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Gas-Phase Chemistry of Protonated Ethylamine: A Mass Spectrometric and Molecular Orbital Study

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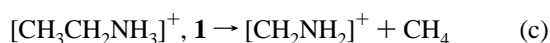
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The unimolecular dissociation of protonated ethylamine, $[\text{CH}_3\text{CH}_2\text{NH}_3]^+$, **1**, has been examined by both mass spectrometric techniques and molecular orbital calculations. Metastable dissociations of various deuterated species demonstrate that the loss of ethene from **1** involves specifically a transfer of a hydrogen atom from the methyl to the NH_2 group. A very limited scrambling (4%) of the hydrogen atoms of the ethyl moiety is observed. Ab initio molecular orbital calculations have been performed at the MP4SDTQ/6-311G**//MP2/6-31G*+ZPE level of theory to examine the mechanism of the unimolecular dissociation of ions **1**. It appears that **1** loses a molecule of ethene after a rate-determining isomerization into a proton-bound complex: $[\text{C}_2\text{H}_4\cdots\text{NH}_4]^+$, **2**. The marginal hydrogen scrambling is accounted for by 1,2-H shifts on the ethyl group inside a second, loosely bonded, complex involving an ethyl cation and a molecule of ammonia: $[\text{C}_2\text{H}_5\cdots\text{NH}_3]^+$, **3**.

Introduction

The chemistry of protonated amines in the gas phase has been the object of only a few reports.^{1–5} The chemical ionization mass spectra of a selection of aliphatic amines demonstrated that isolated protonated amines $[\text{RNH}_3]^+$ react either by loss of ammonia, giving the corresponding R^+ ions, or by elimination of an alkene molecule, yielding $[\text{NH}_4]^+$ ion.² Under high-energy conditions, as revealed for example by collisional experiments,⁴ an alkane elimination leading to iminium ions may enter into competition with the two former processes. The mechanism of both alkene and ammonia eliminations has recently been interpreted in terms of ion–neutral complex mediated reactions, and the potential energy profiles associated with these processes have partly been described in the case of propylamine.^{2,5} From a more general point of view, the β -elimination of an olefin molecule from a cation containing an even number of electrons seems to occur via a proton-bonded intermediate.⁶

In the present study we were interested in the behavior of the simplest protonated alkylamine which is able to undergo an alkene elimination, i.e. protonated ethylamine. The $[\text{CH}_3\text{CH}_2\text{NH}_3]^+$ ion, **1**, may a priori dissociate via three reaction channels:



In fact, only the first reaction (a) is observed from metastable ions **1**; the two latter reactions give rise to noticeable signals only in the high-energy collision-induced mass spectrum.

To investigate accurately the dissociation process leading to C_2H_4 loss, high-level ab initio molecular orbital calculations have also been used in conjunction with deuterium-labeling mass spectrometric experiments.

Experimental and Computational Section

The experiments were carried out with a VG-ZAB-2F double-focusing mass spectrometer (B-E) operating in the chemical ionization mode. The accelerating voltage was set at 8 kV, the electron energy at 150 eV, and the emission current at 0.5 mA. The source temperature was 180 °C. The mass-analyzed ion kinetic energy (MIKE) spectra of metastable ions were obtained, as usual, by selecting with the magnet the ion to be studied and scanning the electrostatic analyzer voltage. Ammonia, methanol, methane, and deuterated homologues were used as reagent gases in the chemical ionization experiments.

Deuterated derivatives $\text{CH}_3\text{CD}_2\text{NH}_2$ and $\text{CD}_3\text{CH}_2\text{NH}_2$ were prepared by reduction of CH_3CN by LiAlD_4 and of CD_3CN by LiAlH_4 , respectively. The standard experimental procedure consists in adding CX_3CN ($\text{X} = \text{H}$ or D) to a solution of LiAlX_4 ($\text{X} = \text{H}$ or D) in ether. After reaction at room temperature for approximately 1 h, the mixture is hydrolyzed by dropwise addition of water. The gaseous ethylamine is then hydrochlorinated by bubbling through a saturated solution of HCl in ether. The solvent and the excess of HCl are removed at reduced pressure to isolate the aminohydrochloride.

Ab initio molecular orbital calculations have been carried out at a theoretical level, allowing an accurate description of the ethyl cation. In fact, recent theoretical studies demonstrated that the bridged ethyl cation is more stable than its classical form by ca. 30 kJ/mol; moreover, the latter has been found to be the transition structure for the hydrogen exchange in the bridged cation rather than an equilibrium structure.⁷ It is noteworthy that these features appear only if the geometry

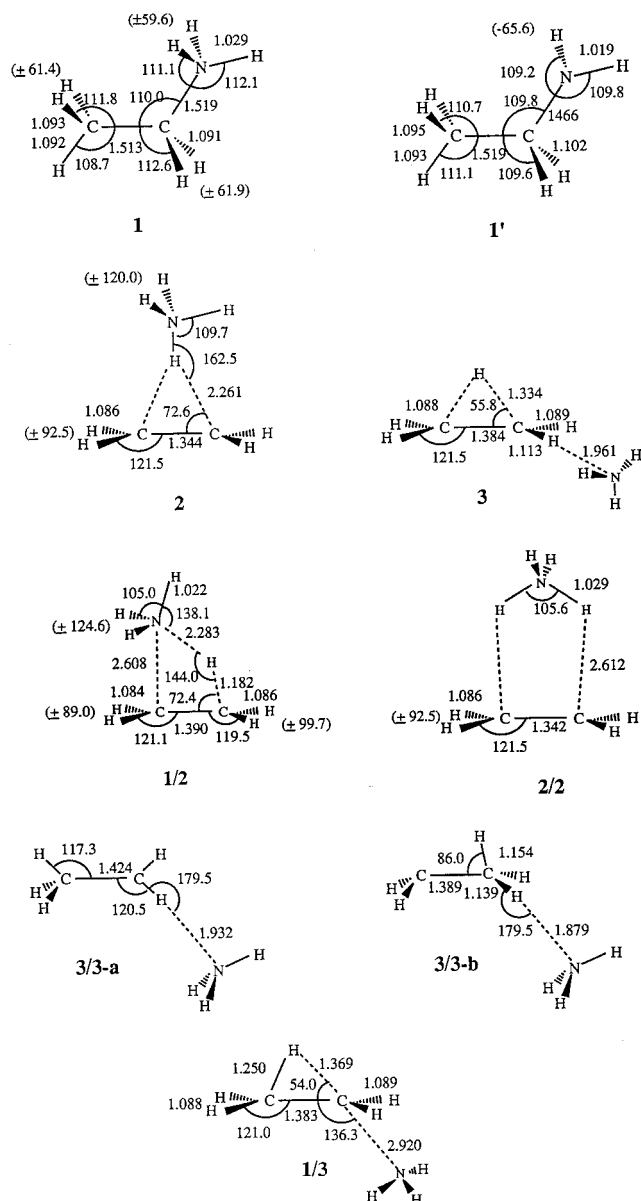
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| precursor | fragment ion (<i>m/z</i>) | | | | |
|---|---|---|--|---|---|
| | [NH ₄] ⁺ (18) | [NH ₃ D] ⁺ (19) | [NH ₂ D ₂] ⁺ (20) | [NHD ₃] ⁺ (21) | [ND ₄] ⁺ (22) |
| [CH ₃ CD ₂ NH ₃] ⁺ | 97 A: 21.4 B: 60.0 C: 100.0 | 3 A: 57.1 B: 40.0 C: 0.0 | 0 A: 21.4 B: 0.0 C: 0.0 | | |
| [CD ₃ CH ₂ NH ₃] ⁺ | 5 A: 7.0 B: 40.0 C: 0.0 | 95 A: 43.0 B: 60.0 C: 100.0 | 0 A: 43.0 B: 0.0 C: 0.0 | 0 A: 7.0 B: 0.0 C: 0.0 | |
| [CH ₃ CH ₂ ND ₃] ⁺ | 0 A: 7.0 B: 0.0 C: 0.0 | 0 A: 43.0 B: 0.0 C: 0.0 | 3 A: 43.0 B: 0.0 C: 0.0 | 97 A: 7.0 B: 100.0 C: 100.0 | |
| [CH ₃ CD ₂ ND ₃] ⁺ | | 0 A: 7.0 B: 0.0 C: 0.0 | 0 A: 43.0 B: 0.0 C: 0.0 | 97 A: 43.0 B: 60.0 C: 100.0 | 3 A: 7.0 B: 40.0 C: 0.0 |
| [CD ₃ CH ₂ ND ₃] ⁺ | | | 0 A: 21.4 B: 0.0 C: 0.0 | 6 A: 57.1 B: 40.0 C: 0.0 | 94 A: 21.4 B: 60.0 C: 100.0 |

Throughout this paper, bond lengths are given in angstroms, bond angles in degrees, total energies in hartrees, and zero-point and relative energies in kJ mol⁻¹. Unless otherwise noted, relative energies in the text refer to the MP4SDTQ/6-311G**/MP2/6-31G*+ZPE level of theory.

It appears clearly that $[\text{NX}_4]^+$ abundances are not consistent with the statistical predictions based on a complete H/D scrambling (Table 1, model A) or on a scrambling limited to the ethyl moiety before an irreversible transfer of a β -hydrogen onto the nitrogen atom (model B). Accordingly, the complete absence of ions $[\text{NH}_2\text{D}_2]^+$ from $[\text{CH}_3\text{CD}_2\text{NH}_3]^+$, $[\text{CD}_3\text{CH}_2\text{NH}_3]^+$, $[\text{CH}_3\text{CD}_2\text{ND}_3]^+$, or $[\text{CD}_3\text{CH}_2\text{ND}_3]^+$ and of ions $[\text{NH}_3\text{D}]^+$ from $[\text{CH}_3\text{CH}_2\text{ND}_3]^+$ excludes any appreciable exchange involving all eight hydrogen atoms. With the exception of the latter precursor, all the data indicate that reaction (a) is virtually



An estimate of the H/D isotope effect and of the participation of the hydrogen atoms from both positions α and β in the $[\text{NX}_4]^+$ ion formation may be done by using the complementary pairs of labeled precursors.⁸ The ratio of peak intensities $[\text{NH}_4]^+ / [\text{NH}_3\text{D}]^+$ and $[\text{NH}_3\text{D}]^+ / [\text{ND}_4]^+$ may be simply related to the total isotope effect, i , and the contributions of each positions, denoted α and β , by

$$[\text{NH}_3\text{D}]^+ / [\text{ND}_4]^+ = i\beta / (1 - \beta) \text{ for } [\text{CH}_3\text{CD}_2\text{ND}_3]^+$$

An isotope effect $i = 1.44$ is deduced from the first pair, while the second leads to $i = 1.30$. Owing to the experimental uncertainties on the determination of peak intensities, we can

TABLE 2: Calculated Total Energies (Hartrees) and Zero-Point Energies (ZPE, kJ/mol) for the Stationary Points Considered

| no. | structure | | HF/6-31G ^a | MP2(F)/6-31G ^{b,c} | MP4/6-311G ^{**b,d} | ZPE ^e |
|-------|--|-----------------|-----------------------|-----------------------------|-----------------------------|------------------|
| 1' | C ₂ H ₅ NH ₂ | C ₁ | -134.247 69 | -134.687 92 | -134.841 27 | 236 |
| 1 | [C ₂ H ₅ NH ₃] ⁺ | C _s | -134.616 52 | -135.054 33 | -135.209 07 | 274 |
| 2 | [C ₂ H ₄ ...NH ₄] ⁺ | C _s | -134.578 84 | -135.017 67 | -135.175 53 | 261 |
| 3 | [C ₂ H ₅ ...NH ₃] ⁺ | C ₁ | -134.524 10 | -134.948 80 | -135.110 18 | 248 |
| 1/2 | TS 1→2 | C _s | -134.523 48 | -134.950 92 | -135.111 21 | 247 |
| 1/3 | TS 1→3 | C _s | -134.522 882 | -134.944 749 | -135.106 322 | 247 |
| 2/2 | TS 2→2 | C _{2v} | -134.573 56 | -135.011 23 | -135.170 550 | 258 |
| 3/3-a | TS 3→3 | C _s | -134.523 12 | -134.940 74 | -135.101 01 | 247 |
| 3/3-b | TS 3→3 | C _s | -134.523 30 | -134.940 30 | -135.101 94 | 247 |
| 5 | C ₂ H ₄ ⁺ [NH ₄] ⁺ | | -134.562 49 | -134.997 87 | -135.158 19 | 256 |
| 6 | [C ₂ H ₅] ⁺ +NH ₃ | | -134.494 30 | -134.918 83 | -135.081 43 | 241 |
| | C ₂ H ₄ | D _{2h} | -78.031 72 | -78.294 29 | -78.382 39 | 130 |
| | [C ₂ H ₅] ⁺ | C _{2v} | -78.309 94 | -78.561 45 | -78.653 39 | 154 |
| | NH ₃ | C _{3v} | -56.184 36 | -56.357 38 | -56.428 04 | 87 |
| | [NH ₄] ⁺ | T _d | -56.530 77 | -56.703 58 | -56.775 80 | 126 |

^a Based on HF/6-31G* geometries. ^b Based on MP2/6-31G* geometries. ^c Full sets of molecular orbitals are used. ^d Core orbitals are frozen. ^e At the HF/6-31G* level and scaled by 0.9 to account for systematic overestimation.

TABLE 3: Calculated Relative Energies (kJ/mol) for the Stationary Points Considered^a

| no. | structure | HF/ 6-31G* | MP2/ 6-31G* | MP4/ 6-311G** | MP4+ZPE ^b |
|-------|--|---------------|----------------|------------------|----------------------|
| 1' | C ₂ H ₅ NH ₂ | -968 | -962 | -965 | -927 |
| 1 | [C ₂ H ₅ NH ₃] ⁺ | 0 | 0 | 0 | 0 |
| 2 | [C ₂ H ₄ ...NH ₄] ⁺ | 99 | 96 | 88 | 75 |
| 3 | [C ₂ H ₅ ...NH ₃] ⁺ | 243 | 298 | 260 | 234 |
| 1/2 | TS 1→2 | 244 | 271 | 257 | 230 |
| 1/3 | TS 1→3 | 246 | 288 | 270 | 243 |
| 2/2 | TS 2→2 | 112 | 113 | 101 | 85 |
| 3/3-a | TS 3→3 | 246 | 298 | 284 | 257 |
| 3/3-b | TS 3→3 | 245 | 299 | 281 | 254 |
| 5 | C ₂ H ₄ ⁺ [NH ₄] ⁺ | 142 | 148 | 134 | 116 |
| 6 | [C ₂ H ₅] ⁺ +NH ₃ | 321 | 356 | 335 | 302 |

^a Based on total and zero-point energies from Table 1. ^b Including MP4/6-311G** relative energies and ZPEs.

consider that both estimates are concordant, and a mean isotope effect of 1.4 ± 0.2 appears to be associated with reaction (a). The values of α and β which are simultaneously deduced from the set of equations are $\alpha = 4 \pm 1\%$ and $\beta = 96 \pm 1\%$, thus providing a confirmation that the [NH₄]⁺ formation from metastable ions **1** occurs via a quasi specific β -elimination.

Molecular Orbital Calculations. Geometrical parameters optimized at the MP2/6-31G* level for the equilibrium and transition structures are given in Figure 1. Relevant total and relative energies are summarized in Tables 2 and 3.

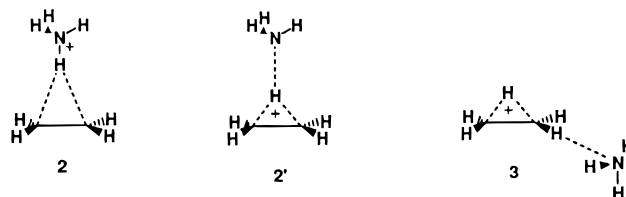
A measure of the accuracy of the computation may be found by comparing the relative energies of **1** and the two sets of products [NH₄]⁺ + C₂H₄, **5**, and NH₃ + [C₂H₅]⁺, **6**. Using the following 298 K heats of formation,⁹ 633, 52, -46, 902, and 574 kJ/mol for [NH₄]⁺, C₂H₄, NH₃, [C₂H₅]⁺, and [CH₃CH₂-NH₃]⁺, respectively, relative enthalpies of 111 and 282 kJ/mol for **5** and **6** with respect to **1** can be calculated. These compare well with the calculated (0 K) values of 116 and 302 kJ/mol (Table 3).

Stable Structures. The most stable conformation of protonated ethylamine (structure **1**, Figure 1) is characterized by the "anti" orientation of one of the N-H bonds with respect to the C-C bond.

Comparison between structures of neutral ethylamine **1'** and its protonated form **1** reveals no spectacular geometrical change upon protonation. We note only a slight lengthening of the C-N bond, pointing to a limited activation of this bond. This is in agreement with the large critical energy for separation of the products NH₃ + [C₂H₅]⁺ (and with the general observation of a limited fragmentation of the [MH]⁺ ions in the proton transfer chemical ionization mass spectrometry of aliphatic amines).

Two ion-neutral complexes [C₂H₄...H⁺...NH₃] are found to correspond to minima on the [C₂H₈N]⁺ potential energy surface. The most stable structure of the two, **2**, is an association between the more stable pair [NH₄]⁺ + C₂H₄, in which one of the four hydrogens of the ammonium ion is in favorable interaction with the π -electron system of the ethene molecule. No stable structure resembling an association between the bridged [C₂H₅]⁺ cation and NH₃, such as **2'**, has been found during our search of stable configurations at both the HF and MP2/6-31G* levels. The stabilization energy of **2** with respect to its components is equal to 41 kJ/mol. Interestingly enough, this energy gain is clearly smaller than that brought by the association of H₃O⁺ with an ethene molecule to give a π -complex [C₂H₄...HOH₂]⁺ similar to **2**. The MP4/6-311G**/MP2/6-31G*+ZPE calculations by Swanton et al.^{6b} indicate an energy difference of 77 kJ/mol between H₃O⁺ + C₂H₄ and the π -complex [C₂H₄...HOH₂]⁺. The better stabilization of the oxygenated complex with respect to the nitrogen one was expected in view of the basicity difference between water and ammonia: PA(H₂O) = 690 kJ/mol, PA(NH₃) = 851 kJ/mol.¹⁰ This is reflected by a larger positive charge on the hydrogen atoms assuming the proton bridge and by a shorter proton bond length in [C₂H₄...HOH₂]⁺ rather than in **2**. This phenomenon is also in keeping with the observation that the stabilization energy of heteroproton-bound dimers [AH...B]⁺ correlates with the difference in proton affinity $\Delta PA = PA(A) - PA(B)$;¹¹ the greater this difference, the smaller the stabilization energy is. In our case, using PA(C₂H₄) = 680 kJ/mol, one calculates ΔPA of 10 and 171 kJ/mol for complexes [C₂H₄...HOH₂]⁺ and **2**, respectively, in clear agreement with the observed stabilization order. We note also that in both cases the structure of the proton-bridged species is such that the proton is covalently bonded to the most basic site.

We indicate above that **2'** is not a stable structure; in fact, [C₂H₅]⁺ and NH₃ may associate to produce the ion-neutral complex **3**, in which the ammonia molecule interacts with one of the peripheral hydrogens of the ethyl cation. This structure is characterized by a stabilization energy of 68 kJ/mol.



Thus, both ion-neutral complexes **2** and **3** may be produced between ethene and ammonia in acidic conditions; however,

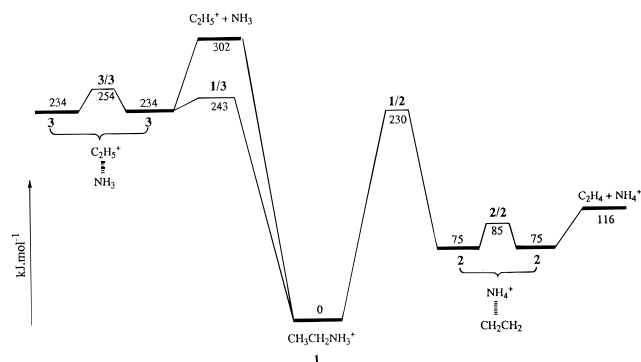


Figure 2. Schematic potential energy profile describing unimolecular reactions of protonated ethylamine, **1**. Energies are calculated at the MP4/6-311G**//MP2/6-31G*+ZPE level of theory.

the large difference in proton affinities between ammonia and ethene favors largely the former structure (**2** is more stable than **3** by 159 kJ/mol) and thrusts aside the possibility of the existence of structure **2'**. The connectivity of complexes **2** and **3** with protonated ethylamine **1** will now be examined.

Channel a: The Ethene Loss. This reaction was found to proceed in two steps. Starting from **1**, the C–N bond lengthening is accompanied by the displacement of the NH₃ group toward the closest H atom of the methyl group. This first step is achieved by the quasi complete abstraction of the hydrogen by the nitrogen atom to produce the complex **2**. This reaction is characterized by the transition structure **1/2**, with an energy barrier of 230 kJ/mol above the most stable form of the protonated ethylamine, **1**. An ion–neutral complex involving an incipient cation bound to the developing ammonia molecule, [R⁺...NH₃], has been proposed to intervene during the formation of NH₄⁺ from protonated amines [RNH₃]⁺.^{3,5a} In fact, our calculation demonstrates that such an [R⁺...NH₃] complex is not a stable species on the [C₂H₇N]⁺ potential energy surface and that it may correspond to the transition structure **1/2**, which looks like an association between NH₃ and a distorted classical ethyl cation.

The formation of the products [NH₄]⁺ + C₂H₄, **5**, implies a simple separation of the two components of the complex **2**, and thus no additional barrier is found in the potential energy curve during this second reaction step. Finally, the possibility of rotation of the ammonium ion inside the complex **2** has been explored. This reaction would render indistinguishable the four hydrogen atoms of the ammonium ion, which eventually participate in a scrambling process. The corresponding transition structure **2/2** has been located, and the calculated critical energy for the rotation **2** ⇌ **2** appears to be equal to 10 kJ/mol.

Figure 2 displays a schematic potential energy profile relevant to these calculations.

Of particular interest is the finding that the transition structure **1/2** is 114 kJ/mol above the fragmentation products and constitutes the rate-determining step of the ethene loss from protonated ethylamine. As long as the dissociation step **2** → [NH₄]⁺ + C₂H₄, **5**, is a simple cleavage with a low critical energy, the ions **2** eventually produced from **1** cannot return back to their original structure; the elementary reaction **1** → **2** is essentially nonreversible. The hydrogen atoms present in the [NH₄]⁺ ions are consequently the three initially attached to the nitrogen atom and one from the original methyl group of **1**. This is in clear agreement with the experimental observation that no hydrogen exchange between the amino and the ethyl moieties occurs before dissociation of metastable ions **1**. Of course the fact that the rotation **2** ⇌ **2** is allowed for those ions **2** coming from **1** is not evidenced by the experiment.

The situation in protonated ethylamine is thus quite different from that in protonated ethanol, [CH₃CH₂OH₂]⁺, in which the [H₃O]⁺ ion formation is accompanied by a total scrambling of the ethyl and hydroxyl hydrogen atoms due to the fact that the transition structure analogous to **1/2** is, in that case, lower in energy than the dissociation products.^{6a,b}

Channel b: The Ammonia Loss. Part of the potential energy profile associated with the loss of ammonia from **1** has been explored by imposing the constraint of a fixed C–N bond length. Starting from the equilibrium value of 1.519 Å, the gradual increase of the C–N bond is accompanied by a closure of one of the H–C–C angles involving a hydrogen atom of the methyl group. The angle value is reduced to about 50° (i.e. its equilibrium value in the ethyl cation) when the C–N distance reaches 3.1 Å (and if the C_s constraint is removed). It consequently appears that the loss of ammonia from **1** is not such a “simple cleavage process”; however, the general shape of its potential energy profile is not greatly affected by the involvement of the 1,2-H assistance. Accordingly, the complete dissociation involves a smooth increase of the potential energy until it reaches the separated products. No reverse critical energy seems to be associated with this reaction.

We also found that, starting from **1** and at the C–N distance close to 3.0 Å, it is easy for the ammonia molecule to turn around the [C₂H₅]⁺ moiety and to allow the isomerization into the complex **3**. Elimination of ammonia can also take place from the latter hydrogen-bridged structure **3**, and MP2(F)/6-31G* optimizations show again that this reaction proceeds without a reverse activation barrier. The transition structure **1/3** has been located at the MP2(F)/6-31G* level, but its potential energy lies only 10 kJ/mol above **3**. This small energy difference is confirmed at the MP4/6-311G**//MP2(F)/6-31G*+ZPE level. At the point **1/3** the potential energy is well below the energy of the products [C₂H₅]⁺ + NH₃, and on this basis, it is not possible to discard the participation of the complex **3** during the ammonia loss.

Hydrogen Scrambling on the Ethyl Moiety inside Complex 3. It has been recalled that the hydrogen scrambling inside the ethyl cation is explained by the passage through its classical form, which represents the transition structure for this process. A critical energy of 30 kJ/mol above the bridged [C₂H₅]⁺ cation has been calculated for this reaction.⁷ In view of the existence of the complex **3** as a stable species we investigated the possibility of occurrence of this scrambling reaction inside this complex. Two transition structures, **3/3-a** and **3/3-b**, have been located. The calculation indicates that both structures lie above **3** by ca. 20 kJ/mol, i.e. that the scrambling reaction possesses a critical energy value slightly less than that calculated for the isolated ethyl cation. Thus, a small but noticeable catalytic effect is exercised by the ammonia molecule on the scrambling process of the ethyl group inside the complex **3**.



Mechanistic Consequences. The experimental observation that metastable ions **1** lead to an ammonium ion containing specifically (96%) one hydrogen atom originally from the β-position of the ethyl group demonstrates that the scrambling of all the hydrogen atoms of the ethyl group is not occurring under this energy regime. This appears to be in agreement with our computational results, which indicate that the isomerization

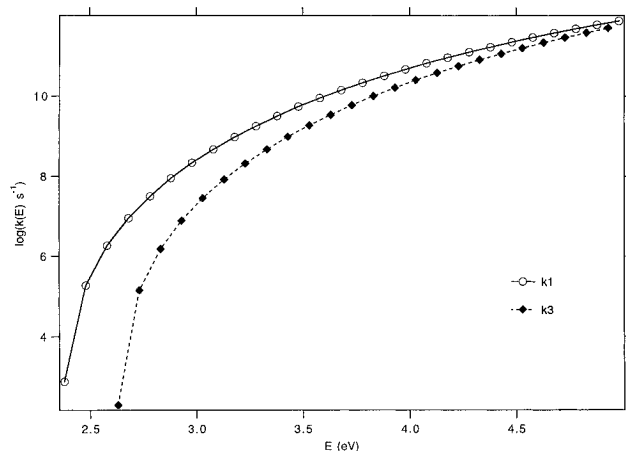


Figure 3. Calculated RRKM rate constants for isomerization and dissociation of protonated ethylamine, **1**.

3 \rightleftharpoons **3** needs more energy than the elimination of ethene via the complex **2**. We should however note that the energy difference between both transition structures TS **3/3** and TS **1/2** (i.e. 24 kJ/mol) is not so important and that it may allow some metastable ions **1** to explore the path **1** \rightarrow **3** \rightleftharpoons **3** before returning back to **1** and then passing irreversibly through the barrier **1/2**. This point may be checked by a simple RRKM treatment. The overall rate constants for (i) the ethene loss from **1**, k_1 , and (ii) the isomerization process **1** \rightarrow **3** \rightleftharpoons **3**, k_3 , can be approximated by

$$k_1 = \sum P_{1/2}^{\ddagger}(E - E_{01})/hN_1(E)$$

$$k_3 = \sum P_{3/3}^{\ddagger}(E - E_{03})/hN_1(E)$$

The sums, $\sum P^{\ddagger}(E - E_0)$, and the densities, $N(E)$, of vibrational states can be evaluated¹² from the HF/6-31G* frequency calculations and using the critical energies $E_{01} = 2.38$ eV and $E_{03} = 2.63$ eV calculated at the MP4SDTQ/6-311G**//MP2/6-31G*+ZPE level. The internal energy dependence of the two corresponding rate constants k_1 and k_3 are displayed in Figure 3.

It appears clearly that the inequality $k_1 > k_3$ holds over the total range of internal energy E examined and particularly in the metastable region (i.e. near $E = 2.5$ eV, where $k_1 = 10^5$ s⁻¹). Hence, most of the ions **1** with internal energy greater than 230 kJ/mol dissociate irreversibly via ethene loss rather than rearrange into **3** and further isomerize by hydrogen scrambling. Furthermore, ions **2** coming from isomerization of **1** via TS **1/2** cannot return back to **1** in view of the large critical energy difference (ca. 110 kJ/mol) between the isomerization **1** \rightarrow **2** and the dissociation **2** \rightarrow [NH₄]⁺ + C₂H₄. Consequently, no mixing of the hydrogen atoms of the protonated amino group with those of the ethyl moiety is expected to occur before dissociation; this conclusion is clearly in agreement with the experimental observations.

One may finally observe that the large energy barrier separating **1** from **2** seems to have little impact on the kinetic energy released during the separation of the [NH₄]⁺ + C₂H₄ fragments. Considering again Figure 3, it appears that metastable ions **1** have about 120 kJ/mol of excess energy above

the fragments. As indicated in the experimental part, only 8.5 kJ/mol of this excess is recovered, on the average, as translational energy. This experimentally determined value may be compared with statistical predictions. The statistical translational energy can be obtained from the simple relationship proposed by Klots.¹³ For a statistically dissociating system at a total energy E_{excess} , the average translational, rotational, and vibrational energies may be expressed in terms of an operational temperature T^* . In this formulation, the average translational energy is simply the term RT^* , and the total energy E_{excess} is given by

$$E_{\text{excess}} = RT^* + (r - 1)RT^*/2 + \sum_{i=1}^{\nu} hv_i/(\exp(hv_i/RT^*) - 1)$$

The parameters r and ν represent the rotational and vibrational degrees of freedom of the products; the ν_i 's are the vibrational frequencies of the reaction products.

By using $E_{\text{excess}} = 120$ kJ/mol for metastable ions **1**, one calculates a term RT^* equal to 11 kJ/mol. This value is comparable to the experimental average kinetic energy release value of 8.5 kJ/mol, thus pointing to a nearly statistical behavior of the dissociating system.

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