Potential Energy Profiles for the Unimolecular Reactions of Organic Ions: Some Isomers of $C_3H_8N^+$ and $C_4H_{10}N^+$

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The slow, unimolecular reactions of the isomeric ions $C_3H_8N^+$ which contain the NH_2 group are discussed in terms of a potential energy profile approach, in conjunction with the organic chemist's concept of mechanism. The approach successfully explains the slow reactions undergone by these ions and also rationalises the results of previous deuterium labelling studies. Extension of the approach to the three isomers of $C_4H_{10}N^+$ which also contain the NH_2 group results in various predictions concerning the reactions undergone by these ions. It is found that the observed behaviour is in excellent agreement with that expected both in the extent of the reactions undergone and also the shapes of the metastable peaks for the processes concerned.

In previous work [1-4] we have emphasised that the slow unimolecular dissociations of organic ions, which give rise to metastable peaks, normally occur with little excess energy in the transition state. Important evidence in favour of this view is found in the frequent observation of primary deuterium isotope effects for the

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[1] G. Hvistendahl and D. H. Williams, *J.C.S. Perkin II*, 1975, 881.

[2] R. D. Bowen and D. H. Williams, *J.C.S. Perkin II*, 1976, 1479.

[3] R. D. Bowen and D. H. Williams, *Org. Mass Spectrometry*, 1977, **12**, 453.

[4] R. D. Bowen, J. R. Kalman, and D. H. Williams, *J. Amer Chem. Soc.*, 1977, **99**, 5481.

decomposition of D-labelled ions. These isotope effects span the entire range known for reactions occurring in solution and in some cases are spectacularly large.[5–7]

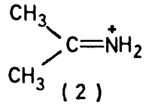
The potential energy profile is a helpful model in discussing the slow unimolecular reactions of organic ions in the gas phase. Application of the model in conjunction with the organic chemist's concept of mechanism frequently explains the slow reactions of ions which have already been investigated. Furthermore, in some cases, the approach may be used to predict correctly the reactions of ions previously uninvestigated.[2,3]

Although studies of oxonium ion systems (for instance $C_2H_5O^+$ [8,9] and $C_3H_7O^+$ [10–12]) are relatively numerous, few have been reported for the corresponding nitrogen analogues. In earlier work [13,14] we had found the potential profile approach instructive in comparing the behaviour of the analogous oxygen and nitrogen ' onium ' ions $C_2H_5O^+$ and $C_2H_6N^+$, and $C_3H_7O^+$ and $C_3H_8N^+$. In view of the success of the approach, it seemed of interest to attempt a more detailed analysis of $C_3H_8N^+$, and, if possible, to extend the method to $C_4H_{10}N^+$.

The metastable dissociations of the five ' onium ' ions (1)—(5) have been documented in an earlier study of $C_3H_8N^+$.[15] In addition, collision activation (CA) spectroscopy has been used to show that each of the isomers, (1)—(5), exists in a potential well.[16]

$CH_3CH_2CH{=}\overset{+}{N}H_2$

(1)



$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!C{=}\overset{+}{N}H_2$

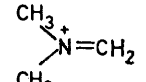
(2)

$CH_3CH_2\overset{+}{N}H{=}CH_2$

(3)

$CH_3CH{=}\overset{+}{N}HCH_3$

(4)



$\genfrac{}{}{0pt}{}{CH_3}{CH_3}\!>\!\overset{+}{N}{=}CH_2$

(5)

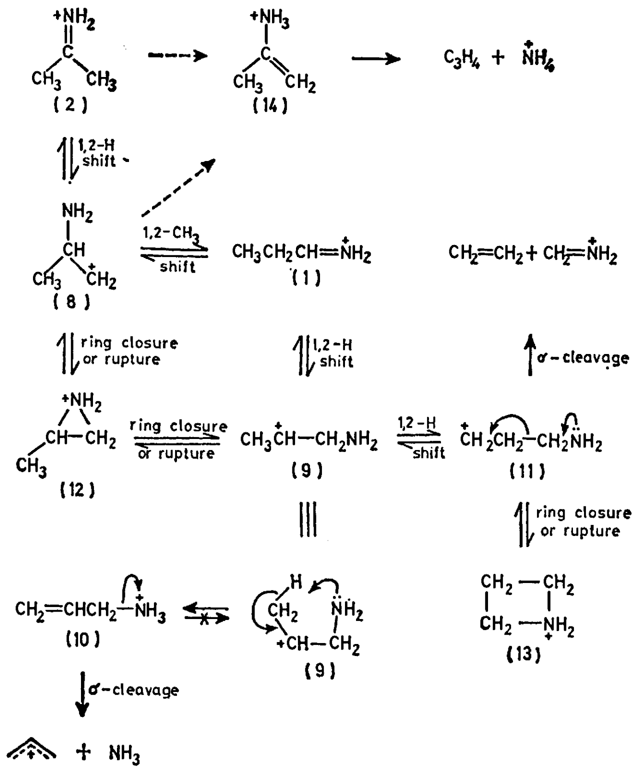
The two isomers, (1) and (2), which contain the NH_2 moiety decompose *via* loss of NH_3 and C_2H_4 in metastable transitions.[15] NH_3 loss dominates and the ratio of NH_3 loss : C_2H_4 loss is roughly the same starting from either isomer [15] thus suggesting interconversion of (1) and (2) prior to dissociation.[17] This conclusion is consistent with D-labelling results, which reveal that the

$CH_3CH_2CH{=}\overset{+}{N}D_2$ (6)

$(CH_3)_2C{=}\overset{+}{N}D_2$ (7)

two hydrogen atoms originally attached to nitrogen retain their identity.[15] Thus, for instance, (6) and (7) eliminate only NHD_2 and C_2H_4 in the first field-free region.[15] This shows that the NH_2 group in (1) and (2) is specifically involved in NH_3 elimination whilst for C_2H_4 loss, the NH_2 group is exclusively retained in the resulting fragment ion $CH_2{=}\overset{+}{N}H_2$.

However, the complete interconversion of (1) and (2) prior to decomposition is precluded because (2) is observed [16,18] to undergo a third reaction, C_3H_4 loss, to a considerable extent (13% [16]); as opposed to (1), which undergoes almost no C_3H_4 loss (*ca.* 0.5% [16]) in slow reactions.



SCHEME 1

DISCUSSION AND RESULTS

The most plausible mechanisms whereby (1) and (2) may interconvert at energies appropriate to metastable transitions are shown in Scheme 1. Here (2) undergoes a 1,2-hydride shift to form the high-energy primary carbonium ion, (8), which may then undergo a 1,2-methyl shift thus producing (1). Alternatively, (8) may undergo ring closure to protonated propylene imine,

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[5] L. P. Hills, M. L. Vestal, and J. H. Futrell, *J. Chem. Phys.*, 1971, **54**, 3834.

[6] Ü. Löhle and Ch. Ottinger, *J. Chem. Phys.*, 1969, **51**, 3097.

[7] C. Lifshitz and L. Sternberg, *Internat. J. Mass Spectrometry Ion Phys.*, 1969, **2**, 303.

[8] T. W. Shannon and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1966, **88**, 5021.

[9] B. G. Keyes and A. G. Harrison, *Org. Mass. Spectrometry*, 1974, **9**, 221.

[10] F. W. McLafferty and I. Sakai, *Org. Mass Spectrometry*, 1973, **7**, 971.

[11] C. W. Tsang and A. G. Harrison, *Org. Mass Spectrometry*, 1973, **7**, 1377.

[12] G. Hvistendahl and D. H. Williams, *J. Amer. Chem. Soc.*, 1975, **97**, 3097; see also references cited therein.

[13] R. Bowen, D. H. Williams, and G. Hvistendahl, *J. Amer. Chem. Soc.*, 1977, **99**, 7509.

[14] D. H. Williams and R. D. Bowen, *J. Amer. Chem. Soc.*, 1977, **99**, 3192.

[15] N. A. Ucella, I. Howe, and D. H. Williams, *J. Chem. Soc.* (*B*), 1971, 1933.

[16] K. Levsen and F. W. McLafferty, *J. Amer. Chem. Soc.*, 1974, **96**, 139.

[17] H. M. Rosenstock, V. H. Dibeler, and F. N. Harllee, *J. Chem. Phys.*, 1964, **40**, 591.

[18] G. Cum, G. Sindona, and N. A. Uccella, *Ann. Chim.* (*Italy*), 1974, **64**, 169.

(12), followed by ring opening to form the secondary cation (9), which may then undergo a 1,2-hydride shift leading to (1). Both these mechanisms seem plausible, although it is known from ^{13}C-labelling results that the former mechanism operates in the analogous oxygen system.[4]

The most direct routes for NH_3 and C_2H_4 elimination from (2) and (1) are also shown in Scheme 1. NH_3 loss proceeds *via* a 1,2-hydride shift in (1), leading to (9) which may then isomerise through a 5-membered ring transition state to protonated allylamine, (10); σ-bond cleavage then results in NH_3 loss. Alternatively, a further 1,2-hydride shift may occur in (9), thus producing (11), which may then eliminate C_2H_4 *via* fission of the central C–C bond.

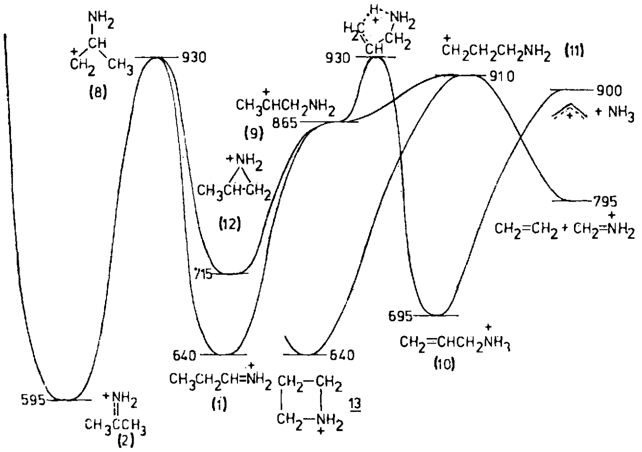

FIGURE 1 Potential energy profile for isomerisation and dissociation of ions (1) and (2)

Use of known heats of formation (ΔH_f) for reactants,* neutrals,[19] and product ions,[19,20] together with a method[21] for estimating heats of formation based on the isodesmic substitution,[22] leads to the potential energy profile shown in Figure 1. Here 1,2-hydride shifts are regarded as proceeding with negligible barriers (*i.e.* with activation energies equal to the reaction endothermicities or exothermicities); this view is supported by calculations[23] and solution n.m.r. experiments.[24] The isomerisation of (9) to (10) is depicted as requiring an activation energy of 65 kJ mol^{-1}; this is consistent with previous findings in analogous systems[25,26] and also with the high degree of retention of the original NH_2 group in the eliminated NH_3 molecule. Clearly (9)→(10) cannot be rapidly reversible because, were this the case, the reversible transfer of hydrogen from carbon to nitrogen would result in loss of identity of the hydrogen atoms attached to nitrogen. Also shown in Figure 1 are protonated propylene imine (12) and protonated azetidine (13); these may be formed by ring closure of the less stable, open-chain isomers, (8) and (9), and (11), respectively. The heats of formation of these ions and protonated allylamine are accessible from the known or estimated proton affinities of propylene imine,[27] azetidine,[27,28] and allylamine,[27] respectively.

It is evident from Figure 1 that isomerisation of (1) to (2) has a very similar activation energy to dissociation. However, the occurrence of a significant amount of C_3H_4 loss only from (2) precludes complete interconversion of (1) and (2) prior to decomposition. A possible explanation is that the isomerisation of (2) to (1) is *just* rate-determining in the dissociation of (2); starting from (1), however, dissociation proceeds more rapidly than isomerisation to (2).

Experimentally, appearance potential measurements reveal that the transition state energies for NH_3 elimination from (1) and (2) are *ca.* 915 and 935 kJ mol^{-1} respectively.* This difference, although small, may be significant.

Two other effects should be observed if the isomerisation of (2) to (1) is the rate-determining step in the decomposition of ions generated as structure (2). First, since the ions formed as structure (1) by rearrangement of (2) possess a higher internal energy than those generated initially as (1), such ions should show a preference for dissociations with high frequency factors.[12,25] In contrast, there will be discrimination against any process which proceeds *via* a highly ordered activated complex because these dissociations are not able to proceed as fast as those involving only simple bond cleavage. Thus, because NH_3 loss must proceed *via* more extensive rearrangement than C_2H_4 loss, the latter process should compete better at high internal energies. Experimentally,[16] a slight but significant trend in this direction is observed; C_2H_4 loss being more abundant relative to NH_3 loss for ions generated as (2) rather than (1). Second, a portion of the excess energy present in rearranged ions of structure (1) is partitioned into the bond which breaks in the dissociation step.[12,25,29] Hence, the metastable peaks should be broader for ions which have undergone rate-determining isomerisation

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* These values were deduced from appearance potential measurements obtained using an energy-resolved electron beam by Professor F. P. Lossing. We thank Professor Lossing for his assistance in making these measurements.

[19] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. L. Herron, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions,' National Bureau of Standards, Washington, D.C., 1969.

[20] F. P. Lossing, *Canad. J. Chem.*, 1971, **49**, 357.

[21] R. D. Bowen and D. H. Williams, *Org. Mass Spectrometry*, 1977, **12**, 475.

[22] L. Radom, J. A. Pople, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 5935.

[23] *E.g.* L. Radom, J. A. Pople, V. Buss, and P. von R. Schleyer, *J. Amer. Chem. Soc.*, 1972, **94**, 311.

[24] G. A. Olah and P. von R. Schleyer, eds., 'Carbonium Ions,' Wiley and Sons Inc., New York; see especially vol. 4, ch. 33.

[25] G. Hvistendahl, R. D. Bowen, and D. H. Williams, *J.C.S. Chem. Comm.*, 1976, 294.

[26] R. D. Bowen and D. H. Williams, *J.C.S. Perkin II*, 1978, 68.

[27] J. F. Wolf, R. H. Staley, I. Koppel, M. Taagepera, R. T. McIver, jun., J. L. Beauchamp, and R. W. Taft, *J. Amer. Chem. Soc.*, 1977, **99**, 5417; we thank Professor Beauchamp for communicating these results prior to publication.

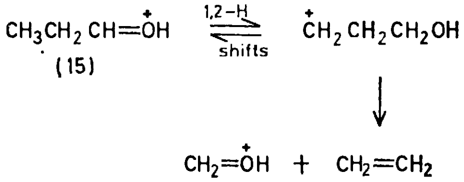
[28] D. H. Aue, H. M. Webb, and M. T. Bowers, *J. Amer. Chem. Soc.*, 1975, **97**, 4137.

[29] R. G. Cooks, J. H. Benyon, R. M. Caprioli, and G. R. Lester, 'Metastable Ions,' Elsevier, Amsterdam, 1973.

than for those which have not. It is found that the gaussian metastable peak for NH_3 loss from (1) and (2) is slightly broader starting from (2) than (1). Average[30] values may be calculated from the width of the metastable peak at half-height; that starting from (2) (17 ± 1 kJ mol^{-1})[31] being reproducibly greater than that (13 ± 1 kJ mol^{-1}) * starting from (1).

Thus, although no drastic differences are observed in the behaviour of (1) and (2), the available experimental evidence is in favour of the view that isomerisation of (2) to (1) is marginally rate-determining in the decomposition of ions generated as (2).

Further support for the general form of the potential energy profile shown in Figure 1 may be deduced from several sources. First, the dissociation of (1) or (2), *via* (11), to $CH_2{=}\overset{+}{N}H_2$ and $CH_2{=}CH_2$ is such that the final step [(11)→products] is exothermic. Therefore, kinetic energy release is possible, and it is found[15] that (1) and (2) both eliminate C_2H_4 with the release of a relatively specific quantity (*ca.* 40 kJ mol^{-1}) of kinetic energy as measured from the flat-topped metastable peak for C_2H_4 loss. In contrast, the metastable peak for C_2H_4 loss from the oxygen analogue (15), *via* the 3-hydroxypropyl cation, is narrow and gaussian because the dissociation step is endothermic.[14]

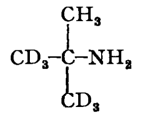
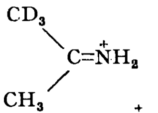


Second, since rapid equilibration of (1), (9), and (11) may occur prior to dissociation, the 1,2-hydride shifts needed to effect these interconversions should lead to loss of identity of all carbon-bound hydrogens in (1) prior to decomposition. In addition, loss of identity of all carbon-bound hydrogens in (2) may occur *via* reversible isomerisation to (8); or, alternatively, *via* isomerisation of (1), (9), and (11) after rearrangement of (2) to (1). Hence, it is probable that the loss of ethylene from deuteriated analogues of (1) and (2) should involve statistical selection of the necessary four hydrogens from the six originally bound to carbon. The predicted and observed decompositions of some deuteriated analogues of (1) and (2) are given in Table 1; the agreement between the observed decompositions and those expected from the model is good.

Third, elimination of NH_3 proceeds *via* formation of protonated allylamine, (10), which dissociates into $C_3H_5^+$ and NH_3 more readily than it returns to (9). The rearrangement of (9) to (10) involves the breaking of a C–H bond and the simultaneous formation of a new N–H bond. Were this step to be rate-determining in the elimination of NH_3 from ions generated as (1) or (2), an isotope effect favouring transfer of H, rather than D, to nitrogen would be expected to operate in the decomposition of suitable D-labelled analogues of (1) and (2).

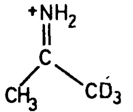
TABLE 1

Expected and observed decomposition of D-labelled analogues of (1) and (2) *via* ethylene loss

Precursor	Ion produced at threshold	Neutral lost[a]							
		C_2H_4		C_2H_3D		$C_2H_2D_2$		C_2HD_3	
		T[b]	O[c]	T[b]	O[c]	T[b]	O[c]	T[b]	O[c]
		0	0	20	19	60	62	20	19
$(CH_3CD_2)_2CHNH_2$	$CH_3CD_2CH{=}\overset{+}{N}H_2$	7	5	53	52	40	43	0	0

[a] Values normalised to a total ion current of 100 units. [b] Expected on basis of model outlined in text. [c] Observed (first field-free region—data from ref. 15).

As it would appear that the isomerisation of (2) to (1) is the rate-determining step in the decomposition of (2), no isotope effect should be observed for loss of NH_3 from this ion. In fact, a small isotope effect (1.5 : 1) is detected; ion (16), for instance, loses more NH_3 (60%) than NH_2D (40%) in the first field-free region.[15] This result probably indicates that isomerisation of (2) to (1) proceeds *via* a transition state of very similar (and, possibly marginally lower energy) than that for (9)→(10). For ion (1) however, the isomerisation (9)→(10) should definitely be rate-determining for NH_3 loss and hence an isotope effect is expected to operate in favour of NH_3 loss. It is found that ion (17), for instance, eliminates NH_3 in preference to NH_2D to the extent of 91 : 9[15] in the first field-free region. These figures



(16)

$CH_3CD_2CH{=}\overset{+}{N}H_2$

(17)

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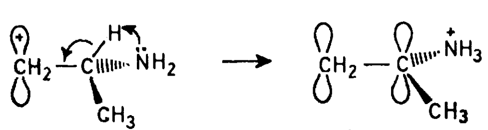
* These energy release measurements were performed using the V.G. Micromass ZAB 2F instrument in the Laboratory of Professor J. H. Beynon, University College of Swansea. In this instrument the ions pass through the magnetic sector before entering the electric sector, metastable decompositions being observed using the MIKES technique. The assistance of Dr. J. R. Kalman in making these measurements is gratefully acknowledged.

[30] D. T. Terwilliger, J. H. Beynon, and R. G. Cooks, *Proc. Roy. Soc. Ser. A*, 1974, **341**, 135.

[31] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 797.

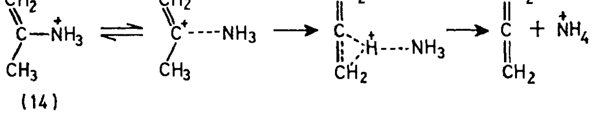
differ substantially from those expected on the basis of statistical selection of the final hydrogen atom needed for NH_3 loss and correspond to an isotope effect of 5 : 1 in favour of H, rather than D, transfer to nitrogen.* An isotope effect of this nature is what is expected on the basis of Figure 1. Moreover, since the isotope effect observed for NH_3 loss from (2) is much smaller, this constitutes more evidence in favour of the rearrangement of (2) *to* (1) being either rate-determining or almost rate-determining. This is because isotope effects are expected to be more pronounced for decompositions of ions of lower internal energy.

Considering the loss of C_3H_4 from (2), it seems probable that this reaction proceeds *via* protonated prop-2-enylamine, (14). This could be formed by 1,3-hydrogen transfer in (2) or by 1,2-hydrogen transfer in (8). The former would be symmetry forbidden[31] if it were a concerted process, and as such would be expected to have a high symmetry-imposed barrier. The latter process, (8)→(14) seems more likely, although this


(8) (14)

rearrangement may well possess an activation energy in view of the rather unfavourable geometry of the transition state (three-membered ring) involved.

Dissociation of (14) to $\overset{+}{N}H_4$ and C_3H_4 may then occur *via* transfer of a hydrogen atom to nitrogen from either the intact methyl group ($CH_2{=}C{=}CH_2$ loss) or from the methylene group ($CH{\equiv}CCH_3$ loss). These processes give rise to products with similar total heat of formation (835 and 830 kJ mol^{-1},[19,27] respectively). It is probable that this reaction proceeds with a very low degree of concert; the N–C bond being considerably stretched before the new N–H bond is formed. Thus, as the N–C bond is stretched, the ion approximates to a loose complex of prop-2-enyl cation solvated by ammonia. A small amount of reorganisation of this complex leads to a complex in which the ammonium cation is loosely solvated by C_3H_4. This complex may now break up to

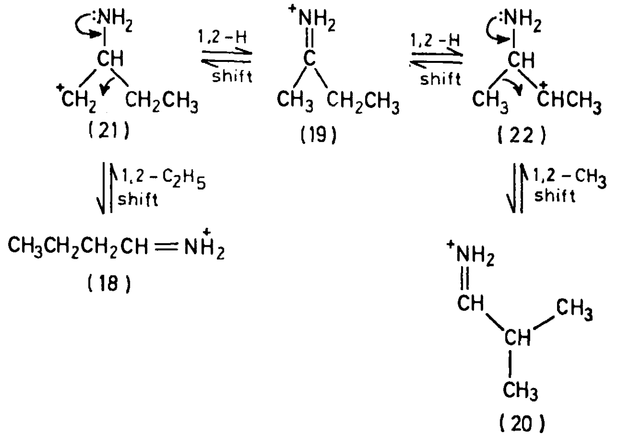

(1)

give $\overset{+}{N}H_4$ and C_3H_4 [equation (1)]; the C_3H_4 fragment is taken to be $CH_2{=}C{=}CH_2$ although $CH_3C{\equiv}CH$ is equally possible.

A necessary condition for this mechanism for C_3H_4 loss to be correct is that the product combination formed (NH_4^+ and C_3H_4) must be lower in energy than prop-2-enyl cation and NH_3. Were this not so, (14) would be expected to undergo NH_3 loss in preference to rearrangement prior to C_3H_4 loss. Using known heats of formation for NH_3,[19] C_3H_4,[19] prop-2-enyl,[32] and NH_4^+ [27] it is found that this condition is satisfied; the total heat of formation of NH_4^+ and C_3H_4 being 830 or 835 kJ mol^{-1} whilst that for prop-2-enyl and NH_3 is considerably higher (945 kJ mol^{-1}).

Thus, the approach outlined above can account in some detail for the major slow reactions undergone by (1) and (2). In particular, it is found that isomerisation of (2) to (1) is close to being rate-determining in the dissociation of (2). The method naturally accommodates the flat-topped metastable peak for C_2H_4 loss from (1) and (2) which is in contrast with C_2H_4 loss from the oxygen analogues of (1) and (2), these reactions being characterised by gaussian metastable peaks.[14]

$C_4H_{10}N^+$.—Since no systematic study of the slow unimolecular reactions of this ion has been reported, we felt it worthwhile to extend the approach used for $C_3H_8N^+$ to this ion. In particular it was hoped that the model would be able to predict successfully the slow dissociations of the isomeric ions (18)—(20) which contain the NH_2 moiety. In view of the fine balance between isomerisation of (2) to (1) and subsequent dissociation observed for the lower homologue $C_3H_8N^+$, it is of interest to enquire which isomers (if any) of $C_4H_{10}N^+$ interconvert before dssociation. Furthermore, does the insertion of a CH_2 residue into (1) and (2) open up new channels for dissociation?



SCHEME 2

The three isomers, (18)—(20), may undergo interconversion *via* a series of 1,2-hydride and alkyl shifts as shown in Scheme 2.

The heats of formation of the species involved in Scheme 2 may be estimated from those known for the lower homologues (1) and (2) or by the use of the iso-

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* The alternative explanation[16] has been postulated that the preference for NH_3 loss from (17) is due to fragmentation of unrearranged (17) with preference for 1,4-transfer of hydrogen [*i.e.* (9)→(10)]. This is possible, but seems less likely in view of the definite existence of an isotope effect for NH_3 loss from (2) and the apparently statistical loss of ethylene observed from both (1) and (2).

[32] D. H. Aue, W. R. Davidson, and M. T. Bowers, *J. Amer. Chem. Soc.*, 1976, **98**, 6700.

desmic substitution.[21] This leads to the potential energy profile of Figure 2. It is apparent from Figure 2 that the energy needed to cause interconversion of (19) and (20) is considerably less than that needed to cause interconversion of these isomers with (18). This is because interconversion of (19) and (20) can proceed *via* a secondary cation whereas isomerisation of (19) and (20) to (18) must proceed *via* a primary cation.

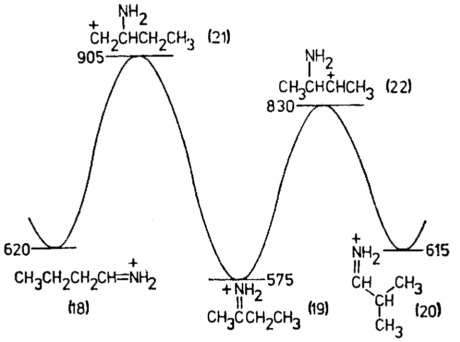
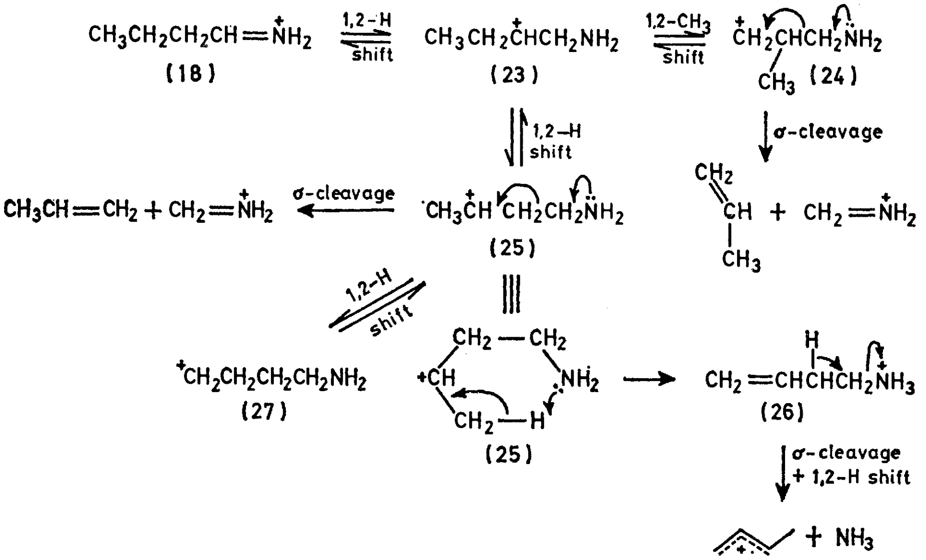


FIGURE 2 Potential energy profile for isomerisation of ions (18), (19), and (20)



SCHEME 3

The most plausible routes for dissociation of (18) are summarised in Scheme 3. Using known heats of formation for product ions [19,33] and neutrals [19] together with estimated [21] heats of formation for reactants and postulated intermediates leads to Figure 3. It is clear from this that dissociation of (18) *via* bond cleavage in (25) is considerably more favourable than isomerisation to (19) [and subsequently (20)]. Thus ion (18) is expected to undergo loss of propene in slow unimolecular dissociations. Another possible decay route is NH_3 loss *via* rearrangement of (25) thus forming protonated homoallylamine, (26), which may then dissociate by σ-cleavage of the C–N bond together with a concomitant 1,2-hydride shift. Although the rearrangement (25)→(26) may proceed *via* a six-membered ring transition state, thus minimising ring strain, it is probable that such a process has an activation energy (say 0—20 kJ mol^{-1}). Hence, NH_3 loss, although possible, may not occur. Experimentally, almost exclusive loss of C_3H_6 is observed for those reactions occurring in metastable transitions. Further support for the proposed reaction profile may be deduced from the shape of the metastable peak for C_3H_6 loss from (18). It is evident from Figure 3 that dissociation of (25) is exothermic, but by only 45 kJ mol^{-1}. This is in contrast to C_2H_4 loss from (1) or (2) *via* (11) which is exothermic by 115 kJ mol^{-1}; this difference arises mainly because (11) is a primary carbonium ion whereas (25) is a more stable, secondary, carbonium ion. By reference to analogous systems,[14] it may be deduced that C_3H_6 loss from (25) will be evidenced by a broad, but gaussian, metastable peak. This is what is observed; a value of 20 kJ mol^{-1} for the average kinetic energy release being deduced from the width of the peak at half height.[30] Thus, approximately half the reaction exothermicity is released as translation; this is consistent with earlier work in analogous systems.[14]

Returning to the isomeric ions, (19) and (20), the most plausible routes whereby these ions may decompose are given in Scheme 4. The corresponding reaction profile is given in Figure 4. The activation energy (65 kJ mol^{-1}) associated with the rearrangement of (29) to (30), *via* a five-membered ring transition state, is assigned on the basis of that postulated and measured in analogous systems ($C_3H_8N^+$ above, $C_3H_7O^+$ [25] and $C_4H_9O^+$ [26]).

From the potential energy profile of Figure 4 it is apparent that, even allowing for an activation energy of 65 kJ mol^{-1} for the rearrangement (29)→(30), NH_3 loss is still the most favourable reaction starting from (19) or (20). The energy needed to cause interconversion

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[33] F. P. Lossing, *Canad. J. Chem.*, 1972, **50**, 3973.

of (19) and (20) is less than that needed to promote dissociation *via* NH_3 elimination. Furthermore, the energy required to dissociate (19) or (20) is less than that needed to cause isomerisation to (18). Hence ions (19) and (20) should (i) isomerise prior to dissociation and (ii) react over a potential surface separate from that over which (18) reacts. This should be evidenced by (i) ions (19) and (20) undergoing the same reaction(s) in the same ratios in slow reactions and (ii) these ions should undergo a different reaction (or reactions) to that of (18). Experimentally, NH_3 loss is the main slow reaction (*ca.* 98% metastable ion current from *m/e* 72) starting from either (19) or (20). Elimination of C_2H_4 or C_3H_6 [*cf.* (18) for which this is the main slow reaction] are very minor processes.

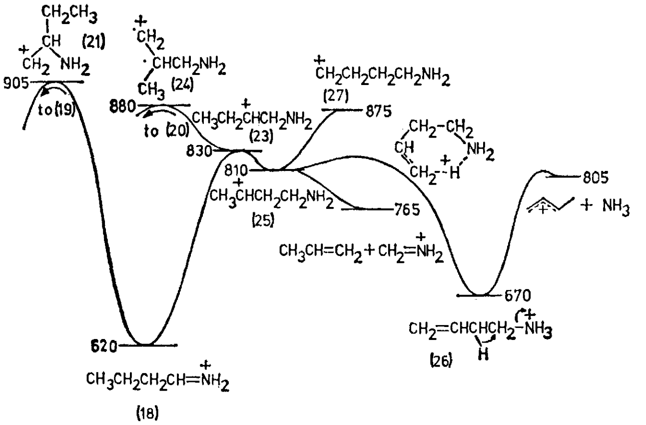


FIGURE 3 Potential energy profile for dissociation of the ion (18)

Thus, although the lower homologues, (1) and (2), undergo a considerable proportion of common slow reactions (C_2H_4 and NH_3 loss), the three isomers of $C_4H_{10}N^+$ which contain an NH_2 group may be divided into two distinct classes. The former class, ion (18), undergo almost exclusively C_3H_6 loss in slow reactions whereas the other class, ions (19) and (20), behave differently in undergoing mainly NH_3 loss.

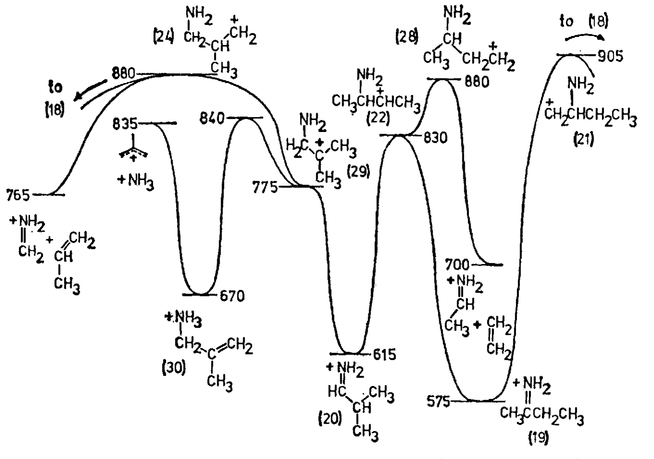


FIGURE 4 Potential energy profile for dissociation of ions (19) and (20)

Further support for the description of reactions given in Figure 4 may be derived from several sources. Thus, the dissociation of (30) to the 2-methylallyl cation and ammonia is finely balanced with isomerisation to (29). Hence, some loss of identity of the hydrogens attached to nitrogen may be expected prior to NH_3 loss. This is observed to be the case, the measured losses of NHD_2 and NH_2D from (31) and (32) being given in Table 2.

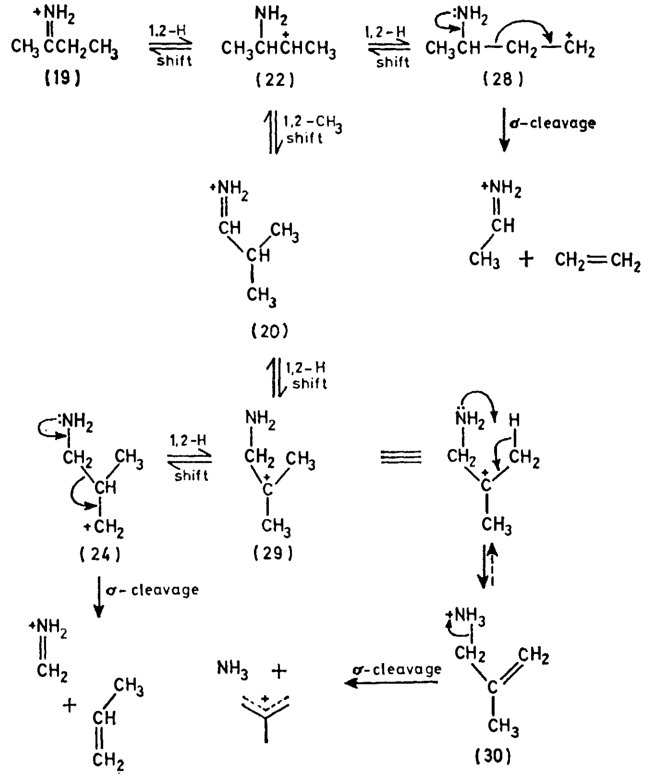
TABLE 2

Loss of deuteriated ammonia from ions (31) and (32)

Ion	Neutral lost [a] First field-free region NH_3	NH_2D	NHD_2	Second field-free region NH_3	NH_2D	NHD_2
(31)	[b]	11	89	[b]	15	85
(32)	[b]	9	91	[b]	18	82

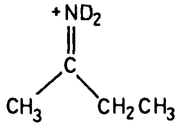
[a] Values normalised to a total metastable ion current due to 'ammonia' loss of 100 units. [b] Too weak to measure.

Two important conclusions stem from the data of Table 2. First, the losses of deuteriated ammonia from the $C_4H_8D_2N^+$ ions of original structures (31) and (32) are very similar. This is further evidence in favour of these ions interconverting prior to dissociation. Second, a significant amount of NH_2D loss is observed, thus indicating partial reversibility of (29)→(30).

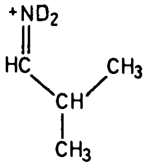


SCHEME 4

Consideration of the route [(28)→products)] for C_2H_4 loss reveals that this proceeds with the release of *ca.* 180 kJ mol^{-1} of energy in the dissociation step. Kinetic energy release is, therefore, expected [14] and it is found that the metastable peak for this process, although very weak, is broad and flat-topped, starting from either (19) or (20).



(31)



(32)

Furthermore, C_3H_6 loss from (19) or (20) may occur either by direct bond fission in the high-energy primary carbonium ion, (24); or, alternatively, (24) may rearrange to (23) and then (25) (Figure 3) and thus undergo C_3H_6 loss *via* σ-cleavage of (25). In the former case, the dissociation of (24) to products is exothermic by 115 kJ mol^{-1} and kinetic energy release is expected.[14] In the latter case, the isomerisation of (19) or (20) to (25) *via* (24) is the rate determining step for C_3H_6 loss; (25) is formed with considerably more internal energy than that needed to cause dissociation. Some of this excess energy is partitioned into the bond that breaks in the dissociation step [12,25,29] thus resulting in a broadening of the metastable peak for the process concerned. Thus, irrespective of the exact mechanism(s) whereby C_3H_6 loss occurs from ions generated as (19) or (20), the metastable peaks associated with these reactions should be broader than that for C_3H_6 loss starting from (18). All three metastable peaks are broad and gaussian. However, those starting from (19) and (20) correspond to an average kinetic energy release of 34 ± 2 kJ mol^{-1} and 30 ± 2 kJ mol^{-1} respectively. These values are significantly greater than that (20 ± 1 kJ mol^{-1}) measured for C_3H_6 loss from (18).

Conclusion.—The approach provides a rationalisation of the slow reactions undergone by two isomers of $C_3H_8N^+$ and accounts, in some detail, for the results of ^2H-labelling studies on these ions. It may be successfully extended to the three isomers of $C_4H_{10}N^+$ which also contain the NH_2 moiety and explains the differences in the reactions undergone by these ions. In particular, the analysis naturally accommodates the independent behaviour of ion (18) as opposed to (19) and (20), which undergo interconversion prior to decomposition *via* a different channel.

EXPERIMENTAL

All compounds were either available commercially or synthesised by unexceptional methods. The mass spectra were obtained using an A.E.I. MS 902 double-focusing mass spectrometer; samples were introduced *via* the All Glass Heated Inlet System (AGHIS). The *N*-deuteriated amines were prepared *in situ* by exchange of the NH_2 protons with D_2O in the AGHIS. The decompositions of ions in the first field-free region were detected by scanning the accelerating voltage at constant electric sector voltage and magnetic field strength.[34]

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[7/1794 *Received*, 12*th October*, 1977]

[34] K. R. Jennings, *J. Chem. Phys.*, 1965, **43**, 4176.