supported by what is known of the geometry[16] of H_3O^+. Therefore we think that the ΔS_{exptl} is not accurate enough.

The $\Delta G°_{600}$ data in Table I give a proton affinity difference between water and ammonia of 31.8 kcal/mol, with an estimated total error of 1 to 2 kcal/mol. This difference corrected for the ΔS change due to rotational symmetry numbers ($RT \ln (18/24) = -0.34$ kcal/mol (at 600 °K)) becomes 31.5 kcal/mol. Since the symmetry numbers involved in proton transfer from water to isobutene cancel, the symmetry correction should be applied to the difference between isobutene and ammonia. Thus the most probable proton affinities for these three compounds are: $\text{PA}(H_2O) = 168.9 \approx 169$, PA(isobutene) = 193, and $\text{PA}(NH_3) = 200.4$ kcal/mol.

Substituent effects on the basicities of oxygen compounds and most other compounds in Table I have been considered previously[7,13] and need not be treated here. The only new compounds are the benzenes. Protonation of these compounds leads to the benzenium ions which have been studied quite extensively in solution.[17] Recently McIver[18] has determined the relative gas-phase basicities of alkyl-substituted benzenes by measuring proton transfer equilibria with an ICR spectrometer. Since his data involved methyl formate as a reference compound the present results for methyl formate, benzene, and the halobenzenes can be connected to his values. The resulting basicities are shown in Table III. Considering only the ΔG changes one finds that the halo substituents decrease the basicity of benzene. However, the deprotonation of benzene is connected with a large symmetry number change with a ratio of symmetry numbers equal to 12. The energy changes corrected for rotational symmetries are shown in the last column of Table III. These numbers show that single fluoro or chloro substitution enhances somewhat the basicity.[19] Introduction of a second fluorine in the meta position reduces the basicity to almost that of benzene and the third fluorine makes 1,3,5-trifluorobenzene less basic than benzene. This reversal can be understood on the basis of the opposing tendencies of the fluorine substituent, which by π donation stabilizes while by σ withdrawal destabilizes the protonated base. Since the π donation effect decreases faster than the σ withdrawal with multiple substitution, a reversal can be expected.

Unfortunately the above entropy correction includes only rotational symmetry numbers, yet other small entropy effects might also be involved. This underlines the desirability for good entropy corrections in all equilibria measurements. It is hoped that better experimental entropy measurements and theoretical considerations will lead to a further increase of the usefulness of the gas-phase equilibria data.

Acknowledgment. The present work was supported by funds from the Canadian National Research Council. Some of the ΔG_{600} measurements given in Table I were performed by Mr. Yan Lau.

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Crossed Beam Studies of Ion–Molecule Reactions in Methane and Ammonia

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Abstract: The dynamics of the following ion-molecule reactions were studied by cross beam techniques at relative (CM) energies of 2-9 eV: $CH_4^+ + NH_3 \rightarrow NH_4^+ + CH_3$ (1); $CH_4^+ + NH_3 \rightarrow CNH_5^+ + H_2$ (2); $NH_2^+ + CH_4 \rightarrow CNH_4^+ + 2H$ (3) $CH_3^+ + NH_3 \rightarrow CNH_4^+ + 2H$ (4). Reaction 1 occurs by a rebound mechanism with two peaks in the forward direction. Labeling studies show proton transfer with no isotopic scrambling. Reaction 2 is direct with the H_2 expelled from the CH_4^+. In (3) and (4), the product internal energy is sufficiently high that dissociation of the H_2 is likely. Labeling studies show limited isotopic scrambling.

Introduction

Using the crossed beam apparatus EVA, we have measured the product ion velocity and angular distributions for the following ion-molecule reactions in the relative (CM) energy range of 2-9 eV:

$$CH_4^+ + NH_3 \rightarrow NH_4^+ + CH_3 \qquad (1)$$

$$CH_4^+ + NH_3 \rightarrow CNH_5^+ + H_2 \qquad (2)$$

$$NH_2^+ + CH_4 \rightarrow CNH_4^+ + H_2 \text{ (or 2H)} \quad (3)$$

$$CH_3^+ + NH_3 \rightarrow CNH_4^+ + H_2 \text{ (or 2H)} \quad (4)$$

As a further probe of the detailed reaction dynamics, we have studied (1)-(4) using deuterium labeling. Previous beam studies of organic ion-molecule reactions[1-3] have shown extensive isotopic scrambling even in cases where the reaction proceeds by a direct mechanism with an intermediate lifetime less than a rotational period. The above cases show less scrambling but show other unusual features, indicating that the dynamics of carbonium ion reactions is still a rich field for study, with many surprises left.

Methane and ammonia are primary constituents of reducing atmospheres such as the outer planets and the early earth. Ion-molecule reactions involving these gases are probably important in discharges and ionospheres composed of these gases. Although the reactions between CH_3^+, CH_4^+, NH_3^+, NH^+ and CH_4 or NH_3 appear superficially similar, they differ markedly in products and mechanism. In order to obtain information about them, it is possible to study the ratio of products and their internal energy as a function of collision energy, to label atoms isotopically to discover whether scrambling processes occur, and to observe the angular distribution of the products in order to obtain information about the detailed reaction dynamics. This paper reports a study of reactions 1-4 through use of information of the kind described above obtained with the ion-molecule reaction apparatus EVA. Reactions in methane-ammonia systems offer a means of examining the family of intermediates, CNH_x^+, both normal and hypervalent. The analogous all-carbon reactions between ions formed from methane and neutral methane have been previously examined in detail[1,2] and will offer an interesting opportunity for comparison. Finally, some previous work on these reactions,[4,5] mostly low energy rates and isotope labeling results, is available to supplement what can be learned from crossed beam experiments.

The crossed beam apparatus EVA is fully described elsewhere.[6] Briefly, the ion beam is formed in an electron bombardment ionizer followed by a small 180° magnetic mass spectrometer and a series of electrostatic deceleration and focusing lenses. The ion beam source and a thermal neutral beam source at 90° are mounted on a rotatable lid to enable the measurement of angular distributions of products. The fixed detection system includes a retarding potential energy analyzer, a 60° magnetic mass spectrometer, and an electron multiplier.

The CH_4^+ beam is probably in its ground electronic state since excited states are very high in energy and would likely radiate or predissociate before reaching the collision zone. Tal'roze[7] has found evidence for an excited state of CH_3^+, but the lifetime is much shorter than the transit time for ions through our lens system. Calculations[8] on NH_2^+, however, indicate a low lying singlet state 1.56 eV above the ground state triplet, and both states are probably present in the beam.

$CH_4^+ + NH_3 \rightarrow NH_4^+ + CH_3$

Huntress et al.[5] report a thermal rate for reaction 1 corresponding to a cross section of roughly 100 Å^2, which decreases with higher energy. In the energy range of our investigation, relative (CM) energies between 1 and 6 eV, the cross section is much smaller. While no direct measurements were attempted, rough comparison with fluxes measured from previously studied reactions indicates cross sections below 1 Å^2. Huntress and Elleman[4] also found that reaction 1 was a simple proton-transfer process since hydrogen labeling produced only one product:

$$CH_4^+ + ND_3 \rightarrow ND_3H^+ + CH_3\cdot$$

At the higher energies of this study, the situation was unchanged. No hydrogen scrambling occurred, and only the one isotopic product was observed for the reaction

$$CD_4^+ + NH_3 \rightarrow NH_3D^+ + CD_3\cdot$$

Figure 1 shows probability contour plots for reaction 1 at various collision energies in Cartesian velocity space. There are two peaks, one of which is slightly forward (direction of the ion beam) of the center of mass. At higher energies, this channel shows more and more backscattering, although still peaking forward. An examination of the reaction energetics in Table I shows the CH_3 product corresponding to the first NH_4^+ peak is formed so close to the center of mass that it could have sufficient internal energy to dissociate to CH_2 + H.

A second, more forward scattered channel is also present at lower energies but falls off rapidly between $E_r = 3$ and 4 eV (CM). Product energy distributions at $E_r = 4.17$ eV show only a small high-energy tail, too small to show up in the contour diagram. The second peak shows quite wide angular distributions. The Q values[9] still indicate considerable internal excitation of the products, but dissociation of CH_3 here would require about 1 eV of internal energy in the CH_4^+ beam plus all the reaction exothermicity to go into internal energy of CH_3. This is highly unlikely.

Both peaks exhibit a rebound type of dynamics in that the nitrogen and carbon atoms have reversed their original directions. It is conceivable that an additional fraction of this reaction occurs by a stripping mechanism, or that some of the reaction exothermicity is converted into translational energy of the products moving in their original directions. For such cases, the large LAB angles and low energies of the product ions would be beyond EVA's ability to detect.

Past experience with many reactions has shown that the sudden disappearance of an ion product at higher energies, such as occurs for the far forward peak here, indicates the dissociation of the ion product. The trend in Q values for this peak in the first two plots of Figure 1 predicts $Q \sim -1.4$ eV for $E_r = 4.17$ eV. If the lack of such a peak is attributable to NH_4^+ dissociation, the NH_4^+ product must receive as internal excitation all the exothermicity of the reaction, the 1.4 eV of initial kinetic energy predicted to be lost above, and 0.5 eV from CH_4^+ initial internal energy. It seems unlikely that NH_4^+ should receive such a large fraction of the available energy as required for dissociation. An alternate explanation may lie in the opening of a new channel (reactive or inelastic) at $E_r = 4$ eV which effectively interrupts the NH_4^+ formation to form a different final product. The new channel could involve production of CNH_5^+, NH_3^+, or CH_5^+ ions which we have also observed from the $CH_4^+ + NH_3$ reaction.

For the similar reason that it seems unlikely that CH_3 corresponding to the peak close to the center of mass should have most (80%) of the product internal energy, the reaction at low energies probably doesn't produce much CH_2 + H. Deposition of even more energy in one product than that required for dissociation is necessary to produce electronic excitation.[10] Thus this also seems unlikely. The two product peaks differ in vibrational energy of the products, but apparently not in electronic state or chemical configuration. At high energies, the peak near the center of mass may leave a dissociating neutral without requiring the deposition of most of the available internal energy in the neutral product, and this process may become increasingly more important.

There are several possible alternative explanations for the

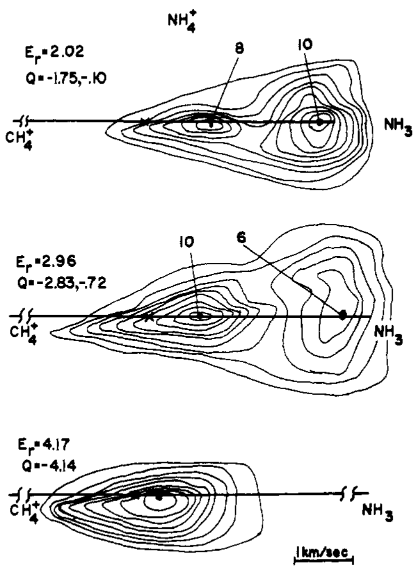


Figure 1. Probability contour plots for reaction 1 in a Cartesian velocity space. The center line is the relative velocity vector of the reactants, with X marking the center of mass. Contours are at 10% intensity intervals, with the relative intensities and Q values of the two peaks indicated in the figure.

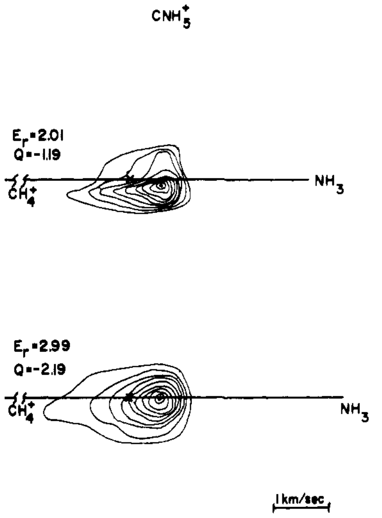


Figure 2. Probability contour plot for reaction 2, similar to that in Figure 1.

two product peaks. One may be due to an electronically excited state in the CH_4^+ beam, producing reaction on a different potential surface. This would require ~10 eV of excitation in the CH_4^+ beam[11] which is unlikely. Second, surface crossings may lead to two or more distinct paths to reaction. The other surface involved would likely be that of the $NH_3^+ + CH_4$ configuration, and the second path would be long-range charge transfer followed by reaction, similar to the situation described theoretically for the $D_2^+ + H$ system.[12] Some NH_3^+ product was also observed so the surface crossing is accessible. It is also possible that a single surface may have two different reaction pathways, which might be chosen preferentially on the basis of initial CH_4^+ vibrational energy, impact parameter, or NH_3 orientation.

Finally, reaction 1 may be compared with the analogous reaction:

$$CH_4^+ + CH_4 \rightarrow CH_5^+ + CH_3\cdot \qquad (5)$$

Reaction 5 shows energy dependent hydrogen scrambling,[13] indicating the operation of some scrambling scheme absent in (1). By contrast, reaction 1 is highly exothermic, and the great disparity in energy between the two configurations apparently limits the system to one, downhill hydrogen jump during a collision. The dynamics of reaction 5, as measured by Henglein,[14] are quite similar to reaction 1, however. Two peaks with nearly equal intensity are seen for collision energies between 2 and 3.5 eV (CM). One peak is at the center of mass, while the other is centered near the spectator stripping point in the original CH_4^+ direction (forward). Caution is due, however, in interpreting this similarity as reaction on similar surfaces. The energetics for the two reactions are so vastly different as to predict quite different surfaces. The difference in scrambling behavior also warns against such conclusions. The first peak of reaction 1 does not show the extensive backscattering that the center of mass peak does for reaction 5, and the stripping peak does not seem to disappear at higher energies for reaction 5. Finally, ^{13}C isotope labeling work has not been done for reaction 5 to indicate if either of the peaks is due to hydrogen transfer to the ion rather than proton transfer to the neutral. The hydrogen isotope work[13] indicates both processes are important. The former channel, which also occurs, is analogous to producing CH_5^+ in reaction 1, which was not investigated.

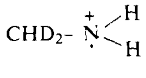
$CH_4^+ + NH_3 \rightarrow CNH_5^+ + H_2$

A second product of the methane ion-ammonia reaction (eq 2), was also investigated. This is a condensation reaction not seen in the analogous $CH_4^+ + CH_4$ system. Huntress[5] did not observe reaction 2 at low energies, suggesting possible threshold for the process. In this study, reaction 2 appeared to have a small cross section (<1 Å^2) and, below $E_r = 2$ eV (CM), product signal was insufficient for accurate work. Above 3 eV, most CNH_5^+ dissociates to $CNH_3^+ + H_2$, a product ion which was also detected at the lower energies. Figure 2 shows a typical probability contour plot for reaction 2. The ion product shows some backward intensity, but clearly peaks forward, in the direction of the original primary ion. Q values at $E_r = 2$ and 3 eV were -1.2 and -2.2 eV, respectively.

Isotope labeling work shows only one isotopic product is formed above $E_r = 1$ eV:

$$CD_4^+ + NH_3 \rightarrow CND_2H_3^+ + D_2$$

The hydrogen product is exclusively expelled from the carbon, and no scrambling takes place. For most collisions, this D_2 recedes in a direction opposite to its original motion, away from the C-N bond. A possible structure for $CNH_3D_2^+$ is



which might result from rearrangement of the initially formed $\cdot CD_2N^+H_3$. If another H_2 is expelled from the carbon atom by a 1-1 elimination to produce CNH_3^+, the isotopic product $CNDH_2^+$ should predominate, and this is observed (70%). Alternatively, $CD_2\text{-}NH_3^+$ could eliminate HD by a 1-2 elimination to form the observed $CD{=}NH_2^+$. Limited scrambling does occur here, but intensities are too low for accurate work. The CNH_5^+ decomposes to $CNH_3^+ + H_2$ rather than to $CNH_4^+ + H$, although the latter is more exothermic. This may indicate a sizable barrier in the CNH_5^+ surface toward decomposition by H atom expulsion.

The large exothermicity of reaction 2, the low Q values, and the possible threshold raises the possibility of atomic

Table I. Heats of Reaction[a] (eV)

(1) $CH_4^+ + NH_3 \rightarrow$	$NH_4^+ + CH_3$	−3.56 eV
	$NH_4^+ + CH_2 + H$	+1.34
	$NH_3^+ + H + CH_3$	+1.91
(2) $CH_4^+ + NH_3 \rightarrow$	$CNH_5^+ + H_2$	−2.69
	$CNH_5^+ + 2H$	+1.82
	$CNH_3^+ + 2H_2$	−0.43
	$CNH_4^+ + H_2 + H$	−1.43
	$CNH_6^+ + H$	−2.69
Reactant	$NH_2^+ + CH_4 \rightarrow$	$CH_3^+ + NH_3 \rightarrow$
Product		
$CH_3NH_3^+$	−5.94	−4.34
$^+CH_2{=}NH_2 + H_2$	−4.69	−3.08
$^+CH_2{=}NH_2 + 2H$	−0.18	+1.43
$CH_3NH^+ + H_2$	−3.21[b]	−1.60[b]
$CNH_3^+ + 3H$	+5.33	+6.94
$CH_3NH_2^+ + H$	−1.43	+0.17

[a] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Draxl, and F. H. Field, *Natl. Stand. Ref. Data Ser., Natl. Bur. Stand.*, No. **26** (1969). [b] Reference 16.

Table II. Q Values and Relative Cross Sections for Reactions 3 and 6

E_r, eV	1.95	4.44	6.55	9.00
$Q(3)$, eV	−1.51		−6.26	−8.78
$Q(6b)$		−4.42	−6.51	
$Q(6c)$		−4.20	−6.15	
$\sigma(6b)$	0.09	0.12	0.19	
$\sigma(6c)$	91	0.88	0.81	

Table III. Q Values and Relative Cross Sections for Reactions 4 and 7

E_r, eV	Thermal[a]	2.09	3.84	5.78	8.89	9.51
$Q(4)$, eV		−2.08				−7.49
$Q(7b)$			−3.78	−5.19	−7.10	
$Q(7c)$			−3.84	−5.65	−7.90	
$\sigma(7a)$	0.35	0.11	0.03	0.03	0.01	
$\sigma(7b)$	0.63	0.60	0.59	0.59	0.76	
$\sigma(7c)$	0.02	0.29	0.37	0.39	0.23	

[a] Reference 4.

hydrogen products. The lack of observable CNH_6^+ or CNH_4^+ products, and the formation of CNH_3^+ decomposition product down to low energies indicates the complex decomposes by elimination of H_2 rather than H, although Table I shows the latter is energetically as favorable. This suggests formation of H_2 product rather than the successive elimination of two hydrogens. A closer look at Q values does not settle the issue but indicates H_2 product is more likely.

At E_r = 3 eV, dissociation of CNH_5^+ is becoming dominant (75%), and only CH_4^+ ions of low internal energy are probably able to form stable CNH_5^+. The products of reaction 2 at the peak will have internal energy of more than 5 eV, 2.7 eV from ΔH_r, 2.2 eV from Q, and the internal energy from CH_4^+. The CNH_5^+ can probably support up to 2.2 eV of internal energy and probably has a large fraction of this, being on the verge of dissociation to $CNH_3^+ + H_2$. This leaves 2.7 eV excitation in H_2 plus the internal energy in the CH_4^+, compared with a dissociation limit of 4.5 eV. Thus, more than 1.7 eV of internal excitation in CH_4^+ is necessary for dissociation of H_2 to be occurring, which is unlikely.

$NH_2^+ + CH_4 \rightarrow CNH_4^+ + H_2$ and $CH_3^+ + NH_3 \rightarrow CNH_4^+ + H_2$

Reactions 3 and 4 are isoelectronic to the well studied $CH_3^+ + CH_4$ reaction,[1,2] although Table I shows reactions 3 and 4 are more exothermic and have an energy well for the intermediate $CH_3NH_3^+$.

These reactions were previously studied at low energies by Huntress and Elleman.[4] They failed to observe reaction 3, which, taken with the decline in cross section with decreasing energy observed in this study at low energy (E_r = 1 eV), indicates a threshold, despite its large exothermicity. Their measurements did, however, indicate a large rate for reaction 4 at thermal energies, 7 × 10^{-10} cm^3/molecule sec,[5] roughly gas kinetic. In addition, they have measured thermal energy relative cross sections for various isotopic products in the labeling experiments $CD_3^+ + NH_3$ and $CH_3^+ + ND_3$.

Both reactions are too low in intensity for work on EVA below E_r = 1 eV, although cross sections do rise to roughly 1 Å^2 at higher energies. This is particularly surprising for reaction 4 in view of the large cross section Huntress observed. This seems to indicate a distinct and separate high-energy mechanism. Above relative energies of 9 eV (CM), CNH_4^+ from both reactions largely decomposes. Some CNH_2^+ decomposition product is formed for collision energies of 4 eV (CM) and up in both reactions. Reaction 3 also produces minor amounts of CNH_3^+ as well.

In addition to reactions 3 and 4, the following isotopically labeled systems were also examined:

$$NH_2^+ + CD_4 \rightarrow CND_4^+ + H_2 \tag{6a}$$

$$\rightarrow CND_3H^+ + HD \tag{6b}$$

$$\rightarrow CND_2H_2^+ + D_2 \tag{6c}$$

$$CD_3^+ + NH_3 \rightarrow CND_3H^+ + H_2 \tag{7a}$$

$$\rightarrow CND_2H_2^+ + HD \tag{7b}$$

$$\rightarrow CNDH_3^+ + D_2 \tag{7c}$$

Intensities for reactions 6a and 7a were too low to measure the reaction dynamics. The product of reaction 6c has a mass identical with that of CND_3^+, a possible decomposition product in the reaction. The percentage of the flux measured at this mass possibly due to the contaminant CND_3^+ is significant (>10%) only at relative energies above 6 eV (CM).

Dynamics

Figure 3 shows probability contour plots for reactions 3, 6b, and 6c. The minor product of the latter two (eq 6b) peaks very close to the center of mass at all energies. Reaction 6c peaks behind the center of mass, with the ion traveling in the original direction of the neutral CH_4. As the collision energy decreases, less and less $CND_2H_2^+$ is forward scattered, and the peak moves further backward. Table II summarizes the Q values and relative cross sections computed[15] by the method of ref 2, for reactions 6b and 6c. Reaction 6a did not occur in our energy range. Note that the relative cross section for reaction 6b, the product peaking near the center of mass, appears to drop at low energies, where formation of the product of (6c) near the center of mass also becomes less likely (see Figure 3).

Typical contour plots for reactions 7b and 7c are shown in Figure 4. Note that the peaks move closer to the center of mass at low energies in contrast to reaction 3. The resulting forward-backward symmetry raises the possibility of a long-lived complex at low energies, in view of the deep energy well for the complex shown in Table I. Higher energy results show the ion product of (7b) slightly further forward peaked than that of (7c), with less backscattering. Table III summarizes the data, including relative cross sections for reaction 7, with Huntress' thermal results[4] added. At the lowest energy of this study, the relative cross section for (7a) is rising as that for (7c) falls, a trend toward the stark-

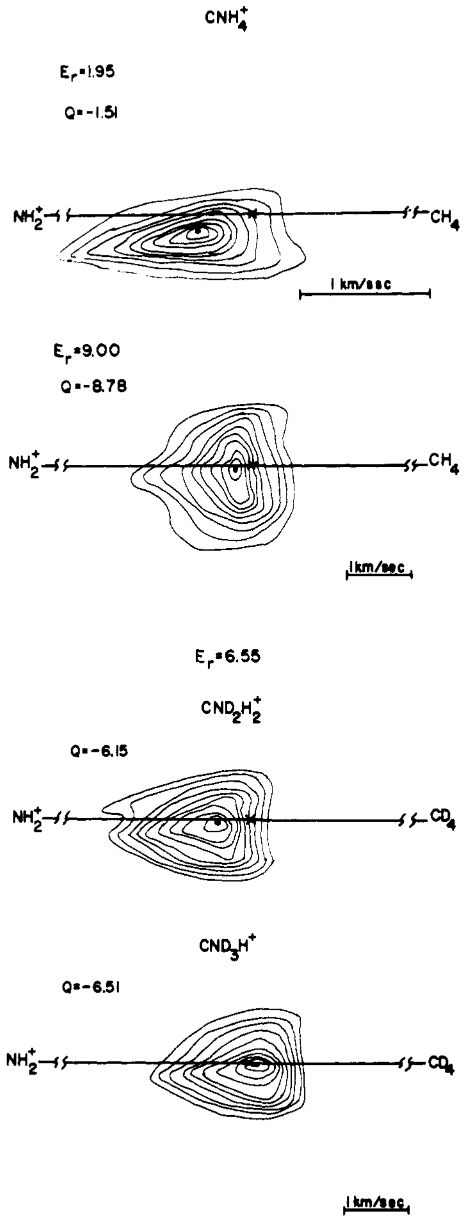


Figure 3. Probability contour plots for reactions 3, 6b, and 6c, similar to those in Figure 1.

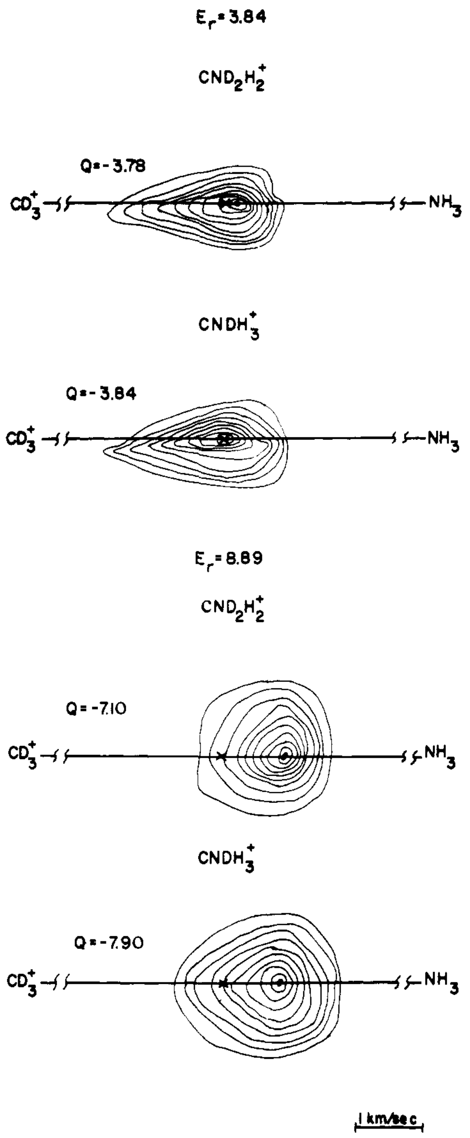


Figure 4. Probability contour plots for reactions 7b and 7c, similar to those in Figure 1.

ly different thermal results. At high energy, the decrease in the product of (7c) may be due to dissociation since Q is more negative for (7c) than (7b).

Examination of the Q values for reaction 3 in Table II reveals large amounts of internal energy in the products, from both the initial collision energy and the reaction exothermicity. According to Table 1, dissociation of both ion and neutral product is possible for Q values below -5.33 eV. Such low Q values are reached at the higher energies studied. The continued presence of CNH_4^+ ion products at such high levels of internal excitation is possible only if the neutral H_2 is dissociated and carries a large fraction of the energy. Thus at high collision energies, the two hydrogen atoms have large velocities relative to each other, although their center of mass is still close to that of the entire system. The hydrogen atoms are likely scattered both forward and back of the center of mass. At low collision energies, hydrogen atoms are also probably produced. For NH_2^+ ions with internal energy of 1 eV, the products formed at the lowest energy studied would still have 1.7 eV in internal energy in excess of that required for H_2 dissociation. The observation of a threshold for reaction 3 at a relative collision energy below 2 eV may indicate a barrier exists on the potential surface for the formation of bound molecular H_2 neutrals. Alternately, a barrier in the incoming portion of the surface may prevent formation of the intermediate for condensation reactions at low collision energies where H_2 of lower internal energy would have been produced. A final possibility arises if triplet ground state NH_2^+ is reacting. The triplet surface on which reaction takes place may correlate to triplet H_2, a dissociative state.

A second possible depository for the large amounts of internal energy is electronic excitation of the products. This mechanism may require surface crossings, and a radiative lifetime shorter than the predissociative lifetime of the excited products. The extra internal energy would thus be removed by a photon rather than by dissociating fragments of the products. There are no bound excited states of H_2 low enough in energy to be consistent with the observed energetics for NH_2^+ with less than 4.5 eV of excitation itself. Also, there is no knowledge of the higher excited states of CNH_4^+ which could be involved. This, therefore, does not seem a likely explanation for reaction 3.

The products of reaction 4, which probably takes place on the singlet ground state CNH_6^+ surface, may be similarly analyzed. Table III shows, for the highest collision energy, a Q value in excess of that required to dissociate both products. Since CNH_4^+ is still being formed, the excess energy must have gone into relative motion of the two hydrogen atoms. At the lowest energy studied, the products formed from CH_3^+ ions with 1 eV internal energy average 1.6 eV internal energy in excess of that needed for H_2 dissociation. At the thermal energies studied by Huntress,[4] however, the system had insufficient energy for H_2 dissociation. The transition from H_2 to 2H as the neutral products may be occurring at the low energy limits of this study, where the cross section appears to go through a minimum, and the isotope labeled relative cross section for reaction 7 shows sharp changes. The change from virtually no $CNDH_3^+$ (eq 7c) at thermal energies to no CND_3H^+ (eq 7a) at high energies suggests separate mechanisms for H_2 and 2H production.

One further feature of both reactions 3 and 4 is the lack of single hydrogen atoms being expelled from the collision intermediate. Although thermodynamically possible and less endothermic than $CNH_4^+ + 2H$ (see Table I), no CNH_5^+ is observed for either reaction at all energies studied. This indicates that reactions 3 and 4 should be viewed as the production of dissociative H_2 rather than the successive expulsion of two hydrogen atoms from the collision intermediate.

Figure 3 shows the dynamics of reaction 6 and the isotope labeling studies of reaction 3. For the product of (6c), $CND_2H_2^+$, the D_2 (or 2D) rebounds away from the carbon end of the intermediate, reversing its initial velocity. The product of (6b), CND_3H^+, however, is formed by expelling hydrogen atoms from opposite ends of the original intermediate. Opposite motions of the two hydrogens might leave the ion product near the center of mass, as observed. Thus the dynamics can be accounted for by a simple model based on the initial positions of the expelled hydrogens. Alternately, one might consider (6) to be the result of a hydrogen scrambling process, a more complicated collision which could also produce products of greater internal energy, hence closer to the center of mass. Another possibility is separate mechanisms for the two products, one perhaps involving triplet NH_2^+ and the other singlet NH_2^+.

Figure 4 shows little difference in the dynamics of reactions 7b and 7c. The product of (7b), $CND_2H_2^+$, is slightly further forward, but the origin of the expelled H_2 or the extent of a possible scrambling scheme has little apparent effect. This is similar to the behavior of the methyl cation-methane system studied previously.[2]

While reactions 3 and 4 show differences in isotope effects on dynamics and variations in the dynamics with energy, similarities do exist. Both produce atomic hydrogen, at least at high energies. In each case, the ion product is predominantly formed in the direction initially traveled by the carbon atom.

Relative Cross Sections

Figure 5 shows the first two steps of a simple hydrogen scrambling scheme to account for the relative cross sections of reaction 6 shown in Table II. Only the first carbonium and ammonium ion intermediates are included since any significant participation by later intermediate species would have produced measurable amounts of the product of (6a), which was not observed. Scrambling occurs by simple proton transfer, and the products are formed by 1,1 elimination from the carbon of the carbonium ion (rate k_1), or 1,2 elimination across the C–N bond for the ammonium ion intermediates (rate k_2). The absence of product in (6a) shows that, in contrast to the methyl cation-methane reaction,[2] scrambling is very slow in this system. Here the scrambling step is not between two carbonium ions of equal energy, but between an ammonium and a higher energy carbonium ion. The substitution of nitrogen for carbon may also produce a barrier to scrambling, in contrast to the stability of bridged carbonium ion transition states. Finally, should reaction 6 take place on a triplet surface, behavior different from the singlet methyl cation-methane system might be expected.

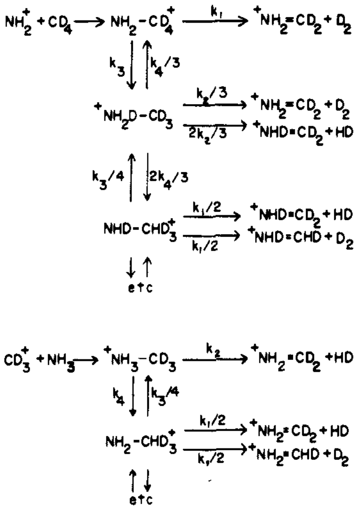


Figure 5. Relevant steps in a proposed scrambling and decomposition scheme for intermediate species in reactions 6 and 7.

Random hydrogen scrambling would produce 40% $CND_2H_2^+$ (eq 6c). The 88% observed at $E_r = 4.44$ eV indicates that roughly 80% of all reactive collisions occur without even the first scrambling step. If most CND_3H^+ (eq 6b) (as well as some of (6c)) is produced from the second rather than third intermediate, the kinematic predictions discussed earlier still hold (the 1,2 elimination producing the product of reaction 6b near the center of mass). Possible 1,1 elimination from $CD_3\text{-}NH_2D^+$ would produce some CND_4^+ (eq 6a) and can be ruled out.

Two other mechanisms are possible for the reaction. Decomposition may be restricted to the carbonium ion intermediates, leaving the ammonium ions as simple scrambling intermediates. This eliminates any 1,2 eliminations, which were not seen in the $CH_3^+ + CH_4$ case. A second alternative eliminates the scrambling scheme altogether. Product of (6b) could be produced by a separate mechanism, forming $CD_3\text{-}NH^+$ by 1,2 elimination from $NH_2\text{-}CD_4^+$.[16] This still fits well with the observed differences in product kinematics as discussed earlier. Also, the percentage of reaction 6b decreases, away from random, at lower energies.[2] One would expect the opposite trend from the single mechanism model, although with three distinct ratios of rates in the scrambling scheme the observed behavior is possible. An energy barrier which would slow down 1,2 elimination from the ammonium ion, for example, would slow reaction 6b product formation at low energies.

Figure 5 also shows the first two intermediates for reaction 7. The third intermediate would produce the product of (7a), and thus must be insignificant at high energies. Following the same dissociation scheme as reaction 6, the data at 3.84 eV (CM) indicate roughly 20% of the dissociations occur from the initial ammonium ion, most occurring from the second intermediate, the carbonium ion. This is consistent with the expectation that carbonium ion 1,1 elimination (k_1) is faster than ammonium ion 1,2 elimination (k_2), as discussed for reaction 6. Since the third and later intermediates must be insignificant, the carbonium ion decomposition rate (k_1) must be much faster than the rate for scrambling to ammonium ions (k_3). At higher energies, the fraction of the product of (7c) falls, indicating faster decomposition of the initial ammonium ion, or the start of dissociation for the lower Q value (eq 7c) product. The prevalence of the carbonium ion decomposition for products of both (7b) and (7c) is also consistent with the similarity of the kinematics, and with the general forward scattering. The hydrogen product rebounds away from the carbon, with the opposite of the original carbon velocity.

At the lowest energy studied, there is significant reaction 7a product. Were this indicative of increased scrambling, one would expect equal, random amounts (20%) of products of (7a) and (7c) at thermal energy. However, Huntress' results[4] show almost no $CNDH_3^+$ (eq 7c) at thermal energies, indicating that a different mechanism is responsible for product of (7a), and probably of (7b) also, at low energies. Huntress[4] has accounted for reaction 7a by 1,1-H_2 elimination from CD_3-NH_3^+, forming the excited CD_3NH^+ configuration, which is still exothermic by 1.65 eV.[16] Perhaps, at higher energies, this process is too slow to be significant compared with the time of collision, the competing ammonium ion 1,2 elimination which produces the product of (7b) similarly becomes less important, and the scrambling process to the quickly decomposing carbonium ion $NH_2CD_3H^+$ becomes energetically allowed and dominant. The transition between these two mechanisms takes place around 2 eV, where the cross section appears to reach a minimum and the complex may become long-lived. This may also be the region of transition between molecular and atomic hydrogen products.

The scrambling process is as slow in reaction 7 as in reaction 6, although singlet and triplet surfaces, respectively, may be involved. In each case, roughly 20% undergoes the slower ammonium ion 1,2 decomposition, and no more than one hydrogen migration appears to take place. This occurs even though the lifetime for the intermediate complex in (6) may be approaching rotational periods at lower energies, and the complex has considerable internal energy. Scrambling and decomposition rates comparable to those in the methyl cation–methane reaction predict[2] that half the intermediates would undergo a second hydrogen migration at E_r = 4 eV (CM), resulting in larger amounts of products of (6a), (6b), and (7a). In neither reaction do the relative cross sections tend toward more scrambled, randomized behavior at low energies, also in contrast to the $CH_3^+ + CH_4$ system.

Huntress and Bowers[17] have formed low energy $CD_3NH_2D^+$ by reacting thermal D_3^+ ions of low internal energy with CD_3NH_2. The resulting decomposition resulted in a 2 to 1 ratio of CND_3H^+ to $CND_2H_2^+$. This is consistent with 1,2-H_2 elimination with little hydrogen scrambling, one of the decomposition steps utilized in the mechanisms proposed for reactions 3 and 4.

The same authors[18] have also studied the ratios of the two decomposition channels, $CNH_6^+ \rightarrow CNH_4^+ + H_2$ and $CNH_6^+ \rightarrow CH_3^+ + NH_3$, for a variety of internal energies of CNH_6^+. The existence of both decomposition channels establishes reaction 4 on the ground state CNH_6^+ surface. Results indicated a barrier in the $CNH_4^+ + H_2$ decomposition channel of 2.4 eV above the thermodynamic limit. These results are added evidence that energy barriers may play a large role in reactions 3 and 4.

These simple ion–neutral condensation reactions in carbon–nitrogen systems are highly exothermic with a deep well for the intermediate complex. Yet in contrast to analogous hydrocarbon systems, little hydrogen scrambling occurs. The energy of the reactions is released mainly as internal energy, even in some cases to the extent of producing two hydrogen atoms rather than one hydrogen atom or molecule. Finally, isotope labeling also indicates that H_2 (or 2H) may be formed by 1,2 elimination to some extent, in contrast to the exclusive 1,1 process attributed to the $CH_3^+ + CH_4$ reaction.

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