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# The rearrangement and simple cleavage of metastable octanamine radical cations

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## Abstract

The isomerization and fragmentation of the straight-chain octanamine radical cations was studied with the aid of deuterium labeling and composite quantum chemical calculations with the G3 and G2 (MP2, SVP) methods. Metastable octan-1-amine molecular ions isomerize to octan-2-amine ions prior to cleavage, and metastable octan-2-amine molecular ions rearrange to the octan-3-amine isomer, but octan-1-amine ions do not isomerize to octan-3-amine, nor are the reverse reactions observed. The competition between cleavage and isomerization is determined by the respective energy barriers and by the internal energy distribution of the metastable molecular ions, which in turn depends on the critical energy for simple cleavage of the molecular ions. (Int J Mass Spectrom 199 (2000) 79–89) © 2000 Elsevier Science B.V.

*Keywords:* Isomerization; Audier mechanism; Ab initio calculations; G3 method; Internal energy distribution

## 1. Introduction

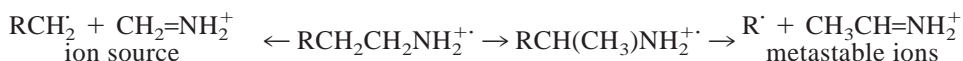
Metastable molecular ions of primary *n*-alkylamines as a rule do not undergo the straightforward simple cleavage reactions that give rise to the characteristic peaks in the electron ionization mass spectra of these compounds [1,2]. Instead, the unimolecular fragmentation that takes place on the microsecond timescale occurs almost exclusively after isomerization of the alkan-1-amine radical cation to the alkan-2-amine isomer. Audier and his co-workers [2] have studied this reaction in detail and shown that the key

step in the isomerization is a 1,2-migration of  $\text{NH}_3$  in a  $\beta$ -distonic isomer of the molecular ion.

The energetics of the dissociation reactions provide a simple reason why rearrangement is the preferred process.  $\alpha$ -cleavage of long-chain alkan-1-amine radical cations (to give  $\text{CH}_2=\text{NH}_2^+ + \text{RCH}_2$ ) requires more energy than does  $\alpha$ -cleavage of alkan-2-amine radical cations (to give  $\text{CH}_3\text{CH}=\text{NH}_2^+ + \text{R}$ ). Assuming that the individual steps of the isomerization process have modest energy requirements, dissociation after isomerization to the alkan-2-amine molecular ion provides a possible reaction path for many of the alkan-1-amine molecular ions that possess less internal energy than required for rapid, direct  $\alpha$ -cleavage.

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Dedicated to Henri Edouard Audier in recognition of his many original contributions to gas-phase ion chemistry.



Scheme 1. The simple cleavage reactions of *n*-alkanamine molecular ions in the ion source and in the field-free regions.

An early observation by Sozzi [3] showed that metastable long-chain alkan-2-amine molecular ions can isomerize in a similar fashion, that is, rearrangement to the alkan-3-amine isomer can precede C–C bond cleavage. However, the metastable molecular ions of alkan-1-amines do not rearrange to alkan-3-amine ions prior to fragmentation, even though alkan-1-amines rearrange to alkan-2-amines and alkan-2-amines rearrange to alkan-3-amines.

In the present study isotope labeling is used to establish the specificity of these reactions, and composite ab initio methods are employed to examine their thermochemistry, in particular the energetics of  $\alpha$ -cleavage of alkan-2-amine and alkan-3-amine molecular ions and the energy barriers involved in the isomerization of metastable alkanamine radical cations. The 1,2-migration of  $\text{NH}_3$  in the  $\beta$  distonic isomers is examined in an accompanying article [4].

## 2. Methods

### 2.1. Synthesis of deuterium labeled amines

[1,1- $\text{D}_2$ ]-octanamine was prepared by reduction of octanenitrile with  $\text{LiAlD}_4$ . [1,1,1- $\text{D}_3$ ]-octan-2-amine was prepared as described by Mitsunobu [5] from [1,1,1- $\text{D}_3$ ]-octan-2-ol, which was obtained by addition of  $\text{CD}_3\text{MgI}$  to heptanal. [1,1,1- $\text{D}_3$ ]-octan-3-amine was prepared analogously (but in much lower yield) from [1,1,1- $\text{D}_3$ ]-octan-3-ol, which was synthesized by the addition of  $\text{CD}_3\text{CH}_2\text{MgBr}$  to hexanal;  $\text{CD}_3\text{CH}_2\text{Br}$  was prepared by  $\text{LiAlH}_4$  reduction of  $(\text{CD}_3\text{CO})_2\text{O}$  and conversion of the labeled ethanol to the bromide with  $\text{HBr}/\text{H}_2\text{SO}_4$ .

### 2.2. Reactions of amine molecular ions

A Jeol four-sector double-focusing JMS-HX110/HX110 mass spectrometer (EBEB geometry) was

used to study the reactions of metastable amine molecular ions. The three first sectors of the instrument were used when recording the mass analyzed ion kinetic energy (MIKE) spectra [6].

### 2.3. Computational thermochemistry

Heats of formation were derived from total energies calculated with composite ab initio methods of the Gaussian and CBS families [7]; the energies were obtained with the Gaussian 94 suite of programs [8] and converted to 298 K heats of formation as described by Nicolaidis et al. [9]; the required auxiliary thermochemical data were taken from the compilation by Wagman et al. [10]. Heats of formation of immonium ions obtained with the G2 (MP2) and CBS-Q methods were reported recently [11]. In the present study the required heats of formation of immonium ions with up to five carbon atoms were determined with the G3 method [12,13]. The values for higher immonium ions were estimated by additivity. Alkyl radical heats of formation were likewise calculated on the basis of G3 total energies. Heats of formation of the isomeric  $\text{C}_5\text{H}_{13}\text{N}^{+\cdot}$  radical cations were calculated with the G2 (MP2, SVP) method [14] rather than with G3, for reasons of computational economy.

## 3. Results

### 3.1. Reactions of metastable molecular ions

Almost all product ions formed by fragmentation of the straight-chain octanamine radical cations arise by expulsion of alkyl radicals.

#### 3.1.1. Octan-1-amine

The MIKE spectrum of octan-1-amine molecular ions (Fig. 1) shows that dissociation is almost exclusively by one reaction only, loss of hexyl radicals. A

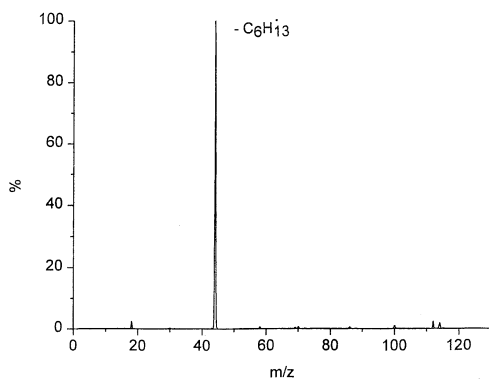
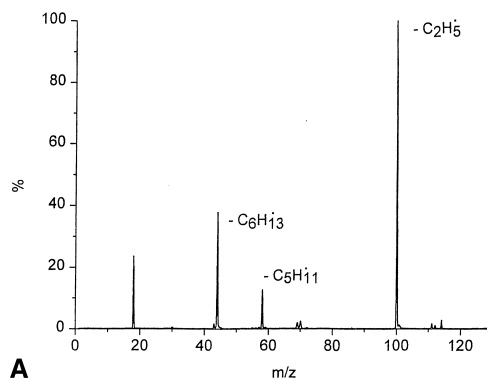


Figure 1. MIKE spectrum of octan-1-amine molecular ions ( $m/z$  129).

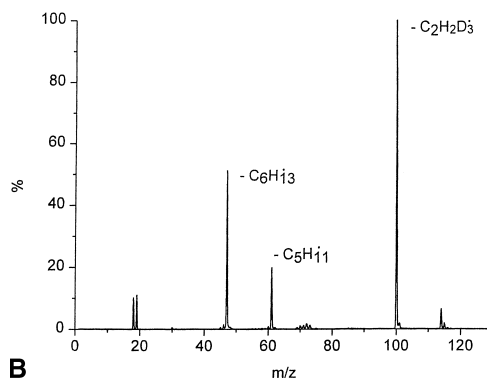
small peak corresponds to loss of a methyl radical, but virtually no  $\text{CH}_2=\text{NH}_2^+$  product ions (formed by  $\alpha$ -cleavage of the unrearranged molecular ion) contribute. As previously reported [2,15], the spectrum of the 1,1- $\text{D}_2$  analog shows that the C-1 hydrogen atoms are not extensively involved in the hydrogen atom exchange reactions and that both C(1) hydrogen atoms are part of the  $\text{CH}_3$  radical expelled from the molecular ion.

### 3.1.2. Octan-2-amine

The major peak in the MIKE spectrum of the octan-2-amine molecular ions [Fig. 2(a)] corresponds to loss of  $\text{C}_2\text{H}_5$ , suggesting isomerization to octan-3-amine; correspondingly,  $[\text{M}-\text{C}_5\text{H}_{11}]^+$  ions are formed.  $\alpha$ -cleavage of the unrearranged molecular ion gives rise to the  $[\text{M}-\text{C}_6\text{H}_{13}]^+$  peak and the very small  $[\text{M}-\text{CH}_3]^+$  peak. The spectrum of the 1,1,1- $\text{D}_3$  analog [Fig. 2(b)] shows that the reactions are quite specific; the terminal methyl group is cleanly eliminated as part of the  $\text{C}_2\text{H}_5$  fragment and completely retained in the  $[\text{M}-\text{C}_5\text{H}_{11}]^+$  and  $[\text{M}-\text{C}_6\text{H}_{13}]^+$  ions. However, the MIKE spectrum of the  $N,N$ - $\text{D}_2$  analog shows that extensive exchange of C- and N-bonded hydrogen atoms takes place prior to dissociation. Loss of pentyl and hexyl radicals from the  $N,N$ - $\text{D}_2$  analog gives rise to  $m/z$  58, 59, 60 ions (relative abundance 40:48:12) and  $m/z$  44, 45, 46 ions (relative abundance 31:54:15); some 3% of the ethyl radicals expelled include one deuterium atom.



A



B

Figure 2. Mike spectra of (a) octan-2-amine molecular ions ( $m/z$  129), (b) [1,1,1- $\text{D}_3$ ]-octan-2-amine molecular ions ( $m/z$  132).

### 3.1.3. Octan-3-amine

Fragmentation of the metastable octan-3-amine molecular ions leads almost exclusively to  $[\text{M}-\text{C}_2\text{H}_5]^+$  ions; a small companion peak corresponding to  $[\text{M}-\text{C}_5\text{H}_{11}]^+$  ions is observed, but the MIKE spectrum (Fig. 3) exhibits no significant signals corresponding to the fragmentation of isomeric species. The spectrum of the 1,1,1- $\text{D}_3$  analog shows that the deuterium atoms of the terminal methyl group are completely retained in the ethyl radical expelled; correspondingly, the spectrum of the  $N,N$ - $\text{D}_2$  analog shows that both deuterium atoms are retained in the  $[\text{M}-\text{C}_2\text{H}_5]^+$  ions.

## 3.2. Reaction thermochemistry

The heats of formation of alkyl radicals and immonium ions, the products of the predominant frag-

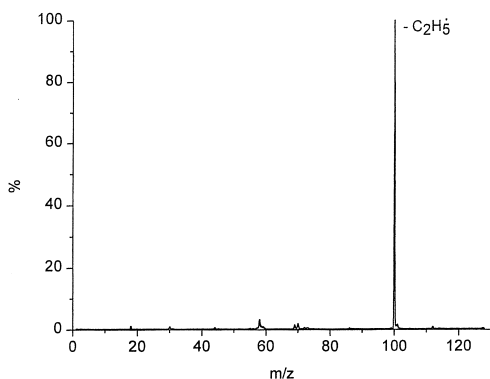


Figure 3. Mike spectrum of octan-3-amine molecular ions ( $m/z$  129).

mentation reactions of the octanamine molecular ions, are given in Table 1. The literature values for the alkyl radicals included in the table are taken from Seetula and Slagle's work [16]; almost the same values were recommended by Tsang [17]. The heats of formation of the  $C_1$ – $C_4$  radicals calculated with the G3 method show very good agreement with the experimental values [18]. The heats of formation given in Table 1 for the hexyl and heptyl radicals are estimated by additivity, based on the literature values for the linear  $C_1$ – $C_5$  alkyl radicals; Cohen [19] has shown that Benson-type additivity methods can provide good estimates of alkyl radical heats of formation.

The heats of formation of immonium ions given in Table 1 were determined with the G3 method, to complement the calculated alkyl radical heats of formation. Very good agreement is obtained with the G2 (MP2) and CBS-Q results recently reported [11]. A small, possibly systematic difference between the results obtained with the latter two methods has been described [11,20]; the G3 values are in most cases very close to the mean of the G2 (MP2) and CBS-Q results. The heats of formation of immonium ions with six and seven carbon atoms were estimated by additivity; it has been shown that Benson-type additivity methods work well for immonium ions [11].

The heats of formation of the octanamine radical cations have not been reported in the literature, and computational limitations prevent us from examining species as large as these with methods like G3 or

Table 1  
Heats of formation of alkyl radicals and immonium ions (298 K,  $\text{kJ mol}^{-1}$ )

	Exp <sup>a</sup>	G3 <sup>b</sup>		G3 <sup>c</sup>
$\text{CH}_3$	146	142	$\text{CH}_2=\text{NH}_2^+$	753
$\text{C}_2\text{H}_5$	121	120	$\text{CH}_3\text{CH}=\text{NH}_2^+$	670
$n\text{-C}_3\text{H}_7$	101	100	$\text{C}_2\text{H}_5\text{CH}=\text{NH}_2^+$	636
$n\text{-C}_4\text{H}_9$	81	80	$n\text{-C}_3\text{H}_7\text{CH}=\text{NH}_2^+$	611
$\text{sec-C}_4\text{H}_9$	67	69	$n\text{-C}_4\text{H}_9\text{CH}=\text{NH}_2^+$	586
$n\text{-C}_5\text{H}_{11}$	61 <sup>d</sup>		$n\text{-C}_5\text{H}_{11}\text{CH}=\text{NH}_2^+$	563 <sup>f</sup>
$n\text{-C}_6\text{H}_{13}$	40 <sup>e</sup>		$n\text{-C}_6\text{H}_{13}\text{CH}=\text{NH}_2^+$	542 <sup>f</sup>
$n\text{-C}_7\text{H}_{15}$	19 <sup>e</sup>			

<sup>a</sup> Experimentally determined values (from [16]).

<sup>b</sup> All-trans conformations.

<sup>c</sup> See [11] for a comparison of calculated and experimental values.

<sup>d</sup> Estimated ([16]).

<sup>e</sup> Estimated by additivity (based on Seetula's results [16]).

<sup>f</sup> Estimated by additivity (based on the G3 heats of formation of the smaller immonium ions; see also [11]).

CBS-Q. The value for the octan-1-amine molecular ion given in Table 2 was determined by additivity, based on the experimentally determined [21] heats of formation of the straight-chain  $C_1$ – $C_5$  amine radical cations. Heats of formation obtained by additivity estimates are not expected to be quite as reliable for radical cations as for neutral molecules or even-electron ions, but, fortunately, the exact value is not of crucial importance to the findings of the present article. To assess the difference between the heats of formation of the isomeric octanamine molecular ions we have examined the corresponding pentanamine molecular ions with the G2 (MP2, SVP) method (Table 2). This estimate is expected to be quite reliable, inasmuch as the G2 (MP2, SVP) and G3 methods yield heats of formation of alkanamine radical cations with up to four carbon atoms that are within  $3 \text{ kJ mol}^{-1}$  of each other and reproduce the experimentally determined values reasonably well (with the exception of the values for methylamine) [4].

The thermochemistry of the  $\alpha$ -cleavage reactions of the four straight-chain octanamines is presented in Table 3; the values given indicate the threshold for simple cleavage of the respective reactant ions in the

Table 2  
Heats of formation of amine radical cations and their distonic isomers<sup>a</sup>

$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2^{+\cdot}$	751 <sup>b</sup>	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{NH}_3^+$	719 <sup>b</sup>
$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{NH}_2^{+\cdot}$	734 <sup>b</sup>	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_2)\text{NH}_3^+$	714 <sup>b</sup>
<i>n</i> -C <sub>4</sub> H <sub>9</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+\cdot</sup>	727 <sup>c,d,e</sup>	$\text{CH}_3\dot{\text{C}}\text{HCH}(\text{CH}_3)\text{NH}_3^+$	698 <sup>b</sup>
<i>n</i> -C <sub>3</sub> H <sub>7</sub> (CH <sub>3</sub> )CHNH <sub>2</sub> <sup>+\cdot</sup>	709 <sup>c,f</sup>	$\text{CH}_3\dot{\text{C}}\text{HCH}_2\text{CH}_2\text{CH}_2\text{NH}_3^+$	697 <sup>c</sup>
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> CHNH <sub>2</sub> <sup>+\cdot</sup>	708 <sup>c,f</sup>	$\text{CH}_3\text{CH}_2\text{CH}_2\dot{\text{C}}\text{HCH}_2\text{NH}_3^+$	698 <sup>c</sup>
<i>n</i> -C <sub>7</sub> H <sub>15</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+\cdot</sup>	660 <sup>g</sup>	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}(\text{CH}_2)\text{NH}_3^+$	691 <sup>c</sup>
<i>n</i> -C <sub>6</sub> H <sub>13</sub> (CH <sub>3</sub> )CHNH <sub>2</sub> <sup>+\cdot</sup>	640 <sup>g</sup>	$\text{CH}_3\text{CH}_2\dot{\text{C}}\text{HCH}(\text{CH}_3)\text{NH}_3^+$	675 <sup>c</sup>
<i>n</i> -C <sub>5</sub> H <sub>11</sub> (C <sub>2</sub> H <sub>5</sub> )CHNH <sub>2</sub> <sup>+\cdot</sup>	640 <sup>g</sup>		

<sup>a</sup> 298 K, kJ mol<sup>-1</sup>.

<sup>b</sup> From [4], based on calculations with the G3 method.

<sup>c</sup> Based on calculations with the G2 (MP2, SVP) method.

<sup>d</sup> All-trans conformation.

<sup>e</sup> Experimental value 726 kJ mol<sup>-1</sup> [21].

<sup>f</sup> All-trans carbon skeleton.

<sup>g</sup> Estimated (see text).

absence of energy barriers toward the reverse reactions.

### 3.3. Intermediate species

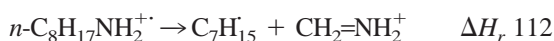
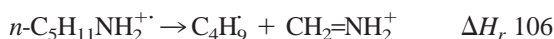
The distonic intermediates (see Schemes 3 and 6) are lower in energy than the isomeric amine molecular ions [4,22]. The difference between the heats of formation of the octanamine molecular ions and their distonic isomers can be estimated from the differences between the ab initio (G3 and G2 (MP2, SVP)) heats of formation of a number of C<sub>4</sub>- and C<sub>5</sub>-amine molecular ions and their β-distonic isomers (Table 2) [4]. The resulting estimates of the heats of formation

of the distonic isomers of the octanamines are included in Schemes 5 and 6. Very similar results are obtained when the estimate is based on the hydrogen atom affinities of amine radical cations and the hydrocarbon bond dissociation energies [23]; Gauld et al. [24] have shown that the heats of formation of distonic ions (excepting α-distonic species) can be estimated by additivity, using bond dissociation energies, refuting earlier suggestions to the contrary [25].

## 4. Discussion

### 4.1. Metastable octan-1-amine molecular ions

Simple α-cleavage of an *n*-alkanamine molecular ion is endothermic by more than 100 kJ mol<sup>-1</sup> (Scheme 2)



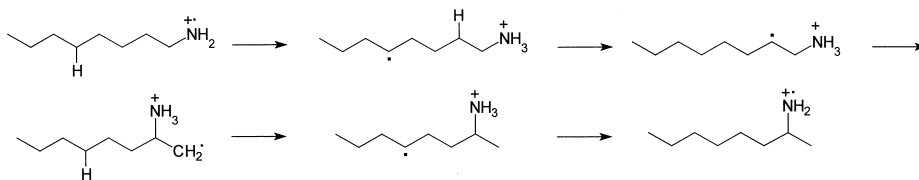
Scheme 2. α cleavage of *n*-alkanamine molecular ions (298 K heats of reaction in kJ mol<sup>-1</sup>, cf. Tables 1 and 2).

It has been shown by Audier et al. [2,26] that the metastable molecular ions of primary amines with five or more carbon atoms react by processes that require less

Table 3  
ΣΔH<sub>f</sub> (products) of the simple cleavage reactions of the octanamine molecular ions

Reactant	Products	ΣΔH <sub>f</sub> (products) <sup>a</sup>
Octan-1-amine <sup>+\cdot</sup>	C <sub>7</sub> H <sub>15</sub> + CH <sub>2</sub> =NH <sub>2</sub> <sup>+</sup>	772
Octan-2-amine <sup>+\cdot</sup>	CH <sub>3</sub> + C <sub>6</sub> H <sub>13</sub> CH=NH <sub>2</sub> <sup>+</sup>	688
	C <sub>6</sub> H <sub>13</sub> + CH <sub>3</sub> CH=NH <sub>2</sub> <sup>+</sup>	710
Octan-3-amine <sup>+\cdot</sup>	C <sub>2</sub> H <sub>5</sub> + C <sub>5</sub> H <sub>11</sub> CH=NH <sub>2</sub> <sup>+</sup>	684
	C <sub>5</sub> H <sub>11</sub> + C <sub>2</sub> H <sub>5</sub> CH=NH <sub>2</sub> <sup>+</sup>	697
Octan-4-amine <sup>+\cdot</sup>	C <sub>3</sub> H <sub>7</sub> + C <sub>4</sub> H <sub>9</sub> CH=NH <sub>2</sub> <sup>+</sup>	687
	C <sub>4</sub> H <sub>9</sub> + C <sub>3</sub> H <sub>7</sub> CH=NH <sub>2</sub> <sup>+</sup>	692

<sup>a</sup> kJ mol<sup>-1</sup>, 298 K; based on the heats of formation in Table 1.



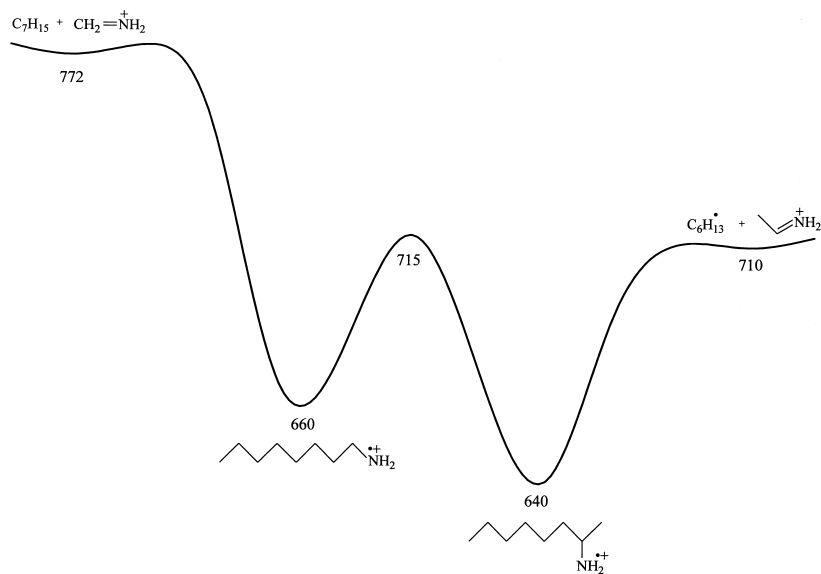
Scheme 3. The Audier mechanism for the isomerization of alkan-1-amine molecular ions; only the reaction initiated by 1,6-hydrogen atom abstraction is shown.

energy than does straightforward simple cleavage. The MIKE spectrum of octan-1-amine molecular ions (Fig. 1) exemplifies the behavior of straight-chain alkan-1-amines. The major product,  $\text{CH}_3\text{CH}=\text{NH}_2^+$ , is formed by cleavage after isomerization to octan-2-amine (Scheme 3).

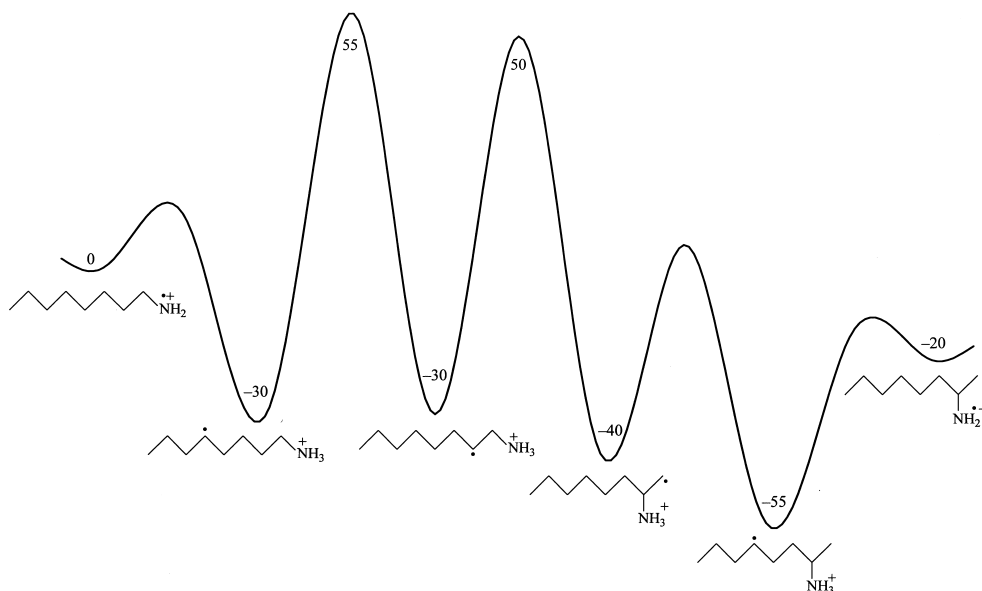
The isomerization is slightly exothermic (by  $\sim 20$   $\text{kJ mol}^{-1}$ , cf. Table 2); however, the exothermicity is less important than the fact that  $\alpha$  cleavage of the resulting octan-2-amine ion requires less energy than does dissociation of the initial octan-1-amine molecular ion (Table 3). Once the isomerization has occurred, fragmentation can be rapid even for ions that do not possess sufficient energy to undergo the simple cleavage of octan-1-amine. This is illustrated in Scheme 4.

The energy required for isomerization can be

estimated with a fair degree of confidence. The barriers toward the hydrogen atom transfer steps that involve the  $-\text{NH}_2^+$  are very low. Yates and Radom [22] estimated a barrier of less than  $10$   $\text{kJ mol}^{-1}$  for the intramolecular 1,5-hydrogen atom abstraction by the  $-\text{NH}_2^+$  from the terminal methyl group in  $n\text{-C}_4\text{H}_9\text{NH}_2^+$ , based on ab initio calculations at the MP2 level. Preliminary G2 (MP2, SVP) calculations [23] suggest an even lower barrier for the 1,5-H transfer from  $-\text{CH}_2-$  to the  $-\text{NH}_2^+$  in  $n\text{-C}_5\text{H}_{11}\text{NH}_2^+$ ; in fact, the barrier for 298 K ions all but disappears when enthalpy contributions and the zero-point vibrational energy are taken into account. However, the hydrogen atom abstraction by the  $-\text{NH}_2^+$  in long-chain amine molecular ions can involve 1,5-, 1,6-, as well as 1,7-hydrogen atom transfer [15]; only transfer



Scheme 4. Potential energy diagram for the fragmentation of octan-1-amine molecular ions; heats of formation in  $\text{kJ mol}^{-1}$ .



Scheme 5. Potential energy diagram for the isomerization of octan-1-amine radical cations to octan-2-amine ions. Numbers indicate energy relative to the octan-1-amine molecular ion ( $\text{kJ mol}^{-1}$ ).

via the 7- and 8-membered cyclic transition states will yield intermediates that can undergo the subsequent 1,4- or 1,5-hydrogen atom transfer from C to C (Scheme 3). We expect that the enthalpy requirements for the C-to-N hydrogen atom transfer reactions do not increase considerably with increasing ring size.

The barrier for the C-to-C 1,4-hydrogen atom transfer is taken to be the same as that suggested by Rabinovitch [27] for 1,4-hydrogen atom transfer between methylene groups in secondary octyl radicals (5ss in Rabinovitch's notation), about  $85 \text{ kJ mol}^{-1}$ , in good agreement with more recent estimates for related systems [28]. For the 1,5-hydrogen atom transfer (6sp), a barrier of about  $60 \text{ kJ mol}^{-1}$  is assumed [27,28].

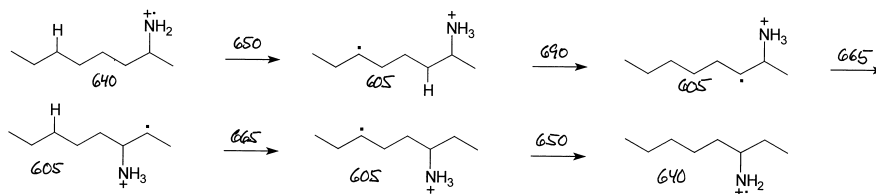
The critical energy for the 1,2-migration of  $\text{NH}_3$  in the  $\beta$ -distonic isomer of octan-1-amine is assumed to be close to that determined for the 1,2- $\text{NH}_3$  migration in the  $\beta$ -distonic isomer of the *n*-butylamine radical cation [4],  $80 \text{ kJ mol}^{-1}$ .

The estimated heats of formation of intermediates and transition states are indicated in Scheme 5. The C-to-C 1,4-hydrogen atom transfer and the  $\text{NH}_3$  migration turn out to be the more energy demanding

steps of the isomerization to the octan-2-amine molecular ion, but inasmuch as formation of the initial distonic intermediate is exothermic, the overall energy barrier toward isomerization is only some  $55 \text{ kJ mol}^{-1}$ , considerably less than that required for simple cleavage.

#### 4.2. Metastable octan-2-amine molecular ions

Direct cleavage of ionized octan-2-amine by loss of a hexyl radical requires some  $70 \text{ kJ mol}^{-1}$  (Tables 2 and 3), in the absence of a barrier for the reverse reaction. Most of the molecular ions with internal energy in appreciable excess of this will dissociate rapidly in the mass spectrometer ion source, but some proportion of the surviving molecular ions possess enough energy to fragment by loss of  $\text{C}_6\text{H}_{13}$  radicals in the field-free regions of the mass spectrometer [see Fig. 2(a)]. Isomerization to octan-1-amine, while in principle possible, would not provide an energetically favorable additional fragmentation pathway, and the absence of hydrogen atom exchange involving the terminal methyl group [see Fig. 2(b)] indicates that this isomerization does not occur at all. On the other



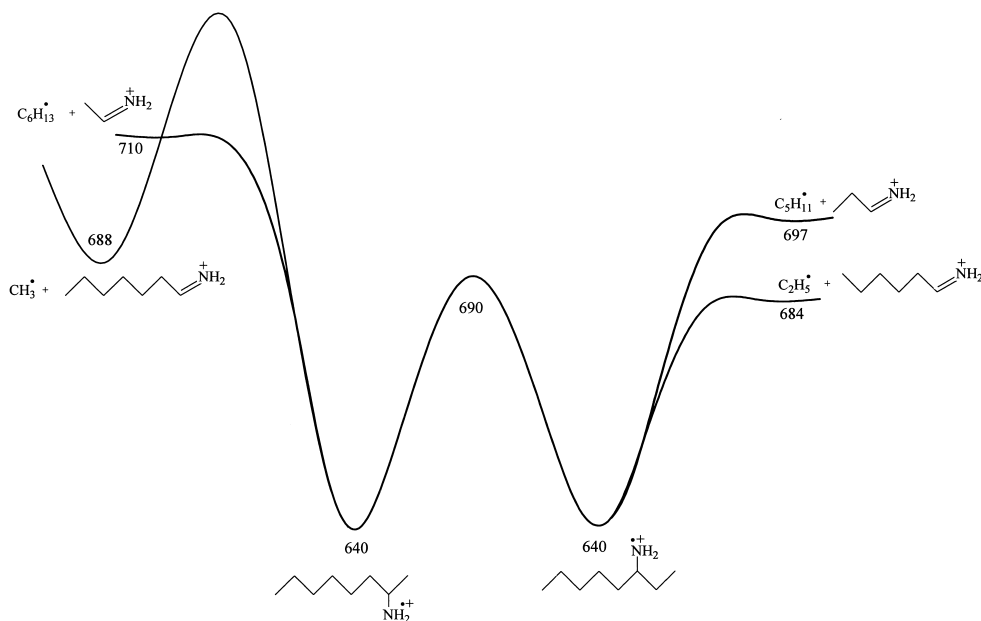
Scheme 6. Audier mechanism for the isomerization of octan-2-amine molecular ions to octan-3-amine ions. Estimated heats of formation of intermediates and transition states in  $\text{kJ mol}^{-1}$ .

hand, isomerization of the octan-2-amine molecular ions to octan-3-amine ions (which by analogy to the pentylamine system is expected to be close to thermoneutral) makes alternative fragmentation reactions possible. This transformation (Scheme 6) probably takes place in a manner analogous to that by which the octan-1-amine molecular ion isomerizes.

Cleavage by loss of  $\text{C}_2\text{H}_5^\bullet$  after rearrangement to the octan-3-amine radical cation yields products that are some  $25 \text{ kJ mol}^{-1}$  lower in energy than the products of direct cleavage by loss of  $\text{C}_6\text{H}_{13}^\bullet$  from the initial octan-2-amine molecular ions (see Table 3), which will also allow some otherwise nonreactive ions to fragment (Scheme 7). The MIKE spectrum of

octan-2-amine (Fig. 2) shows that about two thirds of the metastable molecular ions actually react after isomerization, giving rise to  $\text{C}_5\text{H}_{11}\text{CH}=\text{NH}_2^+$  and  $\text{C}_2\text{H}_5\text{CH}=\text{NH}_2^+$  product ions (cleavage of octan-3-amine) rather than  $\text{CH}_3\text{CH}=\text{NH}_2^+$  and  $\text{C}_6\text{H}_{13}\text{CH}=\text{NH}_2^+$  ions (cleavage of intact octan-2-amine). We note that the MIKE spectrum of *N,N*- $\text{D}_2$ -octan-2-amine molecular ions demonstrates that exchange of carbon- and nitrogen-bonded hydrogen atoms precedes C–C bond cleavage for both isomerizing and nonisomerizing molecular ions, confirming that the energy requirements are lower for hydrogen atom abstraction than for the subsequent steps in the isomerization.

The heats of formation of the distonic intermedi-



Scheme 7. Potential energy diagram for the isomerization and cleavage of octan-2-amine molecular ions; heats of formation in  $\text{kJ mol}^{-1}$ .



ates and the energy barriers for the individual steps indicated in Scheme 6 are estimated in the same manner as described above for the isomerization of octan-1-amine molecular ions. The C–to–C hydrogen atom transfer is probably the more energy-demanding step of the isomerization of octan-2-amine, inasmuch as the barrier to  $\text{NH}_3$  migration between secondary sites is only some  $60 \text{ kJ mol}^{-1}$  [4]. The overall energy barrier toward isomerization is  $50 \text{ kJ mol}^{-1}$ , making isomerization a viable alternative to direct simple cleavage (Scheme 7).

Direct  $\alpha$ -cleavage of the octan-2-amine molecular ions could be by loss of a methyl radical or by loss of a hexyl radical. The MIKE spectrum shows that the latter reaction greatly predominates, even though the products formed by loss of  $\text{CH}_3$  would be considerably lower in energy (Table 3). The most straightforward rationale is that expulsion of the methyl radical has an energy barrier in excess of the reaction endothermicity, that is, that the barrier toward addition of  $\text{CH}_3$  to an immonium ion carbon atom is substantially higher than that for the addition of other alkyl radicals. This is in line with a number of previously reported observations [11,29].

#### 4.3. Metastable octan-3-amine molecular ions

The octan-3-amine radical cations dissociate nearly exclusively by the energetically more favored simple cleavage, expulsion of an ethyl radical (Fig. 3). The alternative  $\alpha$ -cleavage, expulsion of a pentyl radical, does not contribute significantly to the observed reactions of the metastable molecular ions, even though it requires only some  $10\text{--}15 \text{ kJ mol}^{-1}$  more energy (see the discussion below).

Rearrangement of the octan-3-amine molecular ions to octan-2-amine may well be possible, but this would not open for additional favorable reactions; loss of a hexyl radical from the latter ion requires more energy than do the cleavage reactions available to the octan-3-amine molecular ion (Table 3). Cleavage after rearrangement to octan-4-amine molecular ions is also not observed, which indicates that the isomerization does not take place; the energetics of  $\alpha$ -cleavage of the octan-3-amine and octan-4-amine

molecular ions are very similar (Table 3 and Scheme 7). The absence of rearrangement may merely reflect that the rate of simple cleavage will exceed the rate of rearrangement-*cum*-cleavage when the energy requirements are not very different.

#### 4.4. Energy distribution of the metastable molecular ions

The metastable molecular ions are those that did not possess sufficient energy to react in the ion source of the mass spectrometer. In other words, the energy requirements of the efficient ion–source reactions determine the upper limit to the internal energy that the surviving (metastable) ions may possess.

The rate constant  $k(E)$  for loss of a hexyl radical from the octan-2-amine molecular ions will increase rapidly with increasing internal energy, inasmuch as the critical energy is as low as  $70 \text{ kJ mol}^{-1}$ . Only few intact molecular ions with energy well in excess of  $E_0$  will survive long enough to leave the ion source. For octan-3-amine, the reaction that delimits the energy of the surviving molecular ions is loss of an ethyl radical. This process requires only some  $45 \text{ kJ mol}^{-1}$ ;  $k(E)$  for the simple cleavage will rise even more steeply with  $E$ , and the internal energy of the surviving ions will be even more narrowly delimited. In other words, the internal energy of the surviving octan-2-amine molecular ions can be higher than the internal energy of the surviving octan-3-amine molecular ions, owing to the different energy requirements for the predominant ion–source reactions, simple cleavage.

The MIKE spectrum of octan-3-amine demonstrates that the energy distribution of the metastable molecular ions is in fact sufficiently narrow that loss of the pentyl radical cannot compete, even though the energy required for this reaction is only some  $10\text{--}15 \text{ kJ mol}^{-1}$  higher than that required for loss of the ethyl radical (Scheme 7). It follows also that virtually no metastable octan-3-amine molecular ions will possess sufficient energy to fragment via the channel(s) open to the octan-2-amine molecular ions. Isomerization may well take place (the barrier to isomerization is sufficiently low) but fragmentation will not.

Conversely, the internal energy of the octan-3-amine molecular ions that arise by isomerization of octan-2-amine ions is delimited by the energy requirement for the simple cleavage available to octan-2-amine molecular ions, loss of a hexyl radical. The more energetic isomerizing molecular ions will therefore possess sufficient energy to fragment by loss of pentyl as well as by loss of ethyl, once isomerization has occurred. This is borne out by experiment, as the difference between the MIKE spectra of octan-2-amine and octan-3-amine illustrates.

A similar relationship is behind the difference between the reactions of the octan-2-amine ions that arise by rearrangement of octan-1-amine molecular ions and those that are formed by ionization of octan-2-amine. Only the latter undergo isomerization to octan-3-amine. The reason is that the internal energy of the surviving octan-1-amine ions can be relatively high.  $E_0$  for the main ion–source reaction, loss of  $C_7H_{15}$ , is upward of  $100 \text{ kJ mol}^{-1}$ , and many surviving molecular ions will in turn possess enough energy to react rapidly by simple cleavage once rearrangement to octan-2-amine ions has taken place. The internal energy of the octan-2-amine molecular ions that are formed by ionization of octan-2-amine and escape undecomposed from the ion source is lower because  $E_0$  of the ion–source reactions is lower; the more rapid reaction for these ions is the less energy demanding reaction, isomerization.

The behavior of these systems resembles the “rate determining isomerization” first proposed by Hvistendahl and Williams [30]. However, an important difference is found in the reason why only the isomerizing ions have sufficient energy to react via several pathways once rearrangement has taken place. In Hvistendahl and Williams’ case, isomerization involves passage over an appreciable energy barrier, which ensures that the internal energy of all reactant ions formed by isomerization is high enough to allow other than the lowest-energy reaction to occur. For octan-2-amine and octan-3-amine, isomerization poses no great energy requirements, but the different ion–source reactions result in different upper limits to the energy that the surviving ions may possess; the

energy of the isomerizing octan-2-amine ions is less severely delimited.

#### 4.5. Nonreactive molecular ion isomers

A simple Rice–Ramsperger–Kassel–Marcus (RRKM) analysis of systems such as those considered here suggests that nearly all ions with sufficient energy to react at all will react rapidly in the mass spectrometer ion source when the critical energy toward dissociation is as low as is the case for octan-2-amine and octan-3-amine molecular ions. In turn, only very few metastable molecular ions ought to be available for reaction in the field-free regions. However, even though the molecular ions are not very abundant, we find that the reactions of the metastable octanamine molecular ions produce reasonably strong signals, indicating that the ion–source depletion of the molecular ion population is not as severe as suggested by the RRKM considerations. The reason could well be that the surviving molecular ions have to a considerable extent isomerized by hydrogen atom abstraction to distonic isomers (Schemes 3 and 6). The intramolecular hydrogen atom abstraction is rapid and energetically favorable, but the resulting distonic ions have no direct, low-energy dissociation reactions available, only further rearrangement by hydrogen atom abstraction. This assumption is supported by the observation that loss of  $NH_3$  is among the prominent collision-induced reactions of the surviving amine molecular ions [23]. It is therefore possible that the distonic isomers in fact constitute a kinetic reservoir of reactant species, a situation described earlier [31]. Also, Hase [32] has shown that unimolecular reactions in systems with several shallow minima connected by low barriers will be slower than predicted by classical RRKM theory; the interconverting ensemble of distonic isomers of the amine molecular ions may be an additional example.

## 5. Conclusions

The reactions of the octylamine molecular ions provide textbook examples of systems where the

crossing of  $k(E)$  curves determines the outcome of the competition between rearrangement and simple cleavage. In addition, these ions can react after a rate determining isomerization where the difference between the internal energy of the reacting ions is not determined by the presence of substantial energy barriers, but arises because the energy distribution of the metastable ions is determined by the (different) energy requirements of the ion–source processes of the respective reactants.

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