The expulsion of alkyl radicals from the methyliumylaminomethyl radical cation, ${}^{\bullet}CH_2NH_2CH_3{}^{+}$, and related distonic ions

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The dissociation of metastable ${}^{\bullet}CH_2NH_2CH_3{}^{+}$ ions into $CH_3{}^{\bullet}$ and $CH_2{=}NH_2{}^{+}$ is accompanied by a remarkably high translational energy release, demonstrating that the addition of a methyl radical to the *N*-terminus of $CH_2{=}NH_2{}^{+}$ has an appreciable energy barrier. Isotope labelling shows the reaction to be highly specific. Alkyl radical loss from a number of substituted *α*-distonic ions was also examined; the kinetic energy release accompanying loss of ethyl radicals from *N*-ethyl α-distonic ions, $CH_3CH_2\overset{+}{N}H_2\overset{\bullet}{C}HR$, varies with the nature of R. The energy barrier for dissociation and the relative energies of the five $C_2H_7N^{\bullet+}$ isomers was examined with the G2(MP2) and CBS-Q composite theoretical methods.

Nearly all stable organic molecules have a corresponding stable radical cation, but a considerable body of recent work has demonstrated that the converse does not apply. The only stable CH_4O species is methanol, CH_3OH, while two stable $CH_4O^{\bullet+}$ isomers exist,[1] $CH_3OH^{\bullet+}$ and ${}^{\bullet}CH_2OH_2{}^{+}$. The latter, a distonic radical cation,[2,3] has been shown to have the lower heat of formation.[4] Within the last decade, many stable distonic radical cations have been characterized in the gaseous as well as the condensed phase. Formally, these species may be considered to arise by ionization of zwitterions or diradicals by removal of one electron, and charge and radical in distonic ions are consequently located at different atoms in a conventional valence-bond description.[3] The properties of distonic radical cations are often very different from those of conventional molecular ions (formed by removal of one electron from a stable neutral molecule), and interconversion of isomeric pairs such as $CH_3OH^{\bullet+}$ and ${}^{\bullet}CH_2OH_2{}^{+}$ usually involves relatively high energy barriers.[3,5] The literature dealing with these species in gaseous and condensed phase has been reviewed.[6,7]

The simplest possible nitrogen-containing distonic ion is ${}^{\bullet}CH_2NH_3{}^{+}$, **1**, which has been found by calculation[8] to be more stable than its isomer, ionized methylamine, **2**. This agrees well with a simple general chemistry view of the aminomethyl radical as a base: protonation is expected to take place at N at least as readily as at C [eqn. (1)].

$$\underset{\mathbf{1}}{{}^{\bullet}CH_2NH_3{}^{+}} \longleftarrow {}^{\bullet}CH_2NH_2 + H^{+} \longrightarrow \underset{\mathbf{2}}{CH_3NH_2{}^{\bullet+}} \qquad (1)$$

Yates and Radom[9] used high level *ab initio* molecular orbital calculations to predict that five stable $C_2H_7N^{\bullet+}$ radical cations should be independently observable, and four of these, ions **3**–**6**, have previously been observed experimentally.[10] Unambiguous experimental evidence is now presented for the existence of the fifth isomer, **7**. The three distonic $C_2H_7N^{\bullet+}$ isomers can be characterized by their loss of a methyl radical; the present results confirm the theoretical prediction[9] that the dissociation of **7** by simple cleavage of the nitrogen–methyl bond has an appreciable energy barrier in excess of the reaction endothermicity.

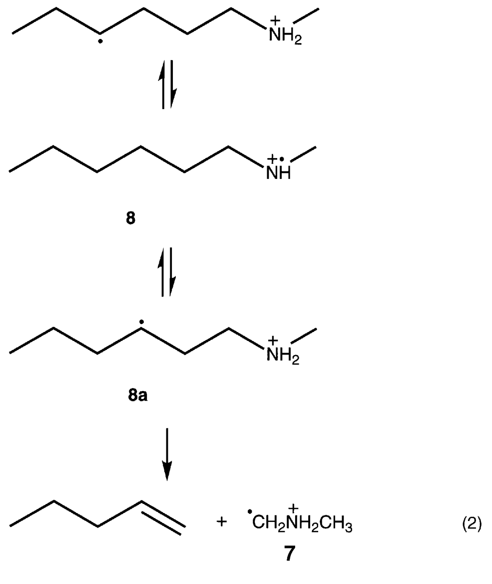
$$\underset{\mathbf{3}}{CH_3CH_2NH_2{}^{\bullet+}} \quad \underset{\mathbf{4}}{CH_3\overset{\bullet}{C}HNH_3{}^{+}} \quad \underset{\mathbf{5}}{{}^{\bullet}CH_2CH_2NH_3{}^{+}}$$
$$\underset{\mathbf{6}}{CH_3NHCH_3{}^{\bullet+}} \quad \underset{\mathbf{7}}{{}^{\bullet}CH_2\overset{+}{N}H_2CH_3}$$

Results and discussion

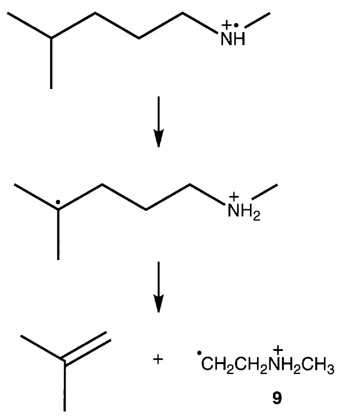
Formation of ${}^{\bullet}CH_2NH_2CH_3{}^{+}$

Secondary aliphatic amine molecular ions formed by 70 eV electron ionization react in the mass spectrometer ion source predominantly by *α*-cleavage;[11] reactions other than simple cleavage proceed only in low ion yield.

Among the lower-yield reactions, loss of alkene molecules from the molecular ion is observed, just as for primary amines;[12] *e.g.* high-resolution measurements show that the *m/z* 45 peak in the 70 eV mass spectrum of *N*-methylhexylamine (6% relative intensity) corresponds to three ionic species, with $C_2H_7N^{\bullet+}$ and $C^{13}CH_6N^{+}$ as the more prominent. The former ion arises by loss of a pentene molecule from the molecular ion, the latter is the natural abundance ${}^{13}C$-analogue of the α-cleavage product ion. The loss of alkene molecules as well as the intramolecular exchange of carbon- and nitrogen-bonded hydrogen atoms observed for metastable secondary amine radical cations[13] show that isomerization of the molecular ions by reversible intramolecular hydrogen atom transfer from carbon to nitrogen [eqn. (2)] can precede fragmentation.



Simple fission of the C1–C2 bond in **8a** yields **7** [eqn. (2)]; ion **9** can be formed analogously, *e.g.* by loss of isobutene from *N*-



(3)

methylisohexylamine molecular ions [eqn. (3)]. The relative ion yield of **7** and **9** increases slightly at low ionizing energy. Similar reactions have previously been observed for primary amine molecular ions.[10,12] We note that ion **7** is produced in rather low yield in reactions such as that shown in eqn. (2), but we currently do not know of a more satisfactory means of preparation. Ion **9** and related species are conveniently obtained in good yield by fragmentation of β-alkoxyethylamine molecular ions.[14,15]

Methyl loss from $^{\bullet}CH_2NH_2CH_3^{+}$

It was not possible to use the collision-induced reactions (CID spectrum)[16] of the ions of *m/z* 45 to characterize unambiguously the $C_2H_7N^{\bullet+}$ ions formed from *N*-alkylamine molecular ions, since the contributions from the collision-induced reactions of $C^{13}CH_6N^{+}$ and $C_2H_6{}^{15}N^{+}$, the natural abundance ^{13}C and ^{15}N containing $CH_2{=}NHCH_3^{+}$ ions formed by α-cleavage, could not be reliably eliminated by subtraction. We note in passing that the collision-induced reactions did not give rise to abundant doubly charged species.

The spontaneous reactions of the metastable $^{\bullet}CH_2NH_2CH_3^{+}$ ions are easily recognized in the mass analysed ion kinetic energy (MIKE) spectrum of the *m/z* 45 ions formed from *N*-methylhexylamine. Two major product species, $CH_2{=}NH_2^{+}$ and NH_4^{+}, are formed. The fragmentation of the ^{13}C-containing metastable $CH_3NH{=}CH_2^{+}$ ions leads only to the latter product,[17] whereas the former arises by methyl loss from the $C_2H_7N^{\bullet+}$ species. The *m/z* 47 ions formed by loss of pentene from *N*-methyl[1,1-$^2H_2$]hexylamine and the *m/z* 48 ions formed by loss of pentene from *N*-(trideuteriomethyl)hexylamine react analogously, both expelling the intact original methyl group [eqn. (4)]. This demonstrates that loss of the *N*-methyl radical

$$\begin{array}{l} ^{\bullet}CD_2NH_2CH_3^{+} \longrightarrow CD_2{=}NH_2^{+} + CH_3^{\bullet} \\ ^{\bullet}CH_2NH_2CD_3^{+} \longrightarrow CH_2{=}NH_2^{+} + CD_3^{\bullet} \end{array} \quad (4)$$

takes place without prior hydrogen rearrangement, *i.e.* $^{\bullet}CH_2NH_2CH_3^{+}$ does not isomerize to $CH_3NHCH_3^{\bullet+}$ by a 1,2-H shift, nor does degenerate isomerization by 1,3-H shifts occur.

The metastable peak corresponding to loss of the methyl radical from $^{\bullet}CH_2NH_2CH_3^{+}$ is broad and flat topped [Fig. 1(*a*)]; the peak width shows that methyl loss occurs with release of *ca.* 255 meV kinetic energy ($T_{0.5}$, Table 1). Expulsion of an alkyl radical by cleavage of the carbon–heteroatom bond is a reaction often encountered for α-distonic ions,[6] *e.g.* methyl radicals are lost from $^{\bullet}CH_2OHCH_3^{+}$ and $^{\bullet}CH_2ClCH_3^{+}$ ions.[18]

Molecular orbital calculations

The release of an appreciable amount of kinetic energy in the elimination of $CH_3^{\bullet}$ from $^{\bullet}CH_2NH_2CH_3^{+}$ agrees well with the results of Yates and Radom's high-level *ab initio* calculations for this system,[9] obtained by an additivity approximation at the UMP3/6-31G(d,p) level. They found an energy barrier of 55 kJ mol^{-1} in excess of the reaction endothermicity for methyl loss. We find the barrier to be somewhat lower, 33 kJ mol^{-1}, when calculated with the G2(MP2) composite procedure, which by an additivity approximation yields results at the QCISD(T)/6-311+G(3df,2p) level (Table 2). The lowering comes primarily from the inclusion of quadratic configuration interaction, in good agreement with Wong and Radom's recent findings.[19] Burgers, Holmes and Terlouw[20] have described a number of instances where the critical energy for loss of small radicals from the heteroatom in distonic ions and related species is considerably in excess of the reaction endothermicity.

Table 1 Kinetic energy release ($T_{0.5}$/meV) for methyl loss from $^{\bullet}CH_2NH_2CH_3^{+}$ formed from the molecular ions of *N*-methylamines

Precursor	Energy release[a]/meV
$CH_3(CH_2)_4CH_2NHCH_3^{\bullet+}$	253
$CH_3(CH_2)_6CH_2NHCH_3^{\bullet+}$	254
$CH_3(CH_2)_4CH_2NHCD_3^{\bullet+}$	261[b]

[a] Reproducibility ±2% [b] Loss of $CD_3^{\bullet}$.

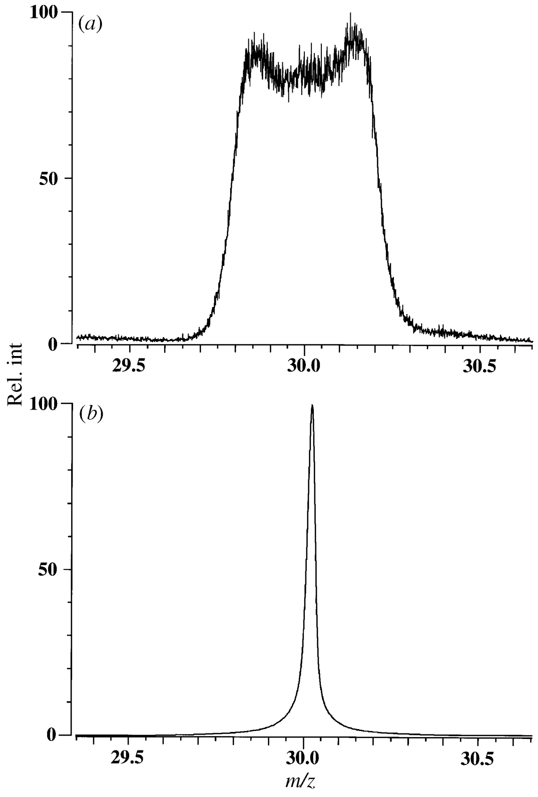


Fig. 1 (*a*) Metastable peak for $^{\bullet}CH_2NH_2CH_3^{+} \longrightarrow CH_2{=}NH_2^{+} + CH_3^{\bullet}$. (*b*) Metastable peak for $CH_3CH_2NH_2^{\bullet+} \longrightarrow CH_2{=}NH_2^{+} + CH_3^{\bullet}$.

We have recalculated the relative energies of the five $C_2H_7N^{\bullet+}$ isomers at the G2(MP2) level,[21] and the results (Table 2) are substantially in agreement with those reported by Yates and Radom.[9] However, quite small differences between the calculated total energies give rise to slightly different relative energies for the five $C_2H_7N^{\bullet+}$ radical cations (Table 3), leading us to expect that the two distonic ions, **4** and **5**, will have heats of formation very close to that of the dimethylamine radical cation. Confirming the earlier results,[9] we find that ion **5** is the more stable $C_2H_7N^{\bullet+}$ species, but the energy differences favouring **5** are quite small at the G2(MP2) level.

We obtain essentially the same results with regard to the relative energies of isomers **3**–**7** and the energy barrier for methyl loss from **7** with the CBS-Q composite procedure of Petersson and co-workers,[22] which has been claimed to give results of the same accuracy as the G2(MP2) procedure,[23] at substantially reduced computational cost. The similarity of our G2(MP2)

Table 2 Total energies calculated for the $C_2H_7N^{\bullet +}$ system

		UMP2/ 6-31G(d,p)[a]	UMP2/ 6-311G(d,p)[b]	UMP2/ 6-311 + G(3df,2p)[b]	QCISD (T)/ 6-311G(d,p)[b]	zpe[c]	QCISD (T)/ 6-311 + G(3df,2p)[d]
$CH_3CH_2NH_2^{\bullet +}$	**3**	−134.434 75	−134.464 90	−134.542 40	−134.527 29	232	−134.604 79
$CH_3\dot{C}HNH_3^+$	**4**	−134.447 41	−134.478 27	−134.556 45	−134.535 81	236	−134.614 00
$^{\bullet}CH_2CH_2NH_3^+$	**5**	−134.449 75	−134.480 87	−134.558 55	−134.538 59	237	−134.616 27
$(CH_3)_2NH^{\bullet +}$	**6**	−134.442 15	−134.471 27	−134.549 87	−134.534 42	231	−134.613 02
$^{\bullet}CH_2NH_2CH_3^+$	**7**	−134.436 52	−134.467 12	−134.545 38	−134.525 34	236	−134.603 61
TS[e]		−134.379 64	−134.409 67	−134.488 83	−134.480 08	222	−134.559 23

[a] Hartrees; energy and geometry optimized at the UMP2(full)/6-31G(d,p) level. [b] Hartrees; calculated using the UMP2(full)/6-31G(d,p) optimized geometry. [c] kJ mol^{-1}; vibrational frequencies calculated at the UHF/6-31G(d,p) level, scaled by 0.91 for calculation of the zero-point energy (R. S. Grev, C. L. Janssen and H. F. Schaefer, *J. Chem. Phys.*, 1991, **95**, 5128; J. A. Pople, A. P. Scott, M. W. Wong and L. Radom, *Isr. J. Chem.*, 1993, **33**, 345). [d] Hartrees; calculated using the G2(MP2) additivity approximation (L. A. Curtiss, K. Raghavachari and J. A. Pople, *J. Chem. Phys.*, 1993, **98**, 1293). [e] $^{\bullet}CH_2NH_2CH_3^+ \longrightarrow CH_2{=}NH_2^+ + CH_3^{\bullet}$; Σzpe(products) = 213 kJ mol^{-1}, ΣE(products) = −134.568 27 Hartrees [G2(MP2) approximation].

Table 3 G2(MP2) and CBS-Q energies for the five $C_2H_7N^{\bullet +}$ isomers

				Relative energies[c]		
		G2(MP2)[a,b]	CBS-Q[a]	Lit.	G2(MP2)	CBS-Q
$CH_3CH_2NH_2^{\bullet +}$	**3**	−134.563 34	−134.567 98	0	0	0
$CH_3\dot{C}HNH_3^+$	**4**	−134.570 89	−134.575 28	−28	−20	−19
$^{\bullet}CH_2CH_2NH_3^+$	**5**	−134.573 02	−134.576 87	−33	−26	−23
$(CH_3)_2NH^{\bullet +}$	**6**	−134.571 92	−134.576 39	−21	−24	−23
$^{\bullet}CH_2NH_2CH_3^+$	**7**	−134.560 62	−134.563 69	4	7	11
TS[d]		−134.521 32	−134.527 14	134	110	107

[a] Hartrees, 0 K. [b] Geometries optimized at the UMP2(full)/6-31G (d,p) level, frequency calculations at the UHF/6-31G(d,p) level (scale factor 0.8929 used). [c] Relative energies in kJ mol^{-1}; literature values from ref. 9; 298 K heats of formation [experimental, G2(MP2), CBS-Q] for **3**: 807, 814, 815 kJ mol^{-1}; for **6**: 776, 790, 794 kJ mol^{-1}. [d] $^{\bullet}CH_2NH_2CH_3^+ \longrightarrow CH_2{=}NH_2^+ + CH_3^{\bullet}$.

Table 4 Kinetic energy release ($T_{0.5}$/meV) for methyl loss from $C_2H_7N^{\bullet +}$ ions formed from various precursors[a]

Reactant ion	Precursor	KER
$CH_3CH_2NH_2^{\bullet +}$	$CH_3CH_2NH_2$	0.6 ± 0.1
$CH_3\dot{C}HNH_3^+$	$CH_3CH(NH_2)CH_2OH$	29.1
$^{\bullet}CH_2CH_2NH_3^+$	$C_8H_{17}NH_2$	21.4
$^{\bullet}CH_2CD_2NH_3^+$	$C_4H_9CH_2CD_2NH_2$	20.8,[b] 21.0[c]
$^{\bullet}CD_2CH_2NH_3^+$	$(CH_3)_2CHCH_2CD_2CH_2NH_2$	20.6,[b] 20.8[c]
$^{\bullet}CH_2NH_2CH_3^+$	(See Table 1)	255[d]

[a] Reproducibility ±2%. [b] Loss of $CH_3^{\bullet}$. [c] Loss of $CHD_2^{\bullet}$. [d] From Table 1.

and CBS-Q results suggest that the accuracy of the two methods is not very different; the available experimental results do not allow a more exacting comparison to be made. The computational cost (measured in units of CPU-time) is considerably lower for the CBS-Q procedure. We find that for open-shell systems of this size, the G2(MP2) procedure takes nearly twice as long as CBS-Q; unless constrained, the disk space requirements of both methods are quite large.

Methyl radical elimination from other $C_2H_7N^{\bullet +}$ isomers

The reactions of the metastable molecular ions of ethylamine, $CH_3CH_2NH_2^{\bullet +}$, **3**, lead to product ions at *m/z* 44 and *m/z* 30 by loss of $H^{\bullet}$ and $CH_3^{\bullet}$. Interestingly, loss of $H^{\bullet}$ from the metastable ethylamine radical cation proceeds in higher yield than does loss of $CH_3^{\bullet}$, whereas the reverse is observed for the reactions taking place in the ion source.[24] The kinetic energy released ($T_{0.5}$) when $CH_3^{\bullet}$ is expelled is unusually low, 0.6 meV (see Fig. 1 and Table 4).

When the α-distonic isomer of the ethylamine radical cation, $CH_3\dot{C}HNH_3^+$, **4**, is formed by fragmentation,[10] it is accompanied by other *m/z* 45 ions. In particular, the precursors of **4** also give rise to a very abundant α-cleavage ion, $CH_3CH{=}NH_2^+$ (*m/z* 44), whose natural abundance ^{13}C- and ^{15}N-containing analogues account for part of the spontaneous and collision-induced reactions of the *m/z* 45 ions. However, the presence of **4** in the *m/z* 45 ion beam is indicated by the formation of a doubly charged species upon collision (the α-cleavage ion undergoes very little charge stripping), and by the presence of a strong peak at *m/z* 30 in the MIKE-spectrum of the *m/z* 45 ions. This corresponds to the elimination of $CH_3^{\bullet}$, a reaction not observed for the $CH_3CH{=}NH_2^+$ α-cleavage ions.[17] Loss of $CH_3^{\bullet}$ from $CH_3\dot{C}HNH_3^+$ is accompanied by the release of 29 meV (Table 4); we presume that this reaction gives rise to $CH_2{=}NH_2^+$ ions. The MIKE-spectrum of $CH_3\dot{C}HND_3^+$ shows almost exclusively loss of $CH_3^{\bullet}$, indicating that exchange of the methyl hydrogens with the hydrogens on the nitrogen atom does not precede C–C bond cleavage; the signal-to-noise ratio was in this case too low for us to measure reliably the kinetic energy release for methyl loss from the labelled ion. Some hydrogen exchange does take place prior to loss of $C_2H_3^{\bullet}$, as NHD_3^+ as well as $NH_2D_2^+$ is formed when $CH_3CHND_3^+$ reacts.

The β-distonic ion $^{\bullet}CH_2CH_2NH_3^+$, **5**, is readily generated in reasonable ion yield from the molecular ions of propane-1,3-diamine, 3-aminopropanol, alkylamines and 2-benzyloxyethylamine.[10,25,26] The metastable $^{\bullet}CH_2CH_2NH_3^+$ ions react by loss of $CH_3^{\bullet}$ to produce $CH_2{=}NH_2^+$, *m/z* 30, and by loss of $C_2H_3^{\bullet}$ to produce NH_4^+, *m/z* 18. The loss of a methyl radical is accompanied by a kinetic energy release of 21 meV (Table 4). The $^{\bullet}CH_2CD_2NH_3^+$ and $^{\bullet}CD_2CH_2NH_3^+$ ions formed by C_4H_8 loss from the [1,1-$^2H_2$] and [2,2-$^2H_2$]-labelled hexylamines show virtually identical reactions; in particular, very nearly the same amount of kinetic energy is released when $CH_3^{\bullet}$ and $CHD_2^{\bullet}$ are expelled (Fig. 2 and Table 4), supporting the conclusion that the methylene groups become equivalent before fragmentation, by rapid, reversible 1,2-NH_3 migration.[10]

Methyl radicals are not lost when metastable molecular ions of dimethylamine, $(CH_3)_2NH^{\bullet +}$, **6**, react; the only process observed is the loss of a hydrogen atom.

Ethyl loss from $CH_3CH_2\overset{+}{N}H_2\dot{C}HR$

The MIKE and CID spectra of the $C_3H_9N^{\bullet +}$ ion formed from *N*-methylalkylamines [eqn. (3)] are identical to those reported[15] for ion **9** formed by fragmentation of *N*-methyl-β-alkoxyethylamines. The predominant spontaneous reaction of **9** is loss of $C_2H_5^{\bullet}$, which occurs as shown in eqn. (5) for the CD_3-analogue.

Table 5 Kinetic energy release ($T_{0.5}$/ meV) for ethyl radical loss from $R\dot{C}H\overset{+}{N}H_2CH_2CH_3$ ions

Reactant		Precursor	Products	KER[a]/meV
$^{\bullet}CH_2\overset{+}{N}H_2CH_2CH_3$	**10**	$CH_3\overset{+}{N}H_2CH_2CH_2^{\bullet}$	$C_2H_5^{\bullet} + CH_2{=}NH_2^+$	7
$^{\bullet}CH_2\overset{+}{N}H_2CD_2CH_3$		$CH_3\overset{+}{N}H_2CD_2CH_2^{\bullet}$	$C_2H_3D_2^{\bullet} + CH_2{=}NH_2^+$	8
$CH_3\dot{C}H\overset{+}{N}H_2CH_2CH_3$	**12**	$CH_3CH_2\overset{+}{N}H_2CH_2CH_2^{\bullet}$	$C_2H_5^{\bullet} + CH_3CH{=}NH_2^+$	105
$CH_3\dot{C}H\overset{+}{N}H_2CD_2CH_3$		$CH_3CH_2\overset{+}{N}H_2CD_2CH_2^{\bullet}$	$C_2H_3D_2^{\bullet} + CH_3CH{=}NH_2^+$	120
$C_2H_5\dot{C}H\overset{+}{N}H_2CD_2CH_3$	**14**	$C_2H_5CH_2\overset{+}{N}H_2CD_2CH_2^{\bullet}$	$C_2H_3D_2^{\bullet} + C_2H_5CH{=}NH_2^+$	240

[a] Reproducibility ±2%.

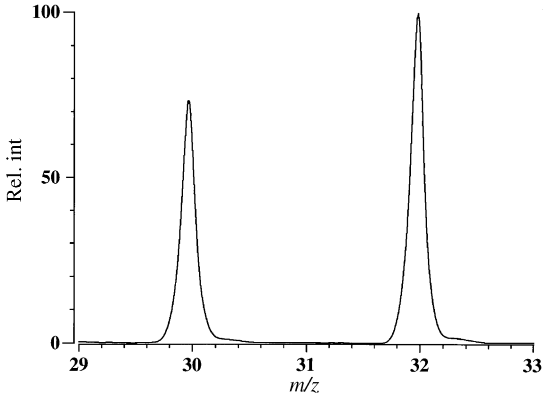


Fig. 2 Excerpt of MIKE spectrum of $^{\bullet}CH_2CD_2NH_3^+$, showing metastable peaks for loss of $CH_3^{\bullet}$ and $CHD_2^{\bullet}$

The metastable peak for this reaction—in which the final step is C–N cleavage in an α-distonic ion, **10**—is a relatively narrow peak of Gaussian shape [Fig. 3(*a*)]; the accompanying kinetic energy release ($T_{0.5}$) is 7 meV (Table 5).

$$\underset{\mathbf{9}}{CD_3\overset{+}{N}H_2CH_2CH_2^{\bullet}} \longrightarrow \underset{\mathbf{10}}{^{\bullet}CD_2\overset{+}{N}H_2CH_2CH_2D} \longrightarrow C_2H_4D^{\bullet} + CD_2{=}NH_2^+ \quad (5)$$

The low kinetic energy release is surprising, in view of the relatively large values observed for the lower homologue, **7**, and for the higher homologues,[15] **12** and **14** [Figs. 1(*a*) and 3(*b*)]. We have therefore remeasured the kinetic energy released in the reactions of **11** and **13** [eqn. (6)] on the instrument used in the present study. The results are given in Table 5. In order to avoid ambiguity with regard to the identity of the ethyl radical expelled (*cf.* ref. 15), the measurements have been performed with deuterium labelled precursors. The metastable peak corresponding to the reaction shown in eqn. (6) [Fig. 3(*b*)] appears to be composite, possibly suggesting more than one reaction path. Exactly the same peak shape is observed when $C_2H_5{\cdot}$ is lost from $CH_3CH_2\overset{+}{N}H_2CH_2CH_2^{\bullet}$; this phenomenon is being studied further.

$$\underset{\mathbf{11}}{CH_3CH_2\overset{+}{N}H_2CD_2CH_2^{\bullet}} \longrightarrow \underset{\mathbf{12}}{CH_3\dot{C}H\overset{+}{N}H_2CD_2CH_3} \longrightarrow C_2H_3D_2^{\bullet} + CH_3CH{=}NH_2^+ \quad (6)$$

$$\underset{\mathbf{13}}{CH_3CH_2CH_2\overset{+}{N}H_2CD_2CH_2^{\bullet}} \qquad \underset{\mathbf{14}}{CH_3CH_2\dot{C}H\overset{+}{N}H_2CD_2CH_3}$$

We have without success attempted to study ion **10** directly, avoiding the **9**→**10** rearrangement step, by isolation of the $C_3H_9N^{\bullet +}$ ions formed by loss of pentene from *N*-ethylhexylamine. Unfortunately, the ^{13}C and ^{15}N contributions from the α-cleavage product ions ($C_3H_8N^+$) are even more pronounced in this case than in the analogous reaction that leads to ion **7** [eqn. (2)]; moreover, the peak corresponding to ethyl loss from any **10** ions formed is obscured by that corresponding to loss of $^{13}CCH_4$ from the α-cleavage ion (loss of C_2H_4 is the major spontaneous reaction of the $CH_2{=}NHCH_2CH_3^+$ immonium ions[17]).

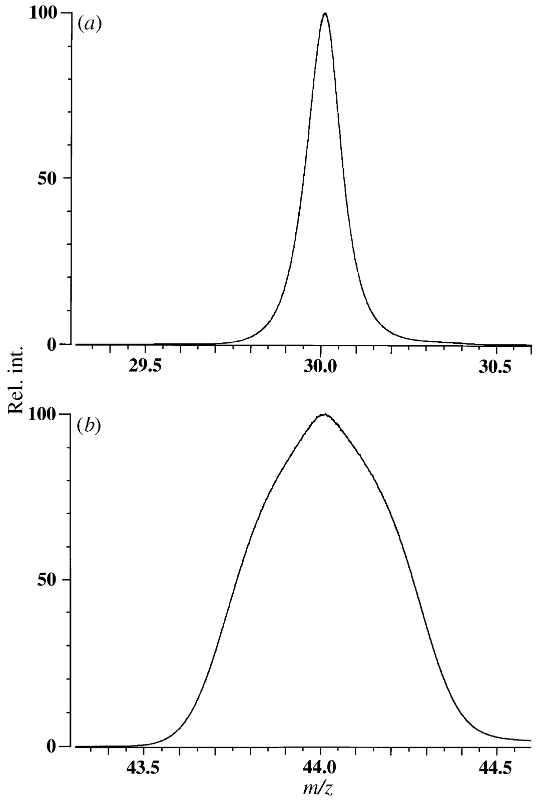


Fig. 3 (*a*) Metastable peak for loss of $C_2H_5^{\bullet}$ from $^{\bullet}CH_2\overset{+}{N}H_2CH_2CH_3$ (formed by rearrangement of $CH_3\overset{+}{N}H_2CH_2CH_2{\cdot}$). (*b*) Metastable peak for loss of $CH_3CD_2^{\bullet}$ from $CH_3\dot{C}H\overset{+}{N}H_2CD_2CH_3$ (formed by rearrangement of $CH_3CH_2\overset{+}{N}H_2CD_2CH_2^{\bullet}$).

McAdoo and co-workers[27] have suggested that expulsion of an ethyl radical from $CH_3\overset{+}{O}HCH_2CH_2^{\bullet}$, the oxygen analogue of ion **9**, takes place *via* intermediate ion–neutral complexes; Brenner *et al.*[28] have made a similar suggestion for the oxygen analogue of **11**. However, the thermochemistry of the nitrogen-containing systems makes it unlikely that the reactions of **9**, **11** and **13** are complex mediated; the energy difference between, *e.g.* $CH_3\overset{+}{N}H_2CH_2CH_2^{\bullet}$ and $[CH_3NH_2^{\bullet +} + C_2H_4]$ would appear to be too large to allow the latter to contribute to the reactions observed.

Ion **9** does not readily form a doubly charged ion by charge stripping, nor does **7**, whereas **1**, **4** and **5** do. The formation of doubly charged species upon collision is probably not a reliable criterion for the recognition of small α- and β-distonic ions, in the absence of guidelines to predict when such ions will undergo high-yield charge stripping reactions.

Experimental

The alkylamines and alkoxyamines examined were prepared by unexceptional methods (usually by reduction of the appropriate amide or carbamate with $LiAlH_4$ or $LiAlD_4$). The $^{\bullet}CH_2CD_2NH_3^+$ ions were formed by loss of C_4H_8 from ionized $[1,1\text{-}^2H_2]$-hexylamine, and $^{\bullet}CD_2CH_2NH_3^+$ was obtained analogously from [2,2-$^2H_2$]-isohexylamine; the $CH_3\dot{C}HNH_3^+$ ions were formed by expulsion of formaldehyde from 2-aminopropan-1-ol molecular ions.[10] Ions **9**, **11** and **13** were formed by loss of acetone from the corresponding *N*-substituted β-isopropyloxyethylamine molecular ions.[14,15]

MIKE and CID spectra were recorded on a Jeol HX/HX110A four sector (EBEB) mass spectrometer in three-sector mode under standard operating conditions; preliminary studies were carried out on VG ZAB-2F instruments at the University of Bielefeld, FRG, and Ecole Polytechnique, Palaiseau, France. The kinetic energy release was determined from the FWHM of the appropriate peaks in the mass analysed ion kinetic energy (MIKE) spectrum, measured under conditions of relatively high energy resolution and corrected for the energy spread of the parent ion beam.

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