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# On the Mechanism of the Reactions of Alkyl Ions with Alkylamines: Competing Proton Transfer and Condensation Reactions

**P. Ausloos and Sharon G. Lias***

*Contribution from the Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899.* *Received June 24, 1985*

**Abstract:** The reactions of ethyl, isopropyl, and *tert*-butyl ions with alkylamines have been examined in an ion cyclotron resonance spectrometer (ICR). Use of deuterium-labeled reactant ions permitted a detailed examination of the relative probabilities of the two competing reaction channels demonstrated previously by Meot-Ner. These are deuteron transfer

$$C_nD_{2n+1}^+ + C_mH_{2m+1}NH_2 \rightarrow C_mH_{2m+1}NH_2D^+ + C_nH_{2n} \quad \text{(a)}$$

and condensation

$$C_nD_{2n+1}^+ + C_mH_{2m+1}NH_2 \rightarrow [(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \quad \text{(b)}$$

At the low pressures of an ICR experiment ($\sim 10^{-6}$ torr), the condensation ions all dissociate through one of two paths

$$[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow C_nD_{2n+1}NH_3^+ + C_mH_{2m} \quad (b_1)$$

and

$$[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow C_mH_{2m+1}NH_2D^+ + C_nD_{2n} \quad (b_2)$$

where ($b_2$) yields products identical with those formed in the direct deuteron transfer, (a). Even though for all reaction pairs both ($b_1$) and ($b_2$) are energetically allowed, the weaker C–N bond in the condensation ion predominantly undergoes scission to give a complex containing an alkyl ion ($C_nD_{2n+1}^+$ or $C_mH_{2m+1}^+$, whichever is energetically favored) and the corresponding amine, as suggested by Moylan and Brauman. This bond cleavage in the condensation ion is followed by proton transfer *in the complex* to yield the final products. The branching ratio (b)/(a), derived from the relative abundances of the $C_nD_{2n+1}NH_3^+$ and $C_mH_{2m+1}NH_2D^+$ products, is greatest for reactions of the ethyl ion and smallest for reactions of the *tert*-butyl ion. A comparison of these results with those obtained in the high-pressure mass spectrometric study of Meot-Ner demonstrates that the branching ratios for alkyl ion–amine reactant pairs are invariant with pressure from $10^{-6}$ to 1 torr. A mechanism involving two independent transition states is proposed to account for this pressure-invariant branching ratio. The study of these systems is complicated by the occurrence of secondary reactions and, in some cases, by the presence of impurities commonly found in commercial amine samples. The uses of deuterium labeling and carefully chosen experimental conditions to circumvent the difficulties are described.

It was reported some time ago[1] that certain ion–molecule reaction pairs undergo two competing reaction channels, proton transfer and condensation, e.g.[1b]

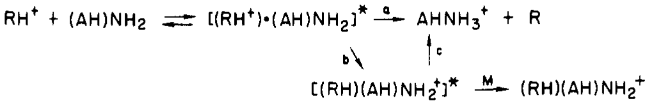
$$i\text{-}C_4H_8^+ + i\text{-}C_4H_8 \rightarrow C_4H_9^+ + C_4H_7 \quad (1)$$

$$i\text{-}C_4H_8^+ + C_4H_8 \rightarrow C_8H_{16}^+ \quad (2)$$

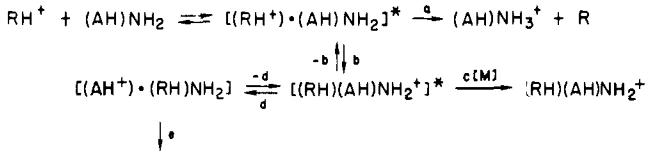
In mass spectrometric studies,[1] the relative probabilities of occurrence of these competitive channels are found to be constant over a wide pressure range; the fact, even at atmospheric pressures in radiolytic systems,[2] evidence for the occurrence of two independent channels has been obtained.

In a detailed high-pressure mass spectrometric study of factors governing competing reaction paths in reactions between alkyl ion and alkylamines, Meot-Ner[3] proposed Scheme I (where (RH) and (AH) are alkyl groups, $[(RH^+)\cdot(AH)NH_2]^*$ is a loose electrostatically bonded complex and $[(RH)(AH)NH_2^+]^*$ is a tight complex (possibility, but not necessarily, a $\sigma$-bonded excited intermediate). This scheme was shown to be consistent with the observed pressure and temperature effects.[3] At low pressures $[(RH)(AH)NH_2^+]^*$ was postulted to undergo a dissociation (channel c) through a four-centered transition state to yield the same products as those formed through channel a.

**Scheme I**



**Scheme II**



In a recent ICR study by Moylan and Brauman[4] of the reactions of the $C_2H_5^+$–$i$-$C_3H_7NH_2$ and $i$-$C_3H_7^+$–$C_2H_5NH_2$ reaction pairs, it was reported that in addition to proton transfer these respective reaction pairs undergo the processes

$$C_3H_7^+ + C_2H_5NH_2 \rightarrow C_3H_7NH_3^+ + C_2H_4 \quad (3)$$

$$C_2H_5^+ + i\text{-}C_3H_7NH_2 \rightarrow C_2H_5NH_3^+ + C_3H_6 \quad (4)$$

with a high probability. From this result it appeared that the mechanism occurring in these systems involved the formation of an excited dialkylammonium ion that could dissociate by loss of

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(1) (a) Sieck, L. W.; Ausloos, P. *J. Chem. Phys.* **1972**, *56*, 1010. (b) Luczynski, Z.; Herman, J. A. *Int. J. Mass Spectrom. Ion Phys.* **1979**, *31*, 237.

(2) (a) Ausloos, P.; Lias, S. G. *J. Am. Chem. Soc.* **1970**, *92*, 5037. (b) Attina, M.; Cacace, F.; Giacomello, P.; Speranza, M. *J. Am. Chem. Soc.* **1980**, *102*, 6896.

(3) Meot-Ner (Mautner), M. *J. Am. Chem. Soc.* **1979**, *101*, 2389.

(4) Moylan, C. R.; Brauman, J. I. *J. Am. Chem. Soc.* **1985**, *107*, 761.

either ethylene or propylene depending on the internal energy content

$$[(C_3H_7)(C_2H_5)NH_2^+] \rightarrow C_2H_5NH_3^+ + C_3H_6 \quad \Delta H = 29\ \text{kcal/mol} \quad (5a)$$

$$[(C_3H_7)(C_2H_5)NH_2^+] \rightarrow C_3H_7NH_3^+ + C_2H_4 \quad \Delta H = 26\ \text{kcal/mol} \quad (5b)$$

Moylan and Brauman[4] also irradiated ethylisopropylammonium ions (generated in ethylisopropylamine) with an infrared laser and found that the fragmentation process favored at low energies is channel 5a rather than the energetically favored channel 5b. Because of this result, (and because they perceived four-center elimination processes such as that posulated[3] for path c to be unlikely in the gas phase), Moylan and Brauman[4] suggested that the $[(RH)(AH)NH_2^+]$ condensation ions (Scheme I) undergo cleavage of a C–N bond to give an alkyl ion–amine complex, either $[(RH^+)\cdot(AH)NH_2]$ or $[(AH^+)\cdot(RH)NH_2^+]$. Proton transfer within this complex would lead eventually to the final observed products. That is, the mechanism occurring in these systems was reinterpreted to be as shown in Scheme II. (Scheme II contains the complete mechanism, including channels d and e, which for the sake of clarity were not explicitly presented in the version of this scheme appearing in Moylan and Brauman's paper.[4]) The fact that a $C_3H_7NH_3^+$ product was observed for the reaction pair $C_3H_7^+$–$C_2H_5NH_2$ in the ICR study[4] but not in the high-pressure mass spectrometric investigation was explained in terms of collisional stabilization of the excited intermediate below the threshold for process 5b at the high pressures of Meot-Ner's experiments.

The current study is a comprehensive examination of the products formed for several alkyl ion–primary amine reactant pairs, carried out to discern factors governing the branching ratios for dissociation of the excited condensation ions, $[(RH)(AH)NH_2^+]^*$, and the relative probabilities of occurrence of the condensation/proton transfer channels ($k_b/k_a$ in Scheme II), as well as to explore possible explanations for the discrepancies between the data reported by Meot-Ner[3] and and those reported by Moylan and Brauman.[4] For example, although Meot-Ner shows that the branching ratio $k_b/k_a$ observed at high pressures for $i$-$C_3H_7^+$–$C_2H_5NH_2$ reactants is 0.20, Moylan and Brauman's reported product ratios indicate that a minimum of 50% of the ion–molecule collision lead to the formation of a $[(C_3H_7)(C_2H_5)NH_2^+]^*$ intermediate in this system.

The results to be presented here demonstrate that the study of these systems is complicated by side reactions that tend to obscure the processes of interest and to make an accurate determination of the relative importances of the primary reaction channels difficult. The ue of deuterium labeling facilities the elucidation of the details of the reaction mechanism.

## Experimental Section

Experiments were performed with the NBS pulsed-ion cyclotron resonance spectrometer[5] provided with a capacitance bridge detector and a computerized data handling system. The electron energy was maintained at 45 eV and the temperature at 325 K.

In order to unambiguously identify the reaction channels, deuterium labeled alkanes were used to generate deuterated alkyl ions in the presence of perprotonated amines. The alkyl ions, $C_2D_5^+$, $i$-$C_3D_7^+$, and $t$-$C_4D_9^+$ were generated respectively from $CD_4$–$C_2D_6$ (10:1) mixtures, pure $C_3D_8$, and pure $(CD_3)_4C$. In the $CD_4$–$C_2D_6$ mixtures, the $C_2D_5^+$ ions are mainly formed via the dissociative deuteron transfer reactions

$$CD_5^+ + C_2D_6 \rightarrow CD_4 + D_2 + C_2D_5^+ \quad (6)$$

and the reaction

$$CD_3^+ + CD_4 \rightarrow C_2D_5^+ + D_2 \quad (7)$$

The net result is that after a sufficient number of collisions more than 80% of the initial ions are converted to $C_2D_5^+$ ions, which are unreactive toward both $CD_4$ and $C_2D_6$. The $i$-$C_3D_7^+$ ion is produced in $C_3D_8$ mainly through $D^-$-transfer reactions from $C_3D_8$ to lower molecular weight fragment ions ($C_2D_5^+$, $C_2D_3^+$, etc.). In $(CD_3)_4C$, $t$-$C_4D_9^+$ is the major fragment ion in the primary mass spectrum and is therefore produced during the electron pulse.

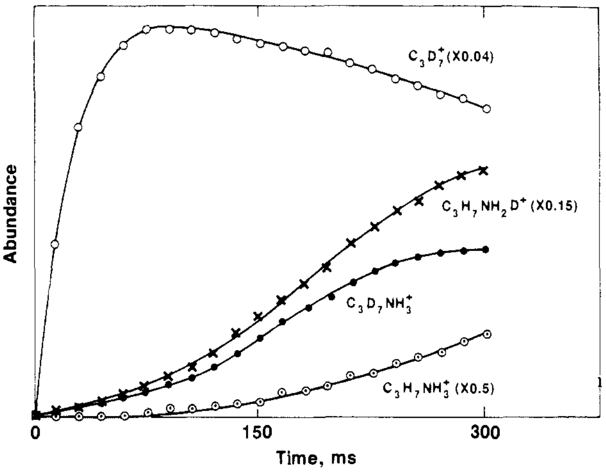

**Figure 1.** Relative abundances of ions in a $C_3D_8$-$i$-$C_3H_7NH_2$ (50:1) mixture as a function of time at a total pressure of $5 \times 10^{-6}$ torr: (○) $C_3D_7^+$; (×) $C_3H_7NH_2D^+$; (●) $C_3D_7NH_3^+$; (⊙) $C_3H_7NH_3^+$.

The perprotonated amines were added to these alkanes or alkane mixtures at low mole fractions [$(1-5) \times 10^{-2}$] in order to (a) allow the alkyl ions to undergo a sufficient number of thermalizing collisions with the alkanes prior to their reaction with the amines, and (b) to minimize electron impact ionization of the amines and the ensuing bimolecular reactions.

The relative abundances of the various reaction channels were determined at reaction times such that only 5–25% of the alkyl ions had reacted. At these short reaction times, secondary reactions involving the product ions of interest are minimized. The latter point is clearly demonstrated by the tracings in Figure 1, which show the abundances of the ions produced in a $C_3D_8$-$i$-$C_3H_7NH_2$ (50:1) mixture. Double resonance ejection shows that the products, $C_3D_7NH_3^+$ and $C_3H_7NH_2D^+$, which grow in with time, do originate from a reaction of $C_3D_7^+$. By the time (300 ms, in these experiments) about 20% of the $C_3D_7^+$ ions have reacted with $C_3H_7NH_2$, there is a distinct leveling off of the abundance of these ions, which at still longer reaction times (not shown in Figure 1) is followed by a decreasing of their abundance. The disappearance of these ions is due to the occurrence of the secondary reactions

$$C_3H_7NH_2D^+ + C_3H_7NH_2 \rightarrow C_3H_7NH_3^+ + C_3H_7NHD \quad (8)$$

$$C_3D_7NH_3^+ + C_3H_7NH_2 \rightarrow C_3H_7NH_3^+ + C_3D_7NH_2 \quad (9)$$

This is confirmed by the sharp rise of the abundance of $C_3H_7NH_3^+$ at long reaction times and the disappearance of that product when $C_3D_7^+$ is ejected. Double resonance ejection experiments show that the disappearance at long times of the $C_nD_{2n+1}NH_3^+$ product ions in all of the various systems is due to proton transfer to the added amine.

An added advantage in monitoring product ions at short time intervals after the ionizing electron pulse is that reactions involving chemical impurities are minimized. Commercial amines contain amine impurities of higher molecules weight and higher proton affinity than the bulk compound. For example, in a $C_3D_8$–$C_2H_5NH_2$ (50:1) mixture a $C_3H_7NH_3^+$ ion was observed as a product. Double resonance ejection showed that $C_3H_7NH_3^+$ is mainly formed by a proton-transfer reaction to a $C_3H_7NH_2$ impurity. Indeed the same product ion was also found to grow in with time in the absence of $C_3D_8$. The approximate concentration of the impurity was obtained by monitoring the time-resolved decay of protonated ethylamine and the concurrent growth of the protonated impurity ion until an equilibrium was reached. Assuming the impurity to be isopropylamine led to an estimate for the impurity concentration in ethylamine of 4 mol %. (If the impurity were taken to be $n$-propylamine, the observed equilibrium ion abundances would have corresponded to 11% of this compound, a result that would have required a reaction rate significantly different from the collision rate to explain the rate of decay of $C_2H_5NH_3^+$ in the bulk ethylamine sample.) The impurity problems and complicating secondary reactions clearly show the need to use deuterium labeling as well as short reaction times in order to pinpoint the relative importances of different reaction channels in these systems.

Because for many reaction pairs the relative abundance of certain product ions was too small to detect under normal ICR operating conditions, the total ion intensity was increased substantially in some ex-

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[5] Lias, S. G.; Buckley, T. J. *Int. J. Mass Spectrom. Ion Proc.* **1984**, *56*, 123.

**Table I.** Percentage of $C_nD_{2n+1}NH_3^+$ Product in Reactions of $C_nD_{2n+1}^+$ with Alkylamines and Related Thermochemical Data

| | | | energetics, kcal/mol | | | |
|---|---|---|---|---|---|---|
| $R^+$ | $R'NH_2$ | % $C_nD_{2n+1}NH_3^+$ | reactn 13b $\Delta H_{Rn}$[b] | proton-transfer reactn 13a $\Delta H_{Rn}$[b] | $\Delta H$(13b) − $\Delta H$(13a) | diff in $R^+$–N bond strengths[c] |
| $C_2D_5^+$ | $C_2H_5NH_2$ | 17 | −54 | −54 | 0 | 0 |
| | $n$-$C_3H_7NH_2$ | 18 | −57 | −55 | −2 | −5 |
| | $i$-$C_3H_7NH_2$ | 30 (18)[a] | −54 | −56 | +2 | −14 (−17) |
| | $t$-$C_4H_9NH_2$ | 53 | −54 | −58 | +4 | −33 (−39) |
| | $t$-$C_5H_{11}NH_2$ | 61 | −57 | −60 | +3 | −34 (−36) |
| $i$-$C_3D_7^+$ | $C_2H_5NH_2$ | <0.1(36)[a] | −41 | −38 | −3 | +14 (+17) |
| | $n$-$C_3H_7NH_2$ | 3 | −42 | −38 | −4 | +9 (+12) |
| | $i$-$C_3H_7NH_2$ | 9 | −39 | −39 | 0 | 0 |
| | $t$-$C_4H_9NH_2$ | 28 | −39 | −41 | +3 | −19 (−22) |
| | $t$-$C_5H_{11}NH_2$ | 34 | −43 | −43 | 0 | −20 (−19) |
| | $c$-$C_6H_{11}NH_2$ | 20 | −40 | −41 | +1 | −9 (−9) |
| $t$-$C_4D_9^+$ | $C_2H_5NH_2$ | <0.1 | −27 | −21 | −6 | +33 (+39) |
| | $n$-$C_3H_7NH_2$ | <0.1 | −28 | −22 | −6 | +28 (+34) |
| | $i$-$C_3H_7NH_2$ | <0.1 | −25 | −23 | −2 | +19 (+22) |
| | $t$-$C_4H_9NH_2$ | 2 | −25 | −25 | 0 | 0 |
| | $t$-$C_5H_{11}NH_2$ | 1 | −28 | −26 | −2 | −1 |
| | $c$-$C_6H_{11}NH_2$ | <0.1 | −26 | −25 | −1 | +10 (+13) |

[a] From ref 4. [b] Thermochemical data from ref 7. [c] Defined as the difference in energy required to break the $R^+$–N bond leading to the $C_nD_{2n+1}NH_3^+$ product (13b) and that required to break the bond leading to a $C_mH_{2m+1}NH_2D^+$ product (13a). Values in parentheses correspond to bond scission without separation of the alkyl ion–amine pair from the complex (estimated from the classical ion–molecule potential, as described in ref 8). Negative sign indicates that bond cleavage leading to process 13b is energetically favored over 13a. The same sign convention is followed in the comparison of overall energetic requirements for processes 13b and 13a ($\Delta H_b - \Delta H_a$). Heats of formation of protonated dialkylamines are from ref 7 or estimated by additivity.

periments. Because this led to saturation of the detector when the reactant ion or major product ions were observed, ion abundances were normalized by focusing on the $^{13}C$ isomers of the major ions and using their magnitudes as a measure of the corresponding ion abundances.

## Results

Table I gives the percent of the reacting alkyl ions, $C_nD_{2n+1}^+$, that yield the product $C_nD_{2n+1}NH_3^+$ in reactions with the primary amines. It is important to note that for all reaction pairs listed in Table I, $C_nD_{2n+1}NH_3^+$ was formed to the exclusion of ions of the same empirical formula but containing fewer deuterium atoms, i.e., there is no H/D shuffling in the intermediate species. Also, in all systems studied, the observed abundances of the dialkylammonium ions corresponding to the condensation ion accounted for <1% of the product ions. Therefore, under the conditions of this study, the percent abundance of the $C_mH_{2m+1}NH_2D^+$ product is [100% − %($C_nD_{2n+1}NH_3^+$)] (Table I).

In order to illustrate the use of deuterium labeling in obtaining mechanistic information about the reactions in these systems, a detailed discussion is given of the results obtained for two complementary reaction systems, ethyl ion plus isopropylamine and isopropyl ion plus ethylamine.

**$i$-$C_3D_7^+$ + $C_2H_5NH_2$.** In the reaction of $i$-$C_3D_7^+$ with $C_2H_5NH_2$, the major product, $C_2H_5NH_2D^+$, is converted to $C_2H_5NH_3^+$ by resonance proton transfer to $C_2H_5NH_2$ and to $C_3H_7NH_3^+$ ($C_3H_7NH_2D^+$) by a subsequent proton/deuteron transfer to the $C_3H_7NH_2$ impurity at long reaction times. An ion of mass 67 ($C_3D_7NH_3^+$) was also seen as a product, but the yield of this ion was less than 0.4% of that of $C_2H_5NH_2D^+$. Double resonance ejection of $C_3D_7^+$ demonstrates that $C_3D_7NH_3^+$ does originate from a reaction of $C_3D_7^+$. However, the results obtained for the $C_3D_8$-$i$-$C_3H_7NH_2$ mixtures demonstrate that 9% of the $C_3D_7^+$ ions reacting with $i$-$C_3H_7NH_2$ undergo the reaction

$$i\text{-}C_3D_7^+ + i\text{-}C_3H_7NH_2 \rightarrow C_3D_7NH_3^+ + C_3H_6 \qquad (10)$$

Therefore, the $C_3D_7NH_3^+$ product ions observed in the $C_3D_8$–$C_2H_5NH_2$ mixture containing 4 mol % propylamine impurity can be entirely accounted for by this reaction. It can therefore be concluded that fewer than 0.1% of the reacting propyl ions undergo reaction 3 in this system. Moylan and Brauman[4] reported that 36% of $C_3H_7^+$ ions react with $C_2H_5NH_2$ through reaction 3; additional experiments would be required to resolve the discrepancy.

Those authors also reported the observation of an ion of mass 88, identified as [($C_2H_5$)($C_3H_7$)$NH_2^+$]), which was estimated to be formed in 14% of the reactive encounters of propyl ions with ethylamine in their system. In the experiments described here, ions of mass 86, 87, and 88 were observed in $C_2H_5NH_2$, both in the absence and presence of added propane. However, since these ions were not present when $C_2H_5NH_3^+$ was ejected, they must have been formed in a secondary process involving this product ion. This conclusion is confirmed by the observation that these ions appear only at long reaction times. Furthermore, in the system studied here, when $C_3H_8$ is replaced by $C_3D_8$, ions corresponding to the [($C_3D_7$)($C_2H_5$)$NH_2^+$] condensation ion are present in an abundance that is <0.1% of that of the $C_2H_5NH_2D^+$ product ion.

**$C_2D_5^+$ + $i$-$C_3H_7NH_2$.** For the $C_2D_5^+$-$i$-$C_3H_7NH_2$ reactant pair, the need to use a low partial pressure of $i$-$C_3H_7NH_2$, and short reaction times for observation of products, is again mandated by the fact that the product $C_2D_5NH_3^+$ will transfer a proton to $i$-$C_3H_7NH_2$ at every collision. In effect, the yield of $C_2D_5NH_3^+$ goes through a maximum as a function of time and eventually approaches zero. The fact that in this study the yield for reaction 4 is nearly a factor of 2 higher than that reported previously[4] remains to be explained.

## Discussion

In $C_nD_{2n+1}^+$–amine reactant systems, the observation of protonated amine products incorporating the deuterated alkyl reactant species (Table I) confirms that even though stabilized condensation ions are not seen at the low pressures of an ICR experiment, a [($C_nD_{2n+1}$)($C_mH_{2m+1}$)$NH_2^+$] intermediate must indeed be formed. The results also show that no scrambling of H/D atoms occurs in the course of the formation and subequent dissociation of the condensation ion.

If in the "symmetrical systems" (ethyl ion plus ethylamine, isopropyl ion plus isopropylamine, and *tert*-butyl ion plus *tert*-butylamine) it is assumed that half of the dissociating $(RH)_2NH_2^{+*}$ species will lead to an ionic product incorporating the deuterium-labeled alkyl group, the fraction of reactive collisions that result in the formation of this intermediate is 34% for ethyl ion plus ethylamine, 18% for propyl ion plus propylamine, and 4% for *tert*-butyl ion plus *tert*-butylamine. This verifies the findings of Meot-Ner[3] that *direct* proton transfer (channel a) is the preferred pathway for isopropyl and *tert*-butyl reactant ions and that the *tert*-butyl ions are least likely to undergo the condensation channel b.

For the nonsymmetrical reactant pairs studied here, the reaction of a deuterated alkyl ion with an amine does not always result in the formation of a $C_nD_{2n+1}NH_3^+$ product. In fact, an examination of results for "complementary" reactant pairs indicates that the $[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]$ intermediates usually dissociate through a single path, rather than through both energetically allowed channels

$$[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow C_nD_{2n+1}NH_3^+ + C_mH_{2m} \quad (11a)$$

$$[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow C_mH_{2m+1}NH_2D^+ + C_nD_{2n} \quad (11b)$$

This is so even though the energy content of the $[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^*$ species is much different if the ion is formed by a reaction of $C_nD_{2n+1}^+$ or $C_mH_{2m+1}^+$, as shown in Table I, i.e., 54 kcal/mol for ethyl ion with isopropylamine as compared to 41 kcal/mol for isopropyl ion with ethylamine. In the ethyl ion–isopropylamine system, reaction 4 occurs, but in the isopropyl ion–ethylamine system, reaction 3 does not; i.e., the ethyl–isopropylammonium condensation ions formed in these systems dissociate only through channel 5a and not through 5b. Simiarly, in the isopropyl ion–*tert*-butylamine system, 28% of the reactive ion-molecule collisions lead to the formation of a protonated isopropylamine product

$$i\text{-}C_3D_7^+ + t\text{-}C_4H_9NH_2 \rightarrow [(C_3D_7)(C_4H_9)NH_2^+] \rightarrow C_3D_7NH_3^+ + C_4H_8 \quad (12a)$$

but in the reaction of $t$-$C_4D_9^+$ with isopropylamine, no $C_4D_9NH_3^+$ is formed

$$t\text{-}C_4D_9^+ + i\text{-}C_3H_7NH_2 \rightarrow [(C_3H_7)(C_4D_9)NH_2^+] \nrightarrow C_4D_9NH_3^+ + C_3H_6 \quad (12b)$$

That is, a $[(C_3H_7)(C_4H_9)NH_2^+]$ intermediate always dissociates to give a protonated propylamine product, even though the condensation process provides sufficient energy (Table I) to split out either olefin.

The enthalpy changes associated with the two possible condensation–dissociation channels

$$C_nD_{2n+1}^+ + C_mH_{2m+1}NH_2 \rightarrow [(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow C_mH_{2m+1}NH_2D^+ + C_nD_{2n} \quad (13a)$$

$$C_nD_{2n+1} + C_mH_{2m+1}NH_2 \rightarrow [(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+] \rightarrow C_nD_{2n+1}NH_3^+ + C_mH_{2m} \quad (13b)$$

(where the overall enthalpy change for reaction 13a is, of course, the same as that for the direct proton-transfer reaction) are summarized in Table I. A column showing the differences in the enthalpy changes of reactions 13b and 13a is also given. It is seen that the enthalpy changes of reactions 13a and 13b are usually about the same (±3 kcal/mol) for a given reactant pair and that the more exothermic of the two channels often does not occur.

The probabilities of observing the condensation–dissociation channel for the various alkyl ion–alkylamine pairs can, in fact, be understood if one accepts that, as suggested by Moylan and Brauman,[4] the dissociation of the $[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^*$ condensation ion involves the initial scission of a C–N bond to give an alkyl ion–amine complex, followed by proton transfer in the complex. For example, for the formation of $C_nD_{2n+1}NH_3^+$ products, this mechanism would be represented

$$[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^* \rightarrow [C_mH_{2m+1}^+ \cdot C_nD_{2n+1}NH_2] \rightarrow [C_mH_{2m} \cdot C_nD_{2n+1}NH_3^+] \rightarrow C_mH_{2m} + C_nD_{2n+1}NH_3^+ \quad (14)$$

The difference in the two N–(alkyl$^+$) bond strengths in these condensation ions, summarized in the last column of Table I, is the decisive factor in determining the channel for dissociation (-b or d in Scheme II) to be followed. An examination of the trends in the N–(alkyl$^+$) bond strengths demonstrates that when the difference is large (greater than approximately 10 kcal/mol in the systems studied here), the excited condensation ion dissociates through a single pathway involving breaking the weaker N–(alkyl$^+$) bond as the first step (i.e., no $C_nD_{2n+1}NH_3^+$ product is formed except when scission of the appropriate corresponding (alkyl$^+$)–N bond is energetically preferred).

**Table II.** Fractions of Collisions Resulting in Condensation Channels in Alkyl Ion–Alkylamine Reactions

| | % condensation channel[a] | | |
|---|---|---|---|
| amine | $C_2H_5^+$ | $i$-$C_3H_7^+$ | $t$-$C_4H_9^+$ |
| $C_2H_5NH_2$ | 34 | [20] | [5] |
| $n$-$C_3H_7NH_2$ | (18)[b] | [15] | [6] |
| $i$-$C_3H_7NH_2$ | 30 | 18 | |
| $t$-$C_4H_9NH_2$ | 53 | 28 | 4 |
| $t$-$C_5H_{11}NH_2$ | 61 | 34 | (1)[b] |
| $c$-$C_6H_{11}NH_2$ | | 20[21] | [6] |

[a] Values in brackets are percentages of stabilized condensation ions observed in a high-pressure mass spectrometer, ref 3. [b] See Discussion; because of the possibility that the condensation ion dissociates through two channels, estimate of relative importance cannot be based on the observed abundance of $C_nD_{2n+1}NH_3^+$.

In addition to the "Symmetric" systems where either of the two C–N bonds may be broken, it appears that two dissociation pathways are possible when the differences in bond energies are small (less than about 10 kcal/mol in these systems). Apparently the $[(C_3D_7)(C_3H_7)NH_2^+]$ ions formed from ($i$-$C_3D_7^+$ + $n$-$C_3H_7NH_2$) reactants undergo two dissociation pathways since the $C_3D_7NH_3^+$ ion is observed even though the bond scission leading eventually to this product is not energetically preferred. However, channel 13a must account for most of the dissociations of these species since this channel accounts for only 3% of the reacting ions, while Meot-Ner reported that at high pressure the dialkyl ammonium ion accounts for 15% of the reactive collisions. Also, in the reactions of ethyl ions with $n$-propylamine (where the energy difference predicted for scission of the two N-alkyl ion bonds is only 5 kcal/mol), it is seen (Table II) that although one might expect the fraction of reactive collisions leading to channel b (Scheme II) to be around 0.3, only 18% of reactive collisions lead to the formation of a $C_2D_5NH_3^+$ product, a result that suggests that in this system both chanels 13a and 13b are occurring.

Accepting that only one dissociation path is followed when there is a significant difference in the C–N bond energies in the $[(C_nD_{2n+1})(C_mH_{2m+1})NH_2^+]^*$ species, the relative abundances of the $C_nD_{2n+1}NH_3^+$ products give an estimate of the importance of the condensation channel relative to *direct* proton transfer in many of these systems. Table II summarizes the percentages of collisions resulting in the occurrence of channel b for the various alkyl ion–amine reactant pairs as derived from the results reported here and/or the study of Meot-Ner.[3] It is seen the Meot-Ner's high-pressure data based on the observation of the stabilized condensation ion are internally consistent with the results of this study. On the basis of this consistency, it can be concluded that the branching ratio for proton transfer/condensation in alkyl ion–amine systems is in fact invariant with pressure from about $10^{-6}$ to 1 torr. Such invariance in branching ratios over pressure ranges of many orders of magnitude has been seen before[1,2] for proton transfer/condensation channels in olefins.

Moylan and Brauman[4] speculated about the factors that might influence the relative probabilities of steps a and b in Schemes I and II, i.e., the factors that determine the relative probability that a given reactant pair undergoes a *direct* proton-transfer reaction or forms an excited condensation ion. These authors suggested that direct proton transfer occurs via a hydrogen-bonded complex, since this channel competes favorably with formation of the condensation ion, which is more exothermic. They suggest that, if this is the case, the proton-bridged ethyl ion[6] then should undergo the proton-transfer channel to a relatively greater extent than should a classical carbonium ion such as the isopropyl ion. The results obtained here taken in conjunction with those reported by Meot-Ner[3] demonstrate that the relative importances of the condensation and direct proton-transfer channels are indeed primarily decided by the identity of the reactant ion (Table II),

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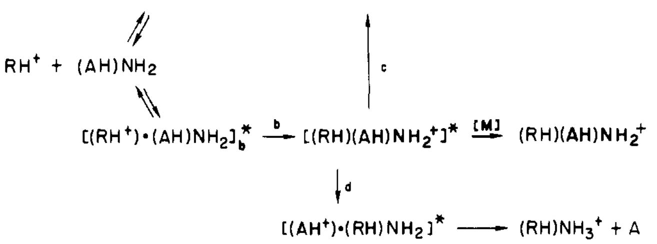
(6) Raghavachari, K.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5469.

**Scheme III**



but do not follow the trend predicted by Moylan and Brauman.[4]

The possibility must be considered that the intermediate generalized here as $[(RH^+)\cdot(AH)NH_2]^*$ initially exists in two or more distinct structures representing different alkyl ion–amine configurations and that the branching ratio for steps a and b in Schemes I and II is decided by the relative probabilities that the ion–molecule collision initially leads to the formation of a particular configuration that may serve as precursor for one reaction or the other (Scheme III, where $[(RH^+)\cdot(AH)NH_2]_a^*$ and $[(RH^+\cdot(AH)NH_2]_b^*$ indicate initial configurations of the collision complex that are respectively predominantly "hydrogen-bonded-like" or "condensation-ion-like"). The prediction of the probabilities of channel a and b would thus require more detailed information about the potential surfaces, particularly of the collision process, than is available from simple thermochemical considerations. This scheme, which is compatible with the pressure and temperature effects on product ratios reported before,[3] provides a simple explanation for the observed pressure-independent competition between two reaction channels without activation energy barriers, in which the energetically less favorable channel (proton transfer is usually about 30 kcal/mol less exothermic) predominates in most systems. Scheme III also offers an intuitively obvious explanation for the trends in branching ratio $k_b/k_a$ summarized in Table II; for a reacting *tert*-butyl ion, a configuration involving close approach of an H atom to the bonding site in the amine would be most likely, while an approaching ethyl ion might be expected to present either an H atom or a C atom to the reactive site with close to equal probability (as is observed). Attina et al.[2b] also suggested that the branching ratio might be determined by some intrinsic feature of the collision process.

Figure 2 shows the major features of a potential surface for Scheme III. Calculations[9] have shown that in such highly exothermic proton-transfer reactions ($\Delta H < -30$ kcal/mol), the first well of the double-welled surface takes on the characteristics of a "bump" on the steep wall of the deeper well. Thus, for any reactant pair approaching along path a, the finite existence of the initial $[(RH^+)\cdot(AH)NH_2]^*$ collision complex that appears in Schemes I and II may be a moot point; i.e., once the reactants have approached to within bonding distances of one another, competition between channels a and b is no longer possible. On the other hand, the energy level of such a $[(RH^+)\cdot(AH)NH_2]^*$ complex must indeed define the transition state for dissociation of the excited condensation ions (see Figure 2).

## Conclusions

The results presented here confirm that the reaction of an alkyl ion with an amine proceeds through two competing pathways, direct proton transfer and condensation, as demonstrated before by Meot-Ner.[3] A comparison of the proton-transfer/condensation branching ratios derived from these results with the corresponding ratios observed in the high-pressure and mass spectrometer study[3] demonstrates that these branching ratios are invariant with pressure from $10^{-6}$ to 1 torr. The proposition of Moylan and Brauman that the initial collision results in the formation of a hydrogen-bonded complex from which proton transfer can occur (or which can surmount a barrier to undergo the condensation process) led to a prediction that for the proton-bridged ethyl ion proton transfer should be more favored over addition than would be the case for the classical propyl ion. The results presented here demonstrate that this is not the case. Although the mechanism of the competition kinetics remains uncertain, it is suggested here on the basis of the pressure invariance that the branching ratio for these two channels is determined by the relative configuration of the reactants when they approach to within bonding distances of one another.

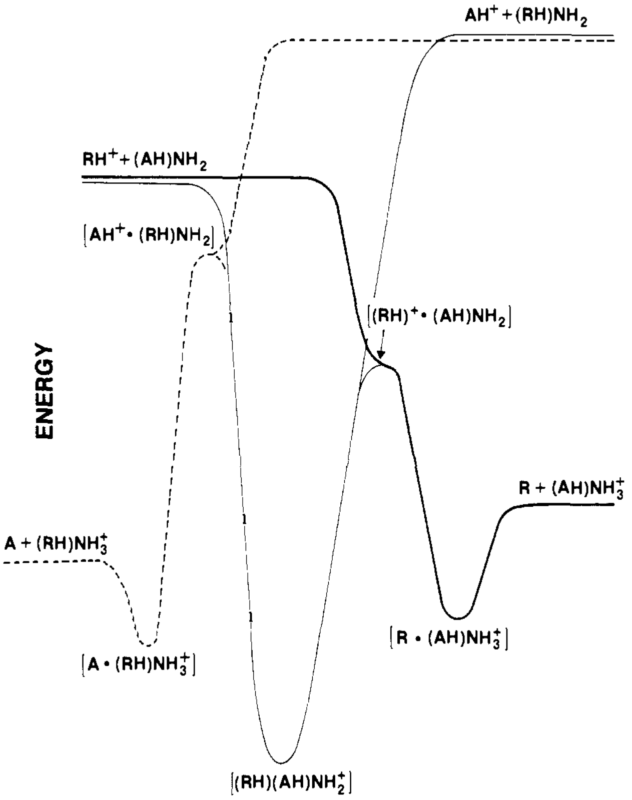


**Figure 2.** Potential surface corresponding to Scheme III.

At the low pressures of an ICR experiment, all the condensation ions dissociate to give a protonated amine product ion, which may have the same identity as the ion formed by direct proton transfer, or may incorporate the reactant alkyl ion in the product protonated amine. Protonated secondary amine condensation ions dissociate through a mechanism in which the weaker of the two C–N bonds undergo scission to form an alkyl ion–amine complex; proton transfer from the alkyl ion to the amine in the complex, followed by dissociation, leads to the final products. In most of the systems studied here the difference in the two C–N bonds in the condensation ion is great enough that the weaker of the two bonds is selectively broken.

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**Registry No.** $C_2H_5NH_2$, 75-04-7; $n$-$C_3H_7NH_2$, 107-10-8; $i$-$C_3H_7NH_2$, 75-31-0; $t$-$C_4H_9NH_2$, 75-64-9; $t$-$C_5H_{11}NH_2$, 594-39-8; c-$C_6H_{11}NH_2$, 108-91-8; $C_2H_5^+$, 14936-94-8; $i$-$C_3H_7^+$, 19252-53-0; $t$-$C_4H_9^+$, 14804-25-2.

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(7) Lias, S. G.; Liebman, J. F.; Levin, R. D. *J. Phys. Chem. Ref. Data* **1984**, *13*, 695.

(8) Lias, S. G. *J. Phys. Chem.* **1984**, *88*, 4401.

(9) Scheiner, S.; Harding, L. B. *J. Phys. Chem.* **1983**, *87*, 1145.