retaining the charge in each case. These results reflect the low heats of formation of the product combinations; there is no energetic preference for undergoing the more extensive rearrangement required to produce $CH_3OH_2^+$. Thus, even in metastable transitions, $C_4H_7^{\cdot}$ loss does not compete; CH_3OH elimination occurs instead.

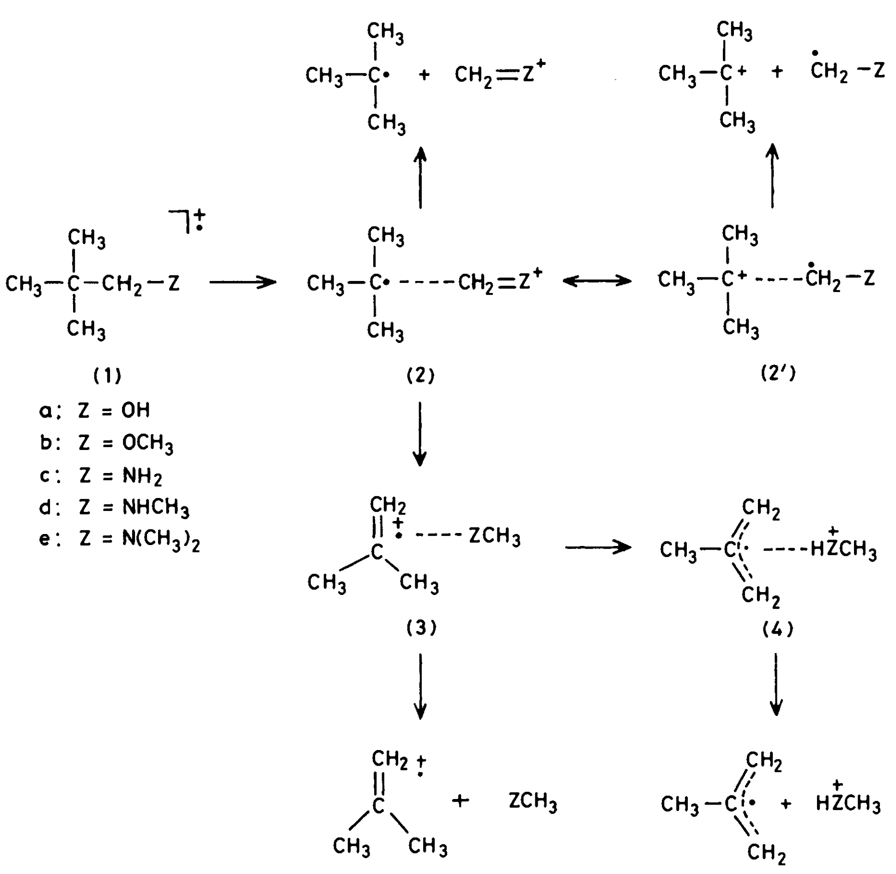
Table 1. 12.0 eV mass spectra of neopentyl derivatives

Compound	*m/z* and relative abundance [a]
$(CH_3)_3CCH_2OH$	88 ($M^{+\cdot}$, 10); 73 (18); 57 (86), 56 (100); 33 (1); 30 (10).
$(CH_3)_3CCH_2OCH_3$	102 ($M^{+\cdot}$, 94); 87 (20); 70 (17); 57 (48); 56 (100); 47 (27); 45 (5).
$(CH_3)_3CCH_2NH_2$	87 ($M^{+\cdot}$, 74); 72 (15); 56 (5); 32 (25); 30 (100).
$(CH_3)_3CCH_2NHCH_3$	101 ($M^{+\cdot}$, 65); 86 (10); 44 (100).
$(CH_3)_3CCH_2N(CH_3)_2$	115 ($M^{+\cdot}$, 60); 100 (7); 58 (100).

[a] Abundances normalised to a value of 100 units for the base peak; ions of abundance lower than 5 units, or arising solely as isotope peaks, are omitted.

On proceeding to the corresponding ether, however, a different picture emerges. Although decompositions to give $C_4H_9^+$ or $C_4H_8^{+\cdot}$ remain the main reactions in the 12.0 eV spectrum, a significant amount of double hydrogen transfer is found [as evidenced by the peak at *m/z* 47 due to $(CH_3)_2OH^+$]. This change in behaviour, relative to the parent alcohol, reflects alterations in the relevant energetics: $C_4H_9^+$ and $C_4H_8^{+\cdot}$ formation are approximately equally favourable, whilst production of $(CH_3)_2OH^+$ requires marginally less energy (Table 2). All the complexes (2b)—(4b) would be easily accessible, even without much ion–dipole stabilisation; consequently, double hydrogen transfer is feasible and occurs. From the data of Table 2, it might have been expected that $C_4H_7^{\cdot}$ loss would become the dominant reaction at the lowest internal energies. However, the decomposition of metastable ions actually involves essentially only CH_3OCH_3 elimination. This anomaly may reflect slight inaccuracies in the thermochemical data: in particular, the heat of formation of methylallyl radical appears to be somewhat uncertain and might be in error by the requisite amount (*ca.* 20 kJ mol^{-1}).

Neopentylamine also exhibits a peak in the 12.0 eV mass spectrum which arises from double hydrogen transfer: $C_4H_7^{\cdot}$ loss from $(CH_3)_3CCH_2NH_2^{+\cdot}$ is evident from the moderately abundant $CH_3NH_3^+$ ion at *m/z* 32. In metastable transitions, $C_4H_7^{\cdot}$ loss dominates the alternative α-cleavage process (relative abundances 75 and 25%, respectively). These data are in sharp contrast with the behaviour of the homologous isobutyl series, where $(CH_3)_2CHCH_2OH^{+\cdot}$ gave an abundant $CH_3OH_2^+$ ion by double hydrogen transfer, $(CH_3)_2CHCH_2OCH_3^{+\cdot}$ showed some double hydrogen transfer, but $(CH_3)_2$-



Scheme.

Table 2. Energetic data relevant to decomposition of ionised neopentyl compounds

Ion	Product and ΔH_f [a]	$\Sigma\Delta H_f$ [a]
$(CH_3)_3CCH_2OH^{+\cdot}$	$(CH_3)_3C^+$ (700) [6,7] + $\dot{C}H_2OH$ (−25) [8]	675
	$(CH_3)_3C^\cdot$ (30) [6,7] + $CH_2{=}OH^+$ (685) [9]	715
	$(CH_3)_2C{=}CH_2^{+\cdot}$ (875) [10] + CH_3OH (−200) [11]	675
	$(CH_3)_2C{=}CH_2$ (−15) [11] + $CH_3OH^{+\cdot}$ (845) [11]	830
	$C_4H_7^\cdot$ (120) [12] + $CH_3\dot{O}H_2^+$ (570) [9]	690
$(CH_3)_3CCH_2OCH_3^{+\cdot}$	$(CH_3)_3C^+$ (700) [6,7] + $\dot{C}H_2OCH_3$ (−10) [13]	690
	$(CH_3)_3C^\cdot$ (30) [6,7] + $CH_2{=}\overset{+}{O}CH_3$ (660) [14]	690
	$(CH_3)_2C{=}CH_2^{+\cdot}$ (875) [10] + CH_3OCH_3 (−185) [11]	690
	$(CH_3)_2C{=}CH_2$ (−15) [11] + $CH_3OCH_3^{+\cdot}$ (775) [11]	760
	$C_4H_7^\cdot$ (120) [12] + $(CH_3)_2\dot{O}H^+$ (550) [9]	670
$(CH_3)_3CCH_2NH_2^{+\cdot}$	$(CH_3)_3C^+$ (700) [6,7] + $\dot{C}H_2NH_2$ (150) [15]	850
	$(CH_3)_3C^\cdot$ (30) [6,7] + $CH_2{=}NH_2^+$ (745) [11]	775
	$(CH_3)_2C{=}CH_2^{+\cdot}$ (875) [10] + CH_3NH_2 (−25) [11]	850
	$(CH_3)_2C{=}CH_2$ (−15) [11] + $CH_3NH_2^{+\cdot}$ (885) [11]	870
	$C_4H_7^\cdot$ (120) [12] + $CH_3\dot{N}H_3^+$ (625) [9]	745
$(CH_3)_3CCH_2NHCH_3^{+\cdot}$	$(CH_3)_3C^+$ (700) [6,7] + $\dot{C}H_2NHCH_3$ (125) [15]	825
	$(CH_3)_3C^\cdot$ (30) [6,7] + $CH_2{=}\overset{+}{N}HCH_3$ (695) [16]	725
	$(CH_3)_2C{=}CH_2^{+\cdot}$ (875) [10] + $(CH_3)_2NH$ (−20) [11]	855
	$(CH_3)_2C{=}CH_2$(−15) [11] + $(CH_3)_2NH^{+\cdot}$ (775) [11]	760
	$C_4H_7^\cdot$ (120) [12] + $(CH_3)_2\dot{N}H_2^+$ (605) [9]	725
$(CH_3)_3CCH_2N(CH_3)_2^{+\cdot}$	$(CH_3)_3C^+$ (700) [6,7] + $\dot{C}H_2N(CH_3)_2$ (110) [15]	810
	$(CH_3)_3C^\cdot$ (30) [6,7] + $CH_2{=}\overset{+}{N}(CH_3)_2$ (660) [16]	690
	$(CH_3)_2C{=}CH_2^{+\cdot}$ (875) [10] + $(CH_3)_3N$ (−25) [11]	850
	$(CH_3)_2C{=}CH_2$ (−15) [11] + $(CH_3)_3N^{+\cdot}$ (730) [11]	715
	$C_4H_7^\cdot$ (120) [12] + $(CH_3)_3NH^+$ (580) [9]	700

[a] All values in kJ mol^{-1} and rounded to the nearest 5 kJ mol^{-1}.

$CHCH_2NH_2^{+\cdot}$ underwent only α-cleavage to $CH_2{=}NH_2^+$.[3] The reversal of this trend in the neopentyl system reflects differences in the energetics associated with dissociation. The inability of $C_3H_5^\cdot$ loss to compete with $C_3H_7^\cdot$ elimination from $(CH_3)_2CHCH_2NH_2^{+\cdot}$ has been ascribed to the high energy of one of the complexes ($CH_3CH{=}CH_2^{+\cdot}$ co-ordinated CH_3NH_2) en route to $CH_3NH_3^+$. This complex would be energetically accessible only if it were stabilised by *ca.* 120 kJ mol^{-1} relative to the separated products. However, in the case of $(CH_3)_3CCH_2NH_2^{+\cdot}$, the required stabilisation is drastically reduced (to *ca.* 70 kJ mol^{-1}) by the greater stability of the ionised alkene [$(CH_3)_2C{=}CH_2^{+\cdot}$] in the corresponding complex (3c). Consequently, an adequate stabilisation by ion–dipole attraction is feasible and the way is opened for formation of the thermodynamically most favourable products, $C_4H_7^\cdot$ and $CH_3NH_3^+$.

Further evidence that the Scheme represents a true description of these reactions is furnished by the deuterium labelled analogue $(CH_3)_3CCD_2NH_2^{+\cdot}$. Ambiguities surround the origin of peaks in the 12.0 eV spectrum; however, this ion undergoes only $C_4H_7^\cdot$ loss (double hydrogen transfer) and $C_4H_9^\cdot$ loss (α-cleavage) in metastable transitions, but no C_4H_6D elimination occurs. These results show that the integrity of the original methylene group is preserved and that it is retained intact in the $CH_3NH_3^+$ daughter ion; this suggests that (2c) $\longrightarrow$ (3c) is essentially irreversible. However, these labelling results do not shed any light on the possible intermediacy of $^\cdot CH_2NH_3^+$ (instead of $CH_3NH_2^{+\cdot}$) in the mechanism whereby $CH_3NH_3^+$ is formed. Nevertheless, since the $^\cdot CH_2ZH^+$ ions are only marginally more stable than their $CH_3Z^{+\cdot}$ isomers, this possibility does not materially alter the conclusions based on the Scheme and Table 2.

No significant double hydrogen transfer occurs for ionised methylneopentylamine or dimethylneopentylamine. Instead, α-cleavage dominates to give ions at *m*/*z* 44 ($CH_3NH{=}CH_2^+$) and 58 [$(CH_3)_2N{=}CH_2^+$], respectively, with elimination of t-$C_4H_9^\cdot$. This trend reflects the changes in energetics of the product combinations when the nitrogen atom in ionised neopentylamine is progressively methylated. The reduction in heat of formation of the imminium ions is 50 kJ mol^{-1} for the first methylation and 45 kJ mol^{-1} for the second. These values are greater than those (20 and 25 kJ mol^{-1}, respectively) occasioned by methylation of $CH_3NH_3^+$. Thus, rearrangement and loss of $C_4H_7^\cdot$ is energetically preferable to α-cleavage for the ionised primary amine, but not in the analogous secondary and tertiary systems.

A final point concerns the direction of charge retention in α-cleavage in the ionised neopentyl species. For the three ionised neopentylamines, production of imminium ions is energetically very preferable to formation of $C_4H_9^+$; this explains the absence of *m*/*z* 56 and 57 in the 12.0 eV mass spectra of these compounds. However, the oxygen analogues undergo α-cleavage or single hydrogen transfer with charge retention at carbon; this is in keeping with the inferior ability of oxygen to stabilise a positive charge on an adjacent carbon atom.

Experimental

The compounds needed for this work were either commercially available or else synthesised by conventional routes. The ^{2}H-labelled analogue of neopentylamine was prepared as in reaction (1).

$$(CH_3)_3CCN \xrightarrow[Et_2O]{LiAlD_4} (CH_3)_3CCD_2NH_2 \qquad (1)$$

The 12.0 eV mass spectra were determined using a modified AEI MS9 double focusing mass spectrometer, at a source temperature of 75 °C, using the procedure previously described.[17]

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