Thermodynamics of Intermediate Ion–Molecule Complexes or Kinetics of Competing Reactions? The Reactions of Low-energy Isobutylamine and Neopentylamine Molecular Ions

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Metastable isobutylamine molecular ions fragment predominantly by loss of either C_2H_5 or C_3H_7 radicals. In contrast, the principal reaction of the closely related metastable neopentylamine ions is loss of C_4H_7 radicals. Claims that competition between simple cleavage and rearrangement is governed in these systems by the heats of formation of transient ion–molecule complexes are shown to be unjustified. It is proposed that, in both systems, rearrangement predominates over 'simple cleavage' for low-energy ions, but that crossing of the $k(E)$ *vs.* E curves occurs at slightly higher energies for neopentylamine than for isobutylamine. Reversible isomerization of the molecular ions to stable distonic isomers is suggested. These isomers are considered to be important intermediates in the rearrangement–fragmentation processes. The involvement of distonic isomers complicates a description of the competing reactions in terms of simple cleavage *vs.* rearrangment. α-Cleavage for the distonic ions is in fact a rearrangement reaction.

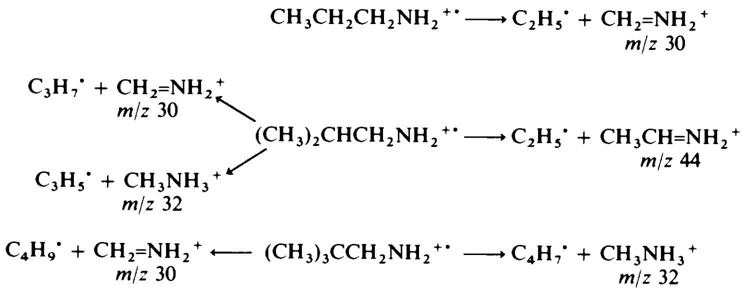
Ions of low internal energy often undergo rearrangement in preference to simple cleavage.[1] The simplest rearrangement, and by far the most common, is intramolecular hydrogen-atom abstraction. This may be followed by simple bond cleavage, as in the McLafferty rearrangement,[2] but more complex reaction sequences are frequently encountered.[3] Reciprocal hydrogen-transfer reactions prior to fragmentation lead in some cases to loss of positional identity among the hydrogen atoms involved ('scrambling'), while in other cases multiple hydrogen transfers occur with a high degree of specificity to (or from) a fragment subsequently expelled. A case in point is the fragmentation of low-energy isobutyl alcohol molecular ions, where the text-book α-cleavage is pre-empted by specific transfer of two hydrogen atoms (Scheme 1).

$$(CH_3)_2CHCH_2OH^{+\cdot} \longrightarrow C_3H_5^{\cdot} + CH_3OH_2^{+}$$

Scheme 1.

This reaction was first described by McFadden, Lounsbury, and Wahrhaftig[4] and has since been studied in detail by Tajima, van der Greef, and Nibbering.[5] Bowen and Williams[6] have proposed a detailed mechanism for this and related reactions, in which intermediate ion–molecule complexes play a central role. The mechanism by which such complexes were to be formed was not delineated.[6] On the basis of estimated heats of formation of the intermediate complexes, Bowen and Williams[6] provided a rationale as to why the metastable molecular ions of isobutyl alcohol and isobutyl methyl ether readily expel an allyl radical while isobutylamine molecular ions do not. That the neutral fragment formed in the reaction of isobutyl alcohol is the allyl radical has recently been confirmed by Burgers *et al.*[7] However, low-energy isobutylamine ions do in fact react by allyl-radical elimination, albeit in low ion yield (see later), and the closely related neopentylamine metastable ions react predominantly[8] by $C_4H_7^{\cdot}$ loss, as evidenced in both cases by formation of ions of *m/z* 32 ($CH_3NH_3^+$). The energetics of these two reactions are closely similar, which has led us to challenge[8] the rationale presented by Bowen and Williams.

Very recently Bowen and Maccoll[9] discussed the low-energy electron ionization mass spectra of neopentyl alcohol, neopentylamine, and related compounds, restating without comment the previously suggested[6] mechanism, which for neopentylamine requires intermediate formation of a [methylamine + butene]$^{+\cdot}$ complex. No indication of how the presumed intermediate CH_3NH_2 species would be formed was given, although this is a crucial step in the suggested mechanism. However, the bone of contention appears to be the estimation of the heats of formation of the putative intermediate complexes, $[C_4H_8 + CH_3NH_2]^{+\cdot}$ for neopentylamine and $[C_3H_6 + CH_3NH_2]^{+\cdot}$ for isobutylamine. It has been assumed[6,9] that the



$$CH_3CH_2CH_2NH_2^{+\cdot} \longrightarrow C_2H_5^{\cdot} + \underset{m/z\ 30}{CH_2{=}NH_2^+}$$

$$(CH_3)_2CHCH_2NH_2^{+\cdot} \longrightarrow C_2H_5^{\cdot} + \underset{m/z\ 44}{CH_3CH{=}NH_2^+}$$

$$(CH_3)_2CHCH_2NH_2^{+\cdot} \longrightarrow C_3H_7^{\cdot} + \underset{m/z\ 30}{CH_2{=}NH_2^+}$$

$$(CH_3)_2CHCH_2NH_2^{+\cdot} \longrightarrow C_3H_5^{\cdot} + \underset{m/z\ 32}{CH_3NH_3^+}$$

$$C_4H_9^{\cdot} + \underset{m/z\ 30}{CH_2{=}NH_2^+} \longleftarrow (CH_3)_3CCH_2NH_2^{+\cdot} \longrightarrow C_4H_7^{\cdot} + \underset{m/z\ 32}{CH_3NH_3^+}$$

Scheme 2.

Table 1. Heats of formation[a] of neutral species, ions, and possible product combinations in the reactions of isobutylamine and neopentylamine ions

		$\Sigma\Delta H_f$
$(CH_3)_2CHCH_2NH_2^{+\bullet}$ (720)[b]	$C_3H_7^{\bullet}$ (75) + $CH_2{=}NH_2^+$ (745)	820
	$C_3H_6^{+\bullet}$ (960) + CH_3NH_2 (-25)	935
	C_3H_6 (20) + $CH_3NH_2^{+\bullet}$ (835)[c]	855
	$C_3H_5^{\bullet}$ (165)[d] + $CH_3NH_3^+$ (610)[e]	775
	$C_2H_5^{\bullet}$ (110) + $CH_3CH{=}NH_2^+$ (655)	765
$(CH_3)_3CCH_2NH_2^{+\bullet}$ (690)[f]	$C_4H_9^+$ (695) + $^{\bullet}CH_2NH_2$ (150)	845
	$C_4H_9^{\bullet}$ (40) + $CH_2{=}NH_2^+$ (745)	785
	$C_4H_8^{+\bullet}$ (875) + CH_3NH_2 (−25)	850
	C_4H_8 (−15) + $CH_3NH_2^{+\bullet}$ (835)[c]	820
	$C_4H_7^{\bullet}$ (125) + $CH_3NH_3^+$ (610)[e]	735

[a] In kJ mol^{-1}, rounded; data for closed shell neutral species from ref. 28, for radicals from ref. 29, and for ionic species from ref. 30, unless otherwise noted. [b] ΔH_f(isobutylamine) − 100 kJ mol^{-1}; ionization energy (isobutylamine) 820 kJ mol^{-1} (ref. 31). [c] Adiabatic ionization energy 8.89 eV (ref. 31); other literature values include 8.80 eV (ref. 32) and 8.97 eV (ref. 33). [d] Ref. 34. [e] Ref. 35. [f] ΔH_f(neopentylamine) −130 kJ mol^{-1} (ref. 35), ionisation energy (neopentylamine) 820 kJ mol^{-1} (ref. 31).

Table 2. Major fragment ion peaks[a] (%) in the MIKE spectra[b] of deuterium-labelled and unlabelled propylamine, butylamine, isobutylamine, and neopentylamine

	m/z								
	30	31	32	33	34	44	45	46	47
$CH_3CH_2CH_2NH_2$	100								
$-ND_2$		19	81						
$-ND_2$[c]		32	68						
$(CH_3)_2CHCH_2NH_2$	40		3			57			
$-ND_2$	9	30	15	1		5	29	11	
$-CD_2NH_2$		5	60		3		8	24	
$(CH_3)_3CCH_2NH_2$	10		85			5			
$-ND_2$		1	16	36	42		5		
$-CD_2NH_2$		1	8		90		1		
$CH_3CH_2CH_2CH_2NH_2$	50					36	14		
$-ND_2$	22	36	8			2	8	21	3

[a] These ions carry more than 95% of the observed fragment ion current, except for propylamine. Other fragment ions correspond to loss of H$^{\bullet}$ and NH_3 from the molecular ions. [b] See Experimental section. [c] From ref. 13; measured with a VG ZAB-2F instrument.

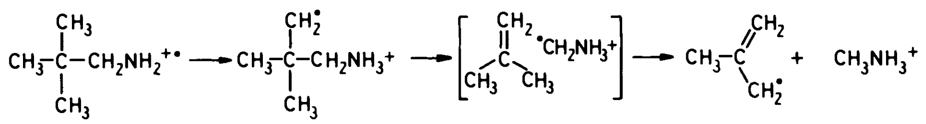
energy of such complexes can be assessed from the heats of formation of the component species. The relevant literature data are given in Table 1. Of the alternatives in each case, that with the lower energy would be that in which $[CH_3NH_2]^{+\bullet}$ interacts with a neutral alkene molecule. The energy of such a complex is in both cases approximately 130 kJ mol^{-1} (less any intra-complex stabilization energy) above that of the parent amine ion. The higher-energy combination, in which an alkene molecular ion interacts with neutral methylamine, was previously[6,9] assumed to describe the complex, in part it seems because the heat of formation assigned to $[CH_3NH_2]^{+\bullet}$ was in error (upwards of 40 kJ mol^{-1} too high). This is in fact a serious discrepancy, since the argument put forward in the various cases considered[6,9] rests explicitly on the difference between the heats of formation of the presumed alkene ion components. The energy required to form the putative complexes from the molecular ions will in fact be virtually the same for isobutylamine and neopentylamine, and it is thus not possible to explain differences between the reactions of these two ions simply in terms of the energetics of such intermediate complexes. We suggest that the observed differences are to some degree exaggerated by the narrow range of rate constants sampled by metastable ions, which in effect favours the observation of slow reactions (the probability for decomposition in a narrow time interval 'tails' towards reactions with low rate-constants), and that the explanation is to be found, instead, in the kinetics of the competing reactions in the systems under consideration.

Results

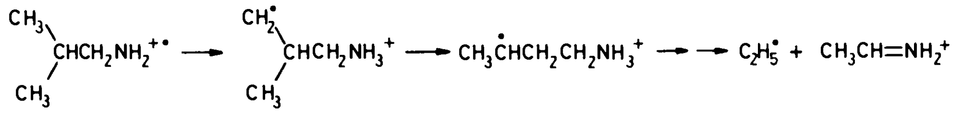
The 70 eV mass spectra of propylamine, isobutylamine, and neopentylamine all have *m/z* 30 ($CH_2{=}NH_2^+$) as the base peak. Only the spectrum of neopentylamine changes appreciably when the energy of the ionizing electrons is reduced; in this case the *m/z* 32 species ($CH_3NH_3^+$) comes to carry a significant portion of the ion current.[9] The reactions of the metastable molecular ions of these three amines are, however, strikingly different. Propylamine reacts virtually exclusively by way of α-cleavage to give *m/z* 30 ions, while the predominant peak for neopentylamine is *m/z* 32 (85% of the total observed fragment ion current). The reactions of isobutylamine lead to *m/z* 44 ($CH_3CH{=}NH_2^+$), *m/z* 32 ($CH_3NH_3^+$), and *m/z* 30 ($CH_2{=}NH_2^+$). The relative abundance of these ions is markedly dependent upon the instrument and the accelerating voltage employed (see Table 3), *i.e.* upon the average lifetime of the reacting ions. The longer-lived ions react preferentially by formation of *m/z* 44 ions, *i.e.* by loss of $C_2H_5^{\bullet}$.

The MIKE spectrum of *N*-methylisobutylamine shows fragmentation only by α-cleavage, while the α-cleavage peak (*m/z* 44) for *N*-methylneopentylamine is accompanied by a peak at *m/z* 46, corresponding to loss of $C_4H_7^{\bullet}$ (82 and 8%, respectively, of the observed fragment ion current).

Deuterium labelling demonstrates that both hydrogen atoms at the α-carbon in neopentylamine are retained in the protonated methylamine ions (Table 2), while one α-hydrogen in isobutylamine can be involved in exchange reactions prior to loss of $C_2H_5^{\bullet}$ and $C_3H_7^{\bullet}$ (Table 2). The $-NH_2$ hydrogen atoms



Scheme 3.



Scheme 4.

Table 3. Major fragment ion peaks[a] (%) in the MIKE spectra of isobutylamine molecular ions as a function of fragmenting ion life-time

Instrument	V^b	t^c	*m/z* 44	32	30
VG ZAB-2F	8 kV	12	15	4	81
	2 kV	24	36	2	62
	1 kV	34	50	3	47
MMM[d]	8 kV	51	57	3	40
	2 kV	103	80	3	17
	800 V[e]	163	80	10	10

[a] These ions carry more than 90% of the fragmenting ion current. [b] Accelerating voltage. [c] Mean lifetime for *m/z* 73 ions (μs) decomposing in the middle of the second field-free region; numbers for the ZAB-2F instrument adapted from ref. 36. [d] An unusually large double-focusing mass spectrometer; see Experimental section. [e] Very low ion current; numbers rounded.

in propylamine are largely retained in the α-cleavage ion, whereas isobutylamine and neopentylamine ions undergo extensive CH/NH exchange before fragmentation (Table 2).

Discussion

Exchange of the hydrogen atoms of the amino group with the methyl group hydrogen atoms (but not with the α-hydrogen atoms) prior to fragmentation suggests the intermediacy of $^{\bullet}CH_2C(CH_3)_2CH_2NH_3^+$ in the case of neopentylamine and of $^{\bullet}CH_2CH(CH_3)CH_2NH_3^+$ in the case of isobutylamine. CH/NH hydrogen exchange and concurrent formation of intermediate distonic ions* such as these has been proposed previously for low-energy aliphatic amine ions,[8,12-17] but the limited exchange observed here demonstrates that an equilibrium-type situation has not been reached, in contrast to the situation for straight-chain primary amines.[18] Furthermore, hydrogen abstraction by the $-NH_2^{+\bullet}$ in straight-chain primary amine ions involves primarily the hydrogen atoms at C(4), C(5), and C(6), while abstraction at C(3) takes place less readily.[18] The reason for this is presumably the ring-strain present in the five-atom cyclic transition state necessary for abstraction at C(3).

The distonic isomers of the molecular ions of isobutylamine and neopentylamine are probably not much different in energy from the initial molecular ions. The bond dissociation energy for a methyl C–H is slightly less than the hydrogen-atom affinity[19] of an $-NH_2^{+\bullet}$, suggesting that the distonic ions are somewhat favoured (by *ca.* 25 kJ mol^{-1}; *cf.* ref. 10).

Formation of the distonic isomers is proposed to be the initial step in the reactions of both the isobutylamine and neopentylamine metastable molecular ions. For neopentylamine the distonic species reacts by cleavage of the α-C–C bond and transfer of a hydrogen atom to the carbon atom of the incipient $CH_3NH_3^+$ fragment. It is convenient to write this as a stepwise process, with C–C cleavage preceding hydrogen transfer (see Scheme 3), but this should not be taken to imply that the $[C_4H_8 \cdots CH_2NH_3]^{+\bullet}$ species represents a local minimum on the reaction path.† The last step prior to final dissociation, hydrogen abstraction by the $^{\bullet}CH_2NH_3$ moiety, may or may not be separated (in time) from C–C bond cleavage, but the evidence in this case (and, indeed, in almost all similar instances of hydrogen transfer occurring as part of rearrangement–fragmentation of saturated cation radicals[21,22]) seems not to allow other than intuitive speculation. However, it should be noted that $^{\bullet}CH_2NH_3^+$ is itself a stable ion,[23] and it could as a (substituted) alkyl radical well be an efficient hydrogen-atom-abstracting species.‡

The reactions of isobutylamine lead primarily to loss of $C_2H_5^{\bullet}$ and $C_3H_7^{\bullet}$. The former reaction is necessarily preceded by skeletal rearrangement to produce a linear chain. This requires, at its simplest, migration of a one-carbon unit, which may occur as shown in Scheme 4, where formation of the distonic ion is followed by 1,2-migration of the $-CH_2NH_3^+$ moiety from C(2) to C(3). 1,2-Migration of alkyl groups is not commonly encountered in radical rearrangement reactions,[24] but a growing body of evidence suggest that incipient ylide ions and oxycarbene ions have high migratory aptitudes in 1,2-radical rearrangements.[25] The mechanism suggested by Audier[16] for apparently similar reactions cannot apply in this case, since it would require the α-carbon atom to become part of the ethyl radical expelled, which is not consistent with the deuterium-labelling results (Table 2).

Migration of $-CH_2NH_3^+$ results in a distonic butylamine ion isomer, which reacts, as does butylamine (presumably after hydrogen migration), by loss of $C_2H_5^{\bullet}$ (*cf.* Table 2). Loss of $C_3H_7^{\bullet}$ may take place from the isomerized ion or from the initial molecular ion. The rearrangement sequence leading to ethyl elimination presumably has not only a low critical energy, but also a tight transition state, inasmuch as it becomes the predominant reaction only at very long ion life-times. Nonetheless, isomerization–cleavage to form *m/z* 44 (and possibly *m/z* 30) is for isobutylamine more favourable (*i.e.* faster) than

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* The term 'distonic ion' has been proposed by Radom to describe radical cations arising formally by ionization from neutral systems which are best written as zwitterions[10,11] or diradicals.[12] Ylide ions are distonic ions in which the charge and radical occupy adjacent positions in a conventional valence bond description.

† '. . . one must take care not to confuse image with fact, which would be like climbing up the signpost instead of following the road.'[20]

‡ Attempts to demonstrate this for $^{\bullet}CH_2NH_3^+$ generated in an ion cyclotron resonance cell have, however, so far been unsuccessful (S. Hammerum, S. Ingemann, and N. M. M. Nibbering, unpublished results, 1984).

hydrogen abstraction by $^{\bullet}CH_2NH_3^+$ to produce allyl radical and $CH_3NH_3^+$, while the converse holds for neopentylamine (see before). One reason for this may be that $CH_2NH_3^+$ migration in neopentylamine would produce a distonic isomer of isopentylamine, $(CH_3)_2\dot{C}CH_2CH_2NH_3^+$, which has been shown[17] to react only after complex skeletal rearrangement. The two rearrangements in sequence would be too slow to compete with hydrogen abstraction. In this context it is of interest that CH/NH exchange is less extensive for neopentylamine than for isobutylamine. A possible reason is that C–C cleavage in the former case is facilitated relative to hydrogen abstraction by the relief of steric strain. 'Steric acceleration' has been observed for carbocation formation in highly substituted systems in solution.[26]

Conclusions

We conclude that initial isomerization of the molecular ions to their distonic isomers slows down the α-cleavage, inasmuch as this reaction for the distonic isomers is a rearrangement rather than a simple cleavage. The isomerization is furthermore seen as the initial step in the rearrangements that lead to more stable product combinations than does α-cleavage.

The various channels open to isobutylamine and neopentylamine molecular ions have, pairwise, quite similar energetic requirements. The reason why the reactions observed in the microsecond time-frame are different is found in the relative rates, not in the accessibility, energetically, of particular intermediates or transition states. This, of course, does not prove that ion–molecule complexes cannot be formed, but in the present system they are not necessary in order to describe and understand the reactions discussed. For neopentylamine, the $k(E)$ *vs.* E curves for simple cleavage and double hydrogen rearrangement are proposed to cross at rates higher than 10^6 s^{-1}. Our results suggest that the cross-over for isobutylamine occurs at k *ca.* 10^5 s^{-1}, and the observed ratio of simple cleavage *vs.* rearrangement therefore depends critically on the actual 'metastable window' of the instrument employed. We suggest that the isobutylamine molecular ion is unusual not because it appears to react by simple cleavage, but because the successfully competing rearrangement is not loss of an allyl radical, as observed for its next of kin, isobutyl alcohol, isobutyl methyl ether, neopentylamine, and similar compounds. An even more favourable path, loss of $C_2H_5^{\bullet}$, is chosen.

Experimental

MIKE spectra were recorded with an unusually large double-focusing mass spectrometer of reverse geometry at the University of New South Wales,[27] in which the field-free region between the analysers is 2.7 m long. The ionizing energy was 70 eV. The compounds examined were commercially available or prepared by unexceptional methods. Where necessary purification of samples was performed by preparative g.l.c.

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