# Potential Energy Profiles for Unimolecular Reactions of Isolated Organic Ions: $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ and $(CH_3)_2C{=}\overset{+}{N}HCH_3$

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The slow unimolecular reactions of metastable $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ and $(CH_3)_2C{=}\overset{+}{N}HCH_3$ ions are reported and discussed. Details of the mechanisms of these reactions are elucidated by $^2H$-labelling studies. Loss of $C_3H_6$ from these $C_4H_{10}N^+$ ions is shown to occur after irreversible isomerisation to $CH_3CH_2CH_2\overset{+}{N}H{=}CH_2$ and related structures. The behaviour of $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ and $(CH_3)_2C{=}\overset{+}{N}HCH_3$ is compared with that of the lower homologues [$CH_3CH_2CH{=}\overset{+}{N}H_2$, $(CH_3)_2C{=}\overset{+}{N}H_2$, and $CH_3CH{=}\overset{+}{N}HCH_3$] and contrasted with that of the oxonium ion analogues $CH_3CH_2CH{=}\overset{+}{O}CH_3$ and $(CH_3)_2C{=}\overset{+}{O}CH_3$.

ALTHOUGH the unimolecular reactions of small $C_nH_{2n+1}O^+$ oxonium ions have been the subject of extensive investigation,[1-22] relatively few studies have been reported of the corresponding immonium ion systems.[16,19,23-29] These immonium ions often exhibit more complicated behaviour than do the analogous oxonium ions; moreover, it is instructive to consider the contrasting roles of oxygen and nitrogen atoms in these ions.[16,19,28] In addition, comparisons between the observed dissociation routes of homologous ions are usually informative. The purpose of this paper is to present and discuss the slow reactions of $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ and $(CH_3)_2C{=}\overset{+}{N}HCH_3$, to compare their behaviour with that of the lower homologues [$CH_3CH_2CH{=}\overset{+}{N}H_2$, $(CH_3)_2C{=}\overset{+}{N}H_2$, and $CH_3CH{=}\overset{+}{N}HCH_3$], and with that of the oxonium ions $CH_3CH_2CH{=}\overset{+}{O}CH_3$ and $(CH_3)_2C{=}\overset{+}{O}CH_3$.

## RESULTS AND DISCUSSION

The unimolecular reactions of metastable $(CH_3)_2C{=}\overset{+}{N}HCH_3$ (1) and $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ (2) ions are given in Table 1. Most of these reactions have been reported

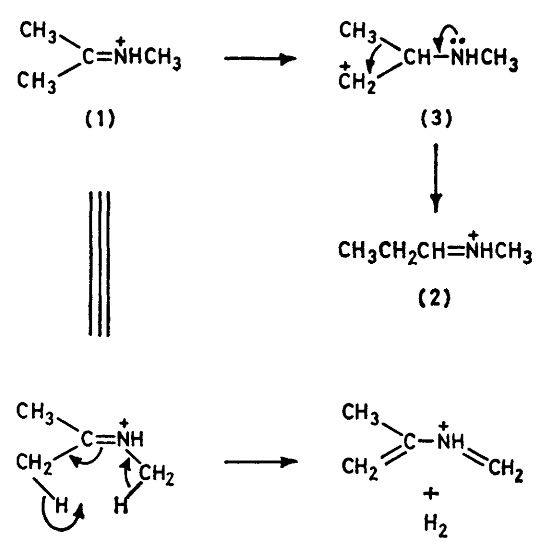
TABLE 1

Unimolecular reactions of metastable $C_4H_{10}N^+$ ions

| Ion | Neutral lost [a] | | | | | |
|---|---|---|---|---|---|---|
| | $H_2$ | $CH_3^{\cdot}$ | $C_2H_4$ | $CH_3NH_2$ | $C_3H_4$ | $C_3H_6$ |
| $(CH_3)_2C{=}\overset{+}{N}HCH_3$ | 55 | 11 | 6 | 4 | 9 | 15 |
| $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ | 14 | 12 | 28 | 9 | *b* | 37 |

[a] Values normalised by peak area and normalised to a total metastable ion current of 100 units; some of these data have previously been reported in ref. 29. [b] Peak present, but too weak to measure accurately.

previously;[29] however, a minor loss of $C_3H_4$ from (1) was omitted. Schemes 1 and 2 give the most plausible mechanisms for decomposition of (1) and (2); several of these pathways (elimination of $C_2H_4$, $CH_3NH_2$, and $C_3H_6$) bear a close resemblance to the decomposition routes proposed for the analogous $C_4H_9O^+$ ions $(CH_3)_2C{=}\overset{+}{O}CH_3$ and $CH_3CH_2CH{=}\overset{+}{O}CH_3$.[15] It is significant that (1) and (2) undergo the five common reactions in somewhat different abundance ratios; this suggests that (1) and (2) do not interconvert rapidly and reversibly prior to dissociation.[2,30] However, the relatively small differences in abundance ratios do not necessarily preclude



SCHEME 1

interconversion of (1) and (2). Nevertheless, the occurrence of $C_3H_4$ loss in moderate abundance from (1), in contrast to the behaviour of (2) which eliminates $C_3H_4$ in very minor abundance (<0.5%), is strong evidence that (1) and (2) interconvert slowly, at most, prior to decomposition.

The observed reactions of (1) and (2) are discussed in detail below.

$H_2$ *Loss*.—This reaction gives rise to a flat-topped metastable peak, corresponding to a kinetic energy release of *ca.* 35 kJ mol$^{-1}$, starting from (1) or (2). An analogous process is observed for the lower homologue, $CH_3CH{=}\overset{+}{N}HCH_3$ (9) which eliminates $H_2$ with the release of a similar amount (*ca.* 25 kJ mol$^{-1}$) of kinetic energy.[23] Further insight is shed on this reaction by

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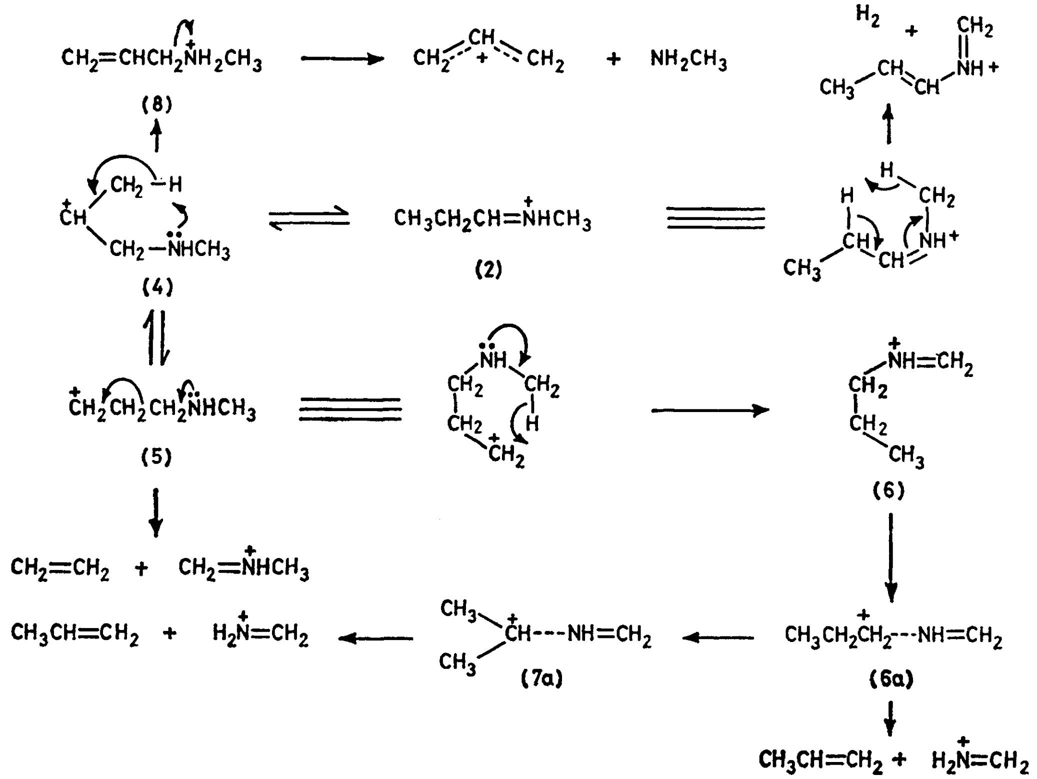


SCHEME 2

the behaviour of ²H-labelled ions (Table 2). It is evident from these data that the hydrogen atom originally attached to nitrogen is retained exclusively in the product ion. One of the two hydrogen atoms expelled as the hydrogen molecule originates from the methyl group bound to nitrogen; the other is selected from those of the $C_3H_6$ side chain in (1) or (2). These reactions are most simply formulated as 1,4-eliminations, occurring through six-membered ring transition states. It is especially instructive to consider the behaviour of

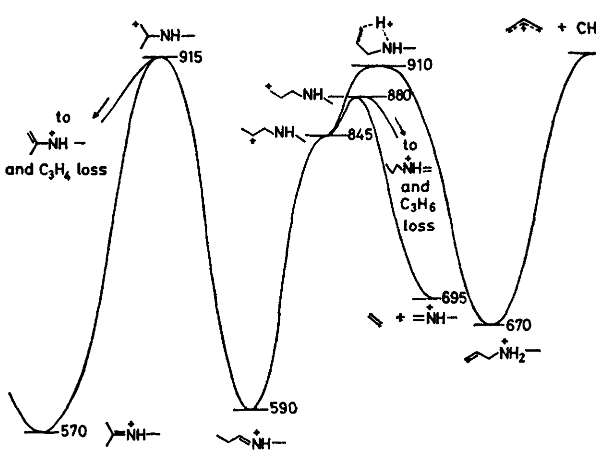



FIGURE Potential energy profile for isomerisation and dissociation of (1) and (2)

$CH_3CD_2CH{=}\overset{+}{N}HCH_3$: the occurrence of both $H_2$ and HD losses from this ion indicates that (2) undergoes at least partial equilibration with (4) and possibly (5). Were hydrogen loss to take place after statistical distribution of hydrogen and deuterium atoms in the $C_3H_4D_2$ side chain of $CH_3CD_2CH{=}\overset{+}{N}HCH_3$, $H_2$ and HD losses would be expected in the ratio 67 : 33. Any primary deuterium isotope effect would increase this ratio. The most likely explanation of the observations is that partial, or complete, equilibration of (2) and (4) precedes elimination of molecular hydrogen and that a primary deuterium isotope effect favours $H_2$ loss over HD loss. The experimental facts can be accommodated on the basis of rapid and reversible isomerisation of (2) and (4),

TABLE 2

Molecular hydrogen loss from ²H-labelled analogues of $C_4H_{10}N^+$

| Ion | Neutral lost [a] | | |
|---|---|---|---|
| | $H_2$ | HD | $D_2$ |
| $(CH_3)_2C{=}\overset{+}{N}DCH_3$ (10) | 100 | | |
| $(CH_3)_2C{=}\overset{+}{N}HCD_3$ (11) | | 100 | |
| $CH_3CH_2CH{=}\overset{+}{N}DCH_3$ (12) | 100 | | |
| $CH_3CH_2CH{=}\overset{+}{N}HCD_3$ (13) | | 100 | |
| $CH_3CD_2CH{=}\overset{+}{N}HCH_3$ (14) | 56 | 44 | <1 |

[a] Values measured by metastable peak heights for ions dissociating in the first field-free region and normalised to a total metastable ion current of 100 units for hydrogen loss.

together with an isotope effect of 2.5 : 1 favouring $H_2$ loss over HD elimination.

It is probable that hydrogen loss from (1) and (2) proceeds through different transition states, despite the similar kinetic energy release associated with each reaction. The behaviour of $CH_3CD_2CH{=}\overset{+}{N}HCH_3$, which does not lose $H_2$ and HD in ratios compatible with statistical distribution of hydrogen and deuterium atoms in the $C_3H_4D_2$ side chain, excludes the possibility of rapid interconversion of (1) and (2).

Finally, in connection with $H_2$ loss, it is significant that a closely similar behaviour is observed for the lower homologue, $CH_3CH{=}\overset{+}{N}HCH_3$, as shown by $^2$H-labelling studies.[23]

$CH_3^{\bullet}$ *Loss*.—This interesting reaction, which constitutes a violation of the even-electron rule,[31] has been discussed in a previous communication.[29] It is perhaps noteworthy that the corresponding oxonium ions, $(CH_3)_2C{=}\overset{+}{O}CH_3$ and $CH_3CH_2CH{=}\overset{+}{O}CH_3$, do not undergo significant methyl radical loss in slow reactions. This difference in behaviour is interpretable in terms of the lower relative heats of formation of ionised imines compared with the analogous ionised aldehydes or ketones.

$C_2H_4$ *Loss*.—This reaction is evidenced by a flat-topped metastable peak; a similar kinetic energy (60—65 kJ mol$^{-1}$) is released upon fragmentation of (1) and (2) as is observed (45 kJ mol$^{-1}$) to accompany $C_2H_4$ elimination from the lower homologues $(CH_3)_2C{=}\overset{+}{N}H_2$ and $CH_3CH_2$-$CH{=}\overset{+}{N}H_2$.[23] Starting from (2), two 1,2-hydride shifts lead to the open-chain carbonium ion (5) which then dissociates exothermically to give $C_2H_4$ and $CH_2{=}\overset{+}{N}HCH_3$ (Scheme 2). This mechanism is established by $^2$H-labelling studies (Table 3) which reveal that the $NHCH_3$ group of (2) is retained completely in the product ion. Moreover, the four hydrogen atoms, required to make up the expelled ethylene molecule, appear to be selected at random from the four protons and two deuterons in the $C_3H_4D_2$ side chain in $CH_3CD_2CH{=}\overset{+}{N}HCH_3$. The statistical ratios for $C_2H_4$, $C_2H_3D$, and $C_2H_2D_2$ losses from (14) are 40 : 53 : 7; the experimental values are 43 : 51 : 6, in satisfactory agreement. This behaviour is identical to that found for the lower homologue, $CH_3CD_2CH{=}\overset{+}{N}H_2$,[23] and shows that (2) interconverts with (4) and (5) at a rate more rapid than that appropriate to ethylene loss. It should be noted that this conclusion is not inconsistent with the earlier deduction that $H_2$ elimination proceeds at a rate faster than (2) isomerises with the primary cation (5). The primary cation is likely to have a relatively high heat of formation, quite plausibly higher than the energy of the transition state for $H_2$ loss. However, $C_2H_4$ loss must proceed *via* the open-chain carbonium ion (5); therefore, interconversion of (2), (4), and (5) can occur before (5) dissociates with loss of $C_2H_4$. Similar effects have been documented in the decomposition of the lower homologues, $C_3H_8N^+$.[23]

It seems probable that $C_2H_4$ loss from (1) occurs after rearrangement to (2) *via* (3) (Scheme 1). If this is the case, the energy needed to cause this isomerisation must be closely similar to the transition state energy for eventual decomposition. This follows from the very similar kinetic energy releases which accompany dissociation of (1) and (2); only a marginally greater kinetic energy release (65 kJ mol$^{-1}$) is observed starting from (1) than is found (60 kJ mol$^{-1}$) for decomposition of (2); these differences are barely greater than the experimental errors involved in the measurements. A similar fine balance exists for the lower homologues, $(CH_3)_2C{=}NH_2^+$ and $CH_3CH_2CH{=}NH_2^+$, for which the energy barriers for dissociation and isomerisation are almost the same.[27]

TABLE 3

Ethylene loss from $^2$H-labelled analogues of $C_4H_{10}N^+$

| Ion | Neutral lost [a] | | |
|---|---|---|---|
| | $C_2H_4$ | $C_2H_3D$ | $C_2H_2D_2$ |
| $(CH_3)_2C{=}\overset{+}{N}DCH_3$ | 100 | | |
| $(CH_3)_2C{=}\overset{+}{N}HCD_3$ | 95 | 5 | |
| $CH_3CH_2CH{=}\overset{+}{N}DCH_3$ | 100 | | |
| $CH_3CH_2CH{=}\overset{+}{N}HCD_3$ | 100 | | |
| $CH_3CD_2CH{=}\overset{+}{N}HCH_3$ | 43 | 51 | 6 |

[a] Values measured by metastable peak heights for ions dissociating in the first field-free region and normalised to a total metastable ion current of 100 units for ethylene loss.

$CH_3NH_2$ *Loss*.—Both (1) and (2) eliminate $CH_3NH_2$ in minor abundance. In each case, the reaction gives rise to a gaussian metastable peak; the average[32] kinetic energy releases associated with $CH_3NH_2$ loss from (1) and (2) are the same within experimental error error (9.6 ± 0.5 and 8.9 ± 0.5 kJ mol$^{-1}$, respectively). By analogy with the mechanisms proposed for $NH_3$ loss from the homologous ions, $(CH_3)_2C{=}NH_2^+$ and $CH_3CH_2CH{=}NH_2^+$, $CH_3NH_2$ elimination from (1) and (2) proceeds *via* (4) and (8) (Scheme 2). Further evidence in favour of these mechanisms stems from the $^2$H-labelling data given in Table 4.

TABLE 4

Methylamine loss from $^2$H-labelled analogues of $C_4H_{10}N^+$

| Ion | Neutral lost [a] | | | |
|---|---|---|---|---|
| | $CH_3NH_2$ | $CH_3NHD$ | $CH_3ND_2$ | $CD_3NH_2$ |
| $(CH_3)_2C{=}\overset{+}{N}DCH_3$ | | 100 | | |
| $(CH_3)_2C{=}\overset{+}{N}HCD_3$ | | | | 100 |
| $CH_3CH_2CH{=}\overset{+}{N}DCH_3$ | | 100 | | |
| $CH_3CH_2CH{=}\overset{+}{N}HCD_3$ | | | | 100 |
| $CH_3CD_2CH{=}\overset{+}{N}HCH_3$ | 94 | 6 | | |

[a] Values measured by metastable peak heights for ions dissociating in the first field-free region and normalised to a total metastable ion current of 100 units for methylamine loss.

It is clear from the data of Table 4 that the expelled methylamine molecule originates from the intact $NHCH_3$ group of (1) and (2), together with one hydrogen atom from the three-carbon chain. The transfer of this hydrogen atom must be irreversible; were this not so, the hydrogen atom attached to the nitrogen atom in (1) and (2) would lose its identity as a result of interconversion of (4) and (8). This requires that (4) ⟶ (8) is the rate-determining step in $CH_3NH_2$ loss from (2); such a view is supported by the behaviour of (14). On the basis of (2), (4), and (5) equilibrating prior to (4) ⟶ (8), the hydrogen and deuterium atoms in the three-carbon chain of (14) should be statistically distributed; in the absence of an isotope effect, $CH_3NH_2$, $CH_3NHD$, and $CH_3ND_2$ losses would be expected in the ratios 67 : 33 : 0. The observed ratios, 94 : 6 : 0, correspond to statistical selection and an isotope effect of 8 : 1 favouring H, rather than D, transfer to nitrogen. This isotope effect is evidence that (4) ⟶ (8) is indeed the rate-determining step in $CH_3NH_2$ elimination from (2). A similar, but smaller, isotope effect is known to operate in ammonia loss from the lower homologue, $CH_3CH_2CH=NH_2^+$.[23]

It is informative to consider the relative abundances of $NH_3$ and $C_2H_4$ losses, from $(CH_3)_2C=\overset{+}{N}H_2$ and $CH_3CH_2CH=\overset{+}{N}H_2$, with the relative abundances of the analogous reactions, $CH_3NH_2$ and $C_2H_4$ eliminations, from (1) and (2). Loss of $NH_3$ dominates, starting from $(CH_3)_2C=NH_2^+$ and $CH_3CH_2CH=NH_2^+$, accounting for seven and eight times the metastable ion current for $C_2H_4$ loss, respectively, from these ions.[23] In contrast, (1) and (2) undergo $CH_3NH_2$ elimination in only minor abundance; $C_2H_4$ and $CH_3NH_2$ losses occur in the ratios 3 : 1 and 1.5 : 1, respectively, from (2) and (1). This change in behaviour, occasioned by substitution of NH by $NCH_3$, can be explained in energetic terms (Table 5).

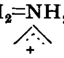
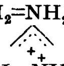
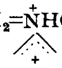
It is clear that the balance between $C_2H_4$ and $NH_3$ losses from the $C_3H_8N^+$ species is altered for the analogous decay routes, $C_2H_4$ and $CH_3NH_2$ eliminations, for (1) and (2). Expulsion of $C_2H_4$ is energetically more favoured for the $C_4H_{10}N^+$ ions; this trend is reflected in the enhanced competition of $C_2H_4$ loss from (1) and (2). However, the energy differences involved are small and it would be unwise to place too great an emphasis on them.

$C_3H_6$ *Loss*.—This reaction, which is also observed in high abundance for the isomeric $C_4H_{10}N^+$ ions $CH_3CH_2CH_2\overset{+}{N}H=CH_2$ (6) and $(CH_3)_2CH\overset{+}{N}H=CH_2$ (7), can be interpreted in terms of isomerisation of (1) and (2) to (6), *via* (4) and (5) (Scheme 2). Three pieces of experimental evidence indicate that this interpretation is correct.

First, $^2$H-labelling studies (Table 6) reveal that the $CH_2=NH_2^+$ daughter ion, produced by $C_3H_6$ loss from (1) and (2), comprises three of the four original hydrogen atoms in the $CH_3NH$ group of these ions. Moreover, the hydrogen atom originally attached to nitrogen is specifically retained in the $CH_2=NH_2^+$ product ion. These data are indicative of irreversible hydrogen transfer from the $NCH_3$ group to the $C_3H_6$ side chain, (5) ⟶ (6); decomposition of (6), thus formed, then occurs. Two possible mechanisms exist whereby this final breakdown of (6) can take place: either isomerisation, *via* (6a), to (7a), followed by hydrogen transfer from the incipient isopropyl cation to nitrogen, or direct dissociation, *via* (6a). Evidence has been cited previously to show that (6) rearranges to (7), *via* (6a) and (7a), prior to $C_3H_6$ loss.[28] However, this conclusion need not necessarily apply at higher internal energies, such as would be expected were (6) formed by rate-determining isomerisation of (1) and (2). In fact, the labelling data suggest that the direct route is dominant; for (2) ⟶ (4) ⟶ (5) ⟶ (6) ⟶ (6a) ⟶ products,

TABLE 5

Energy data relevant to the decomposition of $C_3H_8N^+$ and $C_4H_{10}N^+$ ions

| Ion | Products and $\Delta H_f$ [a] | $\Sigma\Delta H_f$ [a] | Transition state energy [a] |
|---|---|---|---|
| $(CH_3)_2C=NH_2^+$ | $CH_2=NH_2^+$ (745[33]) + $C_2H_4$ (50[33]) | 795 | 930[27] |
| |  (945[34]) + $NH_3$ (−45[33]) | 900 | 930[27] |
| $CH_3CH_2CH=NH_2^+$ | $CH_2=NH_2^+$ (745[33]) + $C_2H_4$ (50[33]) | 795 | 910[27] |
| |  (945[34]) + $NH_3$ (−45[33]) | 900 | 930[27] |
| $(CH_3)_2C=\overset{+}{N}HCH_3$ | $CH_2=\overset{+}{N}HCH_3$ (645[16,35]) + $C_2H_4$ (50[33]) | 695 | 915 [b] |
| |  (945[34]) + $CH_3NH_2$ (−25[33]) | 920 | 915 [b] |
| $CH_3CH_2CH=\overset{+}{N}HCH_3$ | $CH_2=\overset{+}{N}HCH_3$ (645[16,35]) + $C_2H_4$ (50[33]) | 695 | 880 [b] |
| |  (945[34]) + $CH_3NH_2$ (−25[33]) | 920 | 910 |

[a] All values in kJ mol$^{-1}$. [b] Values estimated using isodesmic substitution procedure [36] and by analogy with the values reported for the lower homologues.[27]

TABLE 6

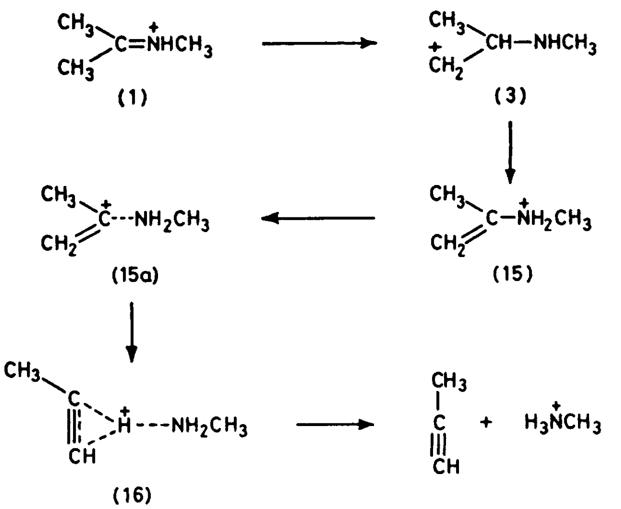
Propene loss from $^2$H-labelled analogues of $C_4H_{10}N^+$ ions

| Ion | Neutral lost [a] | | | |
|---|---|---|---|---|
| | $C_3H_6$ | $C_3H_5D$ | $C_3H_4D_2$ | $C_3H_3D_3$ |
| $(CH_3)_2C=\overset{+}{N}DCH_3$ | 100 | | | |
| $(CH_3)_2C=\overset{+}{N}HCD_3$ | | 100 | | |
| $CH_3CH_2CH=\overset{+}{N}DCH_3$ | 100 | | | |
| $CH_3CH_2CH=\overset{+}{N}HCD_3$ | | 100 | | |
| $CH_3CD_2CH=\overset{+}{N}HCH_3$ | | 8 | 92 | |

[a] Values measured by metastable peak heights for ions dissociating in the first field-free region and normalised to a total metastable ion current of 100 units for propene loss.

the hydrogen atom transferred in the step (5) ⟶ (6) is retained in the expelled propene, as is observed for $(CH_3)_2C{=}\overset{+}{N}HCD_3$ and $CH_3CH_2CH{=}\overset{+}{N}HCD_3$.

Secondly, the average kinetic energies released upon elimination of $C_3H_6$ from (1) and (2) ($10 \pm 0.5$ and $9.5 \pm 0.5$ kJ mol$^{-1}$, respectively) are greater than the corresponding value ($8 \pm 0.5$ [28] kJ mol$^{-1}$) observed starting from (6). This increase in kinetic energy release is consistent with (1) and (2) undergoing irreversible rearrangement to (6).[11]



Scheme 3

Thirdly, the occurrence of relatively high energy decomposition routes (for instance, $CH_3NH_2$ loss) from (1) and (2), but not from (6), is evidence that (1) and (2) are able to reach higher energy transition states when decomposing in metastable transitions. This is consistent with (1) and (2) isomerising to (6) before $C_3H_6$ loss; however, starting from (6), dissociation *via* $C_2H_4$ or $C_3H_6$ loss is energetically preferable to rearrangement to (5) and subsequently (2) or (1).

It is noteworthy that the oxonium ions, $(CH_3)_2C{=}\overset{+}{O}CH_3$ and $CH_3CH_2CH{=}\overset{+}{O}CH_3$, corresponding to (1) and (2), behave in a manner closely resembling (1) and (2), especially in regard to $C_3H_6$ loss.

$C_3H_4$ *Loss*.—This unusual reaction only occurs in significant abundance for (1); it is apparent that considerable rearrangement must precede $C_3H_4$ elimination to form $CH_3NH_3^+$. Several mechanisms can be devised to explain this reaction; of these, that depicted in Scheme 3 is perhaps the most plausible. A 1,2-hydride shift in (1) leads to (3), which could isomerise, *via* a 1,2-methyl shift, to (2) (Scheme 1), or undergo a further 1,2-hydride shift to form (15). Bond stretching in (15) leads to (15a), a species *en route* to the methylvinyl cation and methylamine; however, separation of the incipient products in (15a) is unfavourable on account of their high total heat of formation [990 [37] ($CH_3\overset{+}{C}{=}CH_2$) + (−25) [33] ($CH_3NH_2$)]. Instead, hydride transfer occurs in (15a), producing (16), which is a species in which propyne and methylamine share in binding to a common proton. When (16) decomposes, the incipient neutral species having the greater proton affinity retains the proton. Methylamine has a much greater proton affinity (880 [38] kJ mol$^{-1}$) than propyne (730 [37] kJ mol$^{-1}$); consequently, in this case, $CH_3NH_3^+$ and $C_3H_4$ are produced preferentially. A similar analysis could be presented involving the formation of allene; since allene and propyne have essentially the same proton affinity (735 and 730 kJ mol$^{-1}$, respectively [37]), it is possible that either, or both, neutral $C_3H_4$ isomers are formed. Alternatively, a simple 1,2-elimination in (15) could give rise to the desired products; the mechanism shown in Scheme 3 corresponds to such a 1,2-elimination, occurring with a very low degree of concert.

The proposed mechanism is consistent with $^2$H-labelling results, which show that the $CH_3NH_3^+$ ion is derived from the intact $CH_3NH$ group of (1). Thus, both $(CH_3)_2C{=}\overset{+}{N}DCH_3$ and $(CH_3)_2C{=}\overset{+}{N}HCD_3$ lose $C_3H_4$ but not $C_3H_3D$.

A related observation is that, of the eight $C_4H_9O^+$ oxonium ions, only $(CH_3)_2C{=}\overset{+}{O}CH_3$ eliminates $C_3H_4$.[15] This, together with the occurrence of significant $C_3H_4$ loss from (1), but not (2), suggests that this reaction proceeds by a different route than rearrangement to (2). A final point may be made concerning the lower homologues, $(CH_3)_2C{=}NH_2^+$ and $CH_3CH_2CH{=}NH_2^+$: an analogous loss of $C_3H_4$ in significant abundance is again observed only from the former ion.[25] These observations all point to $C_3H_4$ loss being associated with the $(CH_3)_2C{=}\overset{+}{Z}R$ structure (Z = O or NH); this view is reflected in Scheme 3.

Lack of reliable thermochemical data hampers the construction of detailed potential energy profiles for the decomposition of (1) and (2). However, by employing estimated heats of formation for reactants and the isodesmic substitution method to obtain approximate energy data for open-chain carbonium ions, the energy diagram of the Figure may be deduced.

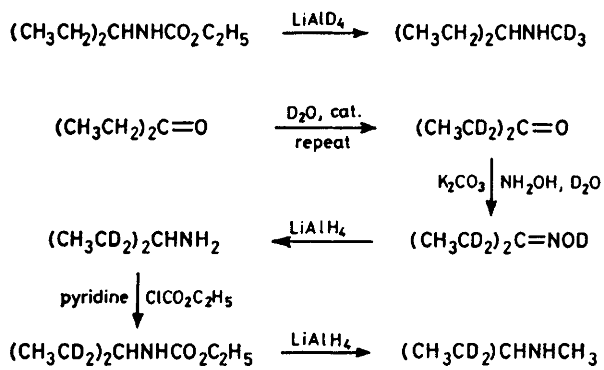
*Conclusions*.—The unimolecular reactions of $(CH_3)_2C{=}\overset{+}{N}HCH_3$ and $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ may be interpreted by means of a potential energy profile approach. Rapid interconversion of these ions does not take place prior to decomposition, but a number of common reactions are observed.

The behaviour of $(CH_3)_2C{=}\overset{+}{N}HCH_3$ and $CH_3CH_2CH{=}\overset{+}{N}HCH_3$ shows a decided similarity to that observed for the lower homologues, $(CH_3)_2C{=}NH_2^+$, $CH_3CH_2CH{=}NH_2^+$, and $CH_3CH{=}\overset{+}{N}HCH_3$. Moreover, there are many parallels between the decomposition routes observed for these $C_4H_{10}N^+$ ions and the analogous $C_4H_9O^+$ ions.

## EXPERIMENTAL

All mass spectra were recorded using an AEI Kratos 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 mass 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.[39] When minor reactions were being investigated, the electric and magnetic field strength was reduced, at constant accelerating voltage and magnetic field strength,[40] in order to achieve maximum sensitivity.




SCHEME 4

The kinetic energy release data were computed from the widths at half-height of the appropriate metastable peak in the normal mass spectrum; 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 releases, associated with dissociation 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 *N*-deuteriated amines were prepared *in situ* by exchanging the NH, of the corresponding undeuteriated amine, with $D_2O$ in the AGHIS. The *C*-deuteriated amines were obtained by the routes in Scheme 4.

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