An Ion Cyclotron Resonance Study of the Ion–Molecule Reactions in Methane–Ammonia Mixtures[1]

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Abstract: The ion–molecule reactions of ions formed by electron impact in methane–ammonia mixtures have been studied by ion cyclotron resonance (icr) techniques, and a number of charge transfer, proton transfer, hydrogen atom abstraction, and condensation reactions have been identified. Ion cyclotron resonance single- and double-resonance techniques using mixtures of isotopically substituted methane and ammonia have been combined to identify and to sort out the masking effects of exchange reactions to study the mechanism of the condensation reaction of methyl cations with ammonia. The condensation is shown to proceed by two distinct channels, one resulting in loss of a hydrogen molecule across the C–N bond, and the other by loss of a hydrogen molecule from the nitrogen end of the intermediate complex. The first process results in an excited $(CH_2NH_2^+)^*$ ion, and the second yields the CH_3NH^+ ion. The ratio of the rates of these two reactions is approximately 3.3, and the total rate for the condensation reaction is $2.0 \pm 0.5 \times 10^{-9}$ cm^3/(molecule sec). The excited $(CH_2NH_2^+)^*$ ion undergoes exothermic proton transfer to NH_3, the proton most likely coming from the carbon end of the molecule. At high pressures, the $(CH_2NH_2^+)^*$ ion is deactivated by nonrearrangement collisions. Proton transfer from ground state $CH_2NH_2^+$ ions to ammonia is endothermic and results in proton loss exclusively from the nitrogen end of the molecule.

The important place methane and the hydrocarbons hold in fundamental organic chemistry has provided a continuing impetus for the study of these molecules. Reactions between ions and molecules are basic processes in radiation chemistry,[3] and the ion–molecule chemistry of the hydrocarbons, methane in particular, has been the most widely studied aspect of the modern investigation of ion–molecule reactions.[4–6]

Hydrocarbon ions exhibit a wide variety of ion–molecule reactions including condensations.[4–6] The primary ions of ammonia do not undergo condensation as readily as in methane,[7–9] and two papers have previously appeared on the ion–molecule reactions in mixtures of methane and ammonia.[10,11] Munson and Field[10] identified the condensation product, $CH_2NH_2^+$, in the high-pressure mass spectrum of the mixture, and correctly inferred the ion–molecule reactions which lead to its formation.

In this study, ion cyclotron magnetic resonance single- and double-resonance techniques are applied to the study of the ion chemistry in methane–ammonia mixtures. A survey of the reactions occurring in the system is made and the condensation reaction producing the $CH_2NH_2^+$ secondary ion from CH_3^+ is examined in detail. The mechanism of condensation and the rate of the reaction are contrasted with the similar condensation of methyl cations with methane, which produces the $C_2H_5^+$ ion.

Experimental Section

Ion cyclotron resonance has quite special advantages for the study of ion–molecule reactions, including the double-resonance technique and long ion reaction path length. The technique has been described extensively in the literature in recent years.[12] The JPL ion cyclotron resonance spectrometer used in this study is equipped for pulsed-drift modulation, resulting in an absorption rather than a derivative signal. The polarity of the dc drift voltages applied to the source region top and bottom plates are alternately reversed at 45 Hz so that during the "off" part of the cycle, ions are drifted out the back end of the cell. This helps eliminate line shape problems caused by trapping ions in the source region when only one of the source region drift plates is pulsed. The voltages applied to the source region drift plates were typically 0.8–1.0 V. A marginal oscillator frequency of 458 kHz was used in order to take advantage of the maximum magnetic field possible. This markedly increases the resolution and the signal-to-noise ratio. The electron energy normally used was 30 eV.

The single most important factor for successful operation of the spectrometer is regulation of the electron emission current below 0.02 μA at pressures greater than 5×10^{-6} Torr in order to avoid excessive space charge and excessive ion densities. High emission currents result in a shift in resonant frequency and a loss of ions from the cell. Artifacts are observed in double-resonance spectra at high ion densities due to ion–ion coupling, space–charge shift, and loss of ions from the cell. Such artifacts can also be induced by gross imbalance and poor matching of the applied drift fields in the source and analyzer regions of the icr cell. Double-resonance spectra in this study were recorded at electron emission currents of between 0.01 and 0.02 μA at irradiating field strengths of 0.04–0.10 V/cm, and were tested for artifacts by doubling or halving the emission current. The maximum ion kinetic energy at these irradiating field strengths and at the pressures used in double-resonance experiments is estimated to be approximately 2 eV.

Pressure measurements were made with a GE 22GT103 ion gauge, and are reported uncorrected for gas composition. Spectra were taken both with prepared mixtures of CH_4 and NH_3 and by introducing the pure gases through two separate sample inlet systems. Some difficulty is encountered with ammonia, since this gas is

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[6] Reviews by J. H. Futrell and T. D. Tiernan and by G. G. Meisels, contained in ref 3.

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strongly adsorbed on metal and glass walls in the spectrometer. For this reason, reported ammonia concentrations and partial pressures may be somewhat in error. The gases were from commercial sources and were used without further purification. The methane was obtained from Phillips, 99.56% grade; the ammonia from J. T. Baker, anhydrous grade; and the CD_4, $^{15}NH_3$, and ND_3 were obtained from Merck Sharpe and Dohme, 99 atom % grades.

Ion–Molecule Reactions in Methane–Ammonia Mixtures

Table I summarizes ion–molecule reactions which have been previously observed in pure methane or pure ammonia and which have been observed by double resonance in the mixtures in the course of this study. The third column in Table I shows the direction of the change in reaction rate with increasing kinetic energy of the reactant ion as determined from the sign of the double-resonance signal.[13] Reaction 1 has been studied extensively in studies of ion–molecule reactions,[4–6] and reaction 2 is the major condensation reaction observed in methane at thermal ion kinetic energies.[4–6]

Table I. Reactions of Methane and Ammonia Primary Ions in the Pure Gases

	Reaction	Ref	dk/dE_{ion}
(1)	$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3$	4–6	–
(2)	$CH_3^+ + CH_4 \rightarrow C_2H_5^+ + H_2$	4–6	–
(3)	$CH_2^+ + CH_4 \rightarrow C_2H_4^+ + H_2$	4–6	–
(4)	$NH_3^+ + NH_3 \rightarrow NH_4^+ + NH_2$	7–9	–
(5)	$NH_2^+ + NH_3 \rightarrow NH_4^+ + NH$	8	–
(6)	$NH_2^+ + NH_3 \rightarrow NH_3^+ + NH_2$	7, 9	+

The rates for the condensation reactions in ammonia are too slow[7,9] to be observed. The protonation reaction 4 is observed, and the NH_2^+ ion is observed to undergo concurrent and competing reactions with NH_3. The proton transfer reaction 5 shows a decrease in rate with increasing reactant ion kinetic energy, while the charge transfer reaction 6 shows an increase in rate with increasing kinetic energy. Charge transfer reactions generally appear to exhibit an increase in rate with reactant ion energy, unlike most proton transfer, atom transfer, and condensation reactions, which generally exhibit a decrease in rate with increasing ion kinetic energy.

Table II. Reactions of Ions in Methane–Ammonia Mixtures

	Reaction	Ref	dk/dE_{ion}
	Primary Ions		
(7)	$CH_4^+ + ND_3 \rightarrow ND_3H^+ + CH_3$	10	–
(8)	$CH_4^+ + ND_3 \rightarrow ND_3^+ + CH_4$	10	+
(9)	$CH_4^+ + ND_3 \rightarrow CH_4D^+ + ND_2$	11	(?)
(10)	$CH_3^+ + ND_3 \rightarrow CH_2ND_2^+ + HD$	10	–
(11)	$CH_3^+ + ND_3 \rightarrow ND_3H^+ + CH_2$	10	(–)
(12)	$CH_3^+ + ND_3 \rightarrow ND_3^+ + CH_3$		(+)
(13)	$CH_2^+ + ND_3 \rightarrow CH_2ND_2^+ + D$	10	–
(14)	$CH_2^+ + ND_3 \rightarrow ND_3H^+ + CH$	10	(–)
(15)	$NH_3^+ + CD_4 \rightarrow NH_3D^+ + CD_3$		–
	Secondary Ions		
(16)	$CH_5^+ + ND_3 \rightarrow ND_3H^+ + CH_4$	10	–
(17)	$C_2H_3^+ + NH_3 \rightarrow NH_4^+ + C_2H_2$		–
(18)	$C_2H_4^+ + NH_3 \rightarrow NH_4^+ + C_2H_3$		–
(19)	$C_2H_5^+ + NH_3 \rightarrow NH_4^+ + C_2H_4$	10	–
(20)	$(CH_2NH_2^+)^* + NH_3 \rightarrow NH_4^+ + CH_2NH(?)$		–

In Table II are listed the ion–molecule reactions observed by double resonance in methane–ammonia mixtures between an ion of one species and neutrals of the other. In performing these identifications, it was helpful to employ mixtures containing isotopically substituted methane and ammonia in order to distinguish between ions which fall at the same mass in one or another mixture. To illustrate the origin of the hydrogen atoms in the product ions, reactions in Table II are shown between the ion and the fully deuterated complementary neutral molecule. Both CH_3-ND_3 and CD_4-NH_3 mixtures were used in these studies.

The methane parent ion undergoes a variety of reactions with ammonia including proton transfer, charge transfer, and hydrogen atom abstraction. Munson and Field[10] have observed the proton transfer reaction, and Harrison and Thynne[11] have reported hydrogen atom abstraction from neutral NH_3 by CD_4^+ ions. Only a very small peak is observed at *m/e* 21 in the icr spectrum of CD_4-NH_3 mixtures. This peak corresponds either to CD_4H^+ produced by proton transfer from CD_3H^+ impurity to methane or to the hydrogen atom abstraction reaction 9. Because of the low signal strength of the CD_4H^+ ion, reliable double resonance was not obtained for this reaction.

The thermal rate constant for the abstraction reaction reported by Harrison and Thynne is small, 1.2×10^{-10} cm^3/(molecule sec), and the proton transfer reactions 1 and 7 compete strongly for this ion. An additional competing channel is charge transfer, reaction 8. This reaction is exothermic since the ionization potentials of CH_4 and NH_3 are 13.0[14] and 10.1 eV,[15] respectively. The reaction shows an increase in rate with kinetic energy typical of charge transfer reactions, so that in encounters between CH_4^+ ions and NH_3 molecules, the charge transfer reaction channel increases with increasing CH_4^+ kinetic energy at the expense of the proton transfer reaction channel.

The methyl cation condenses with ammonia in a manner analogous to the condensation with methane. The ion at *m/e* 30 in CH_4-NH_3 mixtures is the only ion observed in the single-resonance spectrum which is not present in the spectrum of either pure gas, and is the only condensation product observed in which a C–N bond is formed (see Figure 1). Reaction 10 shows that the product ion has the structure $CH_2NH_2^+$. It will be shown later that a small amount of CH_3NH^+ is also formed and that the $CH_2NH_2^+$ ion is formed in an excited state. The CH_2^+ ion also reacts with ammonia to produce the $CH_2NH_2^+$ ion. Reactions 10 and 13 are identified in the pulsed double-resonance spectrum shown in Figure 2. The spectrum clearly illustrates the decrease in rate with ion kinetic energy typical of condensation reactions.

The double-resonance spectrum in Figure 2 was taken at relatively low pressure and short ion residence time (5×10^{-6} Torr and 1.0 μsec). At higher pressures and longer ion residence times (1×10^{-5} Torr and 3.0 μsec), peaks appear in double-resonance spectra which are evidently due to reactions 11 and 14. At high pressure and long ion residence times, indirect couplings due to tertiary reactions may be expected in icr double-resonance spectra, and these particular

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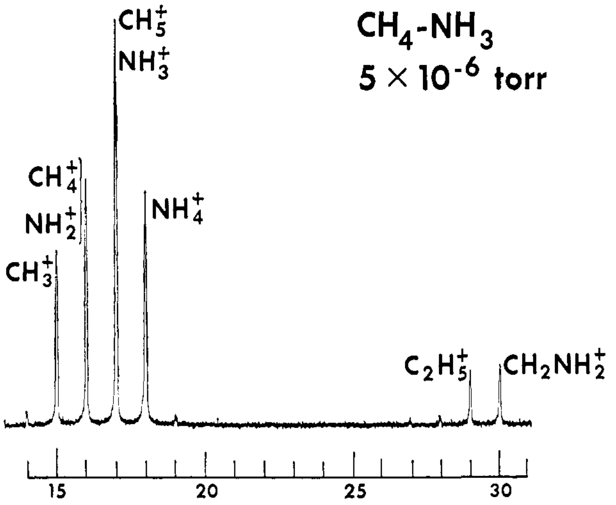

Figure 1. Single-resonance spectrum, 2:1 mixture of CH_4 and NH_3, electron energy 30 eV, ion residence time 2.0 msec.

peaks may also be due to the reaction sequence CH_2^+ or $CH_3^+ \rightarrow (CH_2NH_2^+)^* \rightarrow NH_4^+$ (reaction 10 or 13, followed by reaction 20). The magnitude of the response, however, appears to be more than can be expected on the basis of indirect coupling alone, and reactions 11 and 14 may therefore be responsible. From the pressure and ion residence times required to observe these responses, the proton transfer reactions must have rates an order of magnitude less than the rates for condensation. It is clear that condensation is the major reaction channel in encounters between CH_2^+ or CH_3^+ ions with NH_3 neutrals at thermal ion kinetic energies.

Charge transfer from the methyl cation to ammonia, reaction 12, is slightly endothermic. The recombination energy of CH_3^+ is 9.84 eV,[16,17] and the ionization potential of NH_3 is 10.1 eV.[15] The charge transfer from CH_3^+ to NH_3 can be observed, however, in icr double-resonance spectra at irradiation field strengths sufficient to accelerate the CH_3^+ ion to kinetic energies in excess of 0.26 eV. The response indicates an increase in reaction rate with kinetic energy consistent with an endothermic process.

Reaction 15 is the only reaction observed between ammonium ions and methane neutrals. No reactions between the NH_2^+ ion and CH_4 were observed. This is unusual since several exothermic reactions are possible. To escape detection, the rates for these reactions must be less than 0.5×10^{-10} cm³/(molecule sec). The proton affinity of ammonia is very high, 207 kcal/mol,[18] and all primary and secondary ions in methane undergo proton transfer to ammonia. The CH_5^+ product ion and the condensation productso bserved in methane–ammonia mixtures are all observed to undergo proton transfer to ammonia. Reaction 20 will be shown to occur only for $CH_2NH_2^+$ molecules formed in an excited state by the condensation between CH_3^+ and NH_3.

In addition to double resonance, plots of the normalized single-resonance intensity of the ions in the spectrum *vs.* pressure are useful in illustrating the ion–molecule reactions occurring in the system. Figure 3

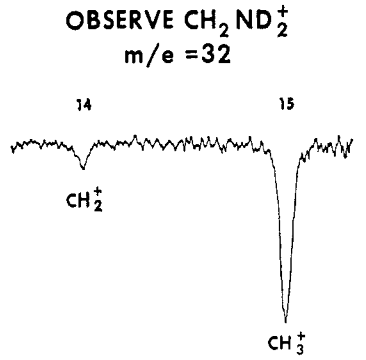

Figure 2. Condensation reactions: double-resonance spectrum observing $CH_2ND_2^+$ at *m/e* 32 in a 2:1 mixture of CH_4 and ND_3, pressure 5×10^{-6} Torr, ion residence time 1.0 msec, irradiation field strength 0.05 V/cm.

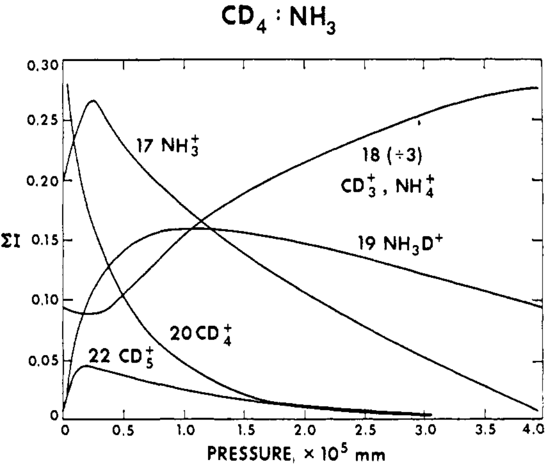

Figure 3. Intensity *vs.* pressure study of the ions *m/e* 17–22 in a 2:1 mixture of CD_4 and NH_3, electron energy 30 eV, ion residence time 2.0 msec.

shows a typical plot for the low mass ions in a 2:1 mixture of CD_4 and NH_3. The initial rise in the curve for the NH_3^+ ion is due to the charge transfer reactions from NH_2^+ and CD_4^+. This is followed by a slow decline due to proton transfer to NH_3 and to D atom abstraction from CD_4. The methane parent ion CD_4^+ shows a monotonic decrease owing to charge transfer to NH_3 and to proton transfer to both CD_4 and NH_3. The initial rise in the CD_5^+ product ion declines sharply owing to proton transfer to NH_3. The initial decline of the curve for *m/e* 18 is caused by the condensation reaction of CD_3^+ with NH_3. This is followed by a steep rise due to the formation of NH_4^+ by proton transfer from NH_3^+ and to resonant proton transfer from NH_3D^+.

$$NH_3D^+ + NH_3 \longrightarrow NH_4^+ + NH_2D \qquad (21)$$

This latter reaction is also evident in the diminution of the NH_3D^+ product ion intensities at elevated pressures, and is readily seen in double resonance. Munson and Field[10] observed this reaction and estimated the rate constant to be on the order of 10^{-9} cm³/(molecule sec).

Internal Excitation of the $CH_2NH_2^+$ Product Ion

Ammonia is a very effective proton scavenger, and at 1×10^{-4} Torr the NH_4^+ ion is the only ion observed

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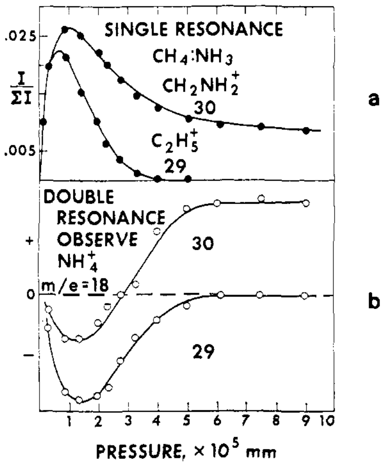

Figure 4. Single- and double-resonance studies of the proton transfer reactions of $C_2H_5^+$ and $CH_2NH_2^+$ in a 2:1 mixture of CH_4 and NH_3. Illustration of the change with pressure from exothermicity to endothermicity of the reaction 30 → 18. Ion residence time 2.0 msec, irradiation field strength (double resonance) 0.10 V/cm.

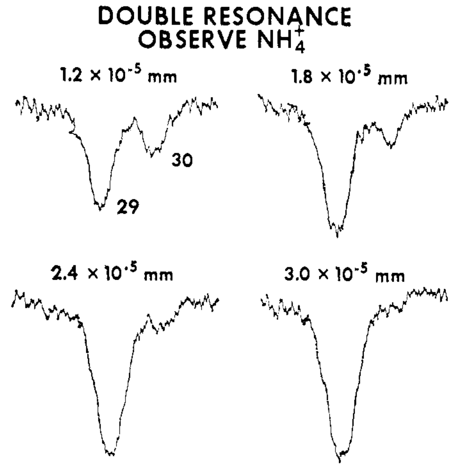

Figure 5. Double-resonance study of the reactions 29 → 18 and 30 → 18 in mixtures of CH_4 and NH_3. The fraction of CH_4 in the mixture was increased at each pressure such that the *single* resonance intensities are *equal* at *m/e* 29 and 30 at each pressure, ion residence time 2.0 msec, irradiating field strength 0.10 V/cm.

in the single-resonance spectrum of CH_4–NH_3 mixtures with the exception of a much smaller peak due to the $CH_2NH_2^+$ ion. This latter ion undergoes proton transfer to ammonia at lower pressures, but at high pressures the proton transfer reaction is no longer observed and the *m/e* 30 ion persists in the CH_4–NH_3 single-resonance spectrum. This behavior is illustrated in Figure 4a, where the other major condensation product, the $C_2H_5^+$ ion at *m/e* 29, is included for comparison. The proton transfer reaction from $C_2H_5^+$ to NH_3 is 50 kcal/mol exothermic and proceeds to completion. It is quite apparent from the intensity *vs.* pressure curve for the *m/e* 30 ion in Figure 4a, that unlike the *m/e* 29 ion, the proton transfer reaction does not proceed to completion and that the reaction is inhibited at higher pressures. This suggests that the ion may possibly be formed initially in an excited state in which the proton transfer reaction is exothermic, and that at higher pressures the excited ion is collisionally deactivated to the ground state ion, for which the proton transfer reaction is evidently endothermic. This hypothesis is supported by the double-resonance data given in Figure 4b.

Figure 4b shows the double-resonance intensity *vs.* pressure for the proton transfer reactions of $C_2H_5^+$ and $CH_2NH_2^+$. The double-resonance intensity *vs.* pressure for reaction 19 parallels the single-resonance intensity almost exactly, and shows a decrease in product ion intensity with increasing kinetic energy of the reactant ion typical of exothermic proton transfer reactions. In order to get a negative response, or decrease in ion intensity, it is a necessary condition that the reaction proceed at thermal ion kinetic energies. The fact that intensity *vs.* pressure curves for double and single resonance exhibit the exact same behavior with pressure indicates that reaction 19 proceeds with the same rate at all pressures.

The initial behavior of the double-resonance intensity *vs.* pressure curve in Figure 4b for reaction 20 at low pressures is similar, and the reaction appears to be exothermic. However, with increasing pressure there is a marked deviation, and the double-resonance response changes sign to become positive. At high pressures the magnitude of the response for reaction 20 reaches a plateau, corresponding to the behavior of the single-resonance intensity for the $CH_2NH_2^+$ ion. The positive response indicates that the product ion intensity increases with increasing reactant ion kinetic energy. This is necessarily the case for an endothermic reaction. The level of this plateau is dependent on irradiating power, decreasing rapidly to zero for decreasing irradiating power.

At high pressures, then, it appears that the proton transfer reaction 20 becomes endothermic, and that this endothermicity is overcome by increasing the translational energy of the reactant ion. The change in reactivity observed for the $CH_2NH_2^+$ ion is consistent with some change in the state of the ion at high pressures. The condensation reaction between CH_3^+ and NH_3 is highly exothermic, releasing 74 kcal/mol of energy. It is therefore not reasonable that the initial product should contain a significant amount of internal energy.

An additional experiment which is consistent with this hypothesis is illustrated in Figure 5. The figure shows the double-resonance spectra for proton transfer to NH_3 from $C_2H_5^+$ and $CH_2NH_2^+$. Unlike the previous experiment, however, the fraction of methane in the sample was increased at each succeedingly higher total pressure, so that the *single-resonance* intensities at *m/e* 29 and 30 were equal at each value of the pressure. Under these conditions, the relative double-resonance intensities for reaction 19 and 20 should not change with pressure since the rate of production of both reactant ions is the same at each pressure, and since the relative rates and dk/dE_{ion} for the protonation reactions should be independent of pressure. It is clear from Figure 5, however, that the rate for reaction 20 must decrease with pressure, indicating that the *m/e* 30 ion is collisionally deactivated at higher pressures.

Mechanism of the Condensation Reaction between CH_3^+ and NH_3

The analogous condensation in methane, reaction 2, has been extensively studied,[4–6] and it has been established that the reaction proceeds with equilibration of

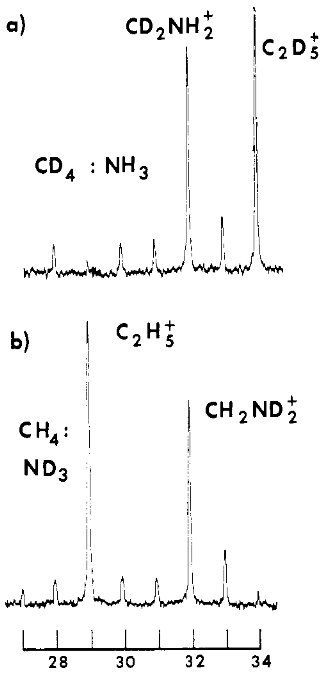

Figure 6. Single-resonance spectra of the condensation products at 5×10^{-6} Torr and 30 eV (a) in a 2:1 mixture of CD_4 and NH_3, and (b) in a 3:2 mixture of CH_4 and ND_3, ion residence time, 2.0 msec.

the protons in the intermediate complex, such that in a reaction between CD_3^+ and CH_4 randomization of the protons occurs in the intermediate and a statistical distribution of products, $C_2(H,D)_5^+$, is observed.[5] Mixtures of CD_4 with NH_3, and of CH_4 with ND_3, were examined in this study in order to determine the fate of the protons during the course of the reaction between methyl cations and ammonia molecules.

The icr single-resonance spectrum of a 2:1 mixture of CD_4 and NH_3 at 5×10^{-6} Torr taken in the high mass portion of the spectrum is given in Figure 6a. The resonances observed at *m*/*e* 31, 32, and 33 are due to the CNH_3D^+, $CNH_2D_2^+$, and $CNHD_3^+$ ions corresponding to the CNH_4^+ ion observed at *m*/*e* 30 in CH_4–NH_3 mixtures. The ion at *m*/*e* 34 is the $C_2D_5^+$ ion from the condensation reaction between CD_3^+ and CD_4. A small amount of the intensity at *m*/*e* 32 must also be due to the $C_2D_4^+$ ion, and the peak at *m*/*e* 30 is due to the $C_2D_3^+$ ion.

The complementary spectrum in Figure 6b is the high mass portion of the single-resonance spectrum of a mixture of CH_4 and ND_3 at 5×10^{-6} Torr. Again resonances are observed at *m*/*e* 31, 32, and 33 corresponding to the CNH_3D^+, $CNH_2D_2^+$, and $CNHD_3^+$ ions from the condensation reaction. In this mixture, the methane condensation products are at *m*/*e* 27, 28, and 29. The ion at *m*/*e* 30 originates from the $C_2H_5^+$ product at *m*/*e* 29 *via* isotope exchange reactions.

The presence of the ions at *m*/*e* 31 and 33 in both spectra suggests that there must be some mechanism for the condensation other than simple loss of HD across the C–N bond. For complete equilibrium in a manner similar to the analogous condensation of methyl cations with methane neutrals, the statistical probabilities for loss of H_2, HD, and D_2 are 1:3:1, respectively, neglecting isotope effects. It is apparent in Figure 6 that the ratio of the intensities of 31, 32, and 33 in both mixtures is significantly different from 1:3:1. More important is the fact that these ratios are a function of the pressure and fraction of ammonia in the sample. For example, as the pressure is raised in CD_4–NH_3 mixtures, the relative peak intensity of the *m*/*e* 31 ion increases dramatically at the expense of the *m*/*e* 33 ion. The change in the relative intensities of the *m*/*e* 31, 32, and 33 ions in CD_4–NH_3 mixtures with increasing ammonia concentration is illustrated in Figure 7a. Extrapolation of the ratios 31/32 and 33/32 to zero total pressure or zero ammonia concentration shows that only the *m*/*e* 32 and 33 ions are initial products of unimolecular decomposition of the $[CD_3NH_3^+]^*$ intermediate complex. The subsequent decrease in the intensity of the ion at *m*/*e* 33 and appearance of the *m*/*e* 31 ion must be due to subsequent reaction with ammonia (*via* exchange as described in the next section).

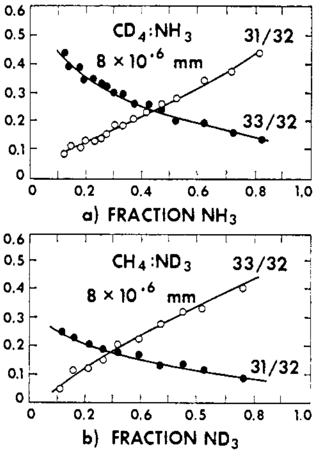

Figure 7. Ratio of the observed single-resonance intensity of the *m*/*e* 31 and 33 ions with *m*/*e* 32 as a function of the fraction of ammonia at constant total pressure (a) in CD_4–NH_3 mixtures, and (b) CH_4–ND_3 mixtures, ion residence time 2.0 msec.

Figure 7b shows the relative intensities of the *m*/*e* 31, 32, and 33 ions in CH_4–ND_3 mixtures. Compared with CD_4–NH_3 mixtures in Figure 7a, the behavior of the curves for the 31/32 and 33/32 ratios is reversed for CH_4–ND_3 mixtures. This result indicates that in the initial decomposition of the complex, a hydrogen molecule is lost either across the C–N bond to form the *m*/*e* 32 product ion, or that the hydrogen molecule is lost from the nitrogen end of the complex ion, forming a *m*/*e* 33 ion from the $[CD_3NH_3^+]^*$ complex and a *m*/*e* 31 ion from the $[CH_3ND_3^+]^*$ complex. These possibilities are illustrated by eq 22–25. Extrapolation of

$$\begin{array}{l} \text{mode 1} \\ (70\%) \end{array} \begin{cases} [\mathrm{CD_3NH_3^+}]^* \longrightarrow \underset{32}{(\mathrm{CD_2NH_2^+})^*} + \mathrm{HD} & (22) \\ [\mathrm{CH_3ND_3^+}]^* \longrightarrow \underset{32}{(\mathrm{CH_2ND_2^+})^*} + \mathrm{HD} & (23) \end{cases}$$

$$\begin{array}{l} \text{mode 2} \\ (30\%) \end{array} \begin{cases} [\mathrm{CD_3NH_3^+}]^* \longrightarrow \underset{33}{\mathrm{CD_3NH^+}} + \mathrm{H_2} & (24) \\ [\mathrm{CH_3ND_3^+}]^* \longrightarrow \underset{31}{\mathrm{CH_3ND^+}} + \mathrm{D_2} & (25) \end{cases}$$

the curves in Figure 7b gives a value of approximately 0.30 for the ratio of $CH_3ND^+/CH_2ND_2^+$ formed. The extrapolation of the curves in Figure 7a is spoiled by the presence at low ammonia concentration of the $C_2D_4^+$ ion at *m*/*e* 32 and the ion $C_2D_4H^+$ at *m*/*e* 33 formed by the condensation of impurities in CD_4.

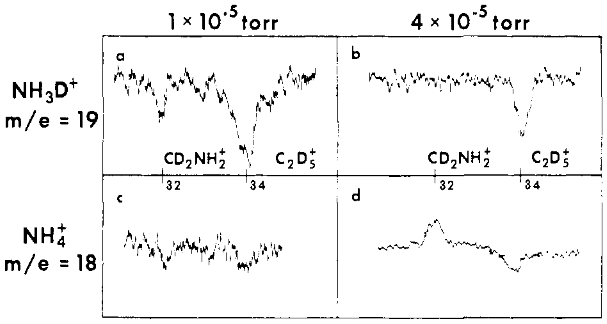

Figure 8. Double-resonance spectra of the NH_3D^+ and NH_4^+ ions in a 2:1 mixture of CD_4 and NH_3, illustrating the origin of the proton transferred from $CD_2NH_2^+$ to NH_3 in the exothermic process at low pressure and in the endothermic process at high pressure, ion residence time 2.0 msec, irradiation field strength 0.10 V/cm.

Exchange Reactions

The effect of increasing pressure and ammonia concentration on the ratio of *m/e* 31, 32, and 33 is seen to shift the weighting in the product distribution toward high mass in the case of CH_4–ND_3 mixtures, and toward low mass in the case of CD_4–NH_3 mixtures. This strongly suggests exchange reactions 26 and 27, in which, during an encounter between the product ion and an ammonia molecule, two atoms of hydrogen are exchanged with no loss in identity of either the ion or molecule. The CD_3NH^+ ion at *m/e* 33 might possibly

$$\underset{33}{CD_2NHD^+} + NH_3 \longrightarrow \underset{32}{CD_2NH_2^+} + NH_2D \qquad (26)$$

$$\underset{32}{CD_2NH_2^+} + NH_3 \longrightarrow \underset{31}{CDHNH_2^+} + NH_2D \qquad (27)$$

undergo collisional rearrangement to CD_2NHD^+ with subsequent exchange, or may possibly undergo exchange directly on collision with NH_3 molecules. Double-resonance results confirm the occurrence of exchange between the *m/e* 33, 32, and 31 ions in these mixtures, and indicate that the rate constant for the exchange reaction increases with increasing ion kinetic energy. Exchange reactions of this type also explain the persistence at high pressures of the *m/e* 30 ion in CD_4–NH_3 mixtures, and the appearance of an ion at *m/e* 34 in CH_4–ND_3 mixtures.

The type of exchange process exhibited by reactions 26 and 27 has been previously observed between isotopically substituted methyl cations and hydrogen molecules.[19–22] Double-resonance results confirm that this same process occurs between methyl cations and ammonia neutrals in CD_4–NH_3 mixtures

$$\underset{18}{CD_3^+} + NH_3 \longrightarrow \underset{17}{CD_2H^+} + NH_2D \qquad (28)$$

$$\underset{17}{CD_2H^+} + NH_3 \longrightarrow \underset{16}{CDH_2^+} + NH_2D \qquad (29)$$

etc. These reactions also show an increase in rate with increasing reactant ion kinetic energy. The formation of isotopically substituted methyl cations by these reactions contributes to the variation of the *m/e* 31, 32, and 33 product ion intensities with pressure and NH_3 concentration, and is evident in the double-resonance spectra of these ions. The double-resonance spectrum of the *m/e* 31 ion at 1 × 10^{-5} Torr in a CD_4–NH_3 mixture contains responses at *m/e* 17 and 16 which must be due to condensation of CD_2H^+ and CDH_2^+ ions with ammonia to produce $CHDNH_2^+$ ions at *m/e* 31. The double-resonance spectrum of the *m/e* 33 ion in CD_4–NH_3 mixtures also shows some coupling to *m/e* 17 and 16 ions, which in this case must be due to condensation of these ions with CD_4 to produce $C_2D_4H^+$. The ion at *m/e* 30 in the single resonance spectrum of CH_4–ND_3 mixtures was shown to be due to the $C_2H_4D^+$ ion produced by condensation of secondary CH_2D^+ ions with CH_4, and by exchange of $C_2H_5^+$ ions with ND_3. This ion disappears with increasing pressure and ammonia concentration by proton transfer to ND_3.

$CD_2NH_2^+$ Proton Transfer Reactions

Double-resonance experiments were performed in the CD_4–NH_3 mixture on the NH_4^+ and NH_3D^+ ions at *m/e* 18 and 19 to determine the origin of the proton transferred from the $CD_2NH_2^+$ ion both in the excited state exothermic proton transfer process and in the ground state endothermic proton transfer process. Figure 8 shows the double-resonance spectra obtained at low pressure and at high pressure for *m/e* 18 and 19. The signal/noise ratio in the low-pressure spectra is very low, which makes it difficult to determine with absolute certainty the origin of the proton in the exothermic process. The spectra in Figures 8a and 8c appear to indicate that the proton most likely transferred from the excited $(CD_2NH_2^+)^*$ at low pressures comes from the carbon end of the molecule. Figures 8b and 8d clearly show that at high pressure, the proton originates exclusively from the nitrogen end of the molecule in the endothermic process.

$$\underset{32}{(CD_2NH_2^+)^*} + NH_3 \longrightarrow \underset{19}{NH_3D^+} + (CDHNH \text{ or } DCN + H_2) \qquad (30)$$

$$\underset{32}{CD_2NH_2^+} + NH_3 + KE \longrightarrow \underset{18}{NH_4^+} + CD_2NH \qquad (31)$$

The spectrum in Figure 8d shows a coupling between the $C_2D_5^+$ ion at *m/e* 34 and the NH_4^+ ion at *m/e* 18. The NH_4^+ ion cannot originate directly by proton transfer from $C_2D_5^+$, and the observed coupling must correspond to the indirect process 34 → 19 → 18. This effect is also observed for the exchange processes, such as 31 → 32 → 33 and 18 → 32 → 31. This effect may also account for any small coupling of 34 or 32 to 18 which may seem to be apparent in Figure 8c, although the possibility still exists that any coupling of 32 to 18 does correspond to the reaction

$$\underset{32}{(CD_2NH_2^+)^*} + NH_3 \longrightarrow \underset{18}{NH_4^+} + CD_2NH \qquad (32)$$

No proton transfer from the CD_3NH^+ isomer is observable because of the low signal/noise ratio.

Rate of the Condensation Reaction

Recent theoretical work[23] has shown how to obtain the rates of ion–molecule reactions from the relative intensities of the primary and secondary ions in the icr single-resonance spectrum. From the relative intensities of the secondary ion peaks at *m/e* 29 and

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(19) S. Wexler, *J. Amer. Chem. Soc.*, **85**, 272 (1963).

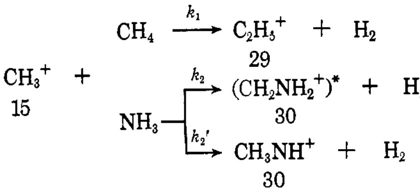
(20) M. S. B. Munson, J. L. Franklin, and F. H. Field, *ibid.*, **85**, 3584 (1963).

(21) M. Inoue and S. Wexler, *ibid.*, **91**, 5730 (1969).

(22) M. T. Bowers and D. D. Elleman, *ibid.*, **92**, 1847 (1970).

(23) S. E. Butrill, *J. Chem. Phys.*, **50**, 4125 (1969).

m/e 30, and from the intensity of the primary ion peak at m/e 15, it is possible to obtain an approximate relative rate for the two condensation reactions of CH_3^+ with CH_4 and NH_3 to form $C_2H_5^+$ and $CH_2NH_2^+$, respectively.



$$CH_3^+ \ (15) + CH_4 \xrightarrow{k_1} C_2H_5^+ \ (29) + H_2 \qquad (33)$$

$$CH_3^+ \ (15) + NH_3 \xrightarrow{k_2} (CH_2NH_2^+)^* \ (30) + H_2 \qquad (34)$$

$$CH_3^+ \ (15) + NH_3 \xrightarrow{k_2'} CH_3NH^+ \ (30) + H_2 \qquad (35)$$

There are several difficulties which prevent an accurate determination of the relative rates. The fact that the secondary ions undergo further reaction makes it necessary to calculate the ratio $(k_2 + k_2')/k_1$ for spectra taken at a low enough pressure where tertiary reactions do not occur. In practice, it proved more convenient to measure the intensities of the ions as a function of pressure at low pressures. The calculated values of $(k_2 + k_2')/k_1$ were extrapolated to zero pressure to obtain the true value.

Another serious difficulty in measuring the relative rates arises from the difficulty of accurately determining the ratio of the concentrations of methane and ammonia in the sample. Ammonia is strongly adsorbed on the walls of the sample bulb, inlet system, and the spectrometer analyzer vacuum system, altering the composition of the gas mixture being examined. To circumvent this difficulty, the fraction of ammonia in the gas stream through the spectrometer analyzer was measured from the intensity of nonoverlapping primary ion peaks in the spectrum of the mixture taken at low pressure.

The results of this procedure yield for the relative rates

$$\frac{k_2 + k_2'}{k_1} = 1.8 \pm 0.5 \qquad (36)$$

These measurements were all made at 15-eV electron energy to eliminate the possibility of the CH_2^+ condensation contributing to the intensity at m/e 30. The relative rates of CH_2^+ condensation *vs.* CH_3^+ condensation with NH_3 is estimated to be 1.3 from the relative contribution of these ions to the double-resonance spectrum of the m/e 30 ion at 30 eV. Munson and Field[10] found that the rate of disappearance of CH_2^+ *vs.* CH_3^+ in CH_4–NH_3 mixtures was approximately 1.5 ± 0.8.

Several measurements of the absolute value for k_1 have been reported,[4–6,24–26] and the most recent of these[25,26] give a value of $k_1 = 1.1 \times 10^{-9}$ cm³/(molecule sec). This value agrees fairly well with the value calculated from the charge–induced dipole model of Gioumousis and Stevenson, 1.3×10^{-9} cm³/(molecule sec).[24] For the reaction of CH_3^+ with NH_3 it may be necessary to include the effect of a charge–permanent dipole potential, which would increase the calculated reaction rate. In this case, the theoretical expression for the thermal rate constant is[27]

$$k = 2\pi e\left(\frac{\alpha}{\mu}\right)^{1/2} + 2\pi e\mu_0\left(\frac{2}{\mu\pi kT}\right)^{1/2} \qquad (37)$$

where α is the angle averaged polarizability of the neutral, μ_0 is the dipole moment of the neutral molecule, and μ is the reduced mass of the ion–neutral pair. The first term is the charge-induced dipole rate of the Gioumousis and Stevenson theory,[28] and the second term is the additional term due to the charge–permanent dipole interaction. The relative efficiency of this latter term in contributing to the reaction rate depends to a large extent on how much the charge–permanent dipole potential is averaged out by rotation of the neutral molecule. Table III shows the measured rates for methyl cation condensation with both methane and ammonia, compared with the theoretical values calculated from both the Gioumousis–Stevenson theory and the expression above. It is quite evident that complete "locking" of the dipolar molecule to the incoming charged ion does not occur. However, it is also clear that the charge–permanent dipole is not completely averaged out by rotations at thermal ion kinetic energies. Fluegge[27] has shown, for example, that the proton-transfer reactions in water are considerably faster than the Gioumousis–Stevenson theory would predict, yet less than the case for complete charge–permanent dipole locking. Further, Munson and Field[10] have reported that the rates for the disappearance of the CH_4^+, CH_3^+, and CH_2^+ ions in ammonia are significantly higher than those with methane, even though the polarizability of ammonia is less.

Table III. Methyl Cation Condensation Rates

		Rate × 10⁹ cm³/(molecule sec)		
Ion	Neutral	Exptl	GS	GS + dipole
CH_3^+	CH_4	1.1 ± 0.1	1.35	1.35
CH_3^+	NH_3	2.0 ± 0.5	1.26	6.07

Discussion

The most interesting results of this study are the identification of the nature of the condensation reaction between methyl cations and ammonia molecules and the subsequent reactions of the product ion. Although analogous, the condensation reactions of CH_3^+ with CH_4 and NH_3 exhibit markedly different behavior. The unimolecular decompositions of the intermediates with loss of H_2 proceed by uniquely different mechanisms. The reaction with CH_4 at thermal kinetic energies proceeds with rearrangement of the protons in the intermediate and statistical loss of H_2.[5] The reaction with NH_3 proceeds by two distinct mechanisms: one resulting in loss of H_2 across the new C–N bond producing an excited $(CH_2NH_2^+)^*$ ion, and the other resulting in loss of H_2 from the nitrogen end of the molecule producing an isomeric CH_3NH^+ ion.

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(24) See also A. G. Harrison, J. J. Myher, and J. C. J. Thynne in "Ion-Molecule Reactions in the Gas Phase," P. Ausloos, Ed., Advances in Chemistry Series, No. 58, American Chemical Society, Washington, D. C., 1966, p 150.

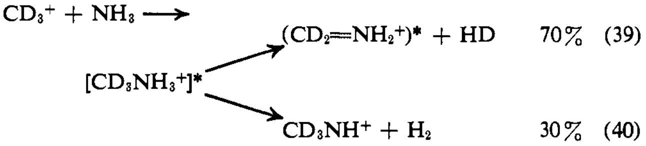
(25) R. P. Clow and J. H. Futrell, presented at the 17th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.

(26) A. G. Harrison and A. A. Herod, presented at the 17th Annual Conference on Mass Spectrometry and Allied Topics, Dallas, Texas, May 1969.

(27) R. A. Fluegge, *J. Chem. Phys.*, **50**, 4373 (1969).

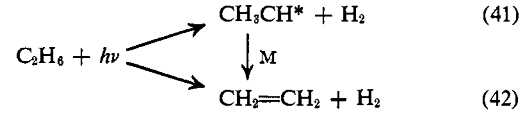
(28) G. Gioumousis and D. P. Stevenson, *J. Chem. Phys.*, **29**, 294 (1958).

$$CD_3^+ + CH_4 \longrightarrow [C_2H_4D_3^+]^* \longrightarrow C_2(H, D)_5^+ + (H, D)_2 \qquad 100\% \quad (38)$$



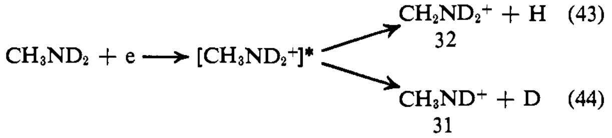
$$CD_3^+ + NH_3 \longrightarrow [CD_3NH_3^+]^* \begin{cases} \longrightarrow (CD_2{=}NH_2^+)^* + HD & 70\% \quad (39) \\ \longrightarrow CD_3NH^+ + H_2 & 30\% \quad (40) \end{cases}$$

The observation of the two separate modes of decomposition for the $[CH_3NH_3^+]^*$ intermediate complex is similar to an isoelectronic process which has been suggested for the photolysis of ethane.[29] In the photolysis of ethane, process 41 is dominant.



$$C_2H_6 + h\nu \begin{cases} \longrightarrow CH_3CH^* + H_2 & (41) \\ \qquad\qquad \downarrow M & \\ \longrightarrow CH_2{=}CH_2 + H_2 & (42) \end{cases}$$

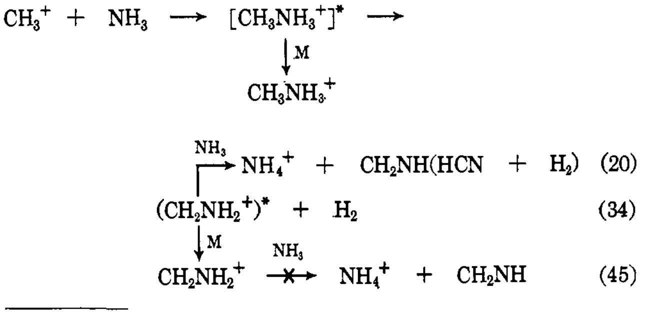
The identification of the ion structure CH_3NH^+ is supported by the observation of this ion in a study of the unimolecular decomposition of $[CH_3ND_2^+]^*$ ions along two similar pathways following electron impact of methylamine–N-d_2.[30]



$$CH_3ND_2 + e \longrightarrow [CH_3ND_2^+]^* \begin{cases} \longrightarrow \underset{32}{CH_2ND_2^+} + H & (43) \\ \longrightarrow \underset{31}{CH_3ND^+} + D & (44) \end{cases}$$

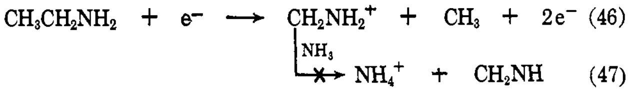
The ratio of the two isomeric ions, 31/32, formed in this process was found to be 0.20–0.30 at 50 eV depending on the amount of rearrangement in the parent ion prior to decomposition. From the appearance potential of the *m/e* 31 and 32 ions in the mass spectrum of CH_3ND_2, Collin and Franklin[30] have calculated the heats of formation of these two isomeric ions and find that the mass 31 ion is 32.8 kcal/mol more energetic ($\Delta H_f(CH_2NH_2^+)$ 174.1, $\Delta H_f(CH_3NH^+)$ 206.9 kcal/mol). Icr studies of the appearance potential of the ions at *m/e* 31, 32, and 33 in the CD_4–NH_3 mixture ranging from the appearance of these ions at the appearance potential of CD_3^+ up to 50 eV show no apparent change in relative intensity as a function of electron energy. If CD_3^+ ions are formed in excited states at higher electron energy, little effect is observed on the ratio for the two modes of decomposition of the intermediate complex.

The behavior of the double-resonance intensity with pressure for the proton transfer reaction of the ($CH_2NH_2^+$) condensation product is unique, and the combination of icr single- and double-resonance results shown in Figures 4 and 5 indicate that $CH_2{=}NH_2^+$ is produced initially in an excited state from which collisonal deactivation is possible at higher pressures. The circumstance which permits this observation is that the proton transfer reaction to ammonia is apparently exothermic for the excited state $CH_2NH_2^+$ ion, but endothermic for the ground state ion.



$$\begin{aligned} &CH_3^+ + NH_3 \longrightarrow [CH_3NH_3^+]^* \longrightarrow \\ &\qquad\qquad \downarrow M \\ &\qquad\quad CH_3NH_3^+ \\ &\xrightarrow{NH_3} NH_4^+ + CH_2NH(HCN + H_2) && (20) \\ &(CH_2NH_2^+)^* + H_2 && (34) \\ &\downarrow M \\ &CH_2NH_2^+ \overset{NH_3}{\nrightarrow} NH_4^+ + CH_2NH && (45) \end{aligned}$$

Several additional experiments were performed in order to confirm this hypothesis. In one experiment, ground state $CH_2NH_2^+$ ions were prepared by electron impact of ethylamine in a mixture of ethylamine and ammonia.[31] Hurzeler, Inghram, and Morrison[32] have conclusively shown that the *m/e* 30 fragment ions produced by photon impact of ethylamine are ground state ions. The $CH_2NH_2^+$ ions produced by electron impact from ethylamine in this mixture do not undergo proton transfer to ammonia.



$$\begin{aligned} &CH_3CH_2NH_2 + e^- \longrightarrow CH_2NH_2^+ + CH_3 + 2e^- && (46) \\ &\qquad\qquad\qquad\qquad \overset{NH_3}{\nrightarrow} NH_4^+ + CH_2NH && (47) \end{aligned}$$

It has been suggested[33] that collision-induced decomposition of the $CH_2NH_2^+$ ion to NH_2^+ and CH_2 and the subsequent reactions of NH_2^+ ion might also account for the observed double-resonance behavior. Decomposition of the ground state $CH_2NH_2^+$ ion into NH_2^+ and CH_2 requires 9.7 eV, based on $\Delta H_f(CH_2NH_2^+)$ 175,[30,34] $\Delta H_f(CH_2)$ 93.7,[35] and $\Delta H_f(NH_2^+)$ 304 kcal/mol.[36] Even assuming that all the exothermicity of the condensation reaction goes into internal excitation of the product ion, 6.5 eV of excess energy would be required to break the C–N bond. The maximum kinetic energy attained by the $CH_2NH_2^+$ ions in double-resonance experiments does not exceed 2 eV, so collision-induced decomposition is not likely. To further strengthen the case for collisional stabilization, large fractions of an inert gas, helium in this case, were successively added through the second sample inlet of the spectrometer while keeping the partial pressure of both CH_4 and NH_3 constant at 4×10^{-6} and 8×10^{-6} Torr, respectively. The electron energy was kept at 20 eV, below the ionization potential of He. Using a long ion residence time, 7.0 msec, the ratio of $CH_2NH_2^+$ to $C_2H_5^+$ increases from 1.3 at zero helium concentration to a maximum value of 1.8 at 95% helium concentration at a total pressure of 2.5×10^{-4} Torr. The increase in the $CH_2NH_2^+/C_2H_5^+$ ratio is clearly consistent with a decrease in the extent of $CH_2NH_2^+$ proton transfer caused by collisional deactivation of the excited $CH_2NH_2^+$ ions.

Collisional stabilization of the intermediate complex for reaction 34 is also possible. In Figure 4a, it is apparent that the single-resonance intensity of the *m/e* 30 ion does not remain entirely constant at elevated pressures, but does show a small constant decrease with increasing pressure. This small decrease is due to collisional stabilization of the intermediate $[CH_3NH_3^+]^*$ complex as indicated in the reaction scheme above. This leads to a decrease in the product

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(29) G. G. Meisels, ref 3, p 374, and references cited therein.

(30) J. E. Collin and M. J. Franklin, *Bull. Soc. Roy. Sci. Liege*, **35**, 267 (1966).

(31) The author is indebted to J. L. Beauchamp of the Department of Chemistry, California Institute of Technology, for his assistance and the use of his laboratory facilities for performing these experiments.

(32) H. Hurzeler, M. G. Inghram, and J. D. Morrison, *J. Chem. Phys.*, **28**, 76 (1958).

(33) This alternative and the experiment with inert gas were suggested by the referee.

(34) W. T. Huntress and J. L. Beauchamp, manuscript in preparation.

(35) W. A. Chupka, *J. Chem. Phys.*, **48**, 2337 (1968).

(36) S. H. Foner and R. L. Hudson, *ibid.*, **29**, 442 (1958).

ion intensity at m/e 30, and at pressures greater than 10^{-4} Torr the signal at m/e 32 from the $CH_3NH_3^+$ ion becomes evident.

At CH_3^+ kinetic energies in excess of 1 eV, an additional endothermic reaction channel becomes available in the condensation of CH_3^+ with CH_4.

$$CH_3^+ + CH_4 \longrightarrow C_2H_3^+ + 2H_2 - 24 \text{ kcal/mol} \qquad (48)$$

This reaction is successfully observed by heating the CH_3^+ primary ion to kinetic energies in excess of 1 eV using high-intensity double-resonance irradiating fields.[25,37] Attempts made to observe by double resonance, or to force by excessive double-resonance heating, the reaction

$$\underset{15}{CH_3^+} + NH_3 \not\twoheadrightarrow \underset{28}{H_2CN^+} + 2H_2 + 25 \text{ kcal/mol} \qquad (49)$$

have been unsuccessful. This result is somewhat surprising in view of the fact that the reaction is exothermic. Assuming that the collision of a methyl cation with either methane or ammonia involves the formation of strongly bound complexes $[C_2H_7^+]^*$ and $[CH_3NH_3^+]^*$, the excitation energies contained in the intermediates are ~30 and 101 kcal/mol, respectively. In the case of $[CH_3NH_3^+]^*$, more than sufficient energy is present for decomposition to H_2CN^+ and yet this reaction is not observed. The reason for this difference in behavior may be that a large portion of the excitation energy contained in the $[CH_3NH_3^+]^*$ intermediate is converted to internal excitation of the $CH_2NH_2^+$ product ion and that this energy is no longer available for further decomposition to H_2CN^+.

Some percentage of the excitation energy of the $[CH_3NH_3^+]^*$ intermediate must go into internal excitation of the product ion. Sjögren[38] has recently suggested that the first electronically excited state of the $CH_2{=}NH_2^+$ ion should be 2 eV above the ground state and should have the structure $^+CH_2{-}NH_2$. The exothermicity of the condensation reaction, 3.2 eV, is sufficient to reach this state, and localization of charge on carbon in the proposed structure for this state is interesting with respect to the origin of the proton transferred to ammonia in this state. The carbon site on the molecule is much less basic than the nitrogen site. Decomposition of the neutral product of the proton transfer reaction 20 to HCN and H_2 requires only 15 kcal/mol of excitation energy for the excited reactant ion, based on $\Delta H_f(CH_2NH_2^+)$ 175[30,34] and $\Delta H_f(CH_2NH)$ 17 kcal/mol.[34]

Acknowledgments. The authors wish to express their appreciation to J. L. Beauchamp and D. Holtz of the California Institute of Technology, Noyes Laboratory for Chemical Physics, for reading the manuscript and providing many hours of helpful conversation.

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[37] L. R. Anders, *J. Phys. Chem.*, 73, 469 (1969).

[38] H. Sjögren, *Ark. Fys.*, 29, 565 (1965).

Triplet–Singlet Energy Transfer in Fluid Solution[1]

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Athens, Georgia 30601. Received August 2, 1969

Abstract: The process of triplet–singlet energy transfer by a dipole–dipole interaction has been studied in fluid solution. The quenching rate constants for the donor–acceptor combinations of phenanthrene–Rhodamine B in ethanol and benzophenone–perylene in Freon are 3.9×10^7 and 7.1×10^9 M^{-1} sec^{-1}, respectively. The ratio of these experimental rate constants is in agreement with the ratio of the relative strengths of the dipole–dipole interactions in these systems. The efficiency of the energy transfer process is governed by the solution lifetime of the triplet state donor and its ability to diffuse to within the critical transfer distance during that lifetime.

Energy transfer from the triplet state of a donor molecule to a singlet state of an acceptor molecule by long-range dipole–dipole resonance interaction was first predicted by Förster (eq 1).[3-6] He stated that the

$$^3D + A_0 \longrightarrow D_0 + {}^1A \qquad (1)$$

forbidden nature of the donor transition will cause the strength of the donor–acceptor interaction to be small, as compared to the totally spin-allowed singlet–singlet process. However, the long lifetime of the spin-forbidden transition in the donor compensates for the weak interaction and consequently large transfer distances are predicted for this process.

By considering a long-range, weak intermolecular interaction between excited donor and ground state acceptor, Förster obtained an expression for the rate of energy transfer

$$k_{D \rightarrow A} = \frac{9000 \ln 10 k^2}{128 \pi^5 n^4 N \tau_0 R^6} \int f_D(\bar{\nu}) \epsilon_A(\bar{\nu}) \frac{d\bar{\nu}}{\bar{\nu}_4} \qquad (2)$$

where N is Avogadro's number, k^2 is an orientation

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[2] NIH Predoctoral Fellow, 1968–1970.

[3] T. Förster, *Z. Naturforsch., A*, 4, 321 (1949).

[4] T. Förster, *Ann. Phys.*, 2, 55 (1948).

[5] T. Förster, *Discuss. Faraday Soc.*, 29, 7 (1959).

[6] T. Förster, *Mod. Quantum Chem. Lect. Istanbul Int. Summer Sch., 1964*, 93 (1965).