

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  $10^{-13}$  and  $10^{-12}$  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  $\text{Ar}_n\cdot\text{CD}_3^+$  or  $\text{Ar}_n\cdot\text{CH}_3^+$ . 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.<sup>36</sup>

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

(36) Stace, A. J., unpublished results.

from the molecular ion to the inert gas cluster. Assuming that energy relaxation is accompanied 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,<sup>37-39</sup> 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.

**Acknowledgment.** I thank the SERC for financial support.

**Registry No.** Ar, 7440-37-1;  $\text{CO}_2$ , 124-38-9;  $(\text{CD}_3)_2\text{CO}^+$ , 666-52-4;  $(\text{CH}_3)_2\text{CO}^+$ , 34484-11-2;  $\text{CD}_3^+$ , 17030-72-7;  $\text{CH}_3^+$ , 14531-53-4;  $\text{CD}_3\text{CO}^+$ , 20063-14-3;  $\text{CH}_3\text{CO}^+$ , 15762-07-9;  $(\text{CH}_3)_2\text{CO}$ , 67-64-1;  $(\text{C-D}_3)_2\text{CO}$ , 666-52-4.

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

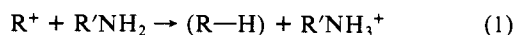
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**Abstract:** Infrared multiple photon decomposition of ethylisopropylammonium ion, the putative intermediate of two different gas-phase proton-transfer reactions, has been carried out. The product distributions for both proton-transfer reactions have 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



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

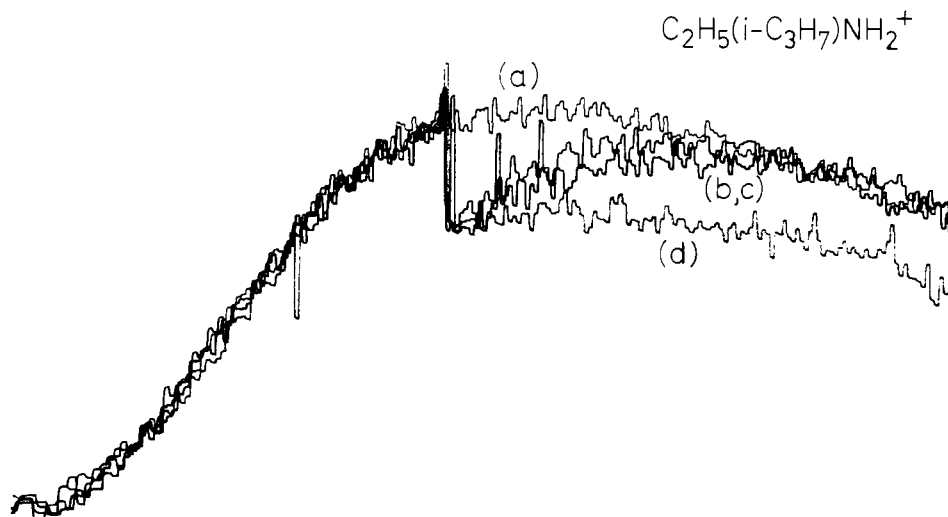
Su and Bowers<sup>1</sup> measured the rates of reaction 1 for several alkyl groups R. They found that the reactions were unit efficient for  $\text{C}_1$ - $\text{C}_3$  cations, but were as low as 60% efficient with the *tert*-butyl cation as the reactant. A subsequent study<sup>2</sup> using several different neutral species as  $\text{C}_4\text{H}_9^+$  sources produced efficiencies 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  $\text{RR}'\text{NH}_2^+$  and subsequent four-center elimination to yield products. Slow proton transfers from  $\text{C}_5\text{H}_{11}^+$  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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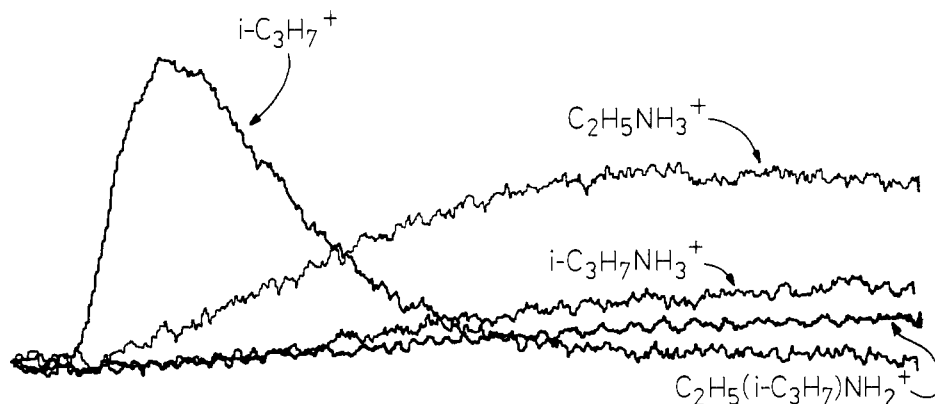
(2) Su, T.; Bowers, M. T. *J. Am. Chem. Soc.* **1973**, *95*, 7611-7613.

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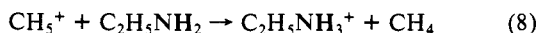
**Figure 1.** Intensity vs. time scan (1 s) of  $C_2H_5(i-C_3H_7)NH_2^+$ : (a) no laser; (b) laser fired at 450 ms; (c) laser at 450 ms, double resonance ejection of  $C_3H_7NH_3^+$ ; (d) laser at 450 ms, double resonance ejection of  $C_2H_5NH_3^+$ . Pressure was  $2.1 \times 10^{-6}$  torr.



**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 eliminated 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:

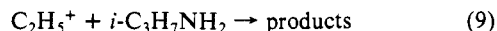


Reaction 8 with ethylamine is 35 kcal/mol more exothermic than the corresponding protonation of propylene. In order to minimize the effect of this side reaction, partial pressures of propylene were adjusted so that they were about three times the partial pressure

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.

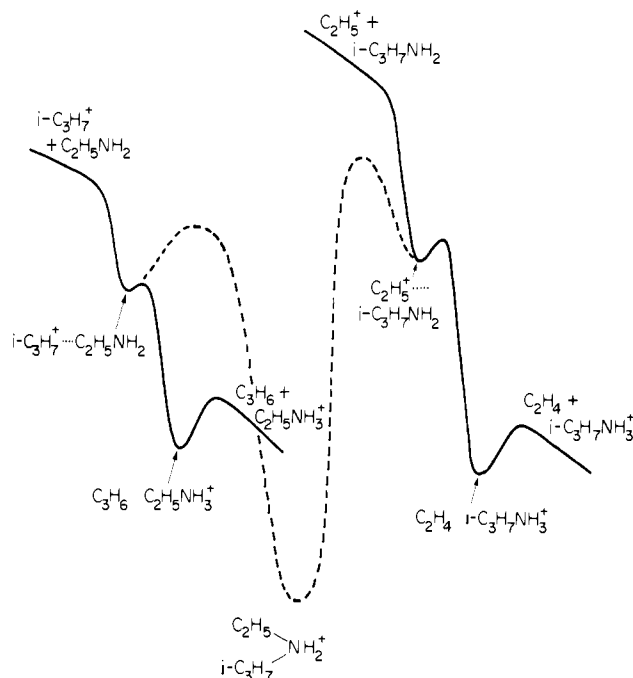
The major product of the reaction was ethylammonium ion; it represented 50% of the yield on average, compared with 80% measured by high-pressure mass spectrometry.<sup>6</sup> Isopropylammonium ion, which was not seen by Meot-Ner, represented 36% of the products. The quaternary ammonium ion, **1**, appeared 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



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





**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, hydrogen-bonded 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 proton-transfer intermediates implies that the reactions follow double-minimum 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 hydrogen-bonded 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.

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