Alpha-cleavage in Amine Molecular Ions. A Not-so-simple Simple Cleavage

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Specific release of translational energy for methyl radical expulsion from certain t-butylamine ions demonstrates the existence of reverse energy barriers to α-cleavage in these amine molecular ions; literature heats of formation of immonium ions may in consequence have a systematic error.

It is a widely held view in mass spectrometry that simple cleavage reactions do not have appreciable reverse critical energies,[1—6] and that flat- or dish-topped metastable peaks are a sign that the reverse reaction has a significant energy barrier.[6] We now draw attention to α-cleavage reactions of certain amine molecular ions, which give rise to broad and strongly dished metastable peaks (see Figure 1). That is to say, the reactions occur with the specific release of considerable translational energy. We suggest that the energy release is caused by the existence of an appreciable energy barrier towards the reverse reaction.

The amine molecular ions, (1), (2), and (3), generated by electron ionization, fragment exclusively by loss of a methyl radical in the microsecond time domain. Methyl loss from the ground-state ion is in all three cases an endothermic reaction (by between 30 and 50 kJ mol^{-1}), if currently accepted values for heats of formation of immonium ions are employed.[8]

$$(CH_3)_3CNHR^{+\bullet} \rightarrow (CH_3)_2C=NHR^+ + CH_3^\bullet$$

Translational energy release

(1) R = H   11 kJ mol^{-1}
(2) R = CH$_3$ 16 kJ mol^{-1}
(3) R = C$_4$H$_9$ 21 kJ mol^{-1}

Methyl radical loss from isopropylamines likewise proceeds with release of translational energy, e.g., 5 kJ mol^{-1} in the

case of N-pentylisopropylamine ($T_{0.50}$), but the metastable peaks are in these instances normally of Gaussian shape. By contrast, α-cleavage loss of a larger alkyl radical from an alkylamine commonly gives rise to narrow, Gaussian-type peaks, which shows that the translational energy released in the dissociation is quite small (see Table 1).

The release of a relatively large amount of translational energy in a dissociation reaction shows either that the products are lower in energy than the transition state for dissociation, or that there is considerable excess energy in the transition state. For reactions with zero or negligible reverse critical energy the excess energy is generally believed to be partitioned among, in effect, roughly half of the degrees of

Table 1. Translational energy release in α-cleavage reactions of some aliphatic amines.[a]

Amine	Radical lost	$T_{0.50}$ kJ mol^{-1}
1-Ethylbutylamine	Et	0.3
1-Methylbutylamine	Pr	0.2
N,N-Dipropylmethylamine	Et	1.5
N,N-Bis(2-methylpropyl)methylamine	Pr^i	1.5
N,N-Dipentylmethylamine	Bu	1.7
N,N-Dimethyl-1-ethylpropylamine	Et	1.3
N,N-Dimethyl-1-propylbutylamine	Pr	1.4

[a] Measurements performed using an unusually large double-focusing mass spectrometer, under conditions of good energy resolution.[7] Translational energy releases ($T_{0.50}$) calculated from the peak width at half height after correction for parent peak width.

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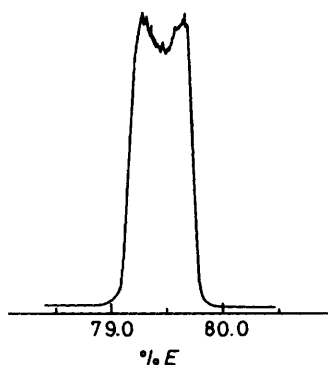
Figure 1. Metastable peak for loss of $CH_3\cdot$ from $(CH_3)_3CNH_2^{+\cdot}$ MIKE spectrum, abscissa in % of the electric sector potential for transmission of the parent ion beam (see footnote to Table 1). Peak shapes similar for $CH_3\cdot$ loss from N-substituted t-butylamines.

freedom of the reacting ion.[2,9] This leads, however, to unacceptably high estimates of the excess energy for these ions [e.g., 7.6 eV for (3)]. In any case, it is highly unlikely that a *specific* energy release would originate from the excess energy term.

It is typically rearrangement reactions that have reverse critical energies, but methyl loss from t-butylamine seems a prototype 'simple cleavage'. The only plausible alternative reaction paths [considering (1)] would be either for hydrogen rearrangement to take place concurrently with C–C cleavage, leading to $CH_2=C(CH_3)NH_3^+$ rather than $(CH_3)_2C=NH_2^+$, or for the molecular ion to have rearranged to $\cdot CH_2C(CH_3)_2NH_3^+$. The former is not likely to occur, because vinylammonium ions are considerably higher in energy than immonium ions.[10] Furthermore, a number of studies[11] of the structure and reactions of the products of α-cleavage in simple amines confirm the immonium ion structure. The latter seems unlikely because isomerization by hydrogen atom transfer from the β-carbon to nitrogen is not observed for other amines.[12] Moreover, distonic amine ion isomers formed from 2-alkoxyethylamines[13] do not expel methyl radicals with release of appreciable translational energy.

We are thus led to the conclusion that the specific translational energy releases in the methyl expulsion process from (1), (2), and (3) are consequences of the existence of energy barriers for the reverse reactions, *i.e.*, the addition of methyl radicals to the immonium ions will in fact have appreciable activation energies. This accords with the fact that the additions of alkyl radicals to (protonated) C=N double bonds proceed with appreciable activation energies in solution.[14]

Given the existence of energy barriers for the addition of methyl radicals to the immonium ions, analogous barriers should in general be found for alkyl radical attack upon immonium ions.[15] It would follow that losses of methyl from the molecular ions of (1), (2), and (3) are distinguished from other α-cleavage reactions of amine molecular ions by a specific partitioning of a significant proportion of the reverse critical energy into translation. In the case of the t-butylamine molecular ion, making the simple assumption that the methyl group departs in the plane of symmetry, treatment of the energy partitioning in terms of the direction of the transition state reaction co-ordinate (dynamical theory) predicts the release of a significant fraction of a reverse critical energy as translational energy,[9,16] whereas reactions in which the neutral released contains more than 4 or 5 atoms normally do not release translational energy to any great extent during dissociation.[9] The reverse critical energies (perhaps 2500

cm^{-1}) proposed for the amine reactions, corresponding to very few quanta of vibrational energy, would require very little reorganization within the incipient products (curvature of the reaction co-ordinate) to be dissipated.

A recent paper by Burgers *et al.*[17] shows that elimination of small radicals from the heteroatom may also occur in apparent contradiction to the widely held view concerning simple cleavages. However, the generalization suggested by these authors is at odds with our observations. The proposal of reverse critical energies for α-cleavage reactions casts doubt on the determination of thermochemical properties of immonium ions from appearance energies for those reactions, and the situation will not be remedied by measuring a number of systems, if in each system the reaction studied is an α-cleavage. Heats of formation determined from such appearance energies may well be too high.

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