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Competitive Condensation and Proton-Transfer Reactions. Temperature and Pressure Effects and the Detailed Mechanism

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Abstract: At high pressures ($P \gtrsim 1$ Torr) carbonium ions (R^+) and amines (A) undergo proton-transfer reactions yielding AH^+ in competition with the formation of condensation products RA^+. For example, t-$C_4H_9^+$ reacts with NH_3 to give NH_4^+ in competition with the formation of t-$C_4H_9NH_3^+$; i-$C_3H_7^+$ reacts with $C_2H_5NH_2$ to give $C_2H_5NH_3^+$ in competition with i-$C_3H_7(C_2H_5)NH_2^+$, etc. The product distribution ratio I_{RA^+}/I_{AH^+} increases linearly with third body pressure at low pressures, but levels off to small finite values at high pressures. The product distribution ratio does not vary significantly with temperature between 200 and 500 K in any of five reactions whose temperature dependence was measured. Displacement-exchange reactions such as i-$C_3H_7^+ + C_2H_5NH_2 \rightarrow i$-$C_3H_7NH_3^+ + C_2H_6$ do not take place even when those reactions would be more exothermic than the proton-transfer reactions. The pressure effects and the absence of exothermic displacement reactions suggest that the major channel for proton transfer does not proceed through the excited condensation-product-like σ-bonded complexes $(RA^{+*})_{tight}$. Rather, the data is consistent with a two-stage mechanism (see Scheme II) in which $(RA^{+*})_{tight}$ and AH^+ are formed from a common precursor. It is proposed that the collision between R^+ and A forms first a loose, electrostatically bonded complex $(R^+{\cdot}A)^*_{loose}$ in which R^+ and A undergo multiple internal collisions, some of which may produce AH^+ or RA^{+*} depending on the geometry of the intracomplex collision. It is further proposed that a similar two-stage mechanism can account for some unexpected pressure and temperature effects in other ion–molecule reactions.

The theoretical treatment of bimolecular and higher order reactions in general, and ion–molecule reactions in particular, should be greatly facilitated if the reactions proceed through intermediates which possess well-defined structures and whose internal energy is distributed statistically among the internal degrees of freedom. The decomposition rates of such intermediates to products or to reactants may then be calculated using unimolecular decomposition theory.[1] However, in order properly to evaluate the role of the intermediate in the overall reaction, the detailed mechanism of the reaction must be known. The present work deals with the detailed mechanism of competitive condensation and proton-transfer reactions between carbonium ions and alkylamines as model ion–molecule processes.

Several authors have applied unimolecular theory to the decomposition of intermediates in ion–molecule reactions. For example, Buttrill[2] applied statistical unimolecular theory to calculate product distributions in the decomposition of the $C_4H_8^{+*}$ and $C_4H_6^{+*}$ intermediates in the reaction of $C_2H_4^+$ with C_2H_4 and C_2H_2. Several workers used statistical unimolecular theory to interpret temperature and pressure effects in clustering reactions of protonated amines.[3-5] Olmstead and Brauman[6] used RRKM theory to calculate reaction efficiencies of nucleophilic displacement reactions involving negative ions. Su and Bowers[7] also considered that such an approach may be applicable to the decomposition of the reaction intermediate in proton transfer from t-$C_4H_9^+$ to ammonia. In these treatments it was generally assumed that a specifically bonded complex with randomized internal energy is formed in every capture collision of the reactants.

The present work deals with reactions between carbonium ions (R^+) and amines (A). At high pressures ($P \gtrsim 1$ Torr) these reactants yield condensation products RA^+, in competition with the major product AH^+ which results from proton transfer. It is safe to assume that the condensation product RA^+ is preceded by a σ-bonded excited species RA^{+*} whose structure is identical with that of RA^+. This intermediate could then be treated by statistical unimolecular theory. The objective of the present study is to use competition kinetics to examine whether proton transfer also proceeds through this

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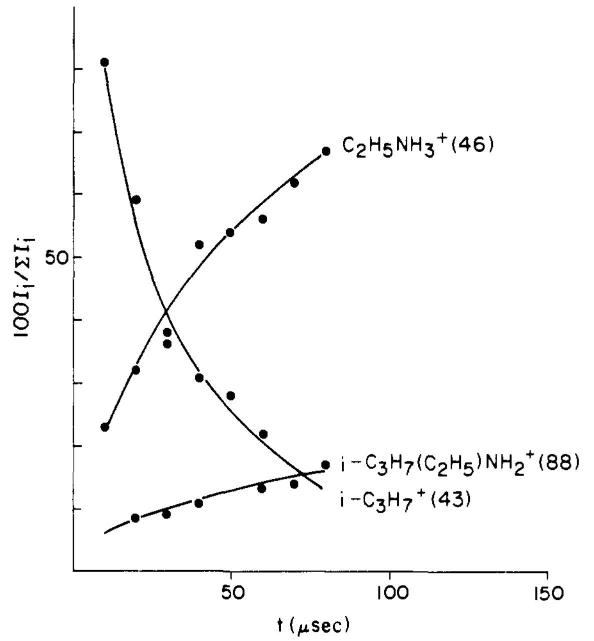


Figure 1. Normalized ion intensities as a function of reaction time in a mixture of 0.1% $C_2H_5NH_3$ in C_3H_8, at T = 462 K, P_{total} = 0.72 Torr. Numbers after ion formulas represent the corresponding *m/e* values.

strongly bound intermediate. The results of pressure and temperature studies and of other observations on these kinetic systems will be presented. The somewhat unexpected results will be used to infer the detailed sequence of events following the capture collision between the reactants.

Experimental Section

1. General. The experiments were performed on the Rockefeller University chemical physics mass spectrometer, used in the pulsed mode.[8] The materials used were isobutane, methane (ultrahigh purity), propane (99.99% purity), and ammonia, all obtained from Matheson; *n*-propylamines, cyclohexylamine, and other alkylamines as reported later, all obtained from MC&B Inc.

Reaction mixtures of known composition were prepared in 5-L bulbs and allowed to flow into the source through a metering needle valve. In most experiments the carbonium ions (R^+), e.g., *i*-$C_3H_7^+$ and *t*-$C_4H_9^+$, were prepared by fast ion-molecule reactions in mixtures of 1% propane or isobutane in CH_4. The reactions yielding *i*-$C_3H_7^+$ or *t*-$C_4H_9^+$ were completed in 10 μs; these ions then reacted more slowly with the amines, which usually constituted 0.05% of the reaction mixture. Some experiments were performed in neat C_3H_8 or *i*-C_4H_{10} as the carrier gas.

The major products of the reactions were protonated amines formed by proton-transfer reactions. In parallel with the formation of the proton-transfer products AH^+, the adduct ions RA^+ were also produced. For example, *i*-$C_3H_7^+ \cdot NH_3$ is formed in parallel with NH_4^+ in the reaction of *i*-$C_3H_7^+$ with NH_3.

At low temperatures the protonated products were observed to add further amine molecules to form cluster ions $AH^+ \cdot nA$, i.e., $NH_4^+ \cdot NH_3$, $NH_4^+ \cdot 2NH_3$, or their analogues in the alkylamines. The adduct ions also formed similar cluster ions, e.g., (*i*-$C_3H_7^+ \cdot NH_3$)$\cdot NH_3$, etc. Owing to the low concentration of the amines, cluster ions with $n >$ 3 were not observed under any conditions in these experiments. The cluster ions always formed after the protonated or adduct ions, as determined by the change of ion intensities with time after the ionizing pulse. For the purposes of the present measurements the intensities of the cluster ions were always added to the intensities of the corresponding nonclustered ion to calculate the total intensity of a given primary reaction product.

The condensation products RA^+ constituted in many reaction systems only 1-5% of the total ion current. The low signal intensity corresponding to these products caused an experimental difficulty, since in the pulsed mode of operation it is necessary to focus on the small peaks for 1-5 min in order to accumulate sufficient ion counts to define an ion time profile. During this time the instrument sensitivity may fluctuate, and this affects adversely the precision of measured relative ion intensities. The effects of the resultant scatter of the data will be noted in later sections.

Table I. Product Distributions, Expressed as the Ratio of Condensation Products to Proton-Transfer Products, i.e., (I_{RA^+}/I_{AH^+}), in Reactions of Carbonium Ions with Amines[a]

expt	reactants	k_f^{300}, 10^{-9} $cm^3\ s^{-1}$	$\frac{I_{RA^+}}{I_{AH^+}}$	$-\Delta H°$ proton transfer, kcal/mol	$-\Delta H°$ condensation, kcal/mol
1	$C_2H_5^+ + NH_3$	2.0	0.12	43.6	68.1
2	*i*-$C_3H_7^+ + NH_3$	1.9	0.065	23.2	51.3
3	$C_2H_5NH_3$		0.20	34.9	
4	*n*-$C_3H_7NH_2$	1.7	0.18	36.4	
5	*n*-$C_6H_{13}NH_2$		0.19		
6	c-$C_6H_{11}NH_2$		0.27	39.4	
7	$(CH_3)_3N$		0.24	43.0	
8	$(C_2H_5)_3N$		0.24	49.9	
9	$(C_3H_7)_3N$		0.061	51.8	
10	*t*-$C_4H_9^+ + NH_3$	1.6	0.025	8.3	38.3
11	$C_2H_5NH_3$	1.8	0.052	20.0	
12	*n*-$C_3H_7NH_2$	1.8	0.065	21.5	
13	*n*-$C_6H_{13}NH_2$		0.016		
14	c-$C_6H_{11}NH_2$	1.5	0.062	24.5	
15	$(CH_3)_2NH$		0.063	23.9	
16	$(CH_3)_3N$		0.055	28.1	
17	$(C_2H_5)_3N$		0.0082	35.0	
18	$(C_3H_7)_3N$		0.0050	36.9	
19	*t*-$C_5H_{11}^+$ + $C_2H_5NH_3$		0.049		

[a] All measurements were made at 300 K, $N_M = 3 \times 10^{16}$ cm^{-3}.
[b] Thermochemical values calculated using the data in ref 16.

In previous work[9] we found that ion intensity distributions obtained in continuous ionization measurements are usually similar to pulsed results at very short reaction times (t = 5-10 μs). In the present experiments the I_{RA^+}/I_{AH^+} ratios obtained in the pulsed mode at short reaction times and those obtained using the continuous mode were generally in good agreement, as will be shown later. We therefore used the continuous mode in some of our investigations to obtain more intense ion signals than are possible with the pulsed mode.

2. Time Profiles of Normalized Ion Intensities. The variation of the normalized intensities ($100I_i/\Sigma I_i$) of reactant and product ions with reaction time in a representative reaction system is illustrated in Figure 1.

The condensation products (RA^+) and proton transfer products (AH^+) are formed by parallel reactions of a common precursor, R^+. Consequently, the product ions are expected to appear in parallel as R^+ disappears, and I_{RA^+}/I_{AH^+} should be independent of reaction time. This behavior is indeed observed in the reaction of *i*-$C_3H_7^+$ with $C_2H_5NH_2$ (Figure 1). Similar behavior was also observed at short reaction times in the reaction of *i*-$C_3H_7^+$ with NH_3 and in the other reactions listed in Table I.

However, in some of the experiments where *i*-$C_3H_7^+$ or *t*-$C_4H_9^+$ reacted with NH_3, I_{RA^+}/I_{AH^+} was observed to increase at long reaction times ($t >$ 100 μs). The increase in $I_{i\text{-}C_3H_7^+ \cdot NH_3}/I_{NH_4^+}$ or $I_{t\text{-}C_4H_9^+ \cdot NH_3}/I_{NH_4^+}$ in these systems, respectively, could reflect the selective depletion of NH_4^+ by impurities. Indeed, ions with *m/e* 32 and 46 were observed, apparently due to protonated CH_3NH_2 and $C_2H_5NH_2$ impurities. The intensities of the impurity ions constituted about 2-6% of the total ion intensity (ΣI_i) at early reaction times, and increased to 10-15% of ΣI_i after 150-200 μs. Since these complications were significant only at later reaction times, the $I_{RA^+}I_{AH^+}$ ratios at early reaction times were used as a measure of product distribution in these systems. No impurity problems were encountered in other systems in this study.

Since impurity ions were observed in the *i*-$C_3H_7^+$ + NH_3 and *t*-$C_4H_9^+$ + NH_3 systems at *m/e* 32 and 46, it was imperative to establish that the *m/e* 60 and 74 ions in these systems, respectively, were indeed formed by condensation reactions and not by the protonation of $C_3H_7NH_2$ and $C_4H_9NH_2$ impurities. For this purpose we obtained the H_2 chemical ionization mass spectrum of the ammonia used in these experiments. The *m/e* 32 and 46 impurities were observed, but the *m/e* 60 and 74 ions were negligible. Similar results were obtained

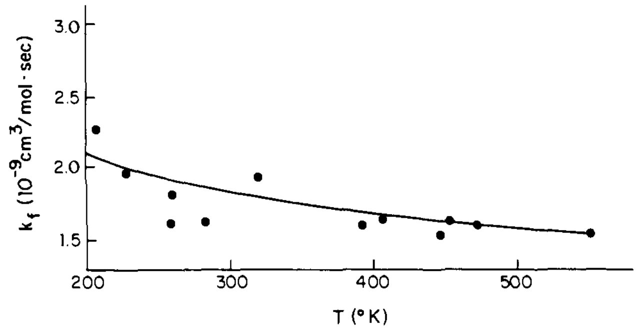


Figure 2. Rate constant for the proton transfer reaction $i\text{-}C_3H_7^+ + NH_3 \rightarrow NH_4^+ + C_3H_6$ as a function of temperature. Solid line represents the collision rate constant calculated from ADO theory.

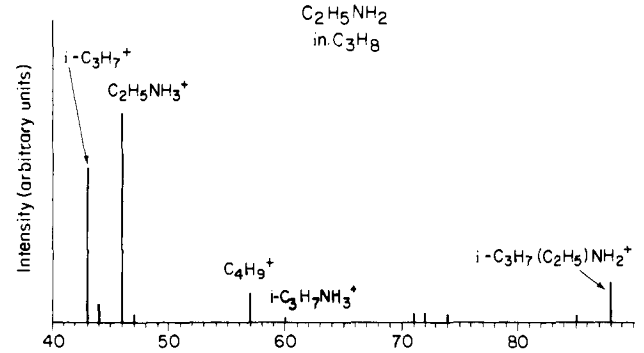


Figure 3. Mass spectrum of a reaction system of 0.1% $C_2H_5NH_3$ in C_3H_8 at 490 K, P = 1.3 Torr. Note that the ion $i\text{-}C_3H_7NH_3^+$ (*m/e* 60) is present only at trace levels.

in the chemical ionization mass spectrum of neat ammonia. Furthermore, we obtained the mass spectrum of a mixture of $ND_3 + i\text{-}C_3H_8$. While no alkylamine impurities were observed in the CIMS of ND_3, the condensation product $C_3H_7ND_3^+$ (*m/e* 63) was still observed in the $ND_3 + C_3H_8$ mixture. These results show that the ions at *m/e* 60 and 74 in the $i\text{-}C_3H_7^+ + NH_3$ and $t\text{-}C_4H_9^+ + NH_3$ systems are not derived from impurities and their formation requires $i\text{-}C_3H_7^+$ or $t\text{-}C_4H_9^+$ as precursors. The identity of the $C_3H_7^+\cdot NH_3$ ion as a condensation product was further verified by deuterium labeling. In the $C_3D_8 + NH_3$ system the condensation ion $C_3D_7^+\cdot NH_3$ (*m/e* 67) was observed, rather than the ion $C_3H_7NH_2D^+$ (*m/e* 61) which would have been formed by the deuteration of a $C_3H_7NH_2$ impurity.

Results

1. Rate Constants of the Overall Reactions $R^+ + A \rightarrow$ Products. Most exothermic proton transfer reactions are fast; i.e., the rate constants are within ±20% of the capture collision rate constants calculated from the ADO theory.[10,11] In the present work we also found that experimental rate constants (Table I) for the reactions of carbonium ions with amines are equal to calculated ADO collision rate constants within experimental accuracy of ±15%. The slight negative temperature dependence of the rate constant for the reaction of $i\text{-}C_3H_7^+$ with NH_3 was also found to agree with the temperature dependence predicted by ADO theory (Figure 2).

2. The Absence of Displacement-Exchange Reactions. In some of the reaction systems represented in Table I displacement-exchange reactions would be more exothermic than proton-transfer reactions. For example, proton transfer from $i\text{-}C_3H_7^+$ to $C_2H_5NH_2$, reaction 3, is exothermic by 34.9 kcal/mol, but the reaction

$$i\text{-}C_3H_7^+ + C_2H_5NH_2 \rightarrow i\text{-}C_3H_7NH_3^+ + C_2H_4$$

would be exothermic by 38.5 kcal/mol.[16] Despite this the product $i\text{-}C_3H_7NH_3^+$ (*m/e* 60) appeared only at trace levels in the mass spectrum of ethylamine in propane, while the proton-transfer product $C_2H_5NH_3^+$ (*m/e* 46) is the major ion, and the condensation product $i\text{-}C_3H_7^+\cdot C_2H_5NH_2$ (*m/e* 88) is also significant (Figure 3). Similarly, the displacement-exchange channel, though thermodynamically favored, was not observed in the reactions of $t\text{-}C_4H_9^+$ and $t\text{-}C_6H_{11}^+$ with $C_2H_5NH_2$.

3. Identity of the Condensation Products. It is expected that condensation reactions of carbonium ions with amines will form protonated alkylamines. For example, the condensation product in the reaction of $i\text{-}C_3H_7^+$ with NH_3, which we denoted as $i\text{-}C_3H_7^+\cdot NH_3$, is expected to be $i\text{-}C_3H_7NH_3^+$; in the reaction of $i\text{-}C_3H_7^+$ with $C_2H_5NH_2$ the condensation product is expected to be $i\text{-}C_3H_7(C_2H_5)NH_2^+$, etc. This result is expected since the formation of the new bond to yield the protonated alkylamine requires only a nucleophilic attack by NH_3 on the positive carbon center of the carbonium ion; no breakage of existing bonds in the reactants is required. The formation of the alkylammonium ions is analogous with the condensation reactions observed between carbonium ions and H_2O to yield protonated alcohols.[12-15]

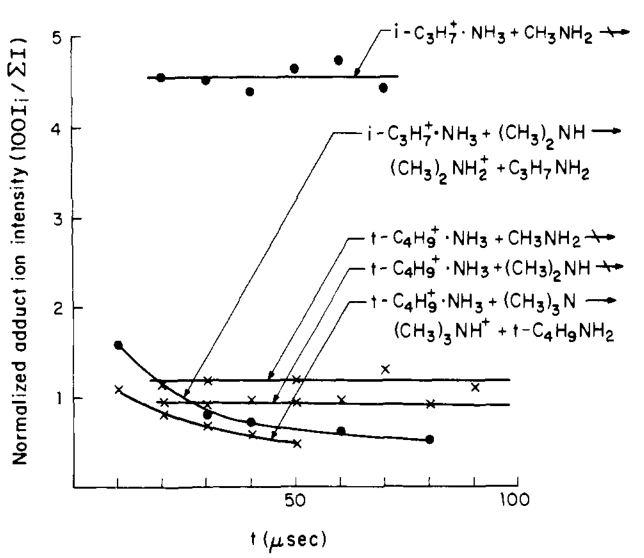


Figure 4. Intensities of the condensation product ions $i\text{-}C_3H_7NH_3^+$ and $t\text{-}C_4H_9NH_3^+$, produced in the reactions of $i\text{-}C_3H_7^+$ and of $t\text{-}C_4H_9^+$, respectively, with NH_3, as a function of reaction time; 0.06% of a reference alkylamine, CH_3NH_2, $(CH_3)_2NH$, or $(CH_3)_3N$, was added in these reaction mixtures. The plots show the occurrence or absence of H^+ transfer reactions from the condensation products to the reference amines, as indicated.

In order to verify the identity of the adduct ions as protonated alkylamines, we performed proton-transfer bracketing experiments. In these experiments small amounts of reference alkylamines were added to the mixture in which the condensation products $i\text{-}C_3H_7^+\cdot NH_3$ or $t\text{-}C_4H_9^+\cdot NH_3$ were formed. For example CH_3NH_2 and $(CH_3)_2NH$ were added, in separate experiments, to a mixture of C_3H_8 and NH_3 in CH_4. The results (Figure 4) show that $i\text{-}C_3H_7^+\cdot NH_3$ did not react in the presence of CH_3NH_2 but was depleted in the presence of $(CH_3)_2NH$. Similarly, $t\text{-}C_4H_9^+\cdot NH_3$ was not depleted by CH_3NH_2 and $(CH_3)_2NH$ but was depleted by $(CH_3)_3N$.

At the concentrations used in the bracketing experiments, proton-transfer reactions to the added reference amines are observable only if they proceed at about collision rate. Exothermic proton-transfer reactions usually proceed at this rate; endothermic reactions are slower. Accordingly, to interpret the results of the bracketing experiments we note the following proton affinities:[16] CH_3NH_2 (211.3), $i\text{-}C_3H_7NH_2$ (216.5), $(CH_3)_2NH$ (217.9), $t\text{-}C_4H_9NH_2$ (218.8), $(CH_3)_3N$ (222.1) kcal/mol. The absence or presence of reactions as observed in Figure 4 is therefore consistent with the identification of the

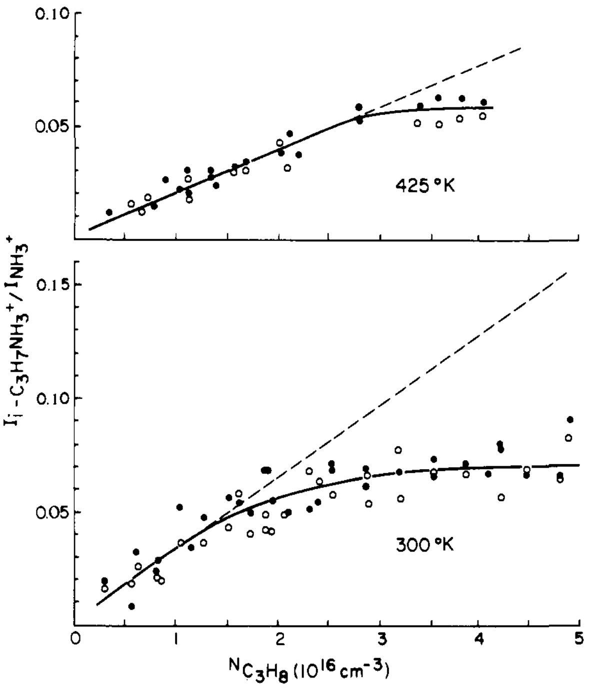


Figure 5. The ratio of condensation product to proton-transfer product as a function of third body density in the reaction of i-$C_3H_7^+$ with NH_3 at two temperatures. Solid circles represent results obtained in the continuous, open circles in the pulsed, ionization mode. Broken line is linear regression plot based on points at $N_{C_3H_8} < 1.5 \times 10^{16}$ cm^{-3}; solid line is drawn through experimental points. Experiments were done with a reaction mixture of 1% NH_3 in propane.

condensation products as protonated isopropylamine and protonated *tert*-butylamine.

4. Pressure Effects. The effects of varying the pressure (or, equivalently, the third body density) on the relative yield of the condensation vs. proton-transfer products was investigated in three reaction systems. The results for the reaction of i-$C_3H_7^+$ with NH_3 at 300 and 425 K are given in Figure 5. As we noted in the Experimental Section, the low intensity of the association product caused considerable scattering of the data. To compensate for the decreased precision of the measurements, a large number of data points were taken. To facilitate the measurements, some of the data was obtained by the continuous ionization technique. As the plots show, the pulsed and continuous results were in good agreement.

Inspection of Figure 5 shows that at both temperatures the ratio of RA^+/AH^+ is proportional to $N_{C_3H_8}$ at low densities. The straight lines in Figure 5 are linear regression plots of $I_{i\text{-}C_3H_7NH_3^+}/I_{NH_4^+}$ vs. $N_{C_3H_8}$, based on the points at $N_{C_3H_8} < 1.5 \times 10^{16}$ cm^{-3}. The intercepts and standard deviations of the intercepts of the plots are 0.0026 ± 0.0040 for the plot at 300 K and 0.0018 ± 0.0038 for the plot at 425 K. The $I_{i\text{-}C_3H_7NH_3^+}/I_{NH_4^+}$ ratio approaches 0 at zero density within experimental error limits at both temperatures.

Even though there is significant scatter, it is evident that the experimental points at high densities deviate from the extension of the line plotted through the points at low densities. In fact, the experimental ratio $I_{i\text{-}C_3H_7NH_3^+}/I_{NH_4^+}$ appears to level off at high densities. The approach to the high pressure limit is faster at the lower temperature; i.e., the slope of the plot through the low density points at 300 K is greater, and the plateau is reached at a lower density, than at 425 K. Note, however, that the limiting high-pressure value, $(I_{i\text{-}C_3H_7NH_3^+}/I_{NH_4^+})_{HP}$, is similar, i.e., ~0.05-0.06, at both temperatures.

Pressure studies were also performed on the system i-$C_3H_7^+$ + $C_2H_5NH_2$ (Figure 6). The general features observed are similar to the i-$C_3H_7^+$ + NH_3 system: the I_{RA^+}/I_{AH^+} ratio levels off at high densities; approach to the high density limit is faster at lower temperatures, and the value of $(I_{RA^+}/I_{AH^+})_{HP}$ is independent of temperature. The high-pressure plateau is achieved at lower densities in this system than in i-$C_3H_7^+$ + NH_3.

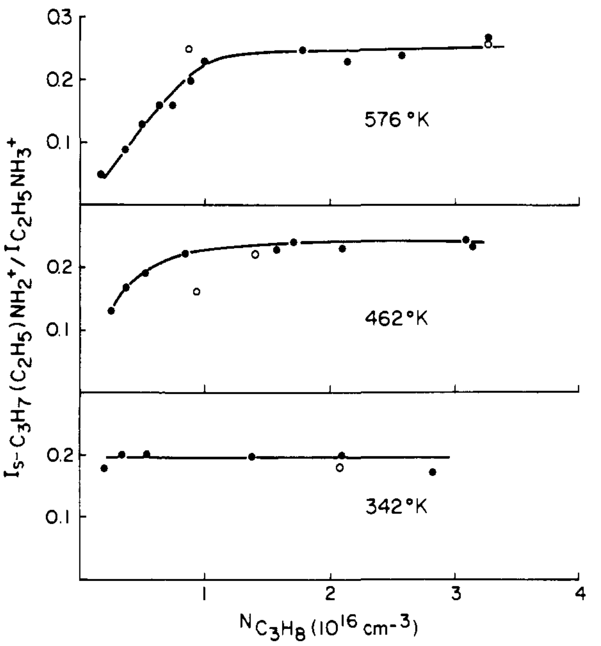


Figure 6. The ratio of condensation product to proton-transfer product as a function of third body density in the reaction of i-$C_3H_7^+$ with $C_2H_5NH_2$ at three temperatures. Solid circles represent results obtained in the continuous, open circles in the pulsed ionization mode. Experiments were done with a reaction mixture of 1% $C_2H_5NH_2$ in propane.

A pressure study was also performed on the reaction of t-$C_4H_9^+$ with $C_2H_5NH_2$ (Figure 7). It appears that, similar to the reaction of i-$C_3H_7^+$ with $C_2H_5NH_2$ at 300 K, the product ratio has already leveled off to $(I_{t\text{-}C_4H_9NH_3^+}/I_{NH_4^+})_{HP} = 0.05$ even at the lowest pressures available.

We also performed some experiments on the product distribution ratio in the t-$C_4H_9^+$ + NH_3 system at 340 and 425 K, in the same range of third body densities as the other pressure studies. At neither temperature did we seem to observe significant leveling off of the $I_{t\text{-}C_4H_9NH_3^+}/I_{NH_4^+}$ ratio at accessible densities, but the results were inconclusive owing to experimental scatter.

5. Temperature Effects. The effect of temperature, at constant third body densities, on the relative yields of condensation and transfer products in five reaction systems is given in Figure 8. We note that the product distribution ratio (I_{RA^+}/I_{AH^+}) is independent of temperature. Figure 8 indicates that this trend is general for all the systems observed, the only exception being a small rise in the $I_{i\text{-}C_3H_7NH_3^+}/I_{NH_4^+}$ ratio at $T < 300$ K.

The temperature studies on the reactions shown in Figure 8 were performed at constant third body densities of 3×10^{16} cm^{-3}, except for the reaction of i-$C_3H_7^+$ with NH_3, which was done at a constant third body density of $N_{C_3H_8} = 2.5 \times 10^{16}$ cm^{-3}. We note that the high-pressure limiting product distribution ratios were generally achieved at these third body densities (Figures 5-7). We therefore interpret the plots in Figure 8 as representing the temperature dependence of the high-pressure limiting product ratios $(I_{RA^+}/I_{AH^+})_{HP}$.

Discussion

1. Is RA^{+*} the Intermediate for the Proton Transfer Reaction? The major question of interest in the present study is whether the proton-transfer reactions proceed through the

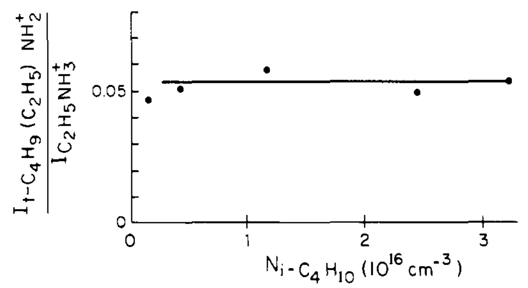
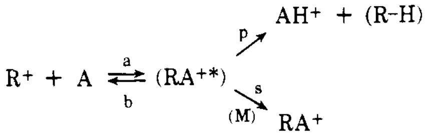


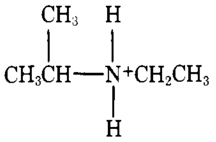
Figure 7. The ratio of condensation product to proton-transfer product as a function of third body density in the reaction of t-$C_4H_9^+$ with $C_2H_5NH_2$ at 340 K. Experiments were done with a reaction mixture of 1% NH_3 in isobutane.

Scheme I



σ-bonded excited condensation products RA^{+*}, such as t-$C_4H_9NH_3^{+*}$ in reaction 10. Evidently, the *condensation* reactions proceed through intermediates of this structure. The mechanistic question is therefore restated as follows. Are the proton-transfer product and the condensation product formed by competition between unimolecular decomposition and collisional deactivation of the common intermediate RA^{+*}? Schematically, the mechanism we wish to test is presented in Scheme I; here RA^{+*} represents the σ-bonded excited intermediate.

We shall propose that Scheme I cannot describe adequately the experimental results. The most direct evidence against Scheme I is the absence of displacement-exchange reactions. Thus RA^{+*} for reaction 3 would represent the ion A. In chemical activation studies it is generally observed that all or most exoergic reactions of the excited reaction intermediate occur. This is observed in neutral as well as ionic systems. For example, the excited methylcyclopropane intermediate formed by the reaction of CH_2 with cyclopropane or propylene rearranges to all possible isomers of isobutene.[17] The excited $H_2O_2^{+*}$ intermediate formed from O_2^+ and H_2 decomposes to OH^+, O_2H^+, and H_2O^+.[18] The relative yields of the products are determined by the relative activation enthalpies and entropies of the accessible channels. Applied to the present system, we may expect that both the proton-transfer and displacement channels should occur since both involve similar decompositions of ion A. Indeed, the decomposition of this intermediate both to i-$C_3H_7NH_3^+$ and to $C_2H_5NH_3^+$ should involve breaking of a C-H bond and forming an N-H bond, probably via similar cyclic intermediates.[7] The energy and entropy of the transition states for the formation of the two products should therefore be comparable. The absence of displacement reactions, even when thermodynamically favored, thus indicates that the major channel for proton transfer does not involve σ-bonded intermediates such as ion A.



A

Scheme I is also inconsistent with the observed pressure effects. According to Scheme I the product distribution ratio would be given by

$$I_{RA^+}/I_{AH^+} = k_s(M)/k_p \qquad (1)$$

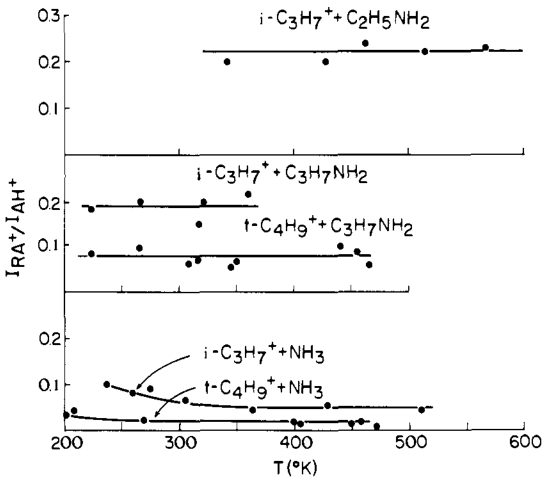


Figure 8. The ratio of condensation to proton-transfer products as a function of temperature for the reactant pairs indicated in the figure. Each temperature study was conducted at a constant third body density of 3 × 10^{16} cm^{-3}, except for the reaction of i-$C_3H_7^+$ with NH_3, which was done at $N_{C_3H_8} = 2.5 \times 10^{16}$ cm^{-3}.

The product distribution ratio should then increase linearly with (M) until condensation becomes the only channel. Figures 6-8 clearly show that, in general, this is not the case and I_{RA^+}/I_{AH^+} levels off to a small finite value.

We can also examine whether Scheme I is consistent with the results of the temperature studies. Qualitatively, the rate constant for decomposition of RA^{+*} may be described by the classical RRK expression[1] for the decomposition of a molecule represented by s coupled classical oscillators of frequency:

$$k_p = [(E - E_0)/E]^{s-1} \qquad (2)$$

E, the total internal energy of RA's, will be given by

$$E = \Delta H_a + E_{th}(R^+) + E_{th}(A) + E_{tr} = \Delta H_a + \Sigma E_{th} \qquad (3)$$

where ΔH_a is the exothermicity of association of R^+ and A to form RA^+, E_{th} is the internal thermal energy of the reactants, and E_{tr} is the relative translational energy of the reactants. ΣE_{th} is the sum of the thermal (including translational) energy terms. E_0 is the critical energy required in the reaction coordinate for decomposition to products. The internal energy in excess of the critical energy is thus given by

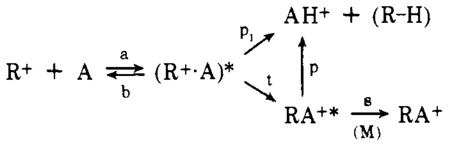
$$E^* = E - E_0 = \Delta H_a - E_0 + \Sigma E_{th} \qquad (4)$$

For the reaction of t-$C_4H_9^+$ with NH_3, $\Delta H_a = 38.3$ kcal/mol. The exothermicity of proton transfer is 8.3 kcal/mol. E_0 will be at least as large as the difference between the deepest point on the reaction surface, which is 38.3 kcal/mol below the separated reactants, and the energy of the separated products, which is 8.3 kcal/mol below the reactants. E_0 will be larger if there is an activation barrier for the inverse reaction. Thus $E_0 \geqslant 38.3 - 8.3 = 30$ kcal/mol. The internal energy in excess of the critical energy is therefore $E^* \leqslant \Sigma E_{th} + 8.3$ kcal/mol.

$E_{th}(t$-$C_4H_9^+)$ may be approximated for the present qualitative purposes by the sum of the average thermal vibrational energies of quantum oscillators of C_4H_{10}. $E_{th}(NH_3)$ is calculated similarly using the vibrational frequencies of NH_3.[19] E_{tr} is calculated from the kinetic energy associated with the average relative molecular velocities.

The result is $\Sigma E_{th} = 1.4$ kcal/mol at 200 K and $\Sigma E_{th} = 5.0$ kcal/mol at 400 K. These values are not negligible even when compared with the largest possible value of $\Delta H_a - E_0$ which is 8.3 kcal/mol. Thus ΣE_{th} constitutes a significant fraction of the excess energy E^* (eq 4). Since $k_p \propto (E^*)^{s-1}$, k_p will thus be significantly affected by the variation of E^* as the temperature changes. This is true even though ΣE_{th} may be small

Scheme II



compared with the *total* internal energy. For example, the change in k_p for the decomposition of $t\text{-}C_4H_9NH_3^{+*}$ between 200 and 400 K may be estimated from eq 2 using the energy values quoted above. For a conservative estimate, the number of active oscillators, s, is taken as $(3N - 6)/3$. Then one finds $k_{400}/k_{200} = 10.1$. In a less conservative estimate, using $s = 3N - 6$, one finds $k_{400}/k_{200} = 2 \times 10^3$.

Since k_s does not depend significantly on the temperature, eq 1 in conjunction with Scheme I would then predict $(I_{t\text{-}C_4H_9NH_3^+}/I_{NH_4^+})_{400}/(I_{t\text{-}C_4H_9NH_3^+}/I_{NH_4^+})_{200} = 10.1$. Therefore, even by a conservative estimate, the temperature effect on the product distribution in reaction 10 should be marked if Scheme I were correct. Evidently, this is in variance with the remarkably temperature independent behavior of I_{RA^+}/I_{AH^+} for this reaction.

For the other reactions whose temperature dependences were studied, ΔH_a and possibly $\Delta H_a - E_0$ is much larger than that for reaction 10. In these cases ΣE_{th} may be only a small fraction of the total excess energy E^* and k_p could be approximately independent of the temperature. The temperature effects are useful as a mechanistic evidence only for reaction 10. For other reactions the observed pressure effects and the absence of displacement reactions provide evidence that, in general, Scheme I does not describe correctly the mechanism of the present competitive reactions.

2. An Alternative Mechanism via a Common Precursor of AH^+ and RA^{+*}. Since Scheme I is not adequate, I shall suggest Scheme II as a mechanism which is consistent with the data. Scheme II is proposed primarily on the basis of the observed pressure effects. It is also consistent with the other experimental results, as will be discussed.

$(R^+{\cdot}A)^*$ in Scheme II represents an intermediate composed of the interacting reactants, but different from RA^{+*}. From the mechanistic point of view the only important feature of $(R^+{\cdot}A)^*$ is that it is a common precursor from which AH^+ and RA^{+*} are formed by unimolecular reactions. Once thus formed from $(R^+{\cdot}A)^*$, RA^{+*} can still react, as in Scheme I, through competitive processes p and s. The intermediate $(R{\cdot}A^+)^*$ could also back-dissociate to reactants. In the present reactions which proceed near collision rate this process is not significant.

Straightforward kinetic analysis of Scheme II shows that the product distribution ratio is given by

$$\frac{I_{RA^+}}{I_{AH^+}} = \frac{k_t k_s(M)}{k_{p_1}[k_p + k_s(M)] + k_p k_t} \tag{5}$$

At low pressures this equation simplifies to

$$\left(\frac{I_{RA^+}}{I_{AH^+}}\right)_{LP} = \frac{k_t k_s(M)}{k_p(k_t + k_{p_1})} \tag{6}$$

while at high pressures

$$\left(\frac{I_{RA^+}}{I_{AH^+}}\right)_{HP} = \frac{k_t}{k_{p_1}} \tag{7}$$

Thus at low pressures I_{RA^+}/I_{AH^+} is proportional to the pressure and approaches 0 as the pressure approaches 0. At high pressures I_{RA^+}/I_{AH^+} achieves a finite ratio which is no longer dependent on the pressure. These features agree with experiment (Figures 5-7).

The observed effects of temperature on the pressure dependence of I_{RA^+}/I_{AH^+} are also consistent with Scheme II. Transition between low-pressure and high-pressure behavior occurs as $k_s(M)$ increases compared with k_p when (M) is increased (eq 5). k_p is a unimolecular dissociation rate constant which is directly related to the temperature as discussed above. k_s is not significantly affected by the temperature. Thus $k_s(M)$ should become comparable with k_p at lower values of (M) as the temperature decreases. Consequently the high-pressure limits should be reached at lower values of (M) at lower temperatures. This trend is also confirmed by experiment, as observed in Figures 5 and 6.

Since RA^{+*} appears in Scheme II, displacement-exchange reactions should still be observed at low pressures according to the arguments given above, but only as a minor channel in the overall scheme. We observed in Figure 4 that the ion corresponding to the displacement-exchange product is present at a small intensity. The data is not sufficient to decide whether the *m/e* 60 ion is formed via the displacement-exchange reaction or from an impurity. This could be better investigated by low pressure ICR studies where the competing condensation channel is absent.

The relation between Scheme II and the observed temperature and steric effects will be discussed in the next section.

3. The Structure of the Primary Complex $(R^+{\cdot}A)^*$. Assigning a structure of a transitory species on the basis of indirect mechanistic evidence must of course be speculative. This is recognized in discussing the following suggestion as to the nature of the precursor complex $(R^+{\cdot}A)^*$ and its relation to the observed temperature and steric effects.

I propose that $(R^+{\cdot}A)^*$ is a loosely bound complex, where the reactants are trapped in a shallow well corresponding to the electrostatic attraction of the reactants. This loose complex may exist for many vibrational periods[20,21] owing to inelastic collisions between the reactants which distribute the relative kinetic energy of the ion-molecule pair among the internal degrees of freedom. The ion-molecule pair will then undergo oscillations between close approach (limited by repulsive forces) and separation to at least a fraction of the initial capture distance, usually 5-10 Å. The reactants are thus trapped to stay together and undergo many collisions, a situation somewhat similar to the cage effect in solution. The actual motion of the reactants in the ion-molecule complex must be quite complicated, involving tumbling and rotation of the reactants about each other. As a first approximation the radial component of the motion can be seen as a low frequency vibration along the weak ion-molecule bond. The vibrational period of weak bonds is usually $10^{13}\text{-}5 \times 10^{-13}$ s^{-1}. A similar number is obtained if the ion and molecule are considered oscillating in a polarization field ($V = e^2\alpha/2r^4$). For example, for $C_3H_7^+$ and NH_3 oscillating between $r = 0$ and $r = 5$ Å, without considering ion-permanent dipole interactions, the period of oscillation is 6.5×10^{-13} s. Since excited ion-molecule complexes can exist to $10^{-8}\text{-}10^{-9}$ s,[23] thousands of intracomplex collisions may be possible. Reactions in the channels p_1 or t will occur when the relative orientation of R^+ and A in the intracomplex collision is appropriate. Since reaction p_1 is exothermic proton transfer and t is association which does not require the breakage of existing bonds, both intracomplex processes may proceed without significant energy barriers. Alternatively, p_1 may be a direct process[22] which competes with the formation of a complex (process t). In either case, k_t/k_{p_1} will be determined only by the geometrical restrictions on the processes p_1 and t. The branching ratio k_t/k_{p_1} will thus be independent of temperature, as is reflected experimentally in $(I_{RA^+}/I_{AH^+})_{HP}$ (Figure 8). However, k_t/k_{p_1} will be affected by steric factors, as is observed in the decrease of I_{RA^+}/I_{AH^+} when A is a highly hindered tertiary amine (reactions 9, 10, 17, 18, Table I).

The possibility that proton transfer between primary and secondary carbonium ions and amines may proceed through a hydrogen bound, rather than σ-bonded intermediate (e.g., $H_3N\cdots H^+\cdots CH_2{-}CH_2$), was proposed by Su and Bowers.[7]

Such structure may be an alternative to the tumbling complex proposed here for $(R^{+}\cdot A)^{*}$.

Conclusion

Our data indicates that Scheme I is not adequate, and that a precursor of the specifically bound complex RA^{+*} plays an important role in the mechanism.

We note that a similar two-stage mechanism can explain some other unexpected ion-molecule phenomena. One such phenomenon is the behavior of several association reactions at high pressures. In general, at the high-pressure limit every complex formed by capture collision of the reactants should be stabilized to form the association products. Thus the overall rate constant for association, $(k_f)_{HP}$, should approach the collision rate constant k_a. This was indeed observed in the clustering of simple amines.[23] However, some association reactions level off to $(k_f)_{HP} \ll k_a$. Also, in these cases $(k_f)_{HP}$ shows a significant negative temperature dependence. Such anomalous behavior was observed in the clustering of N_2^+ with N_2 and of O_2^+ with O_2,[24] in the clustering of sterically hindered amines,[23,25] and in the association of carbonium ions with HCN.[26] This behavior can be explained by competition between back-dissociation of a loose complex and the formation of the tight complex which may be ultimately stabilized. The applicable scheme is a variant of Scheme II, obtained by omitting processes p and p_1, but considering the inverse of process t. Mathematical analysis then gives

$$(k_f)_{HP} = k_a k_t/(k_b + k_t) < k_a \tag{8}$$

The negative temperature dependence of $(k_f)_{HP}$ results from the positive temperature dependence of k_b.

Another example where a variant of Scheme II may be applicable are slow transfer reactions, such as H^- transfer. These reactions exhibit negative temperature coefficients and slow rate constants, both of which correlate with increasing steric crowding of the reactants.[27] If these reactions involve tight, specifically bound complexes, then again competition between back-dissociation of the primary loose complex and the formation of the tight complex may explain these kinetic features.

The theoretical treatment of the dynamics of complex motions in the loose complex may be very involved. If these processes indeed affect the overall rate constant, RRKM treatment of the tight complex will not give the complete kinetic picture. In these cases transition state theory may still be used profitably to calculate the overall rate constant, since in this approach only the equilibrium properties of the tight transition complex have to be known, and knowledge of the detailed dynamics is not necessary.

In conclusion, a long-lived loose complex may be the first intermediate in several types of ion-molecule reactions. Competitive reactions of the original reactants within this complex may result in otherwise unexpected temperature and pressure effects.

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