Reactions of Isolated Organic Ions. Alkene Loss from the Immonium Ions $CH_3CH{=}N^+HC_2H_5$ and $CH_3CH{=}N^+HC_3H_7$

Richard D. Bowen *

Department of Chemistry, University of Warwick, Coventry CV4 7AL

The slow unimolecular reactions of metastable $CH_3CH{=}N^+HR$ [R = C_2H_5, $(CH_3)_2CH$, and $CH_3CH_2CH_2$] ions are reported and discussed in energetic and mechanistic terms. These immonium ions eliminate an alkene (R–H) derived by hydride abstraction from the incipient carbonium ion R^+. This reaction is interpreted as occurring *via* an ion–dipole complex comprising the incipient carbonium ion co-ordinated to $CH_3CH{=}NH$, followed by rearrangement to another complex in which (R–H) and $CH_3CH{=}NH$ are bound to a common proton. ^{2}H-Labelling experiments show a different specificity in the hydrogen-abstraction step for R = ethyl and R = *n*-propyl: transfer of a deuterium atom from the β-carbon predominates when R = CH_2CD_3, but $CH_3CH{=}N^+HCD_2CH_2CH_3$ expels a substantial proportion of C_3H_5D. The behaviour of the $CH_3CH{=}N^+HR$ ions is compared with that of their $CH_2{=}N^+HR$ homologues. An analysis is presented of the influence of the structure of R on the properties of the associated ion–dipole complexes.

The study of the structure and reactivity of charged intermediates is a central theme of organic chemistry.[1] It has been established that mass spectrometers can be applied to good effect in this field as instruments in which interesting ions may be generated and investigated free from interference from solvent molecules.[2–4] An analysis of the behaviour of metastable ions is often especially informative. Such ions have relatively long lifetimes (*ca.* 10 μs); this precludes the intervention of isolated electronic states, except in rare circumstances.[5] Furthermore, there is sufficient time for a very large number (*ca.* 10^8) of bond vibrations to occur before dissociation takes place; this affords ample opportunity for energetically accessible transition states and combinations of possible products to be formed. These circumstances lead to a situation in which the critical[6] energy (corresponding to the activation energy) for a given process is the dominant factor in determining whether or not that reaction will occur.[7,8] A pertinent illustration of this energy discrimination is the occasional observation of very large isotope effects in the dissociation of metastable ions.[9–12] As a general rule, the isotope effects are of comparable magnitude to those encountered in solution experiments, thus underlining the fact that the average internal energies in the transition states are similar for metastable ions and species in condensed phases.

Recent advances in characterising the structures of isolated organic ions and the ionic[13] and neutral[14] products of their decomposition have permitted a more detailed description of their chemistry to be made. It has become clear that unusual intermediates are often involved in the reactions of metastable ions. These species include distonic[15] ions (those with notional charge and radical sites on separate atoms),[16–18] ion–dipole or ion–molecule complexes (in which an incipient cation is co-ordinated to a neutral component),[19–21] and proton-bound complexes (in which two putative neutral components are attached to a common proton).[22–24] The second and third of these classes of ion appear to play an important role in the isomerisation and decomposition of various 'onium' ions $C_nH_{2n+1}Z^+$ (Z = O, S, or NH).[22] The chemistry of the oxonium ions, $C_nH_{2n+1}O^+$, has been extensively investigated by both electron-ionisation and chemical-ionisation methods.[22,25–60] Indeed, it was largely through these studies that the relevance of ion–dipole and proton-bound complexes came to be recognised.[22,43,50] The analogous immonium ions, $C_nH_{2n+2}N^+$, have received much less attention.[21,42,46,61–69] In this paper, the reactions of $CH_3CH{=}N^+HR$ ions (R = C_2H_5 and C_3H_7) are reported, discussed and compared with those of the homologous $CH_2{=}N^+HR$ ions in order to determine the influence of the structure of R on the behaviour of the associated ion–molecule complexes.

Table 1. Reactions of metastable immonium ions.

Ion structure	Neutral lost[a] C_2H_4	C_3H_6	Kinetic energy release[b]
(1) $CH_3CH{=}N^+HCH_2CH_3$	100		3.4 ± 0.2
(2) $CH_3CH{=}N^+HCH_2CH_2CH_3$		100	3.5 ± 0.2
(3) $CH_3CH{=}N^+HCH(CH_3)_2$		100	2.7 ± 0.1
(4) $CH_3CH_2CH{=}N^+HCH_2CH_3$	100		3.5 ± 0.4

[a] Values measured in first and second field-free region and normalised to a total metastable ion current of 100 units. [b] Values computed from the width at half-height of the appropriate metastable peak for ions dissociating in the second field-free region and quoted in kJ mol^{-1}.

Results and Discussion

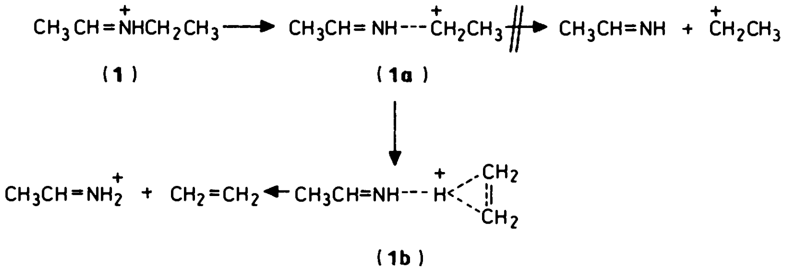
The reactions of metastable $CH_3CH{=}N^+HR$ and the related $CH_3CH_2CH{=}N^+HCH_2CH_3$ immonium ions are given in Table 1. Each of these ions expels an alkene derived by hydrogen abstraction from the original alkyl group. In each case, the reaction is characterised by a Gaussian metastable peak; the kinetic energy release[8,70] computed from the width at half height of the associated metastable peak is also given in Table 1.

The behaviour of the ^{2}H-labelled analogues of (1)–(4) (Table 2) is informative. The hydrogen atom originally bound to nitrogen is exclusively retained in the daughter ion formed by alkene expulsion. This indicates that transfer of hydrogen from carbon to nitrogen is essentially irreversible, regardless of whether the alkyl group R in $CH_3CH{=}N^+DR$ is ethyl, n- or isopropyl. Similar conclusions apply for the higher homologue, $CH_3CH_2CH{=}N^+DC_2H_5$, which loses only C_2H_4. In contrast, the origin of the hydrogen transferred from carbon to nitrogen shows a distinct dependence on the structure of the alkyl group

Table 2. Reactions of metastable ^{2}H-labelled immonium ions.

Ion structure	Neutral lost[a] C_2H_4	C_2H_3D	$C_2H_2D_2$	C_2HD_3	C_3H_6	C_3H_5D	$C_3H_4D_2$
$CH_3CH{=}N^+DCH_2CH_3$	100						
$CH_3CH{=}N^+HCH_2CD_3$			86 ± 3	14 ± 2			
$CH_3CH{=}N^+DCH_2CD_3$			84 ± 3	16 ± 2			
$CH_3CH{=}N^+DCH_2CH_2CH_3$					100		
$CH_3CH{=}N^+HCD_2CH_2CH_3$						31 ± 1	69 ± 2
$CH_3CH{=}N^+DCD_2CH_2CH_3$						30 ± 1	70 ± 2
$CH_3CH{=}N^+DCH(CH_3)_2$					100		
$CH_3CH_2CH{=}N^+DCH_2CH_3$	100						

[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. Very similar results, lying within the quoted error limits, were obtained by measurements of metastable-peak areas for ions dissociating in the second field-free region.



Scheme 1.

in $CH_3CH{=}N^+HR$. When R is ethyl, transfer of a β-hydrogen is predominant: both $CH_3CH{=}N^+HCH_2CD_3$ and $CH_3CH{=}N^+DCH_2CD_3$ eliminate 85% $C_2H_2D_2$ and only 15% C_2HD_3. If the hydrogen and deuterium atoms in the C_2HD_2 group were transferred with equal probability to nitrogen, 60% $C_2H_2D_2$ and 40% C_2HD_3 loss would be expected. Exclusive $C_2H_2D_2$ expulsion would be anticipated if only the β-hydrogens were involved in alkene loss. Thus, the observed ratios of $C_2H_2D_2$:C_2HD_3 loss reveal that specific participation of the β-hydrogen atom accounts for roughly two-thirds of ethylene loss from $CH_3CH{=}N^+HCH_2CD_3$ and $CH_3CH{=}N^+DCH_2CD_3$. The remaining third occurs after the hydrogen and deuterium atoms have acquired a common identity. This analysis neglects isotope effects, which should favour hydrogen transfer (leading to C_2HD_3 expulsion) at the expense of deuterium transfer ($C_2H_2D_2$ loss); the inclusion of an isotope effect in the analysis would mean that the specificity of β-hydrogen participation would be greater than the apparent value (two-thirds) deduced above. On proceeding to the homologues, $CH_3CH{=}N^+HCD_2CH_2CH_3$ and $CH_3CH{=}N^+DCD_2CH_2CH_3$, the observed ratios (69:31) of $C_3H_4D_2$:C_3H_5D losses are very close to that (67:33) expected on the basis of isomerisation of the $CD_2CH_2CH_3$ group to CHD_2CHCH_3, followed by transfer of any one of the six hydrogen and deuterium atoms of the methyl groups to nitrogen. The ratios predicted assuming specific β-hydrogen transfer occurs are 100:0. Consequently, it is evident that the strong preference for β-hydrogen transfer in the loss of ethylene from (**1**) is reduced to nearly negligible importance in propene elimination from (**2**).

This trend appears to be general for alkene expulsions of this type from immonium ions of this structure. Thus, $CH_2{=}N^+HCD_2CH_3$ eliminates $C_2H_2D_2$, but not C_2H_3D.[61] In contrast, $CH_2{=}N^+HCD_2CH_2CH_3$ expels $C_3H_4D_2$ and C_3H_5D in the ratio 71:29, and $CH_2{=}N^+HCD_2CH(CH_3)_2$ loses $C_4H_6D_2$ and C_4H_7D in the ratio 74:26.[66] These values are different from that (100:0) expected for β-hydrogen transfer, but close to those (67:33 and 73:27, respectively) predicted on the basis of isomerisation of the incipient alkyl group, followed by transfer of hydrogen or deuterium from any of the resultant methyl groups.[66] Similarly, the transfer of hydrogens from various sites in the alkyl group R has been reported in alkene expulsion from larger $CH_3CH{=}N^+HR$ immonium ions.[71]

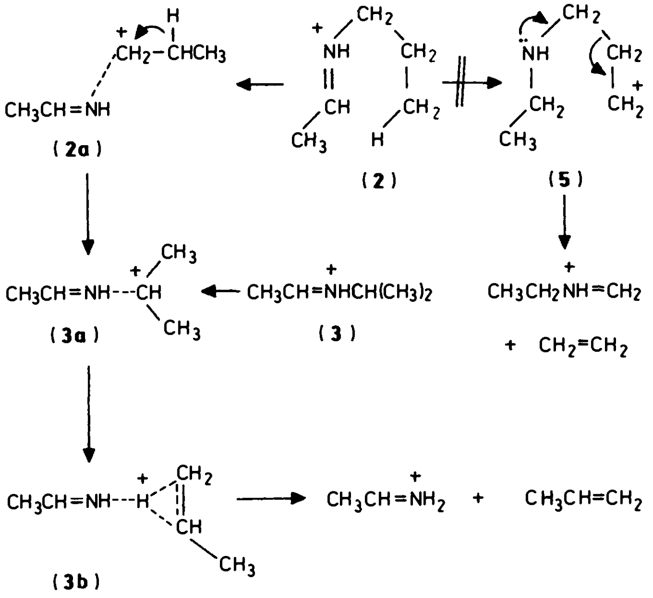
All these results are naturally accommodated by the hypothesis that alkene loss takes place *via* species comprising an incipient carbonium ion co-ordinated to an imine.

Thus, starting from (**1**) (Scheme 1), stretching of the C–N σ-bond leads to structure (**1a**), in which ethanimine ($CH_3CH{=}NH$) is attached to a developing ethyl cation. Continuation of this bond stretching would lead to formation of $CH_3CH{=}NH$ and $C_2H_5^+$; however, this process is energetically unfavourable (Table 3), compared with production of $CH_3CH{=}NH_2^+$ and C_2H_4. Reorganisation of (**1a**) yields (**1b**), in which ethanimine and ethylene are co-ordinated to a common proton. This proton-bound complex eventually dissociates with retention of the proton by the incipient neutral ($CH_3CH{=}NH$) having the greater proton affinity. The observation that $CH_3CH{=}N^+CH_2CD_3$ and $CH_3CH{=}N^+DCH_2CD_3$ lose mainly $C_2H_2D_2$ may be interpreted on the assumption that the hydrogens on the β-carbon atom are preferentially transferred to nitrogen in the sequence (**1a**) ⟶ (**1b**) ⟶ products. This corresponds to poor competition of 1,2-hydride shifts in the incipient ethyl cation with reorganisation of (**1a**) ⟶ (**1b**). An alternative, though related, possibility is that the developing classical ethyl cation rearranges to the non-classical bridged isomer. Since one of the original β-hydrogen atoms would become the bridging hydrogen in such a mechanism, it would be preferentially transferred to nitrogen in the dissociation step. The minor contribution for α-hydrogen transfer reflects a limited amount of hydrogen exchange in the ethyl cation, presumably by interconversion of the bridged and classical forms of the species. One attractive feature of this variation of the mechanism is the correlation with quantum mechanical calculations; these indicate that the bridged structure for $C_2H_5^+$ corresponds to the global minimum on the hypersurface, with the classical (open)

Table 3. Energy data relevant to the dissociation of immonium ions.

Ion	$\Delta H_f{}^a$	Products and $\Delta H_f{}^a$	$\Sigma\Delta H_f{}^a$
$CH_3CH{=}N^+CH_2CH_3$	575^b	$CH_3CH{=}NH$ (5^c) + $C_2H_5^+$ (905^{83})	910
(**5**) $^+CH_2CH_2NHCH_2CH_3$	920^d	$CH_3CH{=}NH_2^+$ (655^{84}) + C_2H_4 (50^{85})	705
$CH_3CH{=}N^+HCH_2CH_2CH_3$	550^b	$CH_3CH{=}NH$ (5^c) + $CH_3CH_2CH_2^+$ (870^{86})	875
$CH_3CH{=}N^+HCH(CH_3)_2$	545^b	$CH_3CH{=}NH$ (5^c) + $(CH_3)_2CH^+$ ($805^{83,86}$)	810
(**6**) $CH_3CH_2NHCH_2CH_2CH_2^+$	855^d	$CH_3CH{=}NH_2^+$ (655^{84}) + C_3H_6 (20^{85})	675
		$CH_3CH_2N^+H{=}CH_2$ (650^{84}) + C_2H_4 (50^{85})	700
$CH_3CH_2CH{=}N^+HCH_2CH_3$	545^b	$CH_3CH_2CH{=}NH$ (-25^c) + $C_2H_5^+$ (905^{83})	880
		$CH_3CH_2CH{=}NH_2^+$ (635^{84}) + C_2H_4 (50^{85})	685

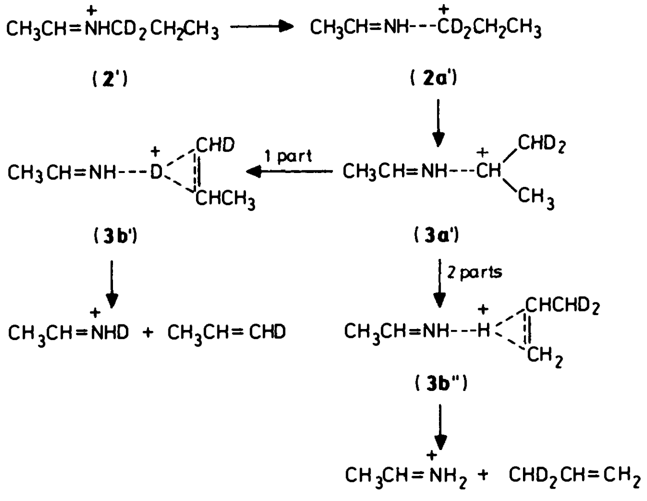
[a] All values in kJ mol^{-1} and rounded to ± 5 kJ mol^{-1}. [b] Value estimated from those reported for lower homologues.[84] [c] Value estimated relative to that (55 kJ mol^{-1}, R. D. Bowen, *J. Chem. Soc., Chem. Commun.*, 1985, 807) assigned to $CH_2{=}NH$ on the assumption that homologation imparts the same stabilisation as is found[85] in the corresponding series of aldehydes. [d] Value obtained using hydride-abstraction energies (F. P. Lossing and J. L. Holmes, *J. Am. Chem. Soc.*, 1984, **106**, 6917) and isodesmic substitution procedures (R. D. Bowen and D. H. Williams, *Org. Mass Spectrom.*, 1977, **12**, 475).



Scheme 2.

$C_2H_5^+$ isomer lying at the higher energy corresponding to a saddle point.[72]

New possibilities are open to the higher homologues $CH_3CH{=}N^+HC_3H_7$ (Scheme 2). Propene loss from (**3**) can occur *via* (**3a**) and (**3b**); this is a mechanism parallel to that for ethylene loss from (**1**), with the modification that the incipient isopropyl cation in (**3a**) is known to exist as a classical isomer in a substantial energy well.[73,74] In contrast, when the C–N bond in (**2**) is partially broken, the developing n-propyl cation undergoes a 1,2-hydride shift to form the thermodynamically more stable isopropyl isomer. This releases *ca.* 65 kJ mol^{-1} of potential energy. Part of this energy appears as kinetic-energy release accompanying C_3H_6 loss from (**2**), thus explaining the broadened metastable peak[8,36] for C_3H_6 expulsion from (**2**), Table 1. In addition, rearrangement of the incipient $CH_3CH_2CD_2^+$ to $CH_3CH^+CHD_2$, followed by near statistical selection of one of two deuterium or four hydrogens atoms in the two methyl groups, explains why $CH_3CH{=}N^+HCD_2CH_2CH_3$ (and $CH_3CH{=}N^+DCD_2CH_2CH_3$) expel $C_3H_4D_2$ and C_3H_5D in a ratio close to 2:1 (Scheme 3). The slight departure from this ratio may reflect a small isotope effect favouring hydrogen transfer to nitrogen or a minor tendency for the migrating β-hydrogen in (**2a**) $\longrightarrow$ (**3a**) to become the central proton in (**3b**). Any residual isotope effect is small, as would be expected since Scheme 2 construes (**2a**) $\longrightarrow$ (**3a**) to be the rate-determining step in C_3H_6 loss from (**2**).



Scheme 3.

The species comprising an incipient cation co-ordinated to $CH_3CH{=}NH$ should be stabilised relative to the separated products by ion–dipole attractions.[47,50] The magnitude of these stabilisations is estimated to be *ca.* 60 kJ mol^{-1} by extrapolation from the value deduced (*ca.* 50 kJ mol^{-1}) for the analogous complexes containing $CH_2{=}NH$.[66] This slight increase reflects the somewhat greater permanent electric dipole moment of $CH_3CH{=}NH$ compared with that of $CH_2{=}NH$.[75] A similar increase in the ion–dipole stabilisation in the corresponding complexes containing $CH_3CH{=}O$ and $CH_2{=}O$ has been reported.[50]

These thermochemical data and mechanistic considerations are conveniently summarised by the potential-energy profile of the Figure. This profile has many features in common with that reported for the $CH_2{=}N^+HC_3H_7$ system. There is, however, one important difference: whereas $CH_3CH{=}N^+HCH_2CH_2CH_3$ expels only C_3H_6, the lower homologue, $CH_2{=}N^+HCH_2CH_2CH_3$ also loses C_2H_4. Ethylene elimination from $CH_2{=}N^+HCH_2CH_2CH_3$ gives rise to a broad dish-topped metastable peak; the associated[8,76,77] kinetic-energy release is very large (65[66] kJ mol^{-1}). This reaction cannot be interpreted as proceeding in a synchronously concerted fashion with little or no reverse critical energy, equation (1), as has been shown by studies on the analogous processes of homologous $CH_2{=}N^+HR$,[66] $CH_2{=}N^+R_2$, and $CH_2{=}N^+RR'$ ions.[69] A better description is one involving a 1,5-hydride shift, followed by σ-

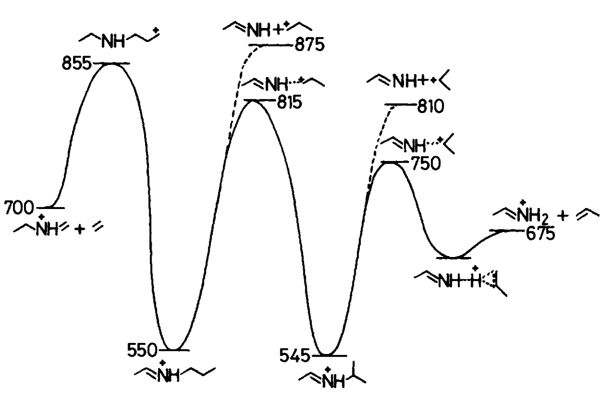
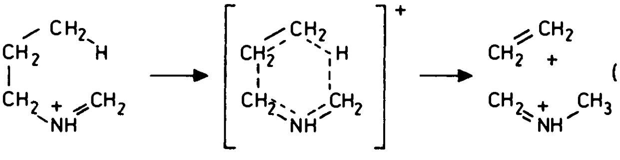
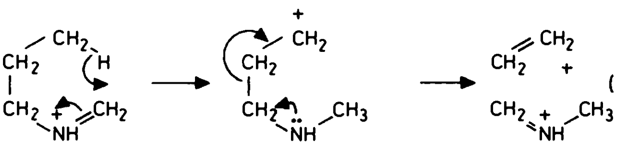


Figure. Potential-energy profile for isomerisation and dissociation of (**2**) and (**3**).



(1)



(2)

cleavage in the resultant open-chain carbonium ion, equation (2). There is a growing body of evidence that suggests that the dissociation of isolated ions usually proceeds by stepwise making and breaking of bonds; synchronously concerted mechanisms apparently operate only under exceptional circumstances.[78–80] In the case in question, the open-chain carbonium ion, *en route* to C_2H_4 loss from $CH_2{=}N^+HCH_2CH_2CH_3$, has a similar energy to the ion–dipole complex involved in C_3H_6 elimination. Consequently, $CH_2{=}N^+HCH_2CH_2CH_3$ expels both C_2H_4 and C_3H_6.[66] Homologation to $CH_3CH{=}N^+HCH_2CH_2CH_3$ evidently destroys the fine energetic balance that exists between C_2H_4 and C_3H_6 elimination from $CH_2{=}N^+HCH_2CH_2CH_3$. This reflects the lower enthalpy of formation of $CH_3CH{=}NH$ and, perhaps to a lesser degree, the superior ion–dipole stabilisation in the complex containing $CH_3CH{=}NH$. Both these factors operate in favour of C_3H_6 loss from $CH_3CH{=}N^+HCH_2CH_2CH_3$, which is estimated to require *ca.* 40 kJ mol^{-1} less energy than C_2H_4 loss. It is also possible that homologation to $CH_3CH{=}N^+HCH_2CH_2CH_3$ introduces a steric obstacle to the initial hydride transfer, because the migration terminus is now a secondary carbon atom.

Two points remain to be made concerning C_2H_4 elimination from $CH_3CH{=}N^+HCH_2CH_2CH_3$. First, this process must have a substantial reverse critical energy; were this not so, C_2H_4 loss would compete effectively with C_3H_6 loss, which must involve species having enthalpies of formation greater than that of $CH_2{=}N^+HCH_2CH_3$ and C_2H_4 (Table 3). Secondly, the failure of C_2H_4 loss to compete from $CH_3CH{=}N^+HCH_2CH_2CH_3$ sets an upper limit of *ca.* 850 kJ mol^{-1} for the transition-state energy for C_3H_6 expulsion. The value utilised in the Figure is 815 kJ mol^{-1}; this is still substantially higher than the transition state of 750 kJ mol^{-1} for C_3H_6 loss from $CH_3CH{=}N^+HCH(CH_3)_2$. Thus, whereas $CH_3CH{=}N^+HCH_2CH_2CH_3$ rearranges to $CH_3CH{=}N^+HCH(CH_3)_2$, or related species, prior to C_3H_6 elimination, $CH_3CH{=}N^+HCH(CH_3)_2$ undergoes loss of C_3H_6 at lower energies than that required for rearrangement to $CH_3CH{=}N^+HCH_2CH_2CH_3$. This explains the larger kinetic-energy release and the results of ^2H-labelling experiments for propene expulsion from $CH_3CH{=}N^+HCH_2CH_2CH_3$.

Other primary open-chain carbonium ions also are energetically inaccessible to these immonium ions. Thus, for example, $^+CH_2CH_2NHCH_2CH_3$ has an estimated enthalpy of formation of 920 kJ mol^{-1} (Table 3). This is 10 kJ mol^{-1} more than the combined enthalpies of formation of the products ($CH_3CH{=}NH + C_2H_5^+$, $\Sigma\Delta H_f = 910$ kJ mol^{-1}) of C–N σ-cleavage in $CH_3CH{=}N^+HC_2H_5$. The estimated transition-state energy for C_2H_4 loss $910 - 60 = 850$ kJ mol^{-1}; well below the enthalpy of formation of $^+CH_2CH_2NHCH_2CH_3$. Production of this cation is also excluded by the ^2H-labelling results for $CH_3CH{=}N^+HCH_2CD_3$. If $^+CH_2CH_2NHCH_2CD_3$ were formed, a 1,5-deuteride shift would be expected to lead to $CH_2DCH_2NHCH_2CD_2^+$ and $CH_2DCH_2N^+H{=}CHCHD_2$; this last ion would then eliminate C_2H_4 and C_2H_3D. Experimentally, however, $CH_3CH{=}N^+HCH_2CD_3$ loses only C_2H_2D and C_2HD_3.

Conclusions

Alkene (R–H) loss from the immonium ions $CH_3CH{=}N^+HR$ ($R = C_2H_5, C_3H_7$) and $CH_3CH_2CH{=}N^+HR$ ($R = C_2H_5$) may be logically interpreted as occurring *via* ion–dipole complexes comprising an imine co-ordinated to the incipient cation, R^+. The behaviour of these complexes reflects the structure and stability of R^+, thus furnishing an explanation for the reactions of ^2H-labelled immonium ions such as $CH_3CH{=}N^+HCH_2CD_3$ and $CH_3CH{=}N^+HCD_2CH_2CH_3$. When R = ethyl, alkene loss involves exclusively ($CH_2{=}N^+HCD_2CH_3$) or predominantly ($CH_3CH{=}N^+HCH_2CD_3$) β-hydrogen transfer to nitrogen. In contrast, when R = n-propyl, the preference for β-hydrogen transfer is greatly diminished because the incipient unstable primary carbonium ion undergoes irreversible isomerisation to the thermodynamically more stable isopropyl cation.

Experimental

All mass spectra were recorded using an AEI MS 902 double-focusing mass spectrometer operating at a source pressure of *ca.* 2×10^{-6} Torr.* Ionisation was effected by bombardment of the sample with electrons of nominal energy 70 eV. Samples were introduced through the all-glass heated inlet system (AGHIS).

Normal spectra were obtained using an accelerating voltage of 8 kV. Metastable 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 magnetic- and electric-field strengths.[81] Alternatively, when low-abundance reactions were under investigation, the electric-field strength was reduced at constant accelerating voltage and magnetic-field strength,[82] in order to maximise sensitivity.

The kinetic-energy release data were computed from the widths at half height of the appropriate second field-free region metastable peaks:[8,70] no correction was applied for the width of the main beam. When 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. The unlabelled compounds were commercially available (di-isopropylamine) or synthesised by routine methods (*N*-ethyl-s-butylamine and *N*-isopropylpropylamine). The *C*-deuteriated amines were prepared by the routes summarised in Scheme 4; the *N*-deuteriated amines were obtained *in situ* by exchanging the NH with D_2O in the AGHIS.

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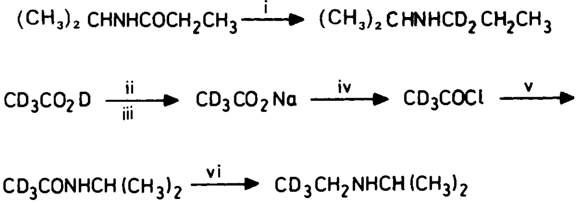
* 1 Torr = 133.322 Pa.



$$(CH_3)_2CHNHCOCH_2CH_3 \xrightarrow{i} (CH_3)_2CHNHCD_2CH_2CH_3$$

$$CD_3CO_2D \xrightarrow[iii]{ii} CD_3CO_2Na \xrightarrow{iv} CD_3COCl \xrightarrow{v}$$

$$CD_3CONHCH(CH_3)_2 \xrightarrow{vi} CD_3CH_2NHCH(CH_3)_2$$

Scheme 4. *Reagents and Conditions:* i, $LiAlD_4$, Et_2O; ii, NaOD; iii, freeze dry; iv, $POCl_3$; v, $(CH_3)_2CHNH_2$, pyridine, <0 °C; vi, $LiAlH_4$, Et_2O.

Acknowledgements

The award of an Advanced Fellowship and financial support from the SERC is gratefully acknowledged. This work was begun during the tenure of a Research Fellowship at Sidney Sussex College, Cambridge. Thanks are also due to Professor D. J. McAdoo for communicating results prior to publication.

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Received 2nd *August* 1988; *Paper* 8/03153C