with our experimental observations. As to whether charge transfer also places a lower limit on the rate constants remains uncertain. Given that each molecular ion receives an internal energy lying somewhere between the values specified in Table I, then they would all be expected to decompose on a time scale of between 10<sup>-13</sup> and 10<sup>-12</sup> s, and no parent ions should be present. The fact that parent ions are observed means one of two things; either they are stabilized by extensive inert gas evaporation or there is an alternative mechanism, such as direct electron impact, responsible for their formation. If direct electron impact is creating low-energy ions, i.e.,  $E < \epsilon_0$ , then it could equally well produce high-energy ions, some of which might be expected to decompose to  $Ar_n CD_3^+$  or  $Ar_n CH_3^+$ . However, ions such as these are not observed. Also, because of the increased probability of hitting the argon component, direct ionization should lead to a gradual decline in the intensity of parent ions as the cluster size increases. Figures 3-5 show no evidence of such behavior. Further kinetic evidence in support of the charge-transfer mechanism will be presented in a subsequent publication.36

By considering each unimolecular decomposition as a clock, we have been able to obtain a certain degree of time resolution against which we have measured the rate of vibrational relaxation from the molecular ion to the inert gas cluster. Assuming that energy relaxation is accompanyed by argon atom loss from the cluster, we can equate the relaxation times with the time scale for vibration predissociation. The results from our simple model would suggest that the time scale for vibrational predissociation in argon lies in the range  $10^{-12}$ – $10^{-10}$  s. Although this time range compares favorably with the 1-20-ps range for the vibrational relaxation of guest molecules in inert gas solids and liquids, 37-39 it is shorter than the  $10^{-8}$ – $10^{-9}$  s suggested by Jortner et al. from a study of the vibrational relaxation of aromatic molecules in large argon clusters.<sup>40</sup> By studying a number of the cluster reactions, we hope to be able to reduce the uncertainty on the vibrational predissociation time range presented above.

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**Registry No.** Ar, 7440-37-1; CO<sub>2</sub>, 124-38-9; (CD<sub>3</sub>)<sub>2</sub>CO<sup>+</sup>, 666-52-4; (CH<sub>3</sub>)<sub>2</sub>CO<sup>+</sup>, 34484-11-2; CD<sub>3</sub><sup>+</sup>, 17030-72-7; CH<sub>3</sub><sup>+</sup>, 14531-53-4; CD<sub>3</sub>CO<sup>+</sup>, 20063-14-3; CH<sub>3</sub>CO<sup>+</sup>, 15762-07-9; (CH<sub>3</sub>)<sub>2</sub>CO, 67-64-1; (C-D<sub>3</sub>)<sub>2</sub>CO, 666-52-4.

# Mechanistic Information from Infrared Multiple Photon Decomposition. The Ethylisopropylamine Proton-Transfer System

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Abstract: Infrared multiple photon decomposition of ethylisopropylammonium ion, the putative intermediate of two different gas-phase proton-transfer reactions, has been carried out. The product distributions for both proton-transfer reactions have been determined. These have been compared with the photochemical results as well as with the high-pressure product distribution for the reaction of isopropyl cation with ethylamine. We conclude that proton transfers from carbonium ions to amines do not follow addition-elimination mechanisms even if such pathways are available. The role of the addition product in the reaction dynamics is clarified.

Determining which of several available pathways a chemical reaction follows is an inherently interesting problem in chemistry. This is just as true for gas-phase reactions as it is for solution-phase ones, although the number of different possible mechanisms for ionic reactions in the gas phase is smaller because of the absence of solvent participation. In some cases, competition can arise between multiple unimolecular reactions of a single intermediate; the outcomes of such competitions determine reaction mechanisms. Photochemical activation of putative intermediates yields product distributions that can provide information sufficient to rule out certain possible mechanisms.

There has been continuing interest in the mechanism of proton transfers from alkyl carbonium ions to alkyl amines (eq 1). This

$$R^{+} + R'NH_{2} \rightarrow (R-H) + R'NH_{3}^{+}$$
(1)

interest stems from the interesting proposal by Bowers and coworkers that these reactions may occur via addition-elimination mechanisms rather than direct mechanisms featuring hydrogenbound complexes, which are normally the only pathways available.

Su and Bowers<sup>1</sup> measured the rates of reaction 1 for several alkyl groups R. They found that the reactions were unit efficient for  $C_1-C_3$  cations, but were as low as 60% efficient with the tert-butyl cation as the reactant. A subsequent study<sup>2</sup> using several different neutral species as  $C_4H_9^+$  sources produced efficiences for proton transfer to ammonia ranging from 50 to 80%. The lower limit of this range agreed with an earlier measurement of the tert-butyl cation/ammonia reaction rate.<sup>3</sup> The authors proposed that tertiary carbonium ions follow a mechanism different from that of the other cations, namely, addition to form a complex RR'NH<sub>2</sub><sup>+</sup> and subsequent four-center elimination to yield products. Slow proton transfers from  $C_5H_{11}^+$  formed from *n*-pentyl chloride were attributed to isomerization of the carbonium ion before reaction, yielding the tertiary species. Modeling studies

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<sup>(1)</sup> Su, T.; Bowers, M. T. Int. J. Mass Spectrom. Ion Phys. 1973, 12, 347-356.

<sup>(2)</sup> Su, T.; Bowers, M. T. J. Am. Chem. Soc. 1973, 95, 7611-7613.

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Scheme I

$$R^{+} + R'NH_{2} \xleftarrow{k_{1}}_{k_{-1}}$$

$$R^{+} \cdots R'NH_{2} \xleftarrow{(R-H) + R'NH_{3}^{+}}_{k_{4}}$$

$$R^{+} \cdots R'NH_{2} \xleftarrow{k_{3}}_{RR'NH_{2}^{+}} \xleftarrow{k_{5}[M]} RR'NH_{2}^{-}$$

$$(Y)$$

for the *tert*-butyl cation-ammonia reaction were undertaken.<sup>4</sup> with the uncomfortable conclusion that the elimination step had to be modeled as proceeding through a loose transition state, despite the well-known tendency of such reactions to exhibit small A factors.5

Meot-Ner studied several (eq 1)-type proton transfers<sup>6</sup> at high pressures (above 1 torr) where one would expect addition products to be collisionally stabilized in competition with the elimination step that yields proton-transfer products. Meot-Ner did in fact observe condensation products as minor competitors to all the proton-transfer products. Basicity bracketing experiments on the addition products confirmed that these side products were the  $\sigma$ -bonded species RR'NH<sub>2</sub><sup>+</sup>. These observations did not, of course, prove that the dialkyl ammonium ions are intermediates in proton-transfer reactions.

In order to shed some light on this question, Meot-Ner measured the product ratio for reaction 2. The addition product for this

$$i-C_3H_7^+ + C_2H_5NH_2 \rightarrow \text{products}$$
 (2)

reaction is the ethylisopropylammonium ion (1), which has two elimination pathways available. The first, reaction 3, yields

$$i - C_3 H_7 N^+ H_2 C_2 H_5 \rightarrow C_3 H_6 + C_2 H_5 N H_3^+$$
 (3)

proton-transfer products. The second, reaction 4, yields

$$1 \to C_2 H_4 + i - C_3 H_7 N H_3^+$$
 (4)

"displacement-exchange" (addition-elimination) products which are more stable<sup>7</sup> than the proton-transfer products by 4 kcal/mol. Meot-Ner reasoned that the isopropylammonium ion should be formed in greater abundance than ethylammonium ion, because the A factors for the two eliminations are expected to be equal. Given similar A factors, the lower threshold energy process should dominate. Nevertheless, only ethylammonium ion was observed. Furthermore, neither the temperature dependence nor the pressure dependence of reaction 2 was consistent with direct formation of ethylisopropylammonium ion from reactants.

Meot-Ner therefore proposed the reaction mechanism shown in Scheme I. Both proton transfer and addition proceed out of intermediate X; the chemically activated addition product Y undergoes direct elimination to yield proton-transfer products in competition with collisional stabilization. The intermediate X was presumed to be an ion-molecule complex between the isopropyl cation and ethylamine, although a hydrogen-bound species was also mentioned as a possibility. This mechanism was shown to be consistent with the observed pressure and temperature effects on the addition/proton transfer branching ratio.

Cacace and co-workers<sup>8</sup> investigated the tert-butyl cation-ammonia system at very high pressures (1 atm), forming the carbonium ion from neopentane radiolytically. The observed ratio of addition products to proton-transfer products was almost identical with Meot-Ner's results at 1 torr, ruling out the addition-elimination mechanism for that system as well. Clearly, the two sets of products do not arise from a competition between fragmentation and collisional stabilization of vibrationally hot tert-butylammonium ion.

Although the results of the latter two investigations seem reasonable, the assertion<sup>6</sup> that reactions 3 and 4 are single-step elimination reactions is inconsistent with evidence<sup>9</sup> that such eliminations do not occur easily in the gas phase. Indeed, based on neutral product analyses<sup>10</sup> and RRKM calculations,<sup>11</sup> Morton has concluded that proton transfer from the methylcyclopentyl cation to triethylamine cannot follow an addition-elimination mechanism. Moreover, the assertion can be tested by forming ion 1, trapping it, and photolyzing it with a high-power infrared laser. We have therefore performed photochemical experiments on presumed intermediate 1 as well as observing the product distributions in both the reaction between the isopropyl cation and ethylamine and the cross-reaction between the ethyl cation and isopropylamine, in order to test the assumed decomposition branching ratio for ion 1 and to clarify the ion's role in the proton-transfer reaction mechanism.

### **Experimental Section**

Experiments were performed with a pulsed ion cyclotron resonance spectrometer, modified for infrared photochemical experiments as described previously.<sup>12</sup> The marginal oscillator detector used in previous studies was replaced by a capacitance bridge detection system<sup>13</sup> that allows mass scans to be taken at constant magnetic field.

All reactant ions were prepared by chemical ionization, as follows:

$$CH_4 + e^- \rightarrow CH_4^+ + 2e^-$$
 (5)

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3^-$$
 (6)

$$\mathrm{CH}_{5}^{+} + \mathrm{B} \to \mathrm{BH}^{+} + \mathrm{CH}_{4} \tag{7}$$

Reactions 5-7 went to completion in less than 100 ms at the pressures employed in these experiments (about 10<sup>-6</sup> torr).

Photochemical experiments were carried out as previously described,<sup>12</sup> using a Lumonics 103-2 TEA CO<sub>2</sub> laser beam collimated in the ICR cell with a gradually focusing (f = 5 m) external mirror. Photolysis product distributions were determined in two ways. First, since each possible product ion is acidic enough to protonate ethylisopropylamine, ammonium ion 1 would be regenerated after the laser pulse. Double resonance ejection of each product ion formed should prevent part of the signal recovery of 1; this part equals the branching fraction for that particular product ion. Second, mass scans of the possible product ions were taken shortly after the laser pulse, before reaction with ethylisopropylamine was complete.

### Results

 $C_2H_5(i-C_3H_7)NH_2^+$ . The ethylisopropylammonium ion was prepared by reaction 7 and photolyzed after all  $CH_5^+$  had reacted. Despite the exothermicity of the chemical ionization reaction (97 kcal/mol), which suggests that the ions possessed a significant degree of thermal excitation, a maximum of only 25% of the ions decomposed with the most resonant line of the laser—P(18), 9.6  $\mu$ m. Optical pumping is apparently slow, even in the quasicontinuum. This observation is consistent with separate photochemical experiments on the tert-butylamm mium ion, which did not decompose using any line of the  $CO_2$  laser.

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Figure 1. Intensity vs. time scan (1 s) of  $C_2H_5(i-C_3H_7)NH_2^+$ : (a) no laser; (b) laser fired at 450 ms; (c) laser at 450 ms, double resonance ejection of  $C_3H_7NH_3^+$ ; (d) laser at 450 ms, double resonance ejection of  $C_2H_5NH_3^+$ . Pressure was  $2.1 \times 10^{-6}$  torr.



Figure 2. Intensity vs. time scans (800 ms) of a 15:7:3 mixture of methane, propylene, and ethylamine for  $C_3H_7^+$ ,  $C_2H_5NH_3^+$ ,  $i-C_3H_7NH_3^+$ ,  $C_2H_5(i-C_3H_7)NH_2^+$ . Pressure was  $4.9 \times 10^{-6}$  torr.

The identification of the products of the multiple photon decomposition was first determined by the signal recovery-double resonance method. All possible product ions are acidic enough to protonate ethylisopropylamine, and would therefore cause the signal of ion 1 to recover. This indeed proved to be the case (Figure 1). Double resonance ejection of the most stable product ion, the isopropylammonium ion, did not prevent the signal recovery. Ejection of the ethylammonium ion, however, completely eliininated the recovery. Results of mass scans taken shortly after the laser pulse confirm the signal recovery results; they show that ethylammonium ion was the only product of the photolysis. Thus, only one of the possible sets of products was formed by infrared multiple photon decomposition: ethylammonium ion plus propylene (only the ionic product was detected). Isopropylammonium ion plus ethylene, the set of products 4 kcal/mol more stable, was not formed at all. Neither were the higher energy products containing alkyl carbonium ions formed, although this is not surprising considering the slow photon absorption that appears to have taken place.

 $i-C_3H_7^+ + C_2H_5NH_2$ . Reaction 2 was studied under ICR conditions for comparison with Meot-Ner's high-pressure results. The isopropyl cation was formed by chemical ionization of propylene; the internal energy of the ions was undoubtedly higher than in the earlier study.<sup>6</sup> The reaction sequence is complicated by the possibility that reaction 8 occurs in competition with reaction 7:

$$CH_5^+ + C_2H_5NH_2 \rightarrow C_2H_5NH_3^+ + CH_4$$
 (8)

Reaction 8 with ethylamine is 35 kcal/mol more exothermic than the corresponding protonation of propylene. In order to minimize the effect of this side reaction, partial pressures of propylene were adjusted so that they were about three times the partial pressure of the amine. The observed rate of protonation of ethylamine was thus significantly smaller than the rate of formation of isopropyl cation. In addition, product distributions were checked by double resonance experiments. Ejection of  $CH_5^+$  throughout the duty cycle produced only a slightly greater signal decrease than ejection of the isopropyl cation; since  $i-C_3H_7^+$  is produced from  $CH_5^+$ , the difference between the two signal decreases corresponded to the relative contribution of reaction 8 to the product yield. The size of the product signal is therefore a good estimate of the amount of ethylammonium ion formed by reaction 2.

The major product of the reaction was ethylammonium ion; it represented 50% of the yield on average, compared with 80% measured by high-pressure mass spectrometry.<sup>6</sup> Isopropylammonium ion, which was not seen by Meot-Ner, represented 36% of the products. The quaternary ammonium ion, 1, appeared as a product as well, despite the significantly lower collision frequency in the ICR. It represented a somewhat smaller fraction of the product yield (14%) than it did at 0.3 torr (20%). A time scan of the various concentrations of ions in the cell is shown in Figure 2. The ethylammonium ion signal rises much more slowly than does the isopropyl cation signal; only small corrections for reaction 8 needed to be made.

 $C_2H_5^+ + i-C_3H_7NH_2$ . The cross reaction (reaction 9), which Meot-Ner did not examine, was also studied. The ethyl cation

$$C_2H_5^+ + i - C_3H_7NH_2 \rightarrow \text{products}$$
(9)

was formed by chemical ionization from ethylene; the reactants were thus even hotter than the reactants of reaction 2. This time, no ion 1 was seen; an average of 82% of the product was the direct proton-transfer product, isopropylammonium ion, and 18% was the addition-elimination product, ethylammonium ion. These product yields were determined by double resonance ejection of

Table I. Product Distributions of Thermal and Photochemical Reactions

| reactant(s)                         | products                            | ∆H° | fraction<br>of product<br>yield (%) <sup>a</sup> |
|-------------------------------------|-------------------------------------|-----|--|
| $i-C_{3}H_{7}^{+}+C_{2}H_{5}NH_{2}$ | $C_{3}H_{6} + C_{2}H_{5}NH_{3}^{+}$ | -35 | 50 (80)  |
|                                     | $C_2H_4 + i - C_3H_7NH_3^+$         | -39 | 36 (0)   |
|                                     | $C_2H_5(i-C_3H_7)NH_2^+$            | -65 | 14 (20)  |
| $C_2H_5^+ + i - C_3H_7NH_2$         | $C_{3}H_{6} + C_{2}H_{5}NH_{3}^{+}$ | -55 | 18   |
|                                     | $C_2H_4 + i - C_3H_7NH_3^+$         | -59 | 82   |
|                                     | $C_2H_5(i-C_3H_7)NH_2^+$            | -85 | 0  |
| $C_2H_5(i-C_3H_7)NH_2^+ + nhv$      | $C_2H_5^+ + i - C_3H_7NH_2$         | +85 | 0  |
|                                     | $i-C_{3}H_{7}^{+}+C_{2}H_{5}NH_{2}$ | +65 | 0  |
|                                     | $C_{3}H_{6} + C_{2}H_{5}NH_{3}^{+}$ | +30 | 100  |
|                                     | $C_2H_4 + i - C_3H_7NH_3^+$         | +26 | 0  |

<sup>a</sup> Values in parentheses are high-pressure data from ref 6.

the ethyl cation, because chemical ionization of the amine by CH<sub>5</sub><sup>+</sup> was a much more important pathway in these experiments than in the studies of reaction 2.

The results of all three experiments are listed in Table I. Several conclusions may be drawn from these results in comparison with Meot-Ner's; the earlier work is also listed in the table.

#### Discussion

First, it is clear that the addition product 1 is formed from reactants in both reaction 2 and 9. It need not be formed directly, but it always is formed. It is either detected directly or shown to have been formed by detection of its decomposition products (reaction 9). The mechanism of its decomposition must therefore be understood before the proton-transfer mechanism can be clarified.

Most IR photolyses produce only one set of products, because decomposition rates exceed photochemical pumping rates at energies just above the lowest decomposition threshold. This means that when only one set of products is observed, these products undoubtedly result from the lowest threshold energy process. The observed products do not necessarily represent the specific species formed in that initial process, but they must at least be products of some reaction sequence that starts with the lowest activation energy step. The lowest activation energy decomposition channel of 1 ultimately yields the ethylammonium ion. Meot-Ner's assumption that ion 1 would decompose to yield primarily the isopropylammonium ion is therefore incorrect. Ion 1 does not decompose by direct elimination.

If ion 1 does not decompose by elimination, how does it decompose? We propose that the lowest threshold energy process is fragmentation to a complex between the isopropyl cation and ethylamine. The internal energy is insufficient for the ionmolecule complex to fall apart immediately, so proton transfer within the complex occurs, yielding the observed products. Although ion 1 could also conceivably fragment to form a complex between the ethyl cation and isopropylamine, this complex would be significantly higher in energy. The alternate pathway would be competitive only at internal energies well above the second threshold. Since the separated carbonium ion/amine pairs differ in stability by 20 kcal/mol, and since their complexes would be expected to show similar relative stabilities, photochemical formation of only one set of products is not surprising.

Literature precedent for the two-step decomposition mechanism is extensive. Dialkyl oxonium ions<sup>14-16</sup> and parent ions of alkyl phenyl ethers<sup>17,18</sup> are thought to decompose to elimination products Moylan and Brauman

$$R^{+} + R'NH_{2} \xleftarrow{k_{1}}_{k_{-1}}$$

$$R^{+} \cdots R'NH_{2} \xleftarrow{(R-H) + R'NH_{3}^{+}}_{(X)}$$

$$R^{+} \cdots R'NH_{2} \xrightarrow{k_{3}}_{R-3} RR'NH_{2}^{+} * \xleftarrow{k_{4}[M]}{RR'NH_{2}^{+}} RR'NH_{2}^{+}$$

$$(Y)$$

Scheme II

via cleavage to ion-molecule complexes followed by proton transfer within the complexes. An analogous mechanism has been proposed for the decomposition of immonium ions,<sup>19</sup> which lie on potential surfaces for proton transfers between carbonium ions and imines. Alkoxide ions decompose to give ketone-anion complexes which undergo proton transfer within the complex prior to dissociation.9a,b Parent ions of diamino steroids decompose to products resulting from proton transfer within ion-molecule complexes; the only alternative mechanism is hydrogen transfer across the entire steroid ring system before fragmentation.<sup>20-22</sup> The role of such ionmolecule complexes in both unimolecular and bimolecular reactions has been reviewed by Morton.23

Data on neutral systems analogous to ion 1 also suggest that single-step elimination is highly unfavorable. One example is the unimolecular decomposition of methylbenzylamine. This disubstituted amine does not eliminate either methane or toluene, but fragments to yield benzyl radicals.24

Given the substantial evidence against direct four-center elimination from positive ions, the possibility that ion 1 is an intermediate in reactions 2 and 9 is reopened, because the observed product distributions no longer rule it out. The unfavorability of the elimination step, however, suggests that these reactions would be extremely slow if forced to follow an addition-elimination mechanism, contrary to observations.<sup>6</sup> Furthermore, the postulated existence of hydrogen-bonded species which could act as intermediates suggests that a preferable alternate pathway exists. The pressure dependence of the product distribution for reaction 2 (taken from a comparison of our data with Meot-Ner's) provides the most compelling evidence that the products do not result from competitive decomposition and collisional stabilization of an ammonium ion. We therefore propose the mechanism shown in Scheme II to explain the results. This mechanism contains the essential aspect of Meot-Ner's proposal that proton transfer competes with ammonium ion formation. It is consistent with the observed pressure dependence of the product branching ratio, as shown below.

The branching ratio for addition vs. proton transfer as a function of [M] is given by:

$$\frac{[\text{RR'NH}_2^+]}{[\text{R'NH}_3^+]} = \frac{k_3 k_4 [\text{M}]}{k_2 (k_{-3} + k_4 [\text{M}])}$$
(10)

At high pressure, this expression is approximately equal to  $k_3/k_2$ , independent of pressure as observed. At low pressure, it is equal to  $k_3k_4[M]/k_2k_{-3}$ , linearly dependent upon pressure and also consistent with observations. If 1 were the only (single) intermediate, it would be the sole reaction product at high pressure.

The differences between the high- and low-pressure product distributions for the reaction of isopropyl cation with ethylamine

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**Figure 3.** Proposed (three-dimensional) potential surface for the  $C_5H_{14}N^+$  system. Solid curves are reaction coordinates for proton transfer. Dotted curves are possible reaction coordinates for decomposition of  $C_2H_5(i-C_3H_7)NH_2^+$ . Unless highly energized, the ion decomposes only via the left-hand path.

are consistent with the dialkyl ammonium ion decomposing as described above. At high pressure, any ion 1 formed is collisionally stabilized below the threshold for cleavage to the ethyl cation complex. Any decomposition that occurs goes through the more stable complex to yield ethylammonium ion. At low pressure, the internal energy of the dialkyl ammonium ion is high enough so that both sets of products are observed. The only surprising aspect of the low-pressure product distributions is that any ion 1 is observed at all; three-body-stabilized species are usually not detected in ICR experiments. Because the stability of 1 is so great, however, the density of quantum states of the ion at these energies is high enough so that the lifetime for decomposition is of the same order as the reciprocal of the collision frequency (about 1 ms).

At the higher energies produced in the ethyl cation/isopropylamine reaction, the lifetime for decomposition of 1 would be shorter, while the collisional lifetime would be unchanged. It is entirely reasonable that collisional stabilization cannot compete with unimolecular decomposition at these energies, as observed. Both of these assertions are consistent with quantum RRK estimates.<sup>25</sup>

A potential-energy diagram consistent with all observations appears in Figure 3. Both proton-transfer reactions follow standard double-well surfaces. The ethylisopropylammonium ion (1) also lies on the  $C_5H_{14}N^+$  hypersurface, but it is not the primary intermediate in either proton-transfer reaction. Capture collisions between carbonium ions and amines produce loose, hydrogenbonded complexes (see below), which can rearrange to form ion 1 or react to yield proton-transfer products. Those dialkyl ammonium ions that are formed can either be collisionally stabilized or decompose (preferentially via the isopropyl cation/ethylamine complex).

Bowers' original mechanistic proposal was based in part upon the very reasonable hypothesis that a carbonium ion and an amine would be likely to form an alkyl ammonium ion as the direct result of a collision, with no barrier. Apparently, this is not the case. The question then arises as to the structure of the collision complex that is formed: is it an unstructured ion-molecule complex with free internal rotations, or is it a hydrogen-bonded species?

The existence of carbonium ion/amine complexes as protontransfer intermediates implies that the reactions follow doubleminimum potential surfaces, because the intermediates of single-well reactions would tend to resemble the ammonium ion/ alkene products. Proton transfer therefore involves some kind of barrier, although these reactions are so exothermic that they are still unit efficient. The observation that direct proton transfer, despite its small potential barrier, always competes favorably with collapse to the very stable ion 1 suggests that the complex is hydrogen bonded. If it were unstructured, there would be no barrier to formation of ion 1 and proton transfer would be the minor pathway. Rearrangement of a hydrogen-bonded species to form the dialkyl ammonium ion involves breaking one bond and forming another; it is quite reasonable to propose that this process is slow enough so that proton transfer can compete with it. (Hypothetical effective barriers for the collapse of proton-bound intermediates to ion 1 are shown in Figure 3 for the purpose of illustration.) If the carbonium ion is bridged in structure, the rearrangement will be more extensive and in addition might be expected to have a larger barrier. Calculations indicate that the ethyl cation is bridged but that the isopropyl cation is not;<sup>26</sup> proton transfer should therefore be favored over addition more for reaction of ethyl cation (eq 9) than for reaction of isopropyl cation (eq 2), as observed.

#### Conclusions

We have shown that mechanistic information can be deduced for ion-molecule reactions by taking advantage of the capability to energize possible intermediates past dissociation thresholds. The results provide confirming evidence for the view that gas-phase proton-transfer reactions generally proceed through hydrogenbonded intermediates, even when alternate pathways are available. They also imply that alkyl ammonium ions follow the same decomposition mechanism as the other positive ions mentioned above: rearrangement to ion-molecule complexes followed by proton transfer, rather than single-step eliminations.

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**Registry No.**  $i-C_3H_7^+$ , 19252-53-0;  $C_2H_5NH_2$ , 75-04-7;  $C_2H_5^+$ , 14936-94-8;  $i-C_3H_7NH_2$ , 75-31-0;  $C_2H_5(i-C_3H_7)NH_2^+$ , 94041-96-0.

<sup>(25)</sup> Robinson, P. J.; Holbrook, K. A. "Unimolecular Reactions"; Wiley-Interscience: New York, 1972.

<sup>(26)</sup> Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. J. Am. Chem. Soc. 1981, 103, 5649-5657.