Products of Low Potential Energy in Mass Spectra as a Consequence of Ion–Dipole Attractions; the Case of Isobutyl Alcohol

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Summary The decomposition of ionised isobutyl alcohol to give $CH_3OH_2^+$ and $C_3H_5^+$, rather than $CH_2=OH^+$ and $C_3H_7^+$, may be understood in terms of ion–dipole attractions which facilitate the formation of the products having the lowest potential energy.

It has become apparent, in recent years, that ion–dipole attractions are often extremely important in the unimolecular reactions of organic ions. Two distinct, but related, phenomena can be interpreted by means of ion–dipole interactions, Scheme 1.[1,2] First, rearrangement of incipient carbonium ions ($R^+ \rightarrow R'^+$) can occur in the species [(1a) and (2a), respectively] in which the R–X bond is essentially broken but R^+ and XH are still bound, relative to the separated products, by ion–dipole attraction. This situation is illustrated by the oxonium ions $CH_3CH_2CH_2\overset{+}{O}=CH_2$ and $(CH_3)_2CH\overset{+}{O}=CH_2$, which interconvert, at energies lower than those needed to dissociate either, *via* $C_3H_7^+$ – – –$O=CH_2$. The binding energy in these species, relative to $C_3H_7^+$ and $O=CH_2$, exceeds 75 kJ mol^{-1}; similar values are found in related cases.[3] When the co-ordinated species XH has a zero or negligible permanent electric dipole moment, little stabilisation is conferred upon (1a) and (2a); this shows the importance of the ion–dipole attraction in lowering the potential energy of (1a) and (2a).[4] Secondly, hydrogen transfer can occur in (2a) [or (1a)] to produce (3a),[5] which may decompose to R'H and X$^+$. In favourable cases, two such hydrogen transfers take place, with the formation of products that could not have been expected on the basis of simple cleavage in (1) or (2). This phenomenon occurs in the decomposition of ionised isobutyl alcohol, (4).

In addition to the normal α-cleavage process, leading to $CH_2=OH^+$ and $C_3H_7^+$, (4) undergoes abundant $C_3H_5^+$ loss, leading to $CH_3OH_2^+$. With the exception of m/z 43 ($C_3H_7^+$),

SCHEME 1
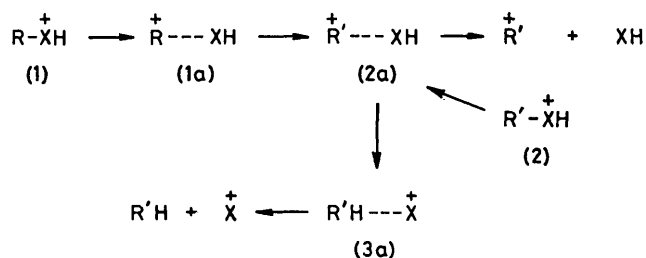
m/z 33 is the most abundant peak in the mass spectrum of isobutyl alcohol at ionising electron energies of 15—70 eV. Moreover, this unusual reaction persists in dissociation of (4) in metastable transitions, whilst the α-cleavage process cannot compete at these low internal energies. It is evident, therefore, that production of $CH_3OH_2^+$ and $C_3H_5^+$ requires less energy than the alternative reaction to form $CH_2=OH^+$ and $C_3H_7^+$.

Scheme 2 shows a mechanism to account for this behaviour. Stretching of a C–C σ-bond in (4) leads to (4a), which corresponds to $(CH_3)_2CH\cdot$ co-ordinated to $CH_2=OH^+$; were this stretching to continue to completion, α-cleavage would result to give $CH_2=OH^+$ and $(CH_3)_2CH\cdot$ ($\Sigma\Delta H_f$ = 765 kJ mol^{-1}).[6,7] However, hydrogen transfer in (4a) can lead to (4b), which comprises ionised propene and methanol bound together by an ion–dipole attraction. Since $CH_3CH=CH_2^+\cdot$ and CH_3OH have $\Sigma\Delta H_f$ = 755 kJ mol^{-1},[7] it is highly likely that (4b) is lower in energy than (4a). Further hydrogen transfer is feasible, to form (4c), which is composed of protonated methanol co-ordinated to allyl radical. Decomposition of (4c) leads to $CH_3OH_2^+$ and $C_3H_5^+$ ($\Sigma\Delta H_f$ = 740 kJ mol^{-1}).[8,9] Thus, ion–dipole attractions provide a method for binding together the constituent
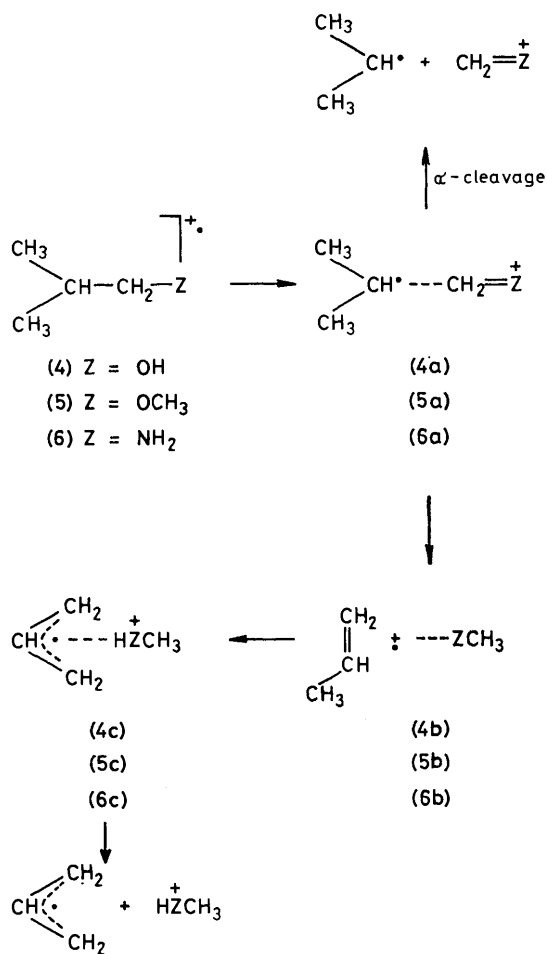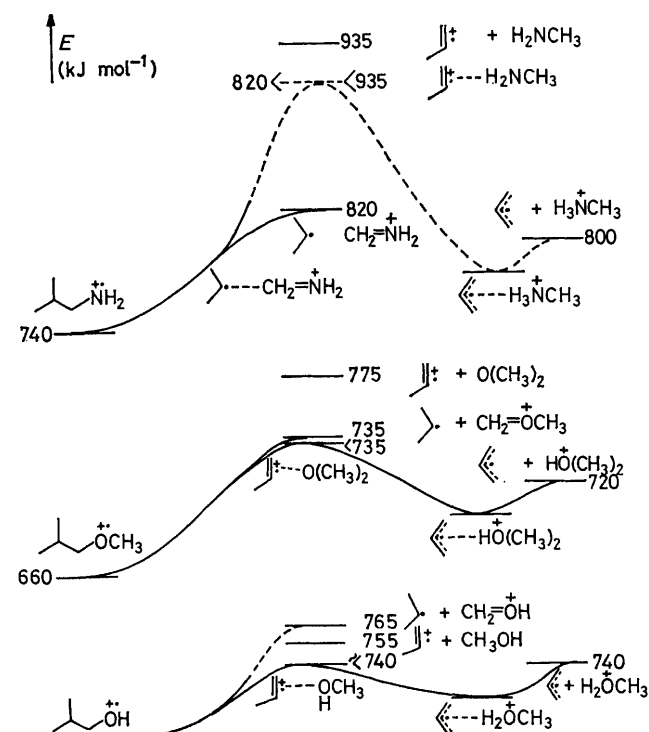
Scheme 2

components of (4a), (4b), and (4c), *en route* to the lowest energy products, $CH_3OH_2^+$ and $C_3H_5^+$.

Further insight is provided into the mechanism by a consideration of the analogous compounds isobutyl methyl ether and isobutylamine. Ionised isobutyl methyl ether, (5), exhibits peaks at m/z 45 and 47 in the ratio 10:1; these peaks correspond to $CH_3\overset{+}{O}=CH_2$ (α-cleavage) and $(CH_3)_2OH^+$ (rearrangement). At low internal energies (metastable ions), the rearrangement reaction dominates, being approximately double the abundance of the α-cleavage process. This change in behaviour, compared to (4), can be understood in terms of the energies of the appropriate product combinations and associated complexes. Although $(CH_3)_2OH^+$ and $C_3H_5^+$ ($\Sigma\Delta H_f = 720$ kJ mol^{-1})[8,9] is the energetically most favourable product combination, $CH_3CH=CH_2^{+\cdot}$ and CH_3OCH_3 ($\Sigma\Delta H_f = 775$ kJ mol^{-1})[7] represents an inferior combination to $C_3H_7^+$ and $CH_3\overset{+}{O}=CH_2$ ($\Sigma\Delta H_f = 735$ kJ mol^{-1}). This means that (5b) is higher in energy relative to (5a), than (4b) is relative to (4a). Consequently, the isomerisation (5a) → (5b) → (5c) competes less successfully with α-cleavage than is the case for the lower homologues (4a) → (4b) → (4c). However, the fact that (5) → (5a) → (5b) → (5c) → $(CH_3)_2OH^+$ + $C_3H_5^+$ does dominate slightly, at low internal energies,

indicates that this route remains energetically preferable to α-cleavage. Thus, (5b) must be bound, relative to $CH_3CH=CH_2^{+\cdot}$ + CH_3OCH_3, by at least $775-735 = 40$ kJ mol^{-1}; this figure, though only approximate, is comparable with values deduced in similar systems.[3,5]

In the case of ionised isobutylamine, (6), the α-cleavage process dominates, both at high and low internal energies: only a very small amount (<1% of the ion current due to α-cleavage) of rearrangement occurs. This cannot be due to the high heat of formation of $CH_3NH_3^+$ + $C_3H_5^+$ ($\Sigma\Delta H_f$ 800 kJ mol^{-1}),[8,9] because this product combination is energetically more favourable than either $CH_2=NH_2^+$ + $C_3H_7^+$ ($\Sigma\Delta H_f = 820$ kJ mol^{-1})[7] or $CH_3CH=CH_2^{+\cdot}$ + CH_3NH_2 ($\Sigma\Delta H_f = 935$ kJ mol^{-1}).[7] Rather, the crucial question concerns the asscessibility of the complex (6b). It is clear that (6b) is composed of high energy components and that the ion–dipole stabilisation is insufficient to permit formation of (6b) to compete with α-cleavage. This allows an upper limit of $935 - 820 = 115$ kJ mol^{-1} to be set for the (hypothetical) ion–dipole stabilisation of (6b). The energy levels relevant to the dissociation of (4), (5), and (6) are summarised in the Figure.

Figure

The mechanism proposed in Scheme 2 is also supported by ^{2}H-labelling results. Thus, $(CH_3)CDCH_2OH^{+\cdot}$ eliminates $C_3H_4D\cdot$ to give $CH_3OH_2^+$, but no contribution can be detected for $C_3H_5^+$ loss either as a daughter ion in the 70 eV spectrum or in metastable transitions. This shows that the methine proton is exclusively retained in the eliminated allyl radical, as depicted in Scheme 2. Furthermore, the spectrum of $(CH_3)_2CHCD_2OH$ shows a large peak at m/z 35 ($CD_2HOH_2^+$) and a small peak at m/z 34 ($CDH_2OH_2^+$); similar behaviour occurs for metastable $(CH_3)_2CHCD_2OH^{+\cdot}$

ions, which lose $C_3H_5^+$ and $C_3H_4D^{\cdot}$ in the ratio $12:1$; no significant $C_3H_3D_2^+$ loss is observed. These data establish that $(\mathbf{4a}) \rightarrow (\mathbf{4b})$ is essentially irreversible, but that a minor fraction ($ca.$ 1/7) of $(\mathbf{4b})$ ions revert to $(\mathbf{4a})$. Finally, $(CH_3)_2CHCH_2OD^{+\cdot}$ eliminates $C_3H_5^+$ and $C_3H_4D^{\cdot}$ in almost equal abundance in metastable transitions. This indicates that $(\mathbf{4b})$ and $(\mathbf{4c})$ interconvert to some extent; the experi-mental facts can be accommodated if $(\mathbf{4b})$ and $(\mathbf{4c})$ inter-convert, on average, once before dissociation takes place.

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