

Potential Energy Profiles for Unimolecular Reactions of Isolated Organic Ions: $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$

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The slow unimolecular reactions of metastable $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$ 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 $\text{C}_4\text{H}_{10}\text{N}^+$ ions is shown to occur after irreversible isomerisation to $\text{CH}_3\text{CH}_2\text{CH}_2\overset{+}{\text{N}}\text{H}=\text{CH}_2$ and related structures. The behaviour of $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$ is compared with that of the lower homologues $[\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{H}_2, (\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{H}_2, \text{and } \text{CH}_3\text{CH}=\overset{+}{\text{N}}\text{HCH}_3]$ and contrasted with that of the oxonium ion analogues $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{CH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3$.

ALTHOUGH the unimolecular reactions of small $\text{C}_n\text{H}_{2n+1}\text{O}^+$ 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 $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$, to compare their behaviour with that of the lower homologues $[\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{H}_2, (\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{H}_2, \text{and } \text{CH}_3\text{CH}=\overset{+}{\text{N}}\text{HCH}_3]$, and with that of the oxonium ions $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{CH}_3$ and $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3$.

RESULTS AND DISCUSSION

The unimolecular reactions of metastable $(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$ (1) and $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ (2) ions are given in Table 1. Most of these reactions have been reported

TABLE 1

Unimolecular reactions of metastable $\text{C}_4\text{H}_{10}\text{N}^+$ ions

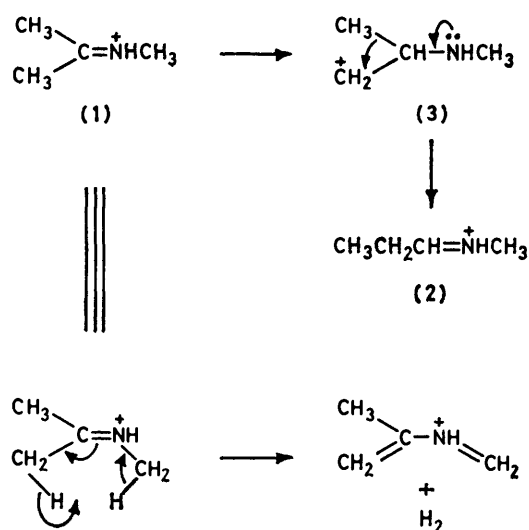
Ion	Neutral lost ^a					
	H_2	CH_3	C_2H_4	CH_3NH_2	C_3H_4	C_3H_6
$(\text{CH}_3)_2\text{C}=\overset{+}{\text{N}}\text{HCH}_3$	55	11	6	4	9	15
$\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$	14	12	28	9	<i>b</i>	37

^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 $\text{C}_4\text{H}_9\text{O}^+$ ions $(\text{CH}_3)_2\text{C}=\overset{+}{\text{O}}\text{CH}_3$

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$\overset{+}{\text{O}}\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\overset{+}{\text{O}}\text{CH}_3$.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

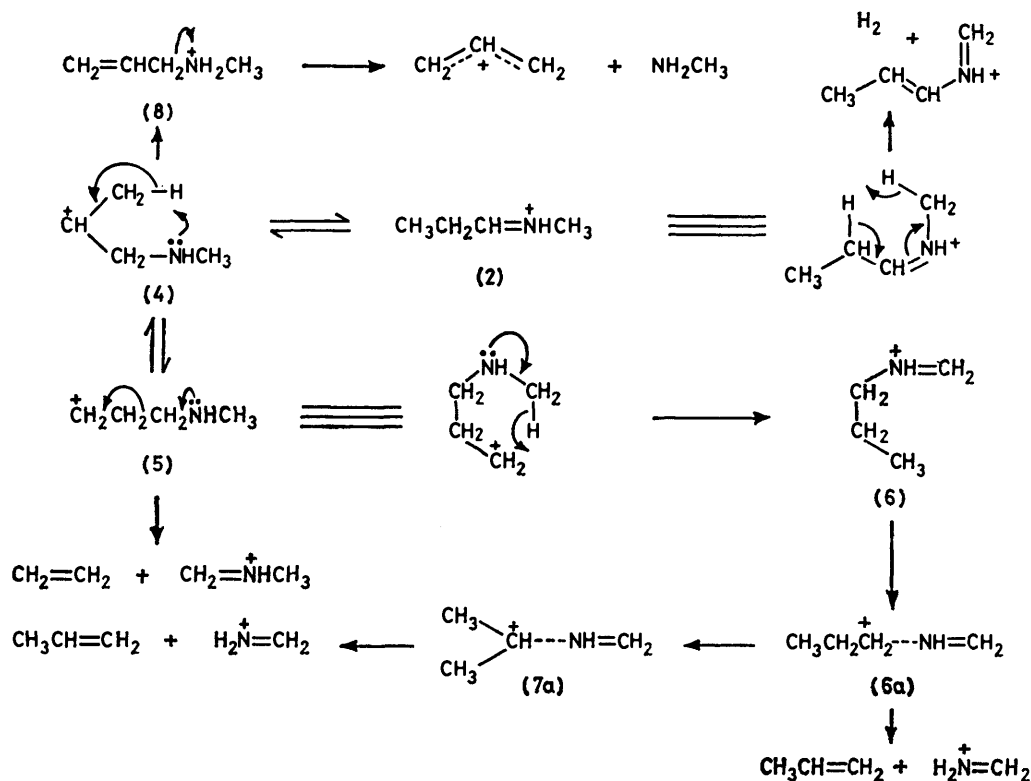


SCHEME 1

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, $\text{CH}_3\text{CH}=\overset{+}{\text{N}}\text{HCH}_3$ (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



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

$\text{CH}_3\text{CD}_2\text{CH}=\overset{\oplus}{\text{N}}\text{HCH}_3$: 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 $\text{C}_3\text{H}_4\text{D}_2$ side chain of $\text{CH}_3\text{CD}_2\text{CH}=\overset{\oplus}{\text{N}}\text{HCH}_3$, 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

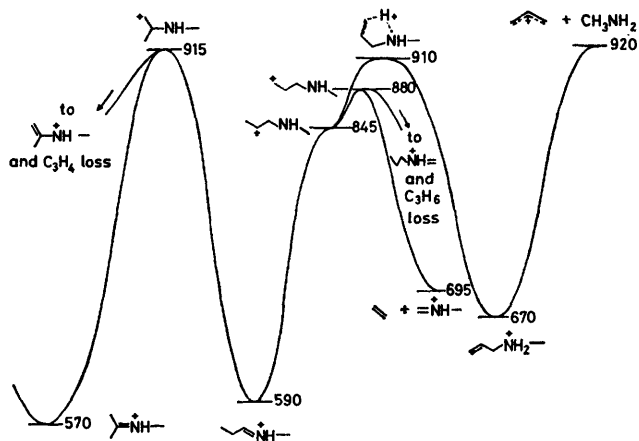


FIGURE Potential energy profile for isomerisation and dissociation of (1) and (2)

group bound to nitrogen; the other is selected from those of the C_3H_8 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

TABLE 2
Molecular hydrogen loss from ^2H -labelled analogues of $\text{C}_4\text{H}_{10}\text{N}^+$

Ion	Neutral lost ^a		
	H_2	HD	D_2
$(\text{CH}_3)_2\text{C}=\overset{\oplus}{\text{N}}\text{DCH}_3$ (10)	100		
$(\text{CH}_3)_2\text{C}=\overset{\oplus}{\text{N}}\text{HCD}_3$ (11)		100	
$\text{CH}_3\text{CH}_2\text{CH}=\overset{\oplus}{\text{N}}\text{DCH}_3$ (12)	100		
$\text{CH}_3\text{CH}_2\text{CH}=\overset{\oplus}{\text{N}}\text{HCD}_3$ (13)		100	
$\text{CH}_3\text{CD}_2\text{CH}=\overset{\oplus}{\text{N}}\text{HCH}_3$ (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.

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),

together with an isotope effect of 2.5 : 1 favouring H₂ 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 CH₃CD₂CH=NHCH₃, which does not lose H₂ and HD in ratios compatible with statistical distribution of hydrogen and deuterium atoms in the C₃H₄D₂ side chain, excludes the possibility of rapid interconversion of (1) and (2).

Finally, in connection with H₂ loss, it is significant that a closely similar behaviour is observed for the lower homologue, CH₃CH=NHCH₃, as shown by ²H-labelling studies.²³

CH₃⁺ 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, (CH₃)₂C=O⁺CH₃ and CH₃CH₂CH=O⁺CH₃, 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.

C₂H₄ 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 C₂H₄ elimination from the lower homologues (CH₃)₂C=NH₂⁺ and CH₃CH₂CH=NH₂⁺.²³ Starting from (2), two 1,2-hydride shifts lead to the open-chain carbonium ion (5) which then dissociates exothermically to give C₂H₄ and CH₂=NHCH₃ (Scheme 2). This mechanism is established by ²H-labelling studies (Table 3) which reveal that the NHCH₃ 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 C₃H₄D₂ side chain in CH₃CD₂CH=NHCH₃. The statistical ratios for C₂H₄, C₂H₃D, and C₂H₂D₂ 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, CH₃CD₂CH=NH₂,²³ 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 H₂ 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 H₂ loss. However, C₂H₄ 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 C₂H₄. Similar effects have been documented in the decomposition of the lower homologues, C₃H₈N⁺.²³

It seems probable that C₂H₄ 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

TABLE 3
Ethylene loss from ²H-labelled analogues of C₄H₁₀N⁺

Ion	Neutral lost ^a		
	C ₂ H ₄	C ₂ H ₃ D	C ₂ H ₂ D ₂
(CH ₃) ₂ C=NDCH ₃	100		
(CH ₃) ₂ C=NHCD ₃	95	5	
CH ₃ CH ₂ CH=NDCH ₃	100		
CH ₃ CH ₂ CH=NHCD ₃	100		
CH ₃ CD ₂ CH=NHCH 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.

of (2); these differences are barely greater than the experimental errors involved in the measurements. A similar fine balance exists for the lower homologues, (CH₃)₂C=NH₂⁺ and CH₃CH₂CH=NH₂⁺, for which the energy barriers for dissociation and isomerisation are almost the same.²⁷

CH₃NH₂ Loss.—Both (1) and (2) eliminate CH₃NH₂ in minor abundance. In each case, the reaction gives rise to a gaussian metastable peak; the average³² kinetic energy releases associated with CH₃NH₂ loss from (1) and (2) are the same within experimental error (9.6 ± 0.5 and 8.9 ± 0.5 kJ mol⁻¹, respectively). By analogy with the mechanisms proposed for NH₃ loss from the homologous ions, (CH₃)₂C=NH₂⁺ and CH₃CH₂CH=NH₂⁺, CH₃NH₂ elimination from (1) and (2) proceeds *via* (4) and (8) (Scheme 2). Further evidence in favour of these mechanisms stems from the ²H-labelling data given in Table 4.

TABLE 4
Methylamine loss from ²H-labelled analogues of C₄H₁₀N⁺

Ion	Neutral lost ^a			
	CH ₃ NH ₂	CH ₃ NHD	CH ₃ ND ₂	CD ₃ NH ₂
(CH ₃) ₂ C=NDCH ₃		100		
(CH ₃) ₂ C=NHCD ₃				100
CH ₃ CH ₂ CH=NDCH ₃		100		
CH ₃ CH ₂ CH=NHCD ₃				100
CH ₃ CD ₂ CH=NHCH 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 NHCH₃ 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) \rightarrow (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) \rightarrow (8), the hydrogen and deuterium atoms in the three-carbon chain of (14) should be statistically distributed;

high abundance for the isomeric $\text{C}_4\text{H}_{10}\text{N}^+$ ions $\text{CH}_3\text{CH}_2\text{-CH}_2\text{NH}=\text{CH}_2$ (6) and $(\text{CH}_3)_2\text{CHNH}=\text{CH}_2$ (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, ^2H -labelling studies (Table 6) reveal that the $\text{CH}_2=\text{NH}_2^+$ daughter ion, produced by C_3H_6 loss from (1)

TABLE 5
Energy data relevant to the decomposition of $\text{C}_3\text{H}_8\text{N}^+$ and $\text{C}_4\text{H}_{10}\text{N}^+$ ions

Ion	Products and ΔH_1^a	$\Sigma\Delta H_1^a$	Transition state energy a
$(\text{CH}_3)_2\text{C}=\text{NH}_2^+$	$\text{CH}_2=\text{NH}_2^+$ (745 ³³) + C_2H_4 (50 ³³)	795	930 ²⁷
	$\text{CH}_2=\text{NH}_2^+$ (945 ³⁴) + NH_3 (-45 ³³)	900	930 ²⁷
$\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$	$\text{CH}_2=\text{NH}_2^+$ (745 ³³) + C_2H_4 (50 ³³)	795	910 ²⁷
	$\text{CH}_2=\text{NH}_2^+$ (945 ³⁴) + NH_3 (-45 ³³)	900	930 ²⁷
$(\text{CH}_3)_2\text{C}=\text{NHCH}_3$	$\text{CH}_2=\text{NHCH}_3$ (645 ^{16,35}) + C_2H_4 (50 ³³)	695	915 ^b
	$\text{CH}_2=\text{NHCH}_3$ (945 ³⁴) + CH_3NH_2 (-25 ³³)	920	915 ^b
$\text{CH}_3\text{CH}_2\text{CH}=\text{NHCH}_3$	$\text{CH}_2=\text{NHCH}_3$ (645 ^{16,35}) + C_2H_4 (50 ³³)	695	880 ^b
	$\text{CH}_2=\text{NHCH}_3$ (945 ³⁴) + CH_3NH_2 (-25 ³³)	920	910

^a All values in kJ mol^{-1} . ^b Values estimated using isodesmic substitution procedure³⁶ and by analogy with the values reported for the lower homologues.²⁷

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) \rightarrow (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, $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$.²³

It is informative to consider the relative abundances of NH_3 and C_2H_4 losses, from $(\text{CH}_3)_2\text{C}=\text{NH}_2^+$ and $\text{CH}_3\text{CH}_2\text{-CH}=\text{NH}_2^+$, 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 $(\text{CH}_3)_2\text{C}=\text{NH}_2^+$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$, 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 $\text{C}_3\text{H}_8\text{N}^+$ 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 $\text{C}_4\text{H}_{10}\text{N}^+$ 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

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 $\text{CH}_2=\text{NH}_2^+$ product ion. These data are indicative of irreversible hydrogen transfer from the NCH_3 group to the C_3H_6 side chain, (5) \rightarrow (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

TABLE 6
Propene loss from ^2H -labelled analogues of $\text{C}_4\text{H}_{10}\text{N}^+$ ions

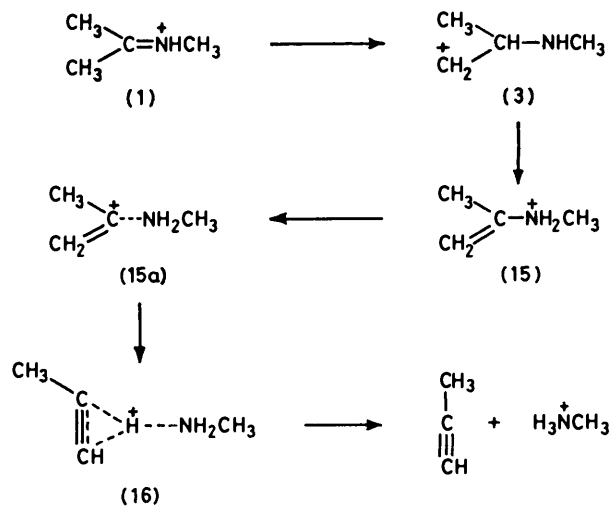
Ion	Neutral lost ^a			
	C_3H_6	$\text{C}_3\text{H}_5\text{D}$	$\text{C}_3\text{H}_4\text{D}_2$	$\text{C}_3\text{H}_3\text{D}_3$
$(\text{CH}_3)_2\text{C}=\text{NDCH}_3$	100			
$(\text{CH}_3)_2\text{C}=\text{NHCD}_3$		100		
$\text{CH}_3\text{CH}_2\text{CH}=\text{NDCH}_3$	100			
$\text{CH}_3\text{CH}_2\text{CH}=\text{NHCD}_3$		100		
$\text{CH}_3\text{CD}_2\text{CH}=\text{NHCH}_3$		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.

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) \rightarrow (4) \rightarrow (5) \rightarrow (6) \rightarrow (6a) \rightarrow products,

the hydrogen atom transferred in the step (5) \rightarrow (6) is retained in the expelled propene, as is observed for $(\text{CH}_3)_2\text{C}=\dot{\text{N}}\text{HCD}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\dot{\text{N}}\text{HCD}_3$.

Secondly, the average kinetic energies released upon elimination of C_3H_6 from (1) and (2) (10 ± 0.5 and 9.5 ± 0.5 kJ mol^{-1} , respectively) are greater than the corresponding value (8 ± 0.5 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, $(\text{CH}_3)_2\text{C}=\dot{\text{O}}\text{CH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\dot{\text{O}}\text{CH}_3$, 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 $(\text{CH}_2\dot{\text{C}}=\text{CH}_2) + (-25)$ 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 ^2H -labelling results, which show that the CH_3NH_3^+ ion is derived from the intact CH_3NH group of (1). Thus, both $(\text{CH}_3)_2\text{C}=\dot{\text{N}}\text{DCH}_3$ and $(\text{CH}_3)_2\text{C}=\dot{\text{N}}\text{HCD}_3$ lose C_3H_4 but not $\text{C}_3\text{H}_3\text{D}$.

A related observation is that, of the eight $\text{C}_4\text{H}_9\text{O}^+$ oxonium ions, only $(\text{CH}_3)_2\text{C}=\dot{\text{O}}\text{CH}_3$ 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, $(\text{CH}_3)_2\text{C}=\text{NH}_2^+$ and $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$: 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 $(\text{CH}_3)_2\text{C}=\dot{\text{Z}}\text{R}$ structure ($\text{Z} = \text{O}$ 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 $(\text{CH}_3)_2\text{C}=\dot{\text{N}}\text{HCH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\dot{\text{N}}\text{HCH}_3$ 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.

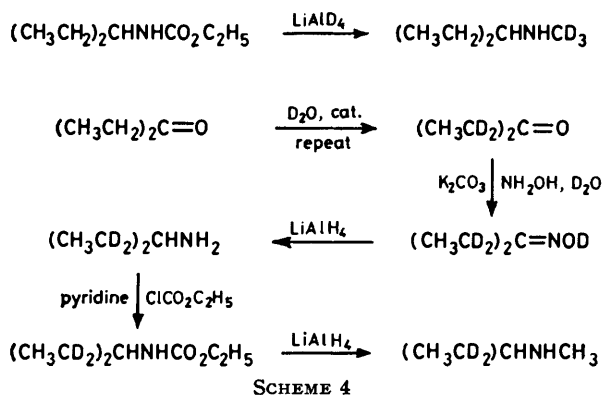
The behaviour of $(\text{CH}_3)_2\text{C}=\dot{\text{N}}\text{HCH}_3$ and $\text{CH}_3\text{CH}_2\text{CH}=\dot{\text{N}}\text{HCH}_3$ shows a decided similarity to that observed for the lower homologues, $(\text{CH}_3)_2\text{C}=\text{NH}_2^+$, $\text{CH}_3\text{CH}_2\text{CH}=\text{NH}_2^+$, and $\text{CH}_3\text{CH}=\dot{\text{N}}\text{HCH}_3$. Moreover, there are many parallels between the decomposition routes observed for these $\text{C}_4\text{H}_{10}\text{N}^+$ ions and the analogous $\text{C}_4\text{H}_9\text{O}^+$ 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.



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 D₂O in the AGHIS. The *C*-deuteriated amines were obtained by the routes in Scheme 4.

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