# Potential Energy Profiles for Unimolecular Reactions of Isolated Organic Ions: Some Isomers of $C_4H_{10}N^+$ and $C_5H_{12}N^+$

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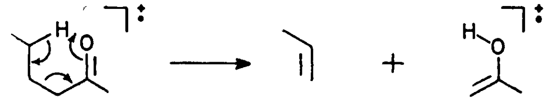
The unimolecular reactions of two isomers of $C_4H_{10}N^+$ and four isomers of $C_5H_{12}N^+$, of general formula $RNH^+{=}CH_2$ ($R = C_3H_7$ or $C_4H_9$), are discussed in terms of a potential energy profile approach. Two main decomposition channels are observed, both of which involve loss of an olefin from the original alkyl side chain. Hydrogen transfer from the alkyl chain to nitrogen can occur in an intermediate in which the incipient carbonium ion $R^+$ is weakly co-ordinated to $NH{=}CH_2$. This process results in the formation of $^+NH_2{=}CH_2$ and expulsion of an olefin containing the same number of carbon atoms as R. Alternatively, a 1,5-hydride shift can take place, from a $\gamma$-carbon atom in $RNH^+{=}CH_2$, to the isolated methylene group. This rearrangement may lead to loss of an olefin containing one less carbon atom than R, thus giving rise to $CH_3NH^+{=}CH_2$ as the daughter ion. The $\gamma$-hydrogen transfer process is analogous to the McLafferty rearrangement which is well known for ionised carbonyl compounds of sufficient chain length. Evidence is presented which shows that the 1,5-hydride shift is not synchronously concerted with olefin loss; instead, the $\gamma$-carbon atom acquires at least a partial positive charge before the olefin is expelled, with kinetic energy release.

THE unimolecular reactions of ions may be investigated conveniently using conventional double-focusing mass spectrometers.[1,2] Slow reactions, occurring in the field-free regions of such instruments, take place after some $10^8$ bond vibrations, thus permitting essentially all energetically accessible decomposition channels to be explored. Consequently, only the lowest activation energy processes give rise to metastable peaks.[3] Moreover, the excess energies present in the transition states for dissociation are comparable to those found in solution. This may be deduced from the frequent observation of primary deuterium isotope effects in the decomposition of metastable ions; in some cases, spectacularly large isotope effects are encountered.[4-7] In addition, although the interference of isolated electronic states is known,[8] this behaviour is unusual, and normally the reactions may be interpreted as involving only the ground electronic state of the ion in question.

Energy is the dominant parameter in determining the occurrence or non-occurrence of a given decay route.[3] Hence, it is often helpful to analyse the chemistry of isolated organic ions in terms of a potential energy profile, over which dissociation is considered to take place.[1,2,9-12] A variety of experimental data may be combined with known heats of formation for reactants, intermediates, and products, to construct these potential energy profiles. In particular, the relative abundances of competing decomposition channels, the kinetic energy release associated with each dissociation, and isotope labelling results are frequently informative.

Site-specific hydrogen transfer reactions are quite well known in the chemistry of isolated ions. An extremely important example is the $\gamma$-hydrogen, or McLafferty rearrangement, which is a common reaction for ionised carbonyl compounds with $\gamma$-hydrogen atoms [equation (1)].

At relatively high internal energy, the McLafferty rearrangement appears to be essentially specific; exclusive $\gamma$-hydrogen transfer occurs. However, at lower internal energies, appropriate to metastable transitions, transfer of other hydrogen atoms is detectable.[13] This suggests that the original hydrogen transfer to oxygen may be reversible. Quantum mechanical calculations also suggest that olefin elimination and hydrogen transfer are not concerted.[14] In this paper, experimental evidence is presented which shows that an analogous $\gamma$-hydrogen transfer rearrangement, observed in the decomposition of some immonium ions, is also not fully concerted.



(1)

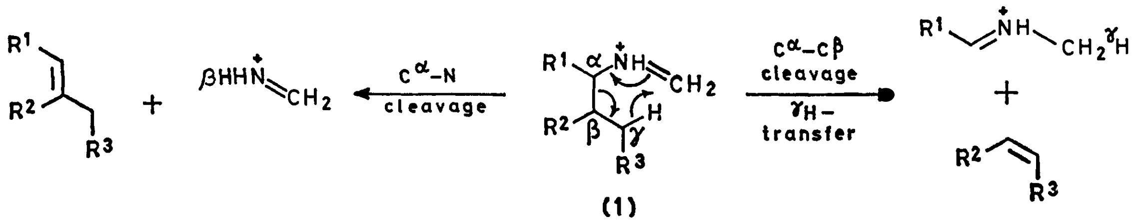
## RESULTS AND DISCUSSION

Loss of olefins is commonly observed as a major decomposition channel of immonium ions of general structure (1). Two distinct processes are frequently encountered; these correspond formally to $C^\alpha$–N and $C^\alpha$–$C^\beta$ cleavages (Scheme 1). Elimination of an olefin, containing one less carbon atom than the original alkyl side chain, can occur with an associated $\gamma$-hydrogen transfer. This may be represented as a concerted process (as depicted in Scheme 1), involving a six-membered ring transition state. Alternatively, the 1,5-hydride shift could occur prior to olefin loss; this would involve an open-chain carbonium ion as an intermediate (or perhaps transition state).

The simplest ion of general structure (1) is $CH_3CH_2\overset{+}{N}H{=}CH_2$. This ion has no $\gamma$-hydrogen atoms and consequently undergoes only the alternative $C^\alpha$–N cleavage process; $^2$H-labelling studies indicate that this reaction involves specifically the transfer of a $\beta$-hydrogen atom to nitrogen when $C_2H_4$ is lost.[15]

For the next homologue, $C_3H_7\overset{+}{N}H{=}CH_2$, two isomeric structures are possible, containing either an n-propyl or an isopropyl side chain. The relative abundances of $C_2H_4$ and $C_3H_6$ losses from these ions, together with the associated kinetic energy releases, are given in Table 1.

It is immediately evident from the data of Table 1 that $C_2H_4$ and $C_3H_6$ losses from (2) are proceeding *via* different mechanisms. Elimination of $C_3H_6$ occurs with only a relatively small and non-specific kinetic energy release, as shown by the gaussian metastable peak for this process. In contrast, $C_2H_4$ loss gives rise to a flat-topped metastable peak and occurs with a large and relatively specific kinetic energy release.



SCHEME 1

The data of Table 1 may be interpreted in terms of a rate-determining rearrangement of (2) to (3) prior to $C_3H_6$ loss. Two pieces of experimental evidence are in favour of this view. First, (2) undergoes loss of both $C_2H_4$ and $C_3H_6$, whereas (3) only eliminates $C_3H_6$. This suggests that $C_3H_6$ loss from (3) requires less energy than isomerisation to (2); however, starting from (2), loss of $C_2H_4$ requires a similar activation energy to that needed for rearrangement to (3). Secondly, the average kinetic energy release accompanying $C_3H_6$ loss from (2) is greater than that for $C_3H_6$ elimination from (3). This is consistent with a rate-determining isomerisation of (2) to (3), prior to $C_3H_6$ loss, followed by decomposition through the same transition states. Part of the excess energy released when the rate-determining rearrangement occurs, is partitioned as translation,[10-12] thus resulting in a larger kinetic energy release associated with $C_3H_6$ loss from (2), compared with (3).

TABLE 1

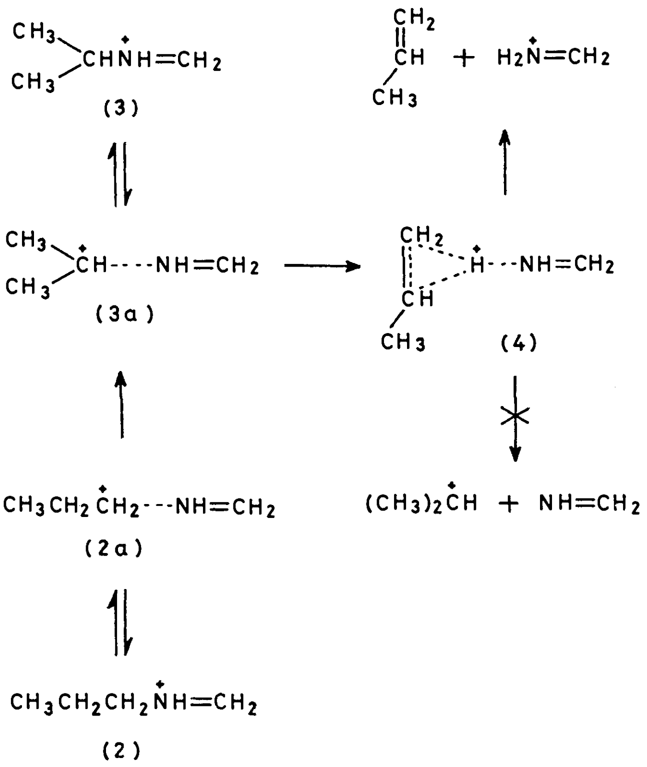
Observed reactions and associated kinetic energy releases for decomposition of isomeric $C_4H_{10}N^+$ ions

| Ion | Neutral Lost [a] | | Associated kinetic energy release [b] | |
|---|---|---|---|---|
| | $C_2H_4$ | $C_3H_6$ | $C_2H_4$ loss | $C_3H_6$ loss |
| $CH_3CH_2CH_2\overset{+}{N}H=CH_2$ | 62 | 38 | 65 [c] | 8 ± 0.6 [d] |
| $(CH_3)_2CH\overset{+}{N}H=CH_2$ (3) | 0 | 100 | | 5 ± 0.2 [d] |

[a] Values measured by second field-free region metastable peak areas and normalised to a total metastable ion current of 100 units. [b] Values in kJ $mol^{-1}$. [c] Flat-topped metastable peak, kinetic energy release measured from width at half height. [d] Gaussian metastable peak, average [16] kinetic energy release; the quoted errors correspond to one standard deviation.

Plausible mechanisms whereby $C_3H_6$ loss can occur from (2) and (3) are given in Scheme 2. These mechanisms are similar to those proposed previously for the oxygen analogues (5) and (6), respectively, of (2) and (3),[12,17] and for higher homologues of these oxonium ions.[18]

Starting from (3), stretching of the N–C σ bond leads to a complex (3a) in which methyleneimine is co-ordinated to an incipient isopropyl cation. Reorganisation of this complex can lead to (4) in which propene and methyleneimine are both co-ordinated to a common proton. This second complex can then break up, with the incipient neutral fragment having the greater proton affinity retaining the proton. In this case, methyleneimine has a much higher proton affinity (850 kJ $mol^{-1}$) than propene (750 kJ $mol^{-1}$ [19]); consequently, propene is eliminated when (3) decomposes *via* (4). Similarly, N–C σ bond stretching in (2) produces (2a), which is a complex in which an incipient n-propyl cation is co-ordinated to methyleneimine. A 1,2-hydride shift in the incipient cation can occur exothermically to form the thermodynamically more favourable isomer (3a). Elimination



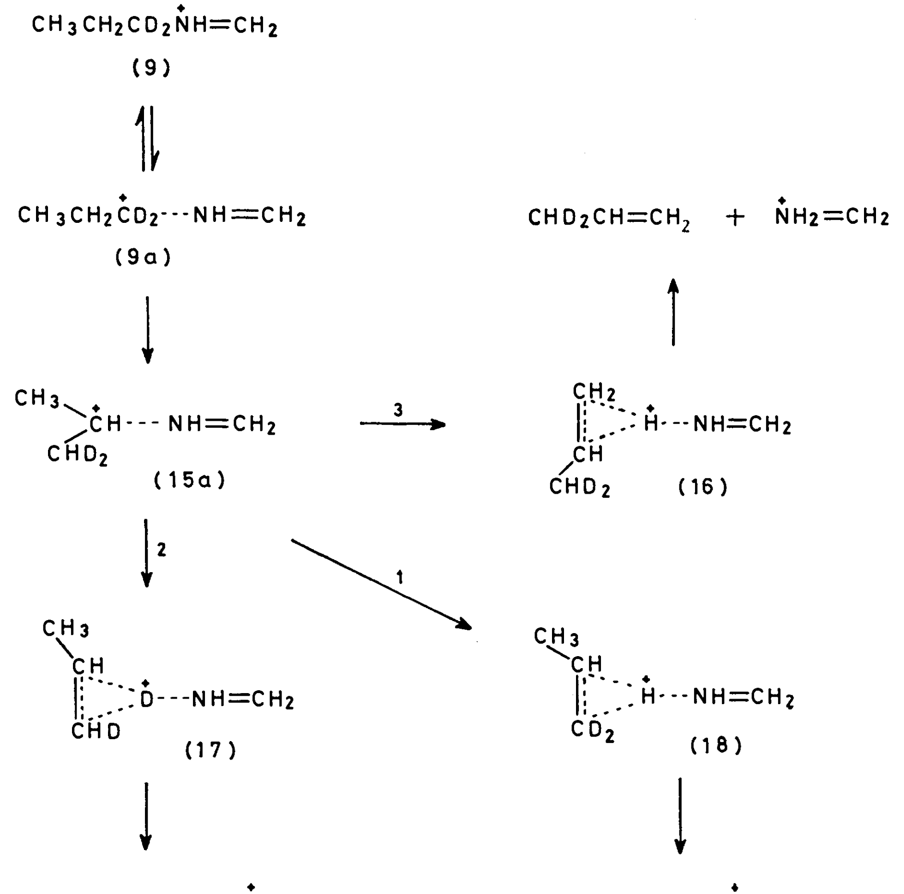
SCHEME 2

$CH_3CH_2CH_2\overset{+}{O}=CH_2$ (5)

$(CH_3)_2CH\overset{+}{O}=CH_2$ (6)

of propene may then take place, *via* (4), in an analogous manner to propene loss starting from (3).

The complexes (2a) and (3a) are stabilised, relative to the separated cation and neutral, by a strong ion dipole attraction. This stabilisation should be quite pronounced, even when the N–C distance is sufficiently long (*ca.* 0.3 nm) that the covalent $\sigma$ bond is essentially broken. For the analogues oxonium ions (5) and (6), the corresponding stabilisation is *ca.* 75 kJ mol$^{-1}$.[18] Higher homologues of (5) and (6), in which the incipient carbonyl compound has a greater dipole moment, exhibit even larger ion–dipole stabilisations (85—105 kJ mol$^{-1}$) when the C–O $\sigma$ bond is stretched.[18] In the case of (2a) and (3a), a smaller stabilisation (50 kJ mol$^{-1}$) is expected on account of the weaker dipole moment (1.4 D) of methyleneimine compared to that (2.3 D [20]) of formaldehyde. However, when the incipient n-propyl cation in (2a) isomerises to the isopropyl structure, *ca.* 65 kJ mol$^{-1}$ of potential energy is released. This is more than enough to overcome the ion–dipole attraction of 50 kJ mol$^{-1}$ which exists in (2a). Consequently, the rearranged ions undergo relatively fast dissociation, *via* isomerisation to (4) followed by $C_3H_6$ loss, with increased kinetic energy release.



SCHEME 3

Other experimental evidence may be cited in favour of the mechanisms given in Scheme 2. The results of $^2H$ labelling studies (Table 2) reveal that the [$CH_2{=}NH$] unit of (2) and (3) is incorporated intact in the $CH_2{=}NH_2^+$ daughter ion, produced when $C_3H_6$ is lost. Thus, the *N*-deuteriated analogues of (2) and (3), and the *C*-deuteriated ions $CH_3CH_2CH_2\overset{+}{N}H{=}CD_2$ and $(CH_3)_2CH\overset{+}{N}H{=}CD_2$, all eliminate only $C_3H_6$ in the propene loss reaction. This is consistent with the mechanisms given in Scheme 1. Moreover, the behaviour of $CH_3CH_2CD_2\overset{+}{N}H{=}CH_2$ is especially informative; this ion eliminates $C_3H_4D_2$ and $C_3H_5D$ in the ratio 71 : 29. The significant competition of $\alpha$-hydrogen transfer to nitrogen may be understood in terms of Scheme 3. The 1,2-hydride shift in (9a) gives rise to (15a), which contains an incipient isopropyl cation with $CH_3$ and $CHD_2$ groups. When rearrangement of (15a) takes place, to give a species in which propene and methyleneimine are co-ordinated to a common proton (or deuteron), any one of these two deuterium or four hydrogen atoms can be transferred. This atom eventually becomes attached to nitrogen in the $\overset{+}{N}H_2{=}CH_2$ (or $\overset{+}{N}HD{=}CH_2$) daughter ion. If rearrangement of (15a) to (16), (17), or (18) occurred, with statistical hydrogen or deuterium selection from the two methyl groups of (15a), then $C_3H_4D_2$ and $C_3H_5D$ losses would be expected in the ratio 2 : 1. The experimental value, 71 : 29, is close to this figure; the slight discrepancy, if significant, may reflect a small isotope effect favouring hydrogen, rather than deuterium, transfer, thus resulting in a slight increase in $C_3H_4D_2$ loss relative to $C_3H_5D$ elimination.

Ions with an n-propyl side chain also undergo $C_2H_4$ loss in metastable transitions. This process could be formulated as a concerted reaction, occurring through a six-membered ring transition state [Scheme (4), (2) ⟶ products]. Alternatively, the open-chain carbonium ion (19) may be produced by a 1,5-hydride shift; this ion can now eliminate $C_2H_4$ by fission of the appropriate C–C σ-bond, with nitrogen lone-pair participation.

TABLE 2

Observed decompositions of $^2$H-labelled analogues of (2) and (3)

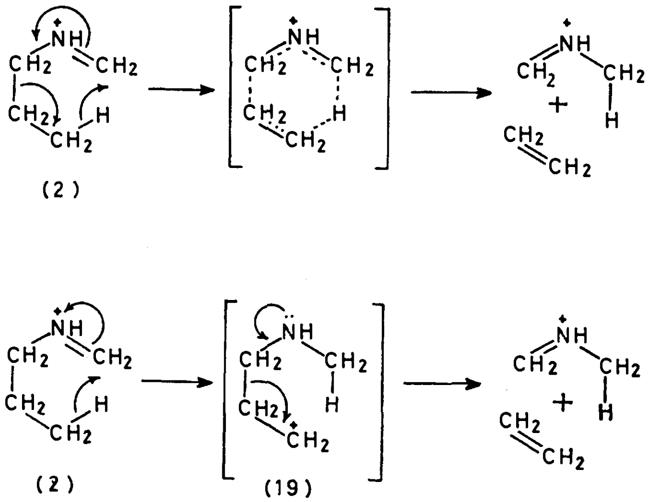
| Ion | Neutral lost [a] | | | |
|---|---|---|---|---|
| | $C_3H_6$ | $C_3H_5D$ | $C_3H_4D_2$ | $C_3H_3D_3$ |
| $CH_3CH_2CH_2\overset{+}{N}D=CH_2$ (7) | 100 | | | |
| $CH_3CH_2CH_2\overset{+}{N}H=CD_2$ (8) | 100 | | | |
| $CH_3CH_2CD_2\overset{+}{N}H=CH_2$ (9) | | 29 ± 2 [b] | 71 ± 3 [b] | |
| $CH_3CH_2CH_2\overset{+}{N}D=CD_2$ (10) | 100 | | | |
| $CH_3CH_2CD_2\overset{+}{N}D=CH_2$ (11) | | 29 ± 1 [b] | 71 ± 3 [b] | |
| $(CH_3)_2CH\overset{+}{N}D=CH_2$ (12) | 100 | | | |
| $(CH_3)_2CH\overset{+}{N}H=CD_2$ (13) | 100 | | | |
| $(CH_3)_2CH\overset{+}{N}D=CD_2$ (14) | 100 | | | |

[a] Values measured by first field-free region metastable peak areas and normalised to a total of 100 units; very similar results are found for dissociations occurring in the second field-free region. [b] The quoted errors correspond to one standard deviation.

It is clear, from the flat-topped metastable peak corresponding to $C_2H_4$ loss, that this reaction proceeds with a substantial reverse activation energy, part of which is translational. Concerted elimination of $C_2H_4$ would be symmetry-allowed [21] and ought not to involve a symmetry-imposed barrier towards either forward or reverse reactions. However, a reverse activation energy could arise from causes other than orbital symmetry. On the other hand, the involvement of the high energy species (19) provides a simple explanation of the kinetic energy release which accompanies $C_2H_4$ loss. Moreover, open-chain carbonium ions such as (19) have previously been postulated as intermediates or transition states in the decomposition of organic ions.[1,2,9-12,21,22]

The potential energy profile of Figure 1 may be constructed using known or estimated heats of formation for reactant ions,[23] open-chain carbonium ions,[24] product ions,[23,25] and neutral species.[25] In addition, the heats of formation of species containing an incipient carbonium ion co-ordinated to methyleneimine are estimated to be stabilised by 50 kJ mol$^{-1}$, relative to the total heat of formation of the isolated carbonium ion [26] and methyleneimine.

The observed behaviour of (2) and (3) can be interpreted in terms of the potential energy profile of Figure 1.



SCHEME 4

Starting from (3), isomerisation to (2), *via* (3a) and (2a), is energetically less favourable than $C_3H_6$ loss. Consequently, (3) eliminates $C_3H_6$ in preference to rearranging to (2). However, starting from (2), isomerisation to (3), *via* (2a) and (3a), requires a very similar activation energy to that needed to promote loss of $C_2H_4$, *via* the open-chain carbonium ion (19). As a result, (2) eliminates $C_2H_4$ and $C_3H_6$ [after rate-determining rearrangement to (3) has occurred]. This behaviour is in contrast to that observed for the oxygen analogues (5) and (6), respectively, of (2) and (3). These oxonium ions interconvert prior to decomposition *via* loss of $CH_2O$ and $H_2O$.[12,17,18] The contrasting behaviour found for the oxygen and nitrogen systems reflects two important differences between aldehydes (or ketones) and imines. Aldehydes and ketones have larger dipole moments and lower proton affinities than the corresponding imines.

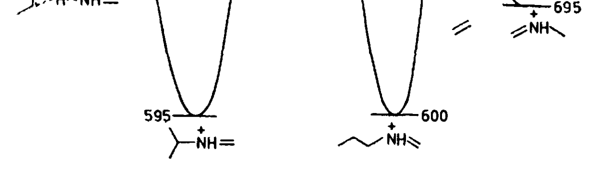
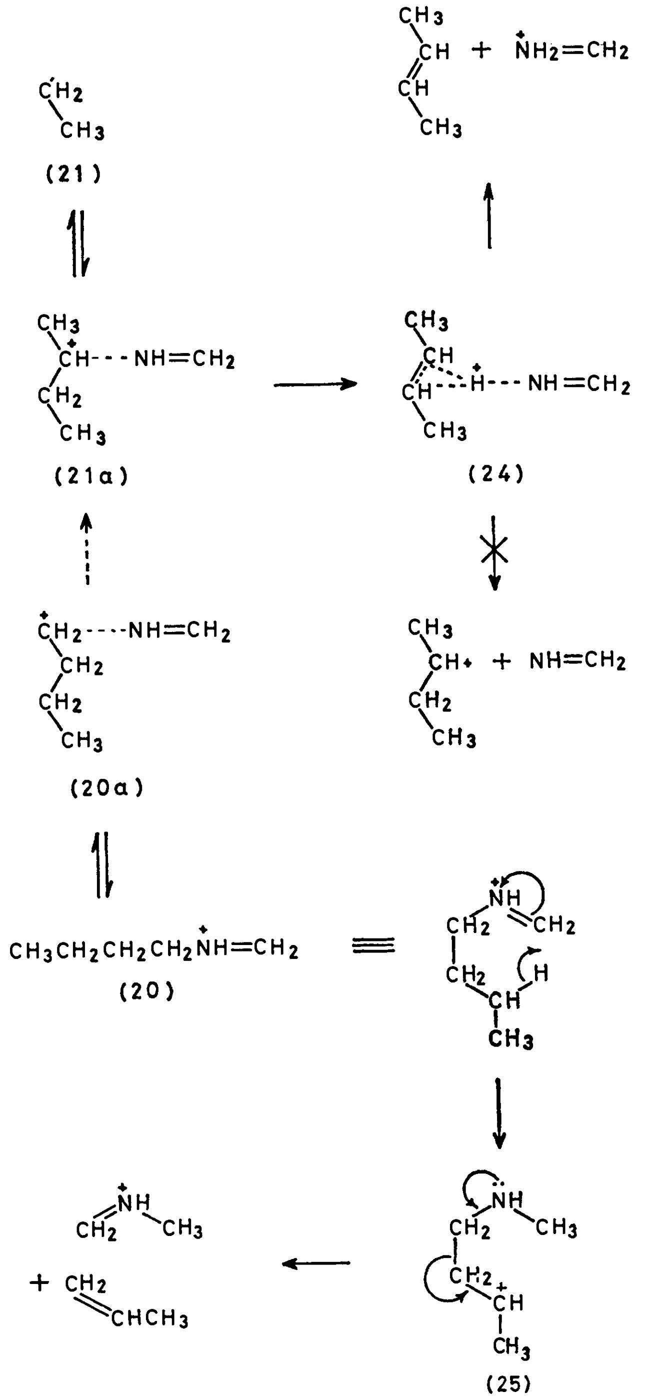


FIGURE 1 Potential energy profile for isomerisation and dissociation of (2) and (3)

Therefore, greater ion–dipole attractions occur between ions co-ordinated to aldehydes or ketones compared with those found when the same cation is co-ordinated to the analogous imine. Thus, interconversion is more facile, compared to dissociation, for oxonium ions such as (5) and (6) than for the corresponding immonium ions (2) and (3). Moreover, when decomposition eventually occurs, the immonium ions tend, almost without exception, to eliminate olefins. whereas the oxonium ions frequently lose aldehydes. This is because most imines have greater proton affinities than almost any small olefin; however, aldehydes and olefins often have comparable proton affinities.



SCHEME 5

It is significant that the intermediacy of the open-chain carbonium ion (19) seems probable in the elimination of $C_2H_4$ from (2). Approximately one-third of the estimated reverse activation energy (180 kJ mol$^{-1}$) is partitioned as translation. This fraction is similar to that observed in analogous and homologous systems.[22]

Further support for the intermediacy of (19) or related species may be deduced from an investigation of the higher homologues, $C_4H_9\overset{+}{N}H{=}CH_2$. The observed dissociations, and accompanying kinetic energy releases, for four isomeric $C_5H_{12}\overset{+}{N}$ ions are given in Table 3.

It is instructive to consider the chemistry of the four isomeric $C_5H_{12}N^+$ ions in two sections, corresponding to two pairs of ions. The first pair, (20) and (21), each contain a straight butyl side-chain; the second pair, (22) and (23), each possess only a branched butyl side chain.

The possible mechanisms whereby (20) and (21) might interconvert or dissociate are depicted in Scheme 5; these mechanisms are analogous to those proposed for the lower homologues (2) and (3) (Scheme 2).

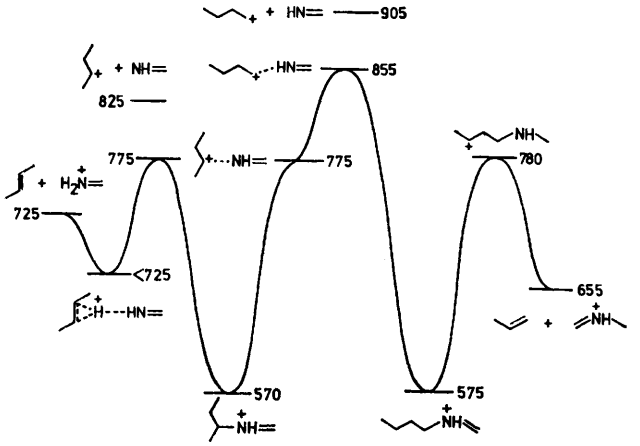


FIGURE 2 Potential energy profile for isomerisation and dissociation of (20) and (21)

It is clear from the fact that (20) and (21) undergo almost exclusively different reactions ($C_3H_6$ and $C_4H_8$ loss, respectively), that these ions do not interconvert prior to dissociation. The very low abundance reaction for $C_4H_8$ loss from (20) takes place with a larger average kinetic energy release than does $C_4H_8$ loss from (21). This is consistent with a minor percentage (<1%) of ions generated as (20) undergoing rate-determining rearrangement to (21) before decomposition. Nevertheless, it is energetically more favourable for (20) and (21) to eliminate $C_3H_6$ and $C_4H_8$, respectively, rather than rearrange to the isomeric structure.

This behaviour may be understood by reference to the appropriate potential energy profile (Figure 2) which is constructed using the same approach as that employed

TABLE 3

Observed reactions and associated kinetic energy releases for decomposition of isomeric $C_5H_{12}N^+$ ions

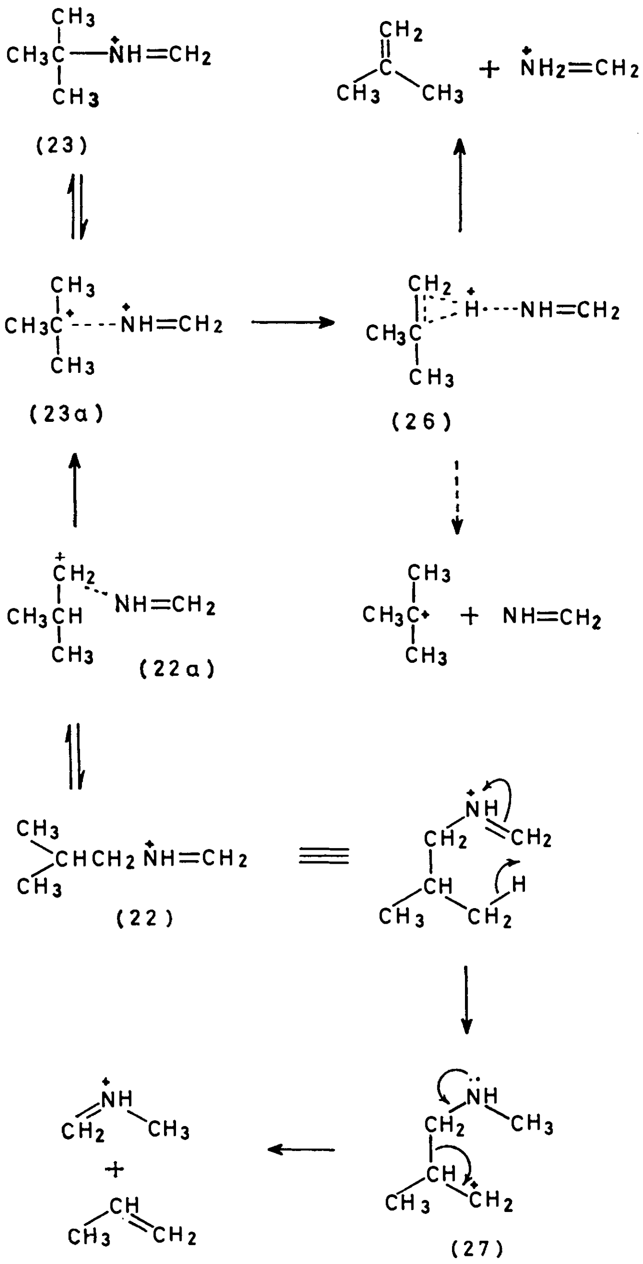
| | Neutral lost[a] | | | Associated kinetic energy release[b] | | |
|---|---|---|---|---|---|---|
| Ion | $CH_3N$ | $C_3H_6$ | $C_4H_8$ | $CH_3N$ loss | $C_3H_6$ loss | $C_4H_8$ loss |
| $CH_3CH_2CH_2CH_2\overset{+}{N}H{=}CH_2$ (20) | 0 | >99 | <1 | | 40 ± 2[e,f] | 13 ± 4[c,d,f] |
| $CH_3CH_2(CH_3)CH\overset{+}{N}H{=}CH_2$ (21) | 0 | 0 | 100 | | | 7 ± 1[c,f] |
| $(CH_3)_2CHCH_2\overset{+}{N}H{=}CH_2$ (22) | 22 | 20 | 58 | 10[c] | 65 ± 3[e,f] | 8 ± 1[c,f] |
| $(CH_3)_3C\overset{+}{N}H{=}CH_2$ (23) | 0 | 0 | 100 | | | 5 ± 1[c,f] |

[a] Values measured by second field-free region metastable peak areas and normalised to a total metastable ion current of 100 units. [b] Values in kJ mol$^{-1}$. [c] Gaussian metastable peak, average[16] kinetic energy release. [d] Peak very minor, result less accurate. [e] Flat-topped metastable peak, kinetic energy release measured from width at half-height. [f] The quoted errors correspond to one standard deviation.

for the lower homologues (2) and (3). Starting from (21), loss of an olefin with the same number of carbon atoms as the intact alkyl group (*i.e.*, $C_4H_8$) is energetically preferable to isomerisation to (20). Similarly, starting from (20), elimination of an olefin with one carbon atom less than the number present in the original alkyl chain (*i.e.*, $C_3H_6$) is energetically more favourable than rearrangement to (21). It is significant that the second process, loss of $C_3H_6$, dominates starting from (20). In contrast, for the lower homologue, (2), the analogous process, $C_2H_4$ loss, occurs in competition with rearrangement, followed by $C_3H_6$ loss. This change in behaviour reflects the intermediacy of a secondary cation (25), in $C_3H_6$ loss from (20), whereas $C_2H_4$ loss from (2) must proceed through the primary carbonium ion (19). Another consequence of the intermediacy of this secondary carbonium ion (25) is that the associated reverse activation energy is reduced to 125 kJ mol$^{-1}$. This is evidenced by a smaller kinetic energy release for $C_3H_6$ loss from (20) compared to that accompanying $C_2H_4$ loss from (2). However, the fraction of this reverse activation energy which appears as translation remains close to one-third, as observed for $C_2H_4$ loss from (2).

Further evidence may be cited in favour of the potential energy profile shown in Figure 2. For example, the observed reactions of several $^2H$-labelled analogues of (20) and (21) reveal that the $CH_2{=}NH_2^+$ ion, produced by decomposition of these ions, is derived from the [$CH_2{=}NH$] unit of (20) and (21). Thus, $CH_3CH_2CH_2CH_2\overset{+}{N}H{=}CD_2$ eliminates only $C_3H_6$ and a very minor (<1%) fraction of $C_4H_8$, in metastable transitions. This shows that the 1,5-hydride shift, (20) ⟶ (25), is irreversible. Furthermore, it also excludes the possibility of a 1,3-propyl shift in (20); such four-electron pericyclic processes are symmetry-forbidden[21] and proceed with very large activation energies. In this case, the activation energy appears to be in excess of 205 kJ mol$^{-1}$; for the lower homologue (2) a similar argument leads to an activation energy >275 kJ mol$^{-1}$ for a 1,3-ethyl shift.

The ions (22) and (23) contain branched butyl side chains; analogous routes for isomerisation and dissociation of these ions are depicted in Scheme 6. The potential energy profile for decomposition of these ions



SCHEME 6

is shown in Figure 3; this profile is constructed using the same approach as that employed for Figures 1 and 2.

Starting from (23), elimination of $C_4H_8$ is energetically more favourable than rearrangement to (22). This process proceeds with retention of the original hydrogen atom bound to nitrogen in the $CH_2{=}NH_2^+$ fragment ion. This suggests that isomerisation of (23a) to (26) is rate determining and irreversible.

Loss of $C_4H_8$ is also observed from (22); however, this process involves more kinetic energy release (8 kJ mol$^{-1}$) than that (5 kJ mol$^{-1}$) associated with $C_4H_8$ loss from (23). This suggests that rate-determining isomerisation of (22) to (23) occurs, prior to $C_4H_8$ loss. Support for this hypothesis is also provided by the observation of $CH_2{=}NH$ loss from (22). As pointed out previously, loss of $CH_2{=}NH$ from immonium ions is rare; presumably, this reaction takes place after the rate-determining rearrangement (22a) $\longrightarrow$ (23a) has occurred. The isomerisation of the incipient isobutyl cation to a t-butyl structure releases *ca.* 135 kJ mol$^{-1}$ of potential energy. This is sufficient to permit $CH_2{=}NH$ loss to compete to some extent with $C_4H_8$ loss, even though the latter is energetically more favourable by *ca.* 35 kJ mol$^{-1}$.

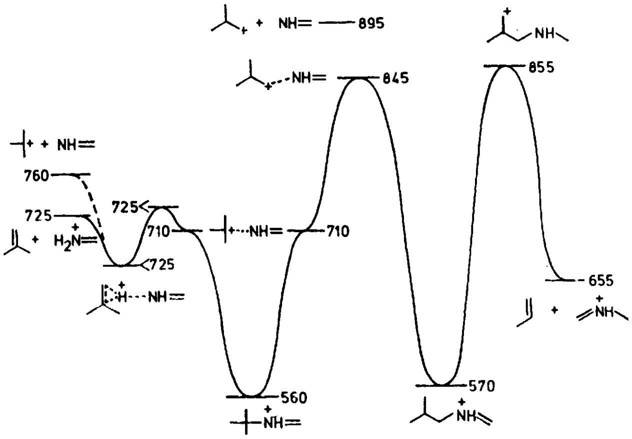


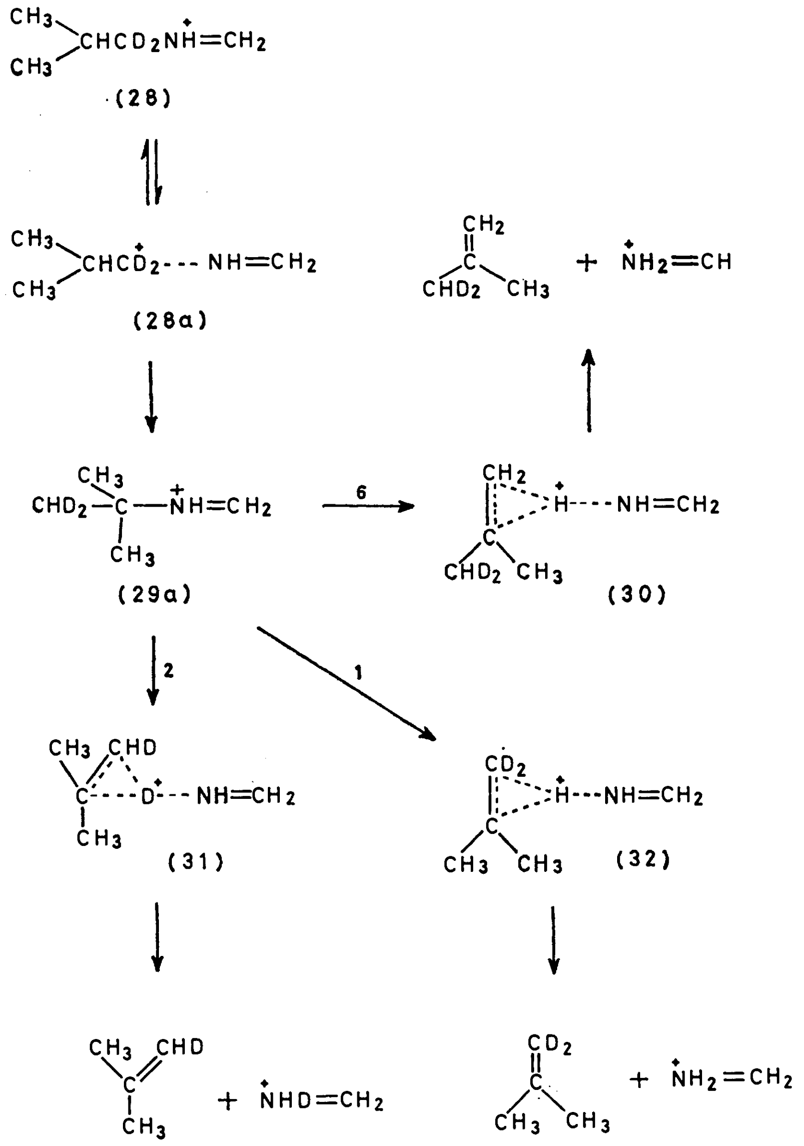
FIGURE 3 Potential energy profile for isomerisation and dissociation of (22) and (23)

In contrast to (20), (22) does not eliminate predominantly $C_3H_6$; instead, $C_3H_6$ and $C_4H_8$ losses are both observed (together with $CH_2{=}NH$ loss). This behaviour is similar to that found for (2), where elimination of $C_2H_4$ and $C_3H_6$ occurs in comparable amounts. A simple explanation of this change in behaviour may be advanced in terms of the stabilities of the relevant open-chain carbonium ions (19), (25), and (27). Whenever the olefin loss process corresponding formally to cleavage of the $C^{\alpha}$–$C^{\beta}$ bond can occur *via* a secondary carbonium ion, this reaction dominates. Thus, (20) loses almost exclusively $C_3H_6$ *via* the secondary carbonium ion (25). However, when this process must involve a primary carbonium ion as an intermediate (or more probably as a transition state), competition occurs between this reaction and rate-determining isomerisation, followed by loss of a different olefin. Hence, (2) and (22) eliminate $C_2H_4$ and $C_3H_6$, and $C_3H_6$, $CH_2{=}NH$, and $C_4H_8$, respectively, because primary carbonium ions are involved in the $C^{\alpha}$–$C^{\beta}$ cleavage process.

The potential energy profile of Figure 3 is also supported by the following data. First, the reverse activation energy associated with $C_3H_6$ loss from (22), *via* (27), is increased compared with that for $C_3H_6$ loss from (20), *via* (25). This effect arises because (27) is a primary carbonium ion, whereas (25) is a secondary carbonium ion, and decomposition of (27) and (25) gives rise to the same products ($CH_3\overset{+}{N}H{=}CH_2$ and $CH_3CH{=}CH_2$). Consequently, a greater kinetic energy release should accompany $C_3H_6$ loss from (22), *via* (27), compared to $C_3H_6$ loss from (20), *via* (25). This is found to be the case (Table 3); in both reactions, flat-topped metastable peaks are observed, corresponding to the release of approximately one-third of the reverse activation energy as kinetic energy.

Secondly, $^2H$-labelling studies reveal that the $CH_2NH$ molecule lost from (22) is derived exclusively from the $[CH_2{=}NH]$ unit of (22). Thus, $(CH_3)_2CHCH_2\overset{+}{N}D{=}CH_2$ loses $CH_2{=}ND$, but no $CH_2{=}NH$; $(CH_3)_2CHCD_2\overset{+}{N}H{=}CH_2$ eliminates $CH_2{=}NH$, but no $CH_2DN$; and $(CH_3)_2CHCH_2\text{-}\overset{+}{N}H{=}CD_2$ loses $CD_2{=}NH$, but no $CH_2DN$. In addition, all these ions eliminate propene derived only from the original isopropyl groups; *i.e.*, each ion loses $C_3H_6$ but not $C_3H_5D$. This reveals that the 1,5-hydride shift, (22) $\longrightarrow$ (27), is irreversible. Finally, loss of $C_4H_8$ involves exclusively the original butyl side chain of (22). Thus, $(CH_3)_2CHCH_2\overset{+}{N}D{=}CH_2$ and $(CH_3)_2CHCH_2\text{-}\overset{+}{N}H{=}CD_2$ lose $C_4H_8$ but no $C_4H_7D$ or $C_4H_6D_2$; however, $(CH_3)_2CHCD_2\overset{+}{N}H{=}CH_2$ eliminates $C_4H_6D_2$ and $C_4H_7D$ in the ratio 74 (±3) : 26 (±2), but no $C_4H_8$ loss is observed. The latter result is in accordance with Figure 3 and may be understood more fully in terms of Scheme 7. After the rearrangement of the incipient isobutyl cation has occurred, (28a) $\longrightarrow$ (29a), transfer of any one of the seven hydrogen atoms, or two deuterium atoms, can take place to nitrogen. On this basis, a ratio of 73 : 27 would be expected for elimination of $C_4H_6D_2$ and $C_4H_7D$ from (28). This ratio is extremely close (within experimental error) to that found experimentally.

*Conclusions.*—The unimolecular reactions of several immonium ions of general formula $R\overset{+}{N}H{=}CH_2$ may be understood in terms of the potential energy profiles, over which dissociation is considered to occur. Two main reactions are observed, loss of olefins containing one less carbon atom than, or the same number of carbon atoms as, the original alkyl group R. The former process gives rise to a flat-topped metastable peak and proceeds with a large reverse activation energy; approximately one-third of this reverse activation energy is partitioned as translation when decomposition occurs. This process proceeds after a 1,5-hydride shift has taken place from the $\gamma$-carbon atom of R to the isolated methylene group in $R\overset{+}{N}H{=}CH_2$. Elimination of the olefin is not fully concerted with this 1,5-hydride shift; instead, the reaction is better interpreted as involving an open-chain carbonium ion, with the γ-carbon atom carrying the formal positive charge. Elimination of olefins containing the same number of carbon atoms as R is evidenced by a gaussian metastable peak. Consequently, no relatively large or specific translational component is present in the reverse activation energy for this reaction. Intermediates in which an incipient carbonium ion is co-ordinated to methyleneimine are involved in this dissociation channel. In some cases, exothermic isomerisation of the incipient cation occurs, thus resulting in rate-determining rearrangements prior to olefin elimination.



SCHEME 7

EXPERIMENTAL

All mass spectra were recorded using an AEI MS 902 double-focusing mass spectrometer operating at a source pressure of *ca.* $10^{-6}$ Torr and with a nominal electron beam energy of 70 eV. Samples were introduced through the all-glass heated inlet system (AGHIS) and normal spectra were obtained using an accelerating voltage of 8 kV.

Ions decomposing in the first field-free region were detected and recorded by increasing the accelerating voltage, from an original value of 2 or 4 kV, at constant electric and magnetic field strengths.[27] Alternatively, when minor reactions were being investigated, the electric field strength was reduced, at constant accelerating voltage and magnetic field strength,[28] in order to achieve maximum sensitivity.

The kinetic energy release data were computed from the widths of the appropriate second field-free region metastable peaks; no correction was applied for the width of the main beam. The results are the means of at least five measurements. Whenever comparisons were to be made between the kinetic energy release, associated with decomposition of isomeric ions, the appropriate compounds were run consecutively under identical operating conditions.

All compounds were available commercially or else synthesised *via* unexceptional procedures. The *C*-deuteriated amines were prepared by reduction of the corresponding amides with lithium aluminium deuteride in diethyl ether or tetrahydrofuran. The *N*-deuteriated amines were obtained *in situ* by exchanging the NH with $D_2O$ in the AGHIS.

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