SELECTED ION FLOW TUBE STUDIES OF INTEREST TO THE CHEMISTRY OF ION-MOLECULE REACTIONS IN THE INTERSTELLAR MEDIUM

by

DOUGLAS M. JACKSON

(Under the Direction of Nigel G. Adams)

ABSTRACT

The possibility of forming organic compounds such as amino acids in the gas phase from observed interstellar species through ion-molecule reactions has been investigated by three studies in a Selected Ion Flow Tube at 298 K. Experiments were conducted examining the reactions of carboxylic acid type ions with CH_3NH_2 and $CH_3CH_2NH_2$, amine-fragment ions with HCOOH, CH_3COOH, and CH_3OCHO, and appropriate ions with H_2COCH_2-c and CH_2CHCHO. The tendency of the neutrals in most cases was to undergo dissociative charge transfer or proton transfer upon reaction with the ions rather than combine to form a product of interest; however, possible intermediates along a pathway to such a product of interest were formed via NH_3^+ reactions resulting in H atom abstraction and NH_4^+ 3 body association reactions. Previously unreported reaction rate coefficients and product distributions useful to astrochemical models have also been determined.

INDEX WORDS: Ion-molecule reaction, Selected Ion Flow Tube, Interstellar medium, Rate coefficient

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CHAPTER 1

INTRODUCTION

The use of various telescopes for analytical spectroscopy of stellar and interstellar regions has greatly aided the field of laboratory astrophysics with the identification of molecules present in the interstellar medium, ISM, and circumstellar medium, CSM. To date over 140 interstellar and circumstellar molecules have been identified [1] and the list of molecules will undoubtedly continue to grow as more powerful telescopes and interferometer arrays are built and utilized. In recent years, spectroscopic studies of hot-core star forming regions such as Sagittarius B2 have led to the discovery of many organic compounds including methylamine [2], acetic acid [3], methyl formate [4], formic acid [5], ethylene oxide [6], and propenal [7]. One study even proposed the detection of the spectral fingerprint of glycine [8], the simplest amino acid, in these hot-core regions, but this claim was later disputed [9]. Regardless of the authenticity of the glycine detection, it may be possible to synthesize glycine or other amino acids via ion-molecule reactions from various ions and neutrals found in these or other regions of space. If synthesized, these amino acids or amino acid precursors could be collected and deposited onto planets by meteorites or comets as the star systems further develop, thus planting the seeds of life [10-13].

Studies of ion-molecule reactions can provide a good understanding of the chemistry of these regions and yield data that can greatly assist in developing astrochemical models. In the evolution of large interstellar dust clouds to hot core regions, the temperatures of the systems increase from about 10 K to ~100-200 K [14]. Room temperature measurements (295 K) give reliable ion product distribution estimates, and temperature adjustment of rate coefficients is not required as long as the reactions proceed near the gas kinetic rate. The total number densities in the hot core regions are of ~10^6-10^7 cm^{-3} [14], which are ~3-4 orders of magnitude less than the reactant neutral number density of the SIFT measurements. However, reactions studied in the SIFT are still relevant to these regions given the considerably longer cloud lifetimes and times for reaction in developing planetary systems. The SIFT experiments also have a He carrier gas pressure of ~0.5 Torr (1.6×10^{16} cm^{-3}), but this does not influence binary collisional reactions since these reactions occur before the reacting species can interact with He. Variation of carrier gas pressure will, however, affect pressure dependent ternary association reactions [15]. Such collisionally stabilized reactions cannot occur in the cloud environments, but their radiatively stabilized analogues can, and the ternary reactions provide data to estimate their binary rate coefficients [15].

This thesis consists of three studies investigating plausible routes to amino acids via the reactions of ISM and CSM molecules and ions. First, the ion-molecule reactions of appropriate ions with methylamine and ethylamine were studied. Then, the reactions of the neutrals acetic acid, formic acid, and methyl formate with several ions were investigated. The final study probed the ion-molecule reactions of the neutral molecules ethylene oxide and propenal, which contain unique functional groups that have not been studied previously [16]. While no direct reaction pathways to amino acids in the gas phase were determined, previously unknown chemistry of these regions was described by determining many reaction rate coefficients and product ion distributions.

CHAPTER 2

A SELECTED ION FLOW TUBE STUDY OF THE REACTIONS OF A SEQUENCE OF IONS WITH AMINES

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[1] Jackson, D. M., Stibrich, N. J., Adams, N. G., and Babcock, L. M. 2005. International Journal of Mass Spectrometry. 243: 115-120.
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ABSTRACT

In seeking a viable pathway from interstellar species to more complex organics such as the amino acids glycine and alanine, it is possible that through a joining of amine and carboxyl functional groups, a product of interest may be obtained. As a prelude to such a study, the ion-molecule reactions of the simple ions N^+, N_2^+, Ar^+, CO_2^+, CO^+, and O_2^+ as well as the protonated species, $HCOOH_2^+$, $CH_3COOH_2^+$, and $HC(OH)OCH_3^+$, with reactant gases CH_3NH_2 and $CH_3CH_2NH_2$ have been investigated in a Selected Ion Flow Tube (SIFT) at 298 K. The neutral amines fragmented to some degree in all cases when reacted with ion species containing no acidic protons, fragmenting more with increasing recombination energy of the primary ion; whereas, the amines readily accept a proton from the protonated acid and methyl formate ions. The rate coefficients of these reactions have also been determined showing that they are nearly gas kinetic with the ethylamine reaction rate coefficients tending to be slightly less than their methylamine counterparts.

1. Introduction

Astrochemical models together with laboratory measurements of reaction rate coefficients and product distributions have provided insight into the earliest routes to the synthesis of the organic matter detected in interstellar clouds [17,18], the regions in which stars and planetary systems form. Some research suggests that comets, asteroids, and other interstellar bodies may have been essential to the formation of Life by depositing large quantities of organic matter on Earth during the pre-Life era [10,12,13,19]. In fact, meteorites impacting Earth have been shown to carry many complex organics including many amino acids [11]. Recently it has been reported that glycine may have been detected in interstellar space [8]. In addition, Blagojevic et al. report that glycine and alanine have recently been synthetically produced in the gas phase in the laboratory [20], indicating many organic syntheses may be possible in interstellar space. However, there is still some uncertainty concerning the exact synthesis and survival of these compounds in interstellar regions, and other routes to amino acid synthesis may be competitive.

The carboxyl and amine functional groups are essential components of the amino acids; thus a series of ion-molecule reactions of species containing these functional groups have been carried out in a SIFT to look for amino acid synthesis. The neutral gases CH_3NH_2 or $CH_3CH_2NH_2$ were used as reactants, and their reactions with the simple ions, N^+, N_2^+, Ar^+, CO_2^+, CO^+, and O_2^+, were performed first to help foster an understanding of this class of reactions of which few have been previously studied [16,21]. CH_3COOH, $HCOOCH_3$, $HCOOH$, and CH_3NH_2 have been detected in the interstellar medium [17,21], and it is from molecules of these types that an initial synthesis point for the formation of more complex amino acid type molecules may have occurred. The previously unknown rate coefficients and product distributions, reported here, will greatly supplement the literature.

2. Experimental

The Selected Ion Flow Tube (SIFT) technique (see Fig 2.1) has been used to introduce a single primary ion species into a flowing He carrier gas. The SIFT technique has been described previously [23,24] and will not be described in detail here; however, several comments are warranted about the ion source. A High Pressure Electron Impact Ion Source (HPIS) with a Rhenium filament was initially employed to produce the ions of interest, the simple ions N^+, N_2^+, Ar^+, CO^+, and CO_2^+ from N_2, Ar, and CO_2. The HPIS allows the simple ions to thermalize through collisions with neutrals in the source chamber and minimizes excitation in the injected ion beam. The HPIS would also have been suitable to produce the protonated species since secondary reactions are possible in this high-pressure source most likely yielding more intact species rather than fragments. Unfortunately, problems arose when HCOOH was first introduced into the source. $HC(OH)_2^+$ was detected in the SIFT and injected into the flow tube, however, the filament corroded and burned out after only about 30 minutes of exposure. The same would occur for any attempt at injecting O_2^+ or any other corrosive or oxidizing gas from the HPIS.

To ionize these species, a Microwave Discharge Cavity (MC) of the type used in Flowing Afterglow (FA) studies was employed [24]. A 1 mm orifice disk was fitted between the microwave discharge plasma and the SIFT chamber to sample ions from the MC but not to overwhelm the SIFT quadrupole mass filter and its pumping system with the source gas. Unfortunately, the MC did not effectively produce the protonated species of interest directly. However, these species could be produced by injecting H_3O^+ from the SIFT (with H_2O in the source) into the flow tube and using it to proton transfer to CH_3COOH, $HCOOCH_3$, and HCOOH. As the flow of a neutral carboxylic acid was increased, H_3O^+ was completely depleted by proton transfer. At the point H_3O^+ was eliminated, the presence of the protonated acid was detected in sufficient quantities, and the flow of the neutral acid was then held steady. Protonated carboxylic acid dimers were also present at this juncture. However, the three body stabilized dimerization reaction does not totally deplete the desired primary ion [25]. The reactions were carried out in a He carrier gas introduced into the flow tube to a total pressure of ~0.5 Torr and evacuated downstream by a Roots pump after sampling the ions with a downstream mass filter and ion counting system. The amine reactant gases were added downstream in the flow through a ring type injector with a flush gas of pure He to ensure a constant flow of the sticky organic gases. Viscous flows of reactant gases were determined by measuring the pressure drop across, and pressure in, a calibrated capillary using the Poiseuille equation. The purities as quoted by the manufacturer of CH_3NH_2 and $CH_3CH_2NH_2$ were 99.5% and 99.8% respectively and these gases were used without additional purification. All measurements were carried out at room temperature (298 K), and the rate coefficients and product ion distributions were determined in the usual way [23,24,26]. Rate coefficients are accurate to ±15% and product ions to ±5 in the percentage.

3. Results and Discussion

The experimental rate coefficients along with literature values [21] where available and the gas kinetic rate coefficients calculated using Variational Transition State Theory [21] with polarizabilities and dipole moments obtained from literature [28] are displayed in Table 2.1. All rate coefficients for the CH_3NH_2 reactions with the simple ions were near the gas kinetic values, and the $CH_3CH_2NH_2$ reactions with the simple ions had rate coefficients just below the equivalent gas kinetic values. The reactions with $HC(OH)_2^+$ were near the gas kinetic rate; whereas, the reactions of the amines with $CH_3C(OH)_2^+$ and $HC(OH)OCH_3^+$ gave rate coefficients above the gas kinetic value. In general, the efficiencies for reactions involving a particular ion and CH_3NH_2 were higher than for $CH_3CH_2NH_2$. Table 2.2 displays the experimental products and percentage product distributions along with literature values [21] where available. The amines exclusively charge transfer with a high degree of fragmentation when reacted with simple ions containing no H atoms and fragment to greater degrees as the recombination energy of the ions increases. Following every fragmentation reaction, secondary reactions occurred involving all primary product ions where these ions proton transfer to the amines. An example decay of a typical primary ion, the rise and decay of primary products, and the rise of a single secondary product is shown in Fig 2.2. Reactions of the amines with

$HC(OH)_2^+$, $CH_3C(OH)_2^+$, and $HC(OH)OCH_3^+$, like the previously mentioned secondary reactions, exclusively result in proton transfer to the neutral amine. The analyses of the reactions with the ions N^+, Ar^+, CO_2^+, $CH_3C(OH)_2^+$, $HC(OH)OCH_3^+$, and $HC(OH)_2^+$ were straightforward; however, the ions N_2^+, CO^+, and O_2^+ posed problems since there were possible products with molecular masses equivalent to those of the primary ions.

3.1 O_2^+, N_2^+, and CO^+ Reactions with CH_3NH_2

O_2^+, N_2^+, and CO^+ when reacted with CH_3NH_2 can possibly generate products of the same charge/mass ratio as the reactant ion. If unaccounted for, these products could distort both the percentage product distributions as well as the rate coefficients for the reactions involved. The reactions of these primary ions with CH_3NH_2 were modeled kinetically to determine whether or not an additional product was present. Though no extra primary product was present for the O_2^+ reaction, its decay was affected by the rise of the secondary product, $CH_3NH_3^+$, also at mass 32. The primary ion decay was largely linear for very low neutral flows, yet the signal increased at higher flows as the rise of the secondary product predominates, obscuring the primary ion decay. A fitting of the kinetic model of this reaction according to the integrated rate laws given by the following equations can be seen in Fig 2.3:

$$[P^+] = [P^+]_o \exp(-k_1[M]t) \qquad (1)$$

$$[A^+] = \frac{k_1 f_a [P^+]_o}{k_{2a} - k_1}\left(\exp(-k_1[M]t) - \exp(-k_{2a}[M]t)\right) \qquad (2)$$

$$\begin{aligned}[MH^+] = {} & \frac{k_1 f_a [P^+]_o}{k_{2a} - k_1}\exp(-k_{2a}[M]t) + \frac{k_1 f_b [P^+]_o}{k_{2b} - k_1}\exp(-k_{2b}[M]t) \\ & - \frac{k_{2a} f_a [P^+]_o}{k_{2a} - k_1}\exp(-k_1[M]t) - \frac{k_{2b} f_b [P^+]_o}{k_{2b} - k_1}\exp(-k_1[M]t)\end{aligned} \qquad (3)$$

[] indicates the concentrations of the primary ion (P^+), CH_3NH_2 (M), a primary product (A^+), and the secondary product (MH^+). The rate coefficient of the primary reaction is given by k_1, and $k_{2a,b,\ldots n}$ and $f_{a,b\ldots n}$ are the rate coefficients and product ratios of the respective primary product decay reactions. Eq. (3) takes two primary products, A and B, into account and thus provides a complete fit for the O_2^+ reaction with CH_3NH_2 but not the reactions of other primary ions which may product different numbers of products. From this fit, a rate coefficient was obtained for the primary O_2^+ reaction and is listed in Table 2.1.

Several trends in the data indicate that N_2^+ could have CH_2N^+ as a product. The other ions of higher recombination energy cause fragmentation into smaller molecules, CH_2N^+ being a common product in these cases. Also, the rate coefficient of this N_2^+ reaction has a greater percent difference from the gas kinetic rate than the other CH_3NH_2 reactions (note that this is in agreement with a previous determination, see Table 2.1). However, the kinetic models according to Eqs. 1,2 of the reactions of N_2^+ as well as CO^+ with CH_3NH_2 fit the data as it exists and allow for no addition of the extra product CH_2N^+.

Literature data [10] for the product distributions of all but one of the reactions for which it is available are in agreement with the present data. Literature values for products of the N_2^+ reaction with CH_3NH_2 conflicts with the experimental data obtained in this study in that the previous data does not report the product CH_3N^+ which is a significant product of this reaction in the present study. The previous study also reports the product percentage of CH_3^+ to be much more significant to the reaction than the present study indicates. The present study is a more extensive study of this particular class of reactions and indicates that CH_3N^+ is a common product ion present in almost every simple ion reaction with CH_3NH_2 making it a likely product of the N_2^+ reaction with CH_3NH_2; moreover, CH_3^+ is no more than a minor product in any reaction of this study if it is a product at all. The reaction in question was repeated several times, and the data presented in Table 2.2 are an accurate representation of the results obtained. No reason can be advanced for the discrepancy especially since the agreement is good in all other cases.

3.2 Kinetic Trends

The simple ions when reacted with CH_3NH_2 have rate coefficients around the gas kinetic values, and these same ions when reacted with $CH_3CH_2NH_2$ react on average to give rate coefficients less than gas kinetic rate and less absolutely than their reactions with CH_3NH_2. The reactive site on the molecules of both classes of reactions lies in the region of the non-bonding electron pair about the N atom. Perhaps the simple ions react with CH_3NH_2 near the gas kinetic rate because the neutral molecule has a short binary backbone; thus the approach of a reactant ion always occurs nearer to the reactive site than the approach would be to a longer molecule. Since $CH_3CH_2NH_2$ has a longer backbone, the reactions of the simple ions with $CH_3CH_2NH_2$ may occur more slowly. The reactions of the protonated species again show the rate coefficients of the $CH_3CH_2NH_2$ reactions are less than those of the CH_3NH_2 reactions supporting the claim that amine chain length and the rate coefficients are inversely related.

The rate coefficients of the majority of the reactions were below or within error of the gas kinetic rate calculated using Variational Transition State Theory; however, the efficiencies of the reactions of both neutral species with $CH_3C(OH)_2^+$ and $HC(OH)OCH_3^+$ were notably above 100%. With these reactant ions, unlike the simple ions studied, the ions will have a significant dipole moment. Such could cause a locking between the ions and neutrals greater than that implicit in the Variational Theory. Calculation of the rate coefficients for which the dipoles of the neutrals are fully locked yields values of the rate coefficients of 3.85×10^{-9} cm^3s^{-1} for the reactions of each ion with CH_3NH_2 and 3.13 x 10^{-9} cm^3s^{-1} for the reactions with $CH_3CH_2NH_2$ [29] which are larger than the experimental values. Note that the reactions with $CH_3CH_2NH_2$ are less efficient than those with CH_3NH_2 (~0.65 to ~0.75 if the dipole is fully locked). Since when proton transfer is energetically possible, it generally occurs at the collisional rate [30], this implies that the protonated acetic acid reactions are actually gas kinetic which would give a locking constant of ~0.65.

3.3 Fragmentation Reactions

3.3.1 Formation of the Products: CH_nN^+ (n = 1-5), $C_2H_6N^+$, and $CH_3CH_2NH_2^+$

The reactions of simple ionic species almost exclusively fragmented CH_3NH_2 and $CH_3CH_2NH_2$. A direct charge transfer from the reactant ion to CH_3NH_2 was the only source of $CH_3NH_2^+$. Clearly only the $CH_3CH_2NH_2$ could have the products $CH_3CHNH_2^+$ and $CH_3CH_2NH_2^+$, but the ions CH_nN^+ (n = 1-4) could be, and were seen to be, produced in reactions involving both neutrals. It is believed that the primary ion is most often drawn to the non-bonding electron pair about the N atom removing an electron from that site. When they are formed in the CH_3NH_2 reactions, the reactions at the amine end would result in H atoms being ejected to various degrees depending on the orientation and energetics of the collision. When these ions are forming in $CH_3CH_2NH_2$ reactions, the H atoms must be ejected leaving the C-N bond intact as in the CH_3NH_2 reactions, rather than leaving the C-C bond intact. It is apparent that the most efficient routes to the product ions involve the cleaving of the C-C bond. If this was not the case, fragments like $C_2H_n^+$ would be formed; however, these products are unlikely and not observed since these fragments have recombination energies higher than their CH_nN^+ counterparts [31]. Furthermore, the limited literature data available [16] shows that the members of the amine series, $CH_3(CH_2)_nNH_2$ (n = 3,4,5), when reacted with O_2^+ each show CH_4N^+ (the observed major product in all simple ion reactions with $CH_3CH_2NH_2$ in this study) as the major product. This indicates that the atoms in the chain play little role in the reaction with the amine terminus serving as the main reaction site.

3.3.2 Formation of the Products: CH_3^+, NH_3^+, and NH_4^+

In addition to causing greater fragmentation in general, the higher recombination energy ions may also remove an electron from a bonding electron pair creating a slightly different class of products. CH_3^+ would be expected to be formed in CH_3NH_2 reactions when an ion approaches the molecule at the C-N bond and has enough energy to cause electron transfer. This would give only a small CH_3^+ product since the orientation of the collision would most often be toward the non-bonding pair about the N. The observed NH_3^+ and NH_4^+ would be expected to form when a high energy primary ion approaches near the C atom of the C-N bond of $CH_3CH_2NH_2$.

3.4 Proton Transfer Reactions

Consistent with the reactivity of the primary product ions with the amines following the simple ion reactions, the reactions of the protonated species, $CH_3C(OH)_2^+$, $HC(OH)OCH_3^+$, and $HC(OH)_2^+$, also proceed by proton transfer. This is consistent with the general trend that proton transfer is efficient when exothermic [30]. No competitive dissociative proton transfer was seen, and, as expected, no ternary association was observed since this would not be competitive with facile proton transfer.

4. Conclusions

The present study has provided insight into one family of gas phase reactions involving the building blocks of amino acids. This study has shown that using amines as neutral reactant gases will not effectively synthesize larger organic molecules and no component of the ions is incorporated into the product ion. Further studies devoted to reactions of these types will likely lead to similar results. Terminal alkanamines appear only to react at the amine end; therefore, it is expected that as the length of the amine molecule chain increases, the ease by which the reactions proceed will decrease due to the orientation factor and steric hindrance, and thus the rate coefficients for amine reactions will decrease as the amine chain length increases and could be confirmed by studies with longer chains. It is apparent that the lone pair of electrons about the N atom of an amine, in addition to serving as the reaction site for the simple ion reactions with the amines, quite readily serves as a base for the protonated carboxylic acids, protonated formate, and the hydrogen containing primary product ions; when energetically possible the amines abstract a proton; otherwise neutral amines demonstrate no tendencies to react to form more complex molecules. The possibility of pathways to complex organics initialized by reactions of amine ion fragments may be more likely.

5. Acknowledgements

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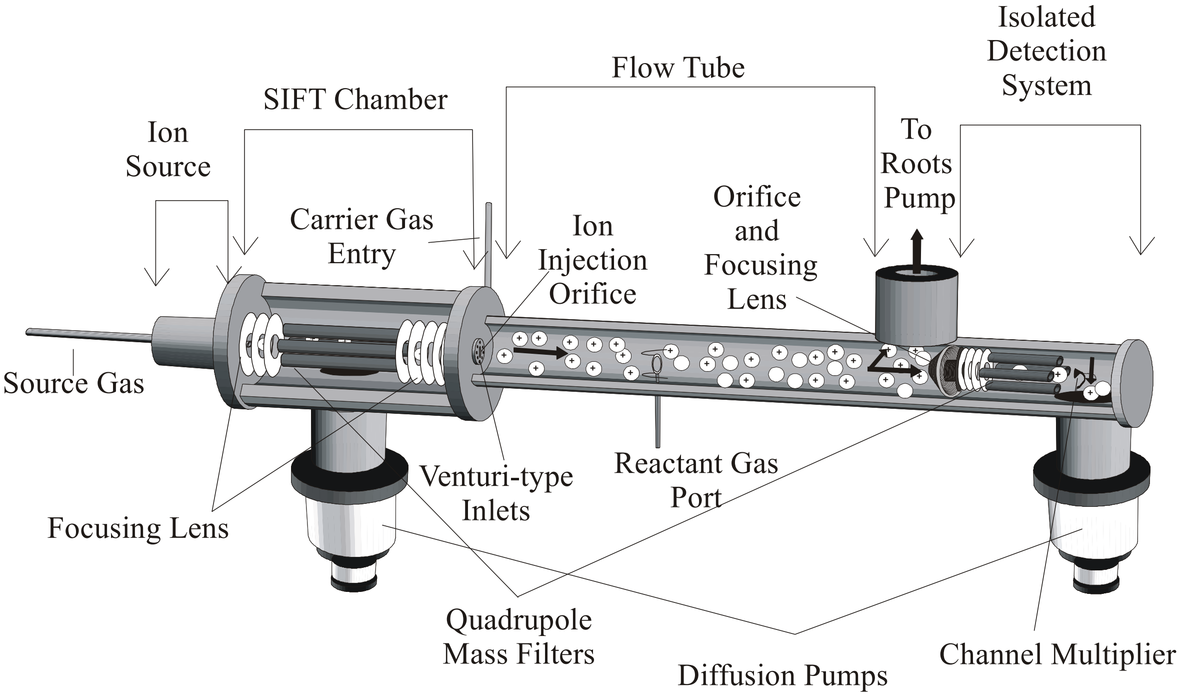

Figure 2.1 A schematic diagram of the University of Georgia SIFT apparatus. Ions are focused from the ion source into a quadrupole mass filter, mass selected, refocused, and injected into the flow tube through the ion injection orifice. These ions are entrained in the He carrier gas flow to which reactant gases are added. Reactant and product ions are sampled at the downstream end of the reaction zone through an orifice into a mass filter/ion counting system.

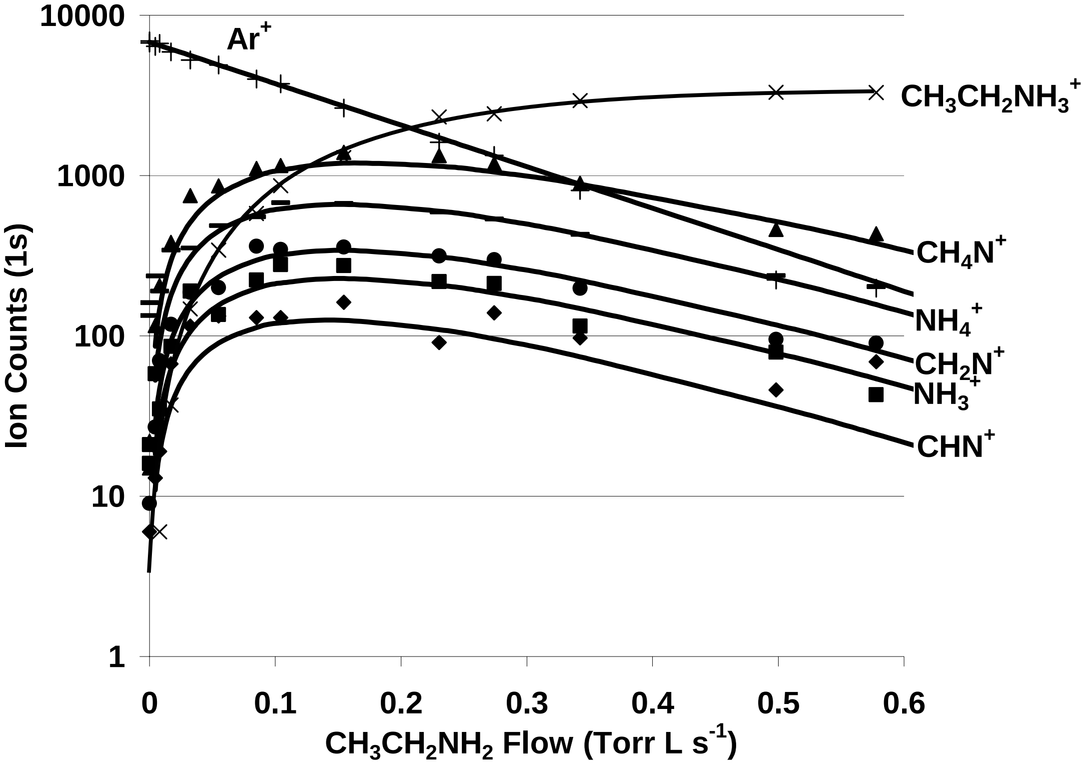

Figure 2.2 Decay of Ar^+ in a typical charge transfer reaction with $CH_3CH_2NH_2$. Note the linear decay of the reactant ion over approximately two orders of magnitude and that the secondary reactions all produce protonated $CH_3CH_2NH_2$.

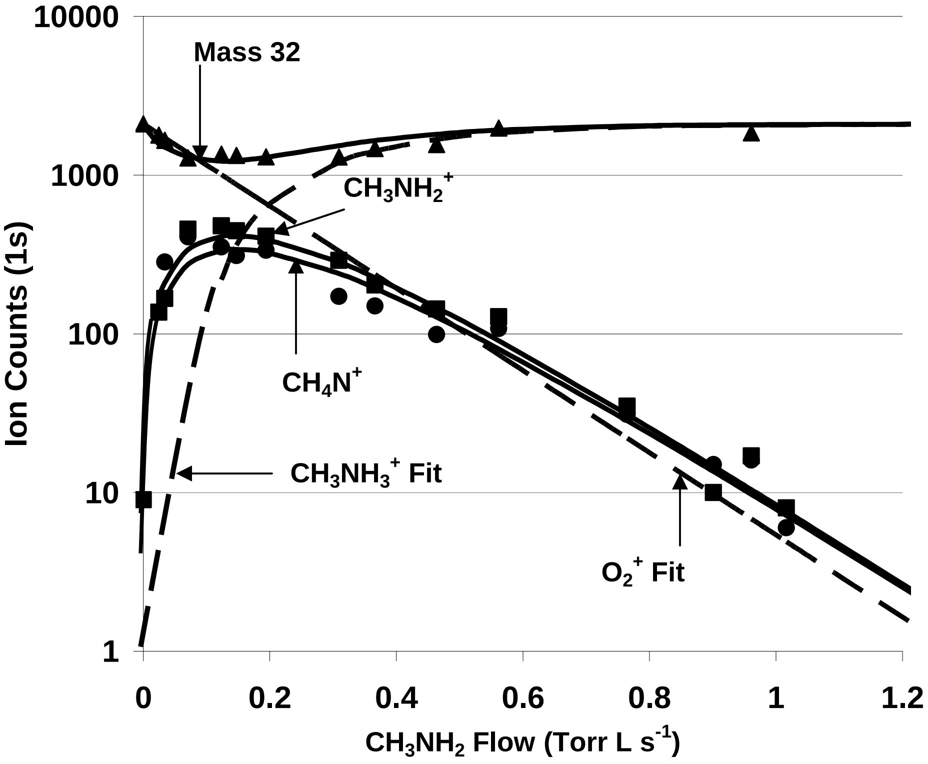

Figure 2.3 Variation of O_2^+ and product ion counts in reaction with CH_3NH_2. The decay of O_2^+ is soon obscured by the rise of the secondary product, $CH_3NH_3^+$. The line through the mass 32 data points is the sum of the modeled decay of O_2^+ and modeled rise of $CH_3NH_3^+$ as shown by the dashed lines. All product ions were modeled in this fit; the mass 32 amu variation could not be improved further without the other fits being substantially degraded.

Table 2.1 Experimental rate coefficients, k_{exp}, of a series of ions (indicated) with CH_3NH_2 and $CH_3CH_2NH_2$ are listed followed by literature rate coefficients, k_{lit}, [21] where available and theoretical collisional rate coefficients, k_{theor}, determined using Variational Transition State Theory [27] with polarizabilities and dipole moments from literature [28]. The reaction efficiency, k_{exp} / k_{theor}, is also given. All rate coefficients are expressed in units of 10^{-9} cm^3/s.

a Obtained by modeling the data in Fig 2.3.

b Within error of the gas kinetic rate.

c The high efficiencies are noted in Section 3.2.

		CH_3NH_2		
Ion	$k_{exp}(10^{-9}\ cm^3s^{-1})$	$k_{lit}(10^{-9}\ cm^3s^{-1})$	$k_{theor}(10^{-9}\ cm^3s^{-1})$	Efficiency
Ar^+	1.92	-	1.99	0.965
N_2^+	1.22	1.20	2.17	0.562
N^+	2.56	2.00	2.68	0.955
CO^+	2.12	-	2.17	0.977
CO_2^+	2.13	-	1.95	1.09^b
O_2^+	2.50^a	1.00	2.10	1.19^b
$HC(OH)_2^+$	1.78	-	1.93	0.922
$CH_3C(OH)_2^+$	2.86	-	1.84	1.55^c
$HC(OH)OCH_3^+$	2.45	-	1.84	1.33^c

		$CH_3CH_2NH_2$		
Ion	$k_{exp}(10^{-9}\ cm^3s^{-1})$	$k_{lit}(10^{-9}\ cm^3s^{-1})$	$k_{theor}(10^{-9}\ cm^3s^{-1})$	Efficiency
Ar^+	0.926	-	1.87	0.495
N_2^+	1.54	-	2.07	0.744
N^+	2.14	-	2.64	0.811
CO^+	1.53	-	2.07	0.739
CO_2^+	1.22	-	1.83	0.667
O_2^+	1.52	-	1.99	0.763
$HC(OH)_2^+$	1.58	-	1.80	0.878
$CH_3C(OH)_2^+$	2.35	-	1.69	1.39^c
$HC(OH)OCH_3^+$	2.11	-	1.69	1.25^c

Table 2.2 Product distributions (%) for the reactions of CH_3NH_2 and $CH_3CH_2NH_2$ with the ions indicated are listed along with literature product ion percentages [21] (in parentheses) where available. Each proposed product channel was exothermic with reaction enthalpies, ΔH_r, ranging from ~ -47 kJ/mol to ~ -840 kJ/mol. Thermochemical data were obtained from the literature [31]. Simple ions are arranged in order of decreasing recombination energy.

	CH_3NH_2 Reactions			$CH_3CH_2NH_2$ Reactions		
Source Ion	Ion Product	Neutral Products	%	Ion Product	Neutral Products	%
	Fragmentation Reactions					
Ar^+	CH_3^+	$NH_2 + Ar$	8	NH_3^+	$C_2H_4 + Ar$	10
15.76 eV	CH_2N^+	$H_2 + H + Ar$	59	NH_4^+	$C_2H_3 + Ar$	25
	CH_3N^+	$H_2 + Ar$	3	CHN^+	$CH_4 + H_2 + Ar$	6
	CH_4N^+	$H + Ar$	30	CH_2N^+	$CH_4 + H + Ar$	12
				CH_4N^+	$CH_4 + Ar$	47
N_2^+	CH_3^+	$NH_2 + N_2$	7 (21)	CH_3N^+	$CH_4 + N_2$	24
15.58 eV	CH_3N^+	$H_2 + N_2$	21 (0)	CH_4N^+	$CH_3 + N_2$	76
	CH_4N^+	$H + N_2$	67 (73)			
	$CH_3NH_2^+$	N_2	5 (6)			
N^+	CH_3^+	$NH_2 + N$	7 (6)	CH_4N^+	$CH_3 + N$	100
14.53 eV	CH_2N^+	$H_2 + H + N$	18 (10)			
	CH_3N^+	$H_2 + N$	7 (7)			
	CH_4N^+	$H + N$	62 (70)			
	$CH_3NH_2^+$	N	6 (7)			
CO^+	CH_3N^+	H_2CO	18	CH_3N^+	$CH_4 + CO$	12
13.99 eV	CH_4N^+	HCO	79	CH_4N^+	$CH_3 + CO$	68
	$CH_3NH_2^+$	CO	3	$C_2H_6N^+$	HCO	20
CO_2^+	CH_2N^+	$HCO_2 + H_2$	4	CH_4N^+	$CH_3 + CO_2$	86
13.75 eV	CH_3N^+	$CO_2 + H_2$	10	$CH_3CH_2NH_2^+$	CO_2	14
	CH_4N^+	HCO_2	72			
	$CH_3NH_2^+$	CO_2	14			
O_2^+	CH_4N^+	HO_2	40 (35)	CH_4N^+	$CH_3 + O_2$	86
12.07 eV	$CH_3NH_2^+$	O_2	60 (65)	$C_2H_6N^+$	HO_2	4
				$CH_3CH_2NH_2^+$	O_2	10
	Proton Transfer Reactions					
$HC(OH)_2^+$	$CH_3NH_3^+$	HCOOH	100	$CH_3CH_2NH_3^+$	HCOOH	100
$CH_3C(OH)_2^+$	$CH_3NH_3^+$	CH_3COOH	100	$CH_3CH_2NH_3^+$	CH_3COOH	100
$HC(OH)OCH_3^+$	$CH_3NH_3^+$	$HCOOCH_3$	100	$CH_3CH_2NH_3^+$	$HCOOCH_3$	100

CHAPTER 3

A SELECTED ION FLOW TUBE STUDY OF THE REACTIONS OF VARIOUS NITROGEN CONTAINING IONS WITH FORMIC ACID, ACETIC ACID, AND METHYL FORMATE

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[2] Jackson, D. M., Stibrich, N. J., McLain, J. L., Fondren, L. D., Adams, N. G., Babcock, L. M. International Journal of Mass Spectrometry. 247: 55-60.
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ABSTRACT

The possibility of forming organic molecules such as the amino acid, glycine, from interstellar species through the ion-molecule reactions of ionized amine fragment compounds with neutral carboxylic acid and ester species has been investigated in a Selected Ion Flow Tube (SIFT) at 298 K. An earlier study showed that reactions of neutral amine species with ionized carboxylic acid or ester fragments does not result in the desired combination of groups but instead results in the fragmentation of the amines [32]. In the present study, the ion product distributions and reaction rate coefficients of the gas phase reactions of HCOOH, CH_3COOH, and CH_3OCHO with the ions Ar^+, N_2^+, NH_2^+, NH_3^+, and $HCNH^+$ have been determined. The ions Ar^+ and N_2^+ fragment the neutral species in dissociative charge transfer, and the reactions of NH_2^+ and $HCNH^+$ with the neutrals result in dissociative proton transfer. NH_3^+ reacts with all three species to form NH_4^+ by H atom abstraction. The reaction rate coefficients were on average within experimental error of the gas kinetic rate and were on the order of 10^{-9} cm^3s^{-1}.

1. Introduction

Astrochemical models and laboratory measurements have aided the understanding of the formation of organic matter in interstellar clouds where planetary systems form [17,18]. If complex organic compounds can be formed in the interstellar regions by gas phase reactions or reactions catalyzed by dust grains, it is possible that comets and meteors could collect and deposit these species onto planets providing the nutrients for life [11-13,19]. In fact meteorites impacting Earth have been shown to carry many amino acids [10]. Indeed it has been reported that the amino acid glycine may have been detected in the gas phase in the interstellar medium [8], but this report has been recently contested [9]. One possible ion-molecule reaction pathway to interstellar amino acid synthesis has already been proposed [20], but competitive routes also may exist. In this paper, the possibility of a gas phase ion-molecule pathway to amino acids involving amine ion fragments and neutral carboxylic acids or esters is explored. The predecessor of this study has already refuted one possible pathway to molecules of this type involving the reactions of neutral amines and ionized carbonyl containing species [32].

The present study has been conducted in a SIFT at 298 K concerning the reactions of the positively charged ammonia and amine ion fragments, NH_2^+, NH_3^+, and $HCNH^+$, and the ions Ar^+ and N_2^+ with the neutrals HCOOH, CH_3COOH, and CH_3OCHO. These neutrals as well as NH_3 and $HCNH^+$ are known to exist in interstellar clouds [1,22]. $HCNH^+$ has been shown to be a primary fragmentation product of the reactions of several ions with the amines $CH_3CH_2NH_2$ and CH_3NH_2 [32], the latter of which has been detected in the interstellar medium [1], and $HCNH^+$ is also believed to play an important role in the atmosphere of Titan [33,34]. The general behavior of the reactions of gaseous HCOOH, CH_3COOH, and CH_3OCHO was determined through preliminary studies with Ar^+ and N_2^+. The reactions of the neutrals with NH_2^+, NH_3^+, and $HCNH^+$ were then analyzed. Several previously unknown ion product distributions and rate coefficients were determined in this study.

2. Experimental

The Selected Ion Flow Tube (SIFT) technique has been used to introduce a single primary ion species into a flowing He carrier gas. The SIFT technique has been described previously [23,24] and will not be described in detail here. A Microwave Cavity (MC) ionization source of the type used in Flowing Afterglow studies [24] was used to create all primary ions. This source was separated from the upstream quadrupole region by a 1 mm orifice disk as in the previous study [32]. The ions Ar^+ and N_2^+ were produced from their respective neutral gases. NH_2^+ and NH_3^+ were produced from ammonia, and $HCNH^+$ was produced from trimethylamine. Attempts were made to produce $HCNH^+$ using methylamine and ethylamine, but these gases when introduced into the MC quickly deposited a carbon layer on the inner surface of the pyrex tube of the MC.

The reactant gases HCOOH and CH_3COOH have low vapor pressures [35] and are notably "sticky" organic liquids that readily dimerize, and for this reason samples of these liquids and the higher vapor pressure liquid CH_3OCHO were prepared by evaporating the pure liquids into an evacuated vessel to a total pressure of 10 Torr and diluting to 1% in He. At this pressure, which is less than the saturated vapor pressure of all the liquids, the compound will be predominantly in the gas phase. However, there will still be a degree of dimerization within the vapors of HCOOH and CH_3COOH and this degree of dimerization can be calculated from the measured literature equilibrium constants [36,37] (no such dimerization occurs for CH_3OCHO so this complication is not present with this higher vapor pressure liquid). When the vapors are introduced into the flow tube, the equilibrium is such that a negligible amount of dimer will be present if there is sufficient time for equilibrium to be approached. That sufficient time is available can be shown by comparing the reduction in dimer concentration due to monomerization in collision with the He carrier gas with that due to the reaction with the primary ions. For these cases $d[D]/dt$ equals $-k_a[D][He]$ and $-k_b[D][+]$ respectively, where k_a and k_b are the rate coefficients of the respective reactions and [D], [He], and [+] represent the concentrations of dimer, He carrier gas, and primary ion respectively. Use of reasonable values for the parameters in these equations shows that the former $d[D]/dt$ is considerably greater than the latter, showing that the presence of dimer in the flow tube is negligible. Thus, the flow of monomer into the flow tube can be determined from the overall flow rate of the mixtures and the total fraction of HCOOH and CH_3COOH in the mixture, whether in monomer or dimer form.

Note that as the gas mixture is consumed and the pressure reduces, the amount of dimer will decrease relative to the monomer but the total fractions of HCOOH and CH_3COOH will remain constant. The purities of the liquids as quoted by the manufacturers were as follows: HCOOH, 99%; CH_3COOH, 99.99%; CH_3OCHO, 99%. The samples of the liquids once attached to the system were additionally purified by freeze-pump-thaw cycles to remove dissolved gases before dilution. The reactant gas mixtures were added downstream in the flow through a ring type injector facing upstream into a carrier gas of pure He at a total pressure of ~0.5 Torr. Flows of the reactant gas mixtures were determined by measuring the pressure drop across, and pressure in, a calibrated capillary under viscous flow conditions using the Poiseuille equation. The He used for the dilutions and as the carrier gas was pre-purified in molecular sieve cooled by liquid nitrogen. All measurements were carried out at room temperature (298 K), and the rate coefficients and product ion distributions were determined in the usual way [23,24,26] accounting for the dilution of the reactant neutral. Note that it is necessary to use the viscosity of He when calculating the rate coefficients instead of the gas phase viscosity of the liquids when a diluted mixture of this type is used as a reactant gas. Rate coefficients are accurate to ±30% and product ions to ±5 in the percentage.

3. Results

The experimental reaction rate coefficients, k_{exp}, are given in Table 3.1 along with the theoretical collisional rate coefficients, k_{theor}, calculated using Variational Transition State Theory [27] and comparative literature values, k_{lit}, are included where available [16,38,39]. The decay of the primary ion versus the flow of neutral gas in a typical reaction is shown in Fig. 3.1. The reaction of N^+ with O_2, a well-established reaction, was performed at the time of this study to confirm the performance of our SIFT apparatus. As can be seen in Table 3.1, our measurement of the rate coefficient with this reaction is in close agreement with literature [16]. The standard reaction was then performed again with a 1% dilution of O_2 in He, and the rate coefficient obtained was unchanged confirming the proper working order of the method of dilution. The reaction efficiencies, k_{exp}/k_{theor}, are given in Table 3.1 as well to demonstrate the correlation of the theoretical and experimental rate coefficients. The experimental rate coefficients are on average within experimental error of those calculated theoretically.

Ionic products, suggested neutral products, ion product percentages, and enthalpies of reaction, ΔH_r, of each reaction deduced using thermodynamic data obtained from literature [28,31,35,40,41] are included in Table 3.2 along with the very limited literature data [16,38,39]. The rapid NH_2^+ and $HCNH^+$ reactions each result in proton transfer from the primary ion to the neutral. The ions Ar^+ and N_2^+ fragmented the neutrals by dissociative charge transfer into the products shown in Table 3.2. NH_3^+ reacted with each of the neutrals via H atom abstraction to form NH_4^+ in a manner which has been reported for the reaction of this ion with several other species containing hydrogen including H_2CO and CH_3OH [42].

4. Discussion

4.1 Kinetics

The rate coefficients, k_{exp}, obtained for many of the reactions in this study are near the k_{theor} values calculated with Variational Transition State Theory [27]. A comparison to the available literature also shows general agreement with our experimental values. The only experiments of the types of reactions investigated in this study that were performed previously were FA studies involving formic acid [38,39]. In each case for k_{lit} values above the gas kinetic rate, k_{exp} is also above k_{theor}; likewise for k_{lit} values below k_{theor}, k_{exp} is below k_{theor} indicating agreement between the current measurements and literature. The agreement of the k_{exp} and k_{lit} in the standard reaction of N^+ and O_2 noted in Section 3 attests to the proper functioning of the apparatus. Note the efficiencies of the reactions are within experimental error equal to the gas kinetic rate.

Some of the differences between k_{exp} and k_{theor} may be attributed to errors associated with the dilution technique and the complications due to carboxylic acid dimerization. If dimerization problems and the equilibrium calculations were a major source of error in the experiment, then the rate coefficients of the reactions of CH_3OCHO, for which dimerization need not be considered, should be closer to k_{theor}. It is observed, however, that they are not relatively closer to 100% efficiency than the rate coefficients of the reactions carboxylic acids. Thus it is likely that the tendency of the organic liquids to adhere to surfaces of the system condensing on and evaporating from the walls is a significant additional source of error in the experiment even though equilibration time was given for the pressures in the dilution chamber to stabilize in the production of the reactant mixtures before pressures were recorded and the flows of the reactants into the flow tube were given sufficient time for the reactant concentrations to stabilize as indicated by the constancy of the ion count rates. It may be noted that some differences between k_{exp} and k_{theor} also may be due to limitations of theory to describe the interactions of ions with complex molecules containing more than one major functional group and not just due to error associated with the experiment.

4.2 Products

4.2.1 Ar^+ and N_2^+

The ion product distributions for the reactant ions Ar^+ and N_2^+ indicate dissociative charge transfer fragmentation for each neutral based on the position of attack. The acids, HCOOH and CH_3COOH, fragment solely into two products based on this principle. An attack claiming an electron from the carboxyl group of the molecules leads to a cleavage of the RCO-OH bond resulting in the ionized product RCO^+ and the OH radical. Alternatively an attack to the R-COOH bond results in $COOH^+$ and a neutral R. In the case of fragmentation of these species, the positive charge resides on the fragment containing the carbonyl which, in the case of the HCOOH, is the only energetic possibility, and in the case of CH_3COOH, is favored by >100 kJmol^{-1} over CH_3^+. Fragmentation of CH_3OCHO gives three products presumably due to the placement of the second C-O bond. An attack to the CH_3O-CHO bond can give either HCO^+ and CH_3O or CH_3O^+ and HCO, and it is also possible to attack the CH_3-OCHO bond, which appears to result in CH_3^+ and the formyloxyl radical, HCOO. This neutral species has not been studied to a large degree, but it has been reported to be unstable, decaying to H and CO_2 in experiments run under single collision conditions [43]. The instability of this species may account for why it does not readily ionize like the hydrocarboxyl radical, COOH, whose ionic form is a product in the reactions of the carboxylic acids, and the product CH_3^+ is seen instead.

With respect to the disagreement of the product distribution of the N_2^+ and HCOOH reaction in Table 3.2 with the literature value which does not report the product $COOH^+$, it may be noted that these old FA measurements can be expected to be relatively accurate concerning rate coefficients but not as accurate concerning products. Unwanted ions may be produced along with the primary ion of interest that may obscure products. Also, neutral source gases had to be added to the flow tube to produce these ions, which complicated product analysis. Electron-ion recombination can also occur further distorting the product distributions of FA experiments. Thus the current SIFT measurements of product distributions are more accurate than previous FA measurements, and the ion products for the reactions of Ar^+ and N_2^+ are very consistent as expected for dissociative charge transfer from species with similar recombination energies.

Because of the above complications, the older FA experiments were often not able to report ion product distributions; thus several reactions for which k_{lit} values are given in Table 3.1 have no corresponding literature products reported.

4.2.2 $HCNH^+$

Each neutral reacted via exothermic proton transfer with the amine fragment $HCNH^+$. Proton transfer from the C of $HCNH^+$ to HCOOH is an endothermic reaction (ΔH_r = ~27 $kJmol^{-1}$) and prevents the formation of HNC, but for CH_3COOH and CH_3OCHO proton transfer from the C of $HCNH^+$ forming HNC is energetically possible with ΔH_r values of -11.4 and -10.2 $kJmol^{-1}$ respectively. Thus reaction pathways leading to HCN are favored energetically, but it is expected that HNC could play a role in the reactions of CH_3COOH and CH_3OCHO with $HCNH^+$. The product channels, which lead to HCN rather than HNC are more exothermic, and the ΔH_r values given in Table 3.2 correspond to the HCN product channels.

4.2.3 NH_2^+ and NH_3^+

The neutrals react in a different manner, although consistently, with NH_2^+ than with NH_3^+ and still differently than with NH_4^+. It has been previously determined that NH_4^+ reacts by rapid association reactions with molecules of the type in this study [15]. This was briefly examined for each neutral in the present study, and the same association as previously was found to occur for the reaction of NH_4^+ with each neutral. An association reaction of either NH_3^+ or NH_2^+ with CH_3COOH could lead to the formation the amino acid glycine or one of its isomeric forms upon electron-ion recombination. However, association does not occur for either species, but NH_2^+ reacts instead via proton transfer with each neutral and NH_3^+ reacts via H atom abstraction. Proton transfer is quite exothermic for the reactions of NH_2^+ with all three species but is endothermic for the corresponding NH_3^+ reactions having ΔH_r values of 49.2, 11.2, and 12.2

$kJmol^{-1}$ for proton transfer to HCOOH, CH_3COOH, and CH_3OCHO respectively. Thus, the reactions of NH_3^+ and the neutrals cannot proceed via proton transfer and proceed instead by H atom abstraction. This sort of H atom abstraction reaction has been reported to occur at the gas kinetic rate for the reactions of NH_3^+ with several species such as H_2CO and CH_3OH but to be much slower in reaction with H_2 [42]. For species with no H atoms to abstract such as CO_2 and CO, no reaction occurs at all with NH_3^+ ($k \leq 5(-13)\ cm^3s^{-1}$) [42]. The reactions of NH_2^+ with the neutrals via H atom extraction are exothermic, and NH_2^+ is known to undergo this sort of reaction as a minor product channel in reactions with H_2CO and CH_3OH [42], but there is no evidence in the data obtained in this study to indicate that this occurs for the reactions of NH_2^+ with the neutrals in the present study.

The neutral products of the abstraction reaction are worth further consideration because it is possible that they are radicals that have been studied very little. Repeating the experiments with the deuterated species could identify which H atom is abstracted preferentially, but these compounds are available either with high impurity or very high expense; thus the ability to positively identify the reaction mechanism is beyond the scope of the present study. A look at the limited literature may prove insightful, however. Experiments in neutral systems have been performed previously indicating the preferential abstraction of the carboxylic hydrogen in reactions of the OH radical with neutral HCOOH and CH_3COOH at or below 300 K [28,33], but to our knowledge no abstractions have been observed in ion-molecule reactions for these types of neutrals. Also in neutral reactions, the HCOO radical has been reported to decompose into H and CO_2 under single-collision conditions [43], and the CH_3COO radical has been reported to decompose into CH_3 and CO_2 at 200 Torr in N_2 [40]. No information is available, however, concerning the time of survival of this species at lower pressures. Alternatively, the species that result from the abstraction of the formyl or acetyl H, COOH and CH_2COOH, have been reported to persist [40,43] and are more thermodynamically stable than the HCOO and CH_3COO radicals. These more stable radicals have been taken as the neutral products in Table 3.2, but may not be the radical isomers produced. CH_3OCHO reactions with the OH radical have been reported and yield two stable radical products. The two abstraction possibilities in this reaction, CH_2OCHO and CH_3OCO, are reported to persist at higher pressures and may play a role in Earth's atmosphere [45]. At room temperature the CH_3OCO radical predominates as the major product in radical-neutral H abstraction reactions by the ratio of 55:45 over CH_2OCHO[34]; CH_3OCO was listed as the product of the reaction of NH_3^+ with CH_3OCHO. There is no thermodynamic data available for the alternative radical, CH_2OCHO, but the abstraction reaction that forms this radical is likely also exothermic.

5. Conclusions

This study has shown the reaction tendencies of a class of reactions involving positively charged ions, including ionized amine fragments, and neutral carboxylic acids and esters. This study and previous literature indicate that the fragment ions of amines and NH_n^+ type ions do not react with either class of neutrals to form C-N bonds. Ions of high recombination energy and no H atoms such as Ar^+ and N_2^+ fragment the neutrals based on the position of the attack. The carboxylic acids, RCOOH, fragment cleaving the R-COOH bond or the RCO-OH bond. Methyl formate indicates the fragmentation pattern of formyl esters of the form ROC(O)H, yielding RO^+ as the major product, with a significant contribution from HCO^+, and R^+ as a minor product. The ions of the form CH_nN^+ ($n = 1$-5) will likely proton transfer as will the ion NH_2^+ depending on relative proton affinities. NH_3^+ reacts with many species including the species in this experiment via H atom abstraction forming NH_4^+. It is obvious that the types of gas phase ion-molecule reactions described in this study do not produce interstellar amino acids, but it is possible that the radicals generated by the NH_3^+ atom abstraction reactions could play a role in forming these species.

6. Acknowledgements

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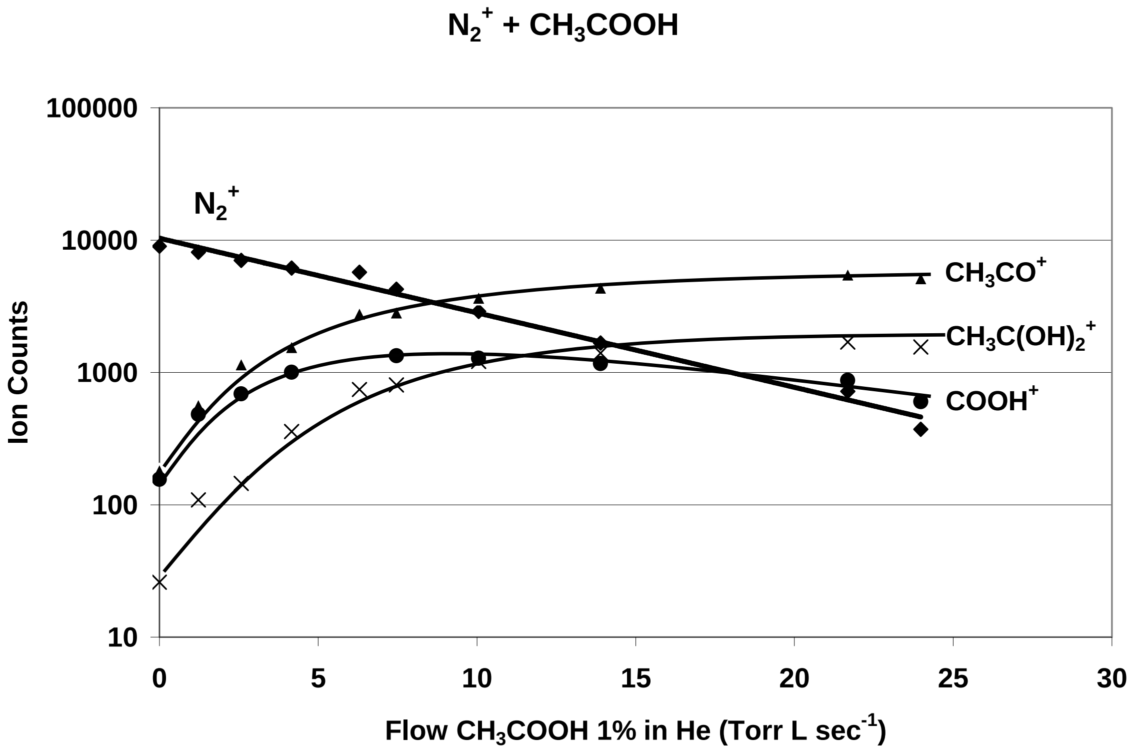

Figure 3.1 Decay of N_2^+ in a typical charge transfer reaction with CH_3COOH is shown above. Note the linear decay of the reactant ion over approximately 1.5 orders of magnitude and that the secondary reaction of $COOH^+$ with the neutral produces protonated CH_3COOH.

Table 3.1 Experimental rate coefficients, k_{exp}, for the gas phase reactions of a series of ions (indicated) with HCOOH, CH_3COOH, and CH_3OCHO are listed followed by theoretical collisional rate coefficients, k_{theor}, determined using Variational Transition State Theory [27] with polarizabilities and dipole moments from literature [28] and literature rate coefficients, $k_{lit,}$ are given where available [16,38,39]. The reaction efficiency, k_{exp} / k_{theor}, is also included. All rate coefficients are expressed in units of 10^{-9} cm^3s^{-1}.

a Used as a standard reaction for comparison with literature to confirm the performance of the University of Georgia SIFT apparatus.

b An average of 5 SIFT literature values[16].

c Previous data obtained using a FA [38,39].

	Primary ion	k_{exp} (10^{-9} cm^3sec^{-1})	k_{theor} (10^{-9} cm^3sec^{-1})	k_{lit} (10^{-9} cm^3sec^{-1})	**Efficiency**
O_2[a]	N^+	0.553	0.937	0.581[b]	0.59
HCOOH	Ar^+	1.9	1.68	-	1.13
	N_2^+	2.05	1.87	4.6[c]	1.1
	NH_2^+	2.53	2.26	2.7[c]	1.12
	NH_3^+	1.06	2.21	0.9[c]	0.48
	$HCNH^+$	1.05	1.87	1.4[c]	0.56
CH_3COOH	Ar^+	1.76	1.98	-	0.89
	N_2^+	2.86	2.22	-	1.29
	NH_2^+	2.41	2.73	-	0.88
	NH_3^+	1.98	2.67	-	0.74
	$HCNH^+$	2.56	2.19	-	1.17
CH_3OCHO	Ar^+	2.52	2.09	-	1.21
	N_2^+	3.12	2.35	-	1.33
	NH_2^+	3.76	2.89	-	1.3
	NH_3^+	2.96	2.82	-	1.05
	$HCNH^+$	2.11	2.29	-	0.92

Table 3.2 Product distributions (%) for the reactions of HCOOH, CH_3COOH, and CH_3OCHO with the ions indicated are listed along with literature product ion percentages where available [38,39]. Reaction enthalpies, ΔH_r, in kJmol^{-1} are also listed showing each proposed product channel is exothermic. Thermochemical data were obtained from the literature [28,31,35,40,41].

a Reaction may also form radical via extraction of the carboxylic H although these are reported to be less thermodynamically and structurally stable [40,43].

b It is also energetically possible to proton transfer from the C forming HNC.

c The less stable radical must be formed in this reaction although this radical has been reported to break up under single collision conditions [43].

d Abstraction may likely also occur from H-CH_2OCHO. However, no thermodynamic data is available for this species.

	Primary Ion	Ion Product	Neutral Products	%	Literature	ΔH_r
HCOOH	Ar^+	HCO^+	$OH + Ar$	70	-	-275.4
		$COOH^+$	$H + Ar$	30	-	-326.9
	N_2^+	HCO^+	$OH + N_2$	85	100	-258.3
		$COOH^+$	$H + N_2$	15	0	-309.7
	NH_2^+	$HCO(OH)_2^+$	NH	100	-	-102.8
	NH_3^+	NH_4^+	$COOH^a$	100	-	-109.4
	$HCNH^+$	$HCO(OH)_2^+$	HCN	100	100	-136
CH_3COOH	Ar^+	CH_3CO^+	$OH + Ar$	55	-	-385.2
		$COOH^+$	$CH_3 + Ar$	45	-	-344.9
	N_2^+	CH_3CO^+	$OH + N_2$	57	-	-368
		$COOH^+$	$CH_3 + N_2$	43	-	-327.7
	NH_2^+	$CH_3CO(OH)_2^+$	NH	100	-	-141.1
	NH_3^+	NH_4^+	CH_2COOH^a	100	-	-103.6
	$HCNH^+$	$CH_3CO(OH)_2^+$	HCN^b	100	-	-174.2
CH_3OCHO	Ar^+	CH_3^+	$HCOO^c + Ar$	17	-	-228.5
		HCO^+	$H_3CO + Ar$	26	-	-262.7
		H_3CO^+	$HCO + Ar$	57	-	-71.9
	N_2^+	CH_3^+	$HCOO^c + N_2$	15	-	-211.3
		HCO^+	$H_3CO + N_2$	25	-	-245.5
		H_3CO^+	$HCO + N_2$	60	-	-54.73
	NH_2^+	$HC(OH)OCH_3^+$	NH	100	-	-139.9
	NH_3^+	NH_4^+	CH_3OCO^d	100	-	-125.3
	$HCNH^+$	$HC(OH)OCH_3^+$	HCN^b	100	-	-173

CHAPTER 4

ION-MOLECULE REACTIONS OF SEVERAL IONS WITH ETHYLENE OXIDE AND PROPENAL IN A SELECTED ION FLOW TUBE

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[3] Jackson, D. M., Adams, N. G., Babcock, L. M. 2006. *Journal of the American Society for Mass Spectrometry*. Available online.
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ABSTRACT

The Selected Ion Flow Tube (SIFT) technique has been used to investigate the ion-molecule reactions of several ions with the neutral molecules ethylene oxide, CH_2OCH_2-c, and propenal, CH_2CHCHO. Both molecules have been identified in hot-core star forming regions and have significance to astrochemical models of the interstellar (ISM) and circumstellar medium (CSM). Moreover, the molecules contain functional groups such as the epoxide group (ethylene oxide) and an aldehyde group which is part of a conjugated π-electron system (propenal) whose reactivities have not been studied in detail in gas phase ion-molecule reactions. The larger recombination energy ions, Ar^+ and N_2^+, were reacted with the neutrals to give insight into general fragmentation tendencies. These reactions proceeded via dissociative charge transfer yielding major fragmentation products of CH_3^+ and HCO^+ for ethylene oxide and CH_2CH^+ and HCO^+ for propenal. The amino acids glycine and alanine are of particular interest to astrobiology especially if they can be synthesized in the gas phase. In an attempt to synthesize amino acid precursors, ethylene oxide and propenal were reacted with NH_n^+ (n=1-4) and $HCNH^+$. As might be expected from the proton detachment energies, NH^+, NH_2^+, and $HCNH^+$ reacted via proton transfer. NH_3^+ reacted with each molecule via H-atom abstraction to produce NH_4^+, and NH_4^+ reacted via a ternary association. All binary reactions proceeded near the gas kinetic rate. Several associated-molecule switching reactions were performed and implications of these reactions to the structures of the association products are discussed.

1. Introduction

The use of various telescopes for analytical spectroscopy of stellar and interstellar regions has greatly aided the field of laboratory astrophysics with the identification of molecules present in the ISM and CSM. To date over 140 interstellar and circumstellar molecules have been identified [1] and the list of molecules will undoubtedly continue to grow as more powerful telescopes and interferometer arrays are built and utilized. In recent years, spectroscopic studies of hot-core star forming regions such as Sagittarius B2 have led to the discovery of many organic compounds including methylamine [2], acetic acid [3], methyl formate [4], formic acid [5], ethylene oxide [6], and propenal [7]. One study even proposed the detection of the spectral fingerprint of glycine [8], the simplest amino acid, in these hot-core regions, but this claim was later disputed [9]. Regardless of the authenticity of the glycine detection, it may be possible to synthesize glycine or other amino acids via ion-molecule reactions from various ions and neutrals found in these or other regions of space. If synthesized, these amino acids or amino acid precursors could be collected and deposited onto planets by meteorites or comets as the star systems further develop, thus planting the seeds of life [10-13].

Studies of ion-molecule reactions can provide a good understanding of the chemistry of these regions and yield data that can greatly assist in developing astrochemical models. In the evolution of large interstellar dust clouds to hot core regions, the temperature of the systems increase from about 10 K to ~100-200 K [14]. Room temperature measurements (295 K) give reliable ion product distribution estimates, and temperature adjustment of rate coefficients is not required as long as the reactions proceed near the gas kinetic rate. The total number densities in the hot core regions are of ~10^6-10^7 cm^{-3} [14], which are ~3-4 orders of magnitude less than the reactant neutral number density of the SIFT measurements. However, reactions studied in the SIFT are still relevant to these regions given the considerably longer cloud lifetimes and times for reaction in developing planetary systems. The SIFT experiments also have a He carrier gas pressure of ~0.5 Torr (1.6×10^{16} cm^{-3}), but this does not influence binary collisional reactions since these reactions occur before the reacting species can interact with He. Variation of carrier gas pressure will, however, affect pressure dependent ternary association reactions [15]. Such collisionally stabilized reactions cannot occur in the cloud environments, but their radiatively stabilized analogues can, and the ternary reactions provide data to estimate such binary rate coefficients [15].

The ion-molecule reactions of the neutral molecules ethylene oxide and propenal, which contain unique functional groups, have not been studied previously [16] and could lead to the formation of amino acids. Ion-molecule reactions of the ISM and CSM molecules, acetic acid, formic acid, methyl formate, and methylamine with several ions of appropriate structure for the formation of amino acids have been studied previously [32,46], and it was determined that many plausible gas phase reactions do not form amino acids. Ethylene oxide is the simplest member of a class of molecules known as epoxides, a compound having a COC ring structure. Epoxides in wet chemistry are susceptible to ring opening reactions due to the ring strain incurred by the three membered ring [47]. Propenal (CH_2CHCHO) on the other hand is an aldehyde whose -CH=O group is part of a conjugated π-electron system. The conjugated system alters the electron density normally found in the aldehyde functional group (ion-molecule reactions involving aldehydes have been studied in detail [16]) and the shape of the molecule. In an attempt to synthesize amino acids, these neutrals were reacted with the ions NH_n^+ (n=1-4) and $HCNH^+$. The ions Ar^+ and N_2^+ are high recombination energy ions and were reacted with the neutrals first to determine general fragmentation tendencies. Some previous success in synthesizing glycine in the gas phase was reported by Blagojevic et al. involving reactions of the ions $NH_{2,3}OH^+$ with acetic acid [20]; however, the interstellar importance of $NH_{2,3}OH^+$ is not known since it has not been observed directly nor has its reactivity with molecular hydrogen been investigated to our knowledge. The ions $NH_{3,4}^+$ have interstellar significance, however, since NH_3^+ reacts slowly with molecular hydrogen in forming NH_4^+, and this is a terminal ion in the presence of molecular hydrogen as is $HCNH^+$ [48]. NH_4^+ is known to associate with various neutrals via a ternary reaction in one of several possible mechanisms [15]. The further reactivities of the associated products observed in this study may shed additional light on the mechanism of these associations and on their prospects for synthesizing amino acids by subsequent reactions.

2. Experimental

The SIFT technique has been described in detail elsewhere [23,24] and will not be reviewed in entirety here; however, several relevant descriptions of, and modifications to, the experimental procedure will be mentioned. A detailed figure of the University of Georgia SIFT apparatus is included in an earlier paper [32]. The SIFT technique uses a quadrupole mass filter to select a single primary reactant ion from an ionization source. Several ionization sources were used to produce the primary ions in this study including a microwave cavity discharge (MC), a low pressure electron impact ionization source (LPIS), and a high pressure electron impact ionization source (HPIS). The MC was used to produce the simple ions, Ar^+ and N_2^+, from their respective gases Ar (Argon, Matheson pre-purified) and N_2 (Nitrogen, BOC grade 5.0). Each of the two electron impact sources was equipped with 0.005 inch diameter tungsten wire filaments. The LPIS was used to produce the ions NH^+, NH_2^+, and NH_3^+ from NH_3 (Ammonia, Matheson anhydrous) and $HCNH^+$ from CH_3NH_2 (Methylamine, Aldrich anhydrous). The HPIS was used to produce NH_4^+ from NH_3. After production and mass selection, the ions were then focused by a series of lens elements through a 1mm orifice and into the flow tube. The ions were drawn from the low pressure mass selection region into the flow tube by a flow of high purity He (National Welders pre-purified) through a Venturi inlet. The He carrier gas was further purified by passage through liquid-nitrogen cooled molecular sieve. Reactant gas was added to the flow in accurately known amounts at one of several known reaction distances. The reactant gas ethylene oxide (Messer 99%) is susceptible to polymerization and must be kept at room temperature or slightly lower temperature environments and has a limited life ~1 year. It may be noted that liquid propenal (Acrolien, Aldrich 97.8%) also polymerizes upon prolonged exposure to light and/or room temperature and was stored in an opaque container under refrigeration. No effects due to polymerization were detected in the reaction data. Propenal and acetic acid (Aldrich 99.99 %), which was used solely in the switching reactions, are viscous liquids with appreciable vapor pressures. To ensure a uniform flow into the flow tube, the vapors of these liquids were diluted in an isolated vessel to a 1% mix in He. Note that the dimerization of acetic acid was accounted for [46] in reporting rate coefficients for the switching reactions. The ternary reactions with NH_4^+ proceeded by successively associating one then two neutrals, X,

$$NH_4^+ + X + He \rightarrow NH_4^+X + He \qquad (1)$$

$NH_4^+X + X + He \rightarrow NH_4^+X_2 + He$ (2)

For the switching reactions it was necessary to use the ion products of (1) and (2) as the primary reactant ions.

$NH_4^+X + Y \rightarrow NH_4^+Y + X$ (3)

$NH_4^+X_2 + Y \rightarrow NH_4^+XY + X$ (4)

Ions of the type $NH_4^+X_{1,2}$ where X is a neutral molecule were produced by addition of a reactant gas (X), ethylene oxide, propenal, or acetic acid, to the flow optimizing the flow of initial reactant gas so that the desired ionic products of (1) and (2) were available in greatest abundance as primary reactant ions in (3) and (4). Additionally, efforts were made to minimize the presence of NH_4^+ before proceeding with the switching reactions. The second gas (Y) was added to the flow sufficiently downstream from the addition of X so that the optimum levels of (1) or (2) were maintained and (3) or (4) could then be studied. Product ions were detected and counted by a quadrupole mass filter detection system equipped with an electron multiplier and a gated photon counter. Ion product distributions are accurate to ±5 in the percentage. Reaction rate coefficients were calculated in the usual way from the exponential decay of the primary ion [23,24,26] and are accurate to ±30% for these sticky vapors.

3. Results

Figure 4.1 displays the data obtained in a typical reaction depicting the exponential decay of a primary ion, the rise of a primary product ion, its decay, and the rise of a secondary product ion.

3.1 Rate Coefficients

The binary rate coefficients, k_b (cm^3s^{-1}), for the reactions of the primary ions, Ar^+, N_2^+, NH_n^+ (n=1-3), and $HCNH^+$, with ethylene oxide and propenal may be viewed in Table 4.1 followed by the theoretical rate coefficients, k_{theor} (cm^3s^{-1}), calculated using Variational Transition State Theory [27]. Molecular dipole moments and polarizabilities were obtained from the literature [28,35]. The reaction efficiency, which is the ratio of k_b to k_{theor}, is also listed. Most of the k_b values are within experimental error (±30%) of the k_{theor} values indicating that the reactions usually proceed at the gas kinetic rate for true binary reactions. The atom abstraction reactions with NH_3^+ occur slightly slower and are known to be slightly less than 100% efficient for various organic molecules [46]. It should be noted that NH_4^+ reacts with the neutrals significantly below the theoretical rate to form single association products and then upon further reactivity double association products as shown in Fig. 4.1. Additionally, the k_b value for these reactions varies as a function of He pressure indicating that ternary reactions, (1) and (2), were occurring. The values of the effective binary rate coefficient at a series of He pressures of the ternary association reactions of NH_4^+ with ethylene oxide and propenal were determined experimentally and three body rate coefficients, $k_3=k_b/[He]$ (cm^6s^{-1}), were calculated yielding values of 2.8(-26) cm^6s^{-1} and 6.2(-27) cm^6s^{-1} for propenal and ethylene oxide respectively where the notation A(B) represents A x 10^B.

3.2 Product Ion Distributions

The ionic product distributions of the reactions of all primary ions with the neutrals are given in Table 4.2 followed by the estimated neutral products and the percentages of the product channels. The enthalpy of reaction, ΔH_r, is given for each reaction channel, and all channels are exothermic. The ΔH_r for the ternary association reactions could not be calculated due to the lack of thermodynamic data on these associations. The ions Ar^+ and N_2^+ react via dissociative charge transfer yielding major fragmentation products of CH_3^+ and HCO^+ for ethylene oxide and CH_2CH^+ and HCO^+ for propenal in similar percentages; possible ambiguities in other fragment products due to mass spectrometric limitations will be discussed. The ions $NH_{1,2}^+$ as well as $HCNH^+$ all reacted via exothermic proton transfer to the neutrals. Since proton transfer tends to occur at the gas kinetic rate when energetically possible [30], no further discussion is necessary of these reactions. For NH_3^+, however, proton transfer is endothermic, and the ion instead reacts with each neutral via H-atom abstraction to form NH_4^+. This is a common mechanism for NH_3^+ reactions with H containing molecules. Switching reactions, (3) and (4), of the type discussed previously [15] were performed by reacting the neutral gas, acetic acid, with the association products of reactions (1) and (2) to investigate mechanisms and structures. Table 4.3 shows the reaction rate coefficients of the switching reactions in all combinations performed. Note some reactions were not performed since they were either mass spectrometrically limited or were not relevant to the goal of the study. Some additional data are included in Table 4.3 from a previous study [15] concerning NH_4^+ association reactions to aid comparison.

4. Discussion

4.1 Products and Product Structures

Two major ionic products appear in Table 4.2 for each of the dissociative charge transfer reactions in relatively high product percentages. These ionic products are HCO^+ and CH_3^+ for the dissociation of ethylene oxide and HCO^+ and CH_2CH^+ for the dissociation of propenal. In the case of ethylene oxide, this indicates that a ring-opening reaction occurs. The likely mechanism involves the breaking of one of the two C-O bonds upon the departure of an electron from this bond. The resulting ion after ring-opening is linear, $[CH_2\text{-}CH_2\text{-}O]^+$, where the positive charge can lie on either end of the molecule but not the central C atom. The appearance of the product CH_3^+ can be explained by considering the case that the charge of the resulting molecule resides on the terminal C atom. One of this atom's bonding orbitals is empty apparently encouraging the migration of an H atom from the central C atom to the terminal C atom while simultaneously weakening the C-C bond enough to break. The observed ionic product CH_3^+ along with neutral HCO is then formed via an intermediate. In the case that the charge of $[CH_2\text{-}CH_2\text{-}O]^+$ resides on the O atom, a radical would then lie on the terminal C atom. If in this case an H atom migration could occur through a similar intermediate, then the observed ionic product HCO^+ would be formed along with neutral CH_3 instead. It might be expected for this mechanism that the two major product channels would occur equally since the pathway of the mechanism is dependent on the chance of charge residing upon one atom rather than the other, and in fact the two product channel percentages are identical within error. It is also possible that charge transfer between a $[CH_3\text{---}CHO]^+$ intermediate after H atom migration might also result in nearly identical product percentages regardless of the atom upon which the positive charge resides. In the dissociation reactions of propenal where the molecule is not symmetric, the two major products occur in different proportions with HCO^+ being the lesser product which is reasonable since the double bond is less likely to be positively charged. This trend of aldehydes (R-CHO) to form HCO^+ in a lesser proportion to R^+ in dissociative charge transfer reactions has been seen in other molecules as well such as methyl formate, CH_3OCHO [46].

The observed ionic products and neutral products listed in Table 4.2 for the dissociative charge transfer reactions can in some cases be ambiguous. We indeed note that for these reactions, ethylene oxide reactions in particular, other plausible isomers or fragments identical in the mass spectrum may be possible. In a simple case, the reaction of Ar^+ with ethylene oxide, the 4 % product $CH_2CH_2^+$ could be mistaken for CO^+ in the mass spectrum. Fortunately, product channels involving CO^+ are sufficiently endothermic to rule out a contribution from this ion. For the product ions in which all three heavy atoms remain of the ethylene oxide ring, the determination between the linear or cyclic isomer was made analytically. This determination may only be made empirically by an extended study of isomeric reactivity. In choosing these isomers the mechanism of fragmentation was envisioned to center on a single C atom. If this is the case, then in the $C_2OH_3^+$ 3% product channel ethylene oxide loses an electron and an H atom from either C atom leaving a C atom with one empty bonding orbital. It is conceivable that the O donates a pair of electrons to form a C=O bond and in doing so breaks the epoxide ring creating a radical-ion at the O atom terminus and leaving an unpaired electron on the C atom terminus. Insufficient thermodynamic data was available to determine the ΔH_r of the reactions producing this ion, $CH_2\text{-}CH{=}O^+$ (note that the molecule has other resonance structures), but this channel is likely endothermic. In the $C_2OH_2^+$ 3 to 4% product channel, consider the point at which the H atom begins to leave as it does in the previous channel. If the leaving H atom bonds with the other H atom of the same C atom, then H_2 is ejected leaving a C atom with both an empty bonding orbital and an unpaired electron. The ring could sensibly open by accepting a pair of electrons from the O atom which would cause the other C-O bond to break leaving adjacent unpaired electrons on the adjacent C atoms. These unpaired electrons would then pair to form linear charged ketene, $CH_2=C=O^+$. Other isomers are possible for each reaction with channels likely to be exothermic; therefore, due to mass spectrometric limitations the product structures suggested here however likely were not implied in Table 4.2.

The neutral products of certain reactions warrant brief discussion of their astrochemical implications. The reactions of NH_3^+ with various saturated compounds such as CH_4 and CH_3OH and unsaturated species such as CH_2CH_2 and CH_3COOH [16,46] have been shown to proceed via H-atom abstraction. This ion's reaction with ethylene oxide and propenal has shown the same trend demonstrating an even wider range of molecules for which this process occurs. H-atom abstraction reactions have possible interstellar implications in that each reaction forms a radical neutral species that may be available for further neutral reactivity providing they retain their characteristic chemical forms after reaction, for example the epoxide ring of the CH_2OCH oxirene radical. The radicals formed may react further with other species whether via ion-molecule reactions, radical-radical reactions, etc. to form species of interest such as amino acids or sugars. Reactions involving radical neutrals have not been studied in great detail especially reactions of interest to astrochemistry due to the difficulty of the experiments. Much more work is needed to investigate the chemical possibilities.

4.2 NH_4^+ Association

The k_b values at a series of He pressures of the association reactions of NH_4^+ with ethylene oxide and propenal plotted in Fig. 4.2 are significantly lower than the k_{theor} values for the corresponding binary reactions. Note the linearity of the plot as the k_b values grow larger at higher pressure. The k_3 values of 2.8(-26) cm^6s^{-1} and 6.2(-27) cm^6s^{-1} for propenal and ethylene oxide respectively were determined from the slopes of the regression lines seen in Fig. 4.2. The approach toward the limiting gas kinetic rate can become relevant at relatively high pressures causing the measured k_b values to level off giving a less accurate k_3 value [49], however, little indication of this effect over the range of pressures studied is seen in Fig. 4.2. The line fitted through the data points in Fig. 4.2 illustrates the linear portion which extrapolates near $k_b = 0$ within experimental error (±30%) at 0 Torr. A wider pressure range was not studied due to experimental limitations. At lower pressures the ion count rate becomes too low for a statistically accurate counting. To obtain higher pressures either the carrier gas flow rate must be increased or the valve leading to the Roots pumping system must be increasingly closed. Higher flow rates could not be obtained due to the flow limit of our carrier gas flow meter. While higher flow rates increase signal by decreasing the ion residence time in the flow and thus decreasing the diffusive loss, closing the valve to the pumping system reduces the flow velocity and rapidly reduces signal due to diffusive loss in spite of the reduction in diffusion which occurs at higher pressures. Though it was not possible to investigate a wider pressure range, this does not adversely affect the data since in fact only the linear portion of the plot is useful in obtaining k_3 values.

4.3 Association Reaction Mechanism

Previously a mechanism, M_1, was proposed for the association reactions (1) by analyzing the results of the switching reactions. It was suggested that a mechanism involving an intermediate complex occurs in which the NH_4^+ ion donates an H atom to the C atom of each organic molecule that is doubly bonded to an O atom thus breaking the π-bond while forming an N-O bond. In the case of propenal the structure would be $CH_2=CHCH_2\text{-}O\text{-}NH_3^+$. The ion formed is likely analogous in reactivity to the NH_3OH^+ ion in the Blagojevich mechanism. A second mechanism, M_2, was reported by Blagojevic et al., involving the ion-molecule reactions of $NH_{2,3}OH^+$ with acetic acid to form charged glycine and protonated glycine respectively. M_2 proceeds by the $NH_{2,3}OH^+$ ion reacting with acetic acid to attach $NH_{2,3}$ group to the acid apparently at the $-CH_3$ end and eject H_2O. Considering the NH_3OH^+ pathway with M_2, it is likely that this reaction proceeds by forming an intermediate in which the -OH group of the ion forms an intermittent bond with an H-atom of acetic acid. The N atom of the ion simultaneously bonds to the C atom allowing the H_2O molecule to detach from both the C and N atoms. Since Blagojevic et al. did not report the flow of acetic acid used in their experiments due to the corrosion of their flow meters by acetic acid, we can not be sure of the rate of reaction; however, if the reaction tendencies of NH_3OH^+ and $CH_2=CHCH_2\text{-}O\text{-}NH_3^+$ are in fact analogous, then the switching reaction of the association product of propenal and NH_4^+ in the present study with CH_3COOH should not switch but rather attach an NH_3 group to CH_3COOH and eject a neutral alcohol, $CH_2=CHCH_2OH$. Providing glycine (or even an isomer) was indeed formed by M_2 in the manner reported by Blagojevic et al, this process should occur for an association product of the type predicted by M_1. It was empirically observed that the reaction between $NH_4^+CH_2$=CHCHO and acetic acid resulted in switching of the neutrals and not the formation of glycine as would be predicted by the previous reasoning. The formation of glycine also did not apparently occur previously [15] for any of the reactions listed. Assuming that M_2 is correct, this would indicate that the covalent nature of the association products suggested by M_1 is not present but rather an electrostatic interaction. The earlier paper acknowledges that for molecules such as CH_3OH which are already saturated this mechanism would likely not apply indicating that the interaction is purely electrostatic or perhaps a proton-bound dimer, CH_2=CHCH=O---H^+---NH_3.

Ethylene oxide, though fully saturated, possesses bonding such that breaking either of the symmetric C-O bonds and attaching an H from NH_4^+ would allow the mechanism to proceed via a ring-opening reaction to form CH_3CH_2-O-NH_3^+. Temporarily assuming that the mechanism proceeds as such according to M_1 for both unsaturated carbonyl containing species as well as epoxides, applying the mechanism to acetaldehyde, CH_3CHO, the association product would be CH_3CH_2-O-NH_3^+ which is identical to that of the proposed association product of the isomeric ethylene oxide. If M_1 does proceed for both of these molecules, then the switching reactions of these two ions should proceed at identical rates. As shown in Table 4.3 the k_b value for (3) between the association product of NH_4^+ with ethylene oxide and acetic acid, 2.2(-10) cm^3s^{-1}, is significantly different than the k_b value for (3) with the association product of NH_4^+ with acetaldehyde and acetic acid, 1.0(-9) cm^3s^{-1}, indicating that the ring of ethylene oxide does not open. This casts doubt on the covalency of a bond of the molecule to the N atom of the ion.

4.4 Trends in the Switching Reactions

It is difficult to determine trends in k_3 values of the association reactions since there appears to be little relation between these values and the theoretical rates, which take into account the neutral dipole moment and neutral polarizability, or the proton affinities which has been shown to affect the relative electrostatic bond strengths of the association products [15]. The trend described previously was that the relative bond strength increases with increasing proton affinity; however, it was reasonably observed that steric effects of the neutrals could cause one to overestimate the bond strength using proton affinity as the lone indicator due to the ease with which a proton can circumvent steric hindrances relative to NH_4^+. The bonds strengths then can truly be said to depend on a sort of "NH_4^+ affinity" which is a combination of effects due to sterics and proton affinity. The relative bond strengths of these association products affect the efficiency of the switching reactions; thus the rate coefficients should also vary in the same way based on the NH_4^+ affinity. In Table 4.3 the switching neutrals (Y) have been listed in order of increasing proton affinity to demonstrate the general trend present without considering sterics: in general rate coefficients increase from top to bottom and decrease from left to right. Additional data from a previous study was also included to aid comparison.

It was presumed in the earlier study that the primary reason the reactions of the ether, $(CH_3)_2O$, did not fit well with the trend in proton affinity, reacting slower than expected in all cases, was due to this molecule's considerable steric inhibition about the O atom. It was also postulated that the lack of a double bond in the molecule may have contributed as well, preventing the covalent bond formed according to M_1 in saturated species. The reactivity of ethylene oxide is of particular relevance to this problem since the steric hindrance present in $(CH_3)_2O$ is eliminated by the 3 member ring which effectively bares the O atom. Note that $NH_4^+CH_3COOH$ switches with ethylene oxide at a rate of 1.3(-10) cm^3s^{-1}, and the same ion switches with $(CH_3)_2O$ at a rate of 3.5(-11) cm^3s^{-1} which is indeed significantly lower even though the proton affinity of $(CH_3)_2O$ is greater than ethylene oxide. Since the data also indicate that the ring of ethylene oxide does not open, the increased rate of switching in the ethylene oxide reaction is likely due to the decreased steric hindrance not the lack of double bond as postulated before.

The k_b values of the switching reactions given in Table 4.3 are listed such that comparison can be made between the rates of switching of the single associations and the double associations of the same neutral. The four k_b values for the reactions of singly and doubly associated ethylene oxide with acetic acid and for singly and doubly associated acetic acid with ethylene oxide are very similar (low 10^{-10} cm^3s^{-1}). On the other hand the k_b value for the reaction of singly associated propenal with acetic acid is 3.9(-10) cm^3s^{-1} and is 1.70(-11) cm^3s^{-1} for doubly associated propenal. The reactions of the singly and doubly associated acetic acid ions with propenal yielded k_b values of 7.2(-10) cm^3s^{-1} and 9.0(-10) cm^3s^{-1} respectively. The data seem to indicate that for neutrals with similar NH_4^+ affinities, apparently such as acetic acid and ethylene oxide, the k_b values will be similar for all combinations of reaction of association and neutral, and for neutrals with very different NH_4^+ affinity the reactions will have markedly different k_b values that will tend to be low when trying to switch out a reactant with a relatively high NH_4^+ affinity and relatively high when trying to switch out neutral with a relatively low NH_4^+ affinity. Also, the ion itself can apparently contribute to sterics in some cases as shown by the considerable decrease in k value between singly and doubly associated propenal reaction with acetic acid.

5. Conclusions

The present study reveals that current efforts to synthesize amino acids in the gas phase using conventional molecules have limited success. Many pathways that seem plausible result in proton transfer or fragmentation stifling a progressive synthesis of more complex organics. Though many plausible gas phase routes to amino acids through ion-molecule reactions have not yielded amino acids, there has been some success, and a great deal of data useful to astrochemical models and mechanistic studies have been collected. The success of Blagojevic et al. with ion-molecule reactions of $NH_{2,3}OH^+$ type species with certain neutrals to form amino acids indicates one possible mechanism which must be investigated further to determine this pathway's relevance to astrochemistry. Also, as indicated by the reactions of NH_3^+ with various neutrals, abstraction of H produces complex radicals whose reactions have not been investigated to this point, but which may react with other radicals or ions to produce more complex species. Additionally, the electron-ion recombination of species such as acetic acid associated with NH_4^+ may also yield a product of interest if during this process rearrangement can occur. Little is known about the structure and bonding of these associated products beyond what has been investigated here, and further study in both theory and experiment is needed. Few plausible routes to amino acids using gas phase ion-molecule reactions remain using currently available laboratory species, yet methods must be developed which can carefully investigate the remaining options in the realm of radical neutrals, electron-ion recombination, or perhaps even combined gas and surface chemistry to verify the possible existence of glycine and other amino acids in the interstellar and circumstellar regions.

6. Acknowledgements

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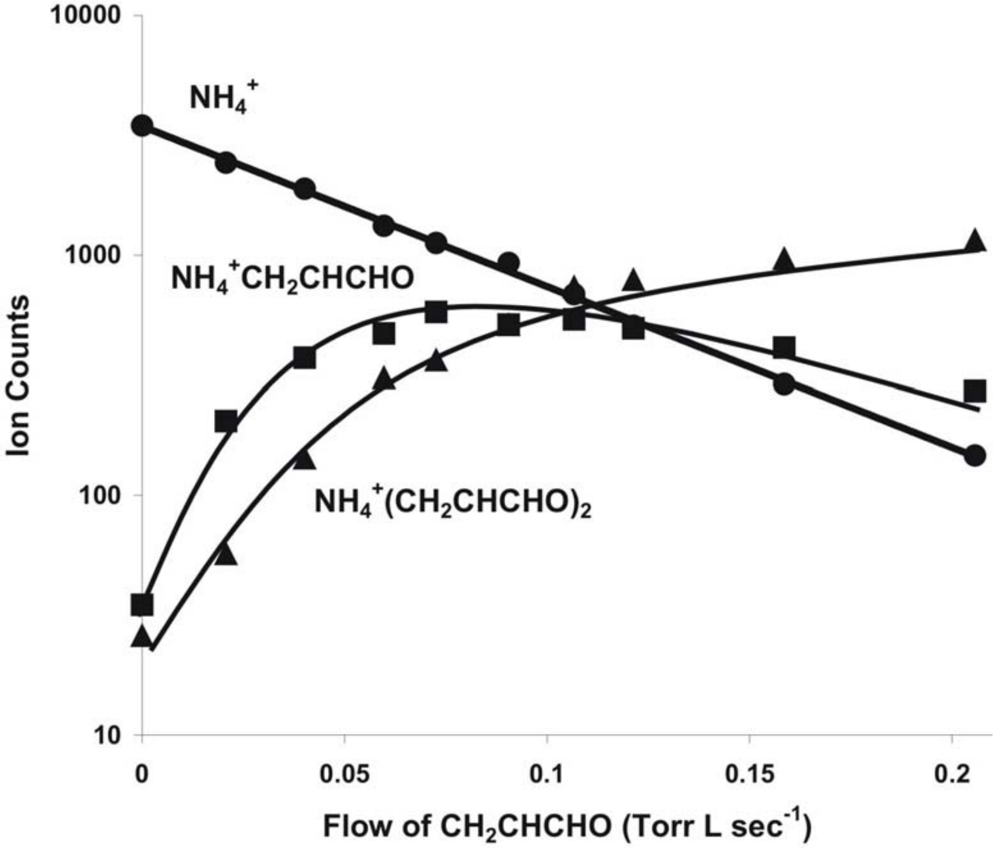

Figure 4.1 NH_4^+ ion counts vs. the flow of reactant gas propenal. Note the linear decay of the primary ion NH_4^+, the rise of the primary association product, $NH_4^+CH_2CHCHO$, and its subsequent reaction with propenal to form the secondary product, $NH_4^+(CH_2CHCHO)_2$.

Table 4.1 The experimental binary reaction rate coefficients, k_b, are listed for each reaction of a primary ion with a given neutral molecule followed by the theoretical reaction rate coefficients, k_{theor}, calculated using Variational Transition State Theory [27] with dipole moments and polarizabilities obtained from the literature [28,35]. The reaction efficiency is given by the ratio k_b/k_{theor}. Note that the k_b values are within experimental error (±30%) of the k_{theor} values indicating that the reactions proceed at or close to the gas kinetic rate for these true binary reactions.

	Primary ion	**k_b** (cm^3sec^{-1})	**k_{theor}** (cm^3sec^{-1})	**Efficiency**
CH_2OCH_2-c	Ar^+	1.8(-9)	2.2(-9)	0.82
	N_2^+	1.8(-9)	2.4(-9)	0.75
	NH^+	3.1(-9)	2.9(-9)	1.07
	NH_2^+	2.6(-9)	2.9(-9)	0.9
	NH_3^+	2.0(-9)	2.8(-9)	0.71
	$HCNH^+$	2.0(-9)	2.4(-9)	0.83
CH_2CHCHO	Ar^+	3.2(-9)	3.3(-9)	0.97
	N_2^+	3.1(-9)	3.7(-9)	0.84
	NH^+	3.9(-9)	4.6(-9)	0.85
	NH_2^+	3.0(-9)	4.5(-9)	0.67
	NH_3^+	2.5(-9)	4.4(-9)	0.57
	$HCNH^+$	2.7(-9)	3.7(-9)	0.73

Table 4.2 The primary reactant ion for each reactant neutral is given followed by ionic products (structures implied) and suggested neutral products. The percentage of each product channel and the ΔH_r (kJmol^{-1}) are also given as calculated with data from the literature [28,35]. Note all channels proposed are exothermic.

a The linear isomer, CH_2-C=O$^+$ (ketene), was chosen as the likely structure.

b The linear isomer, CH_2-CH=O$^+$, was chosen as the likely structure.

c It was not possible to give the ΔH_r for these reactions due to the lack of thermodynamic data.

d HNC is also thermodynamically possible for reactions with both propenal/ethylene oxide with ΔH_r = -25/-2.2 kJmol^{-1} respectively.

e The structures CH=CH-CH=O or CH_2=C-CH=O are also energetically possible.

CH_2OCH_2

Primary ion	Ion Product	Neutral Products	%	ΔH_r ($kJmol^{-1}$)
Ar^+	CH_2^+	$CH_2O + Ar$	3	-194.3
	CH_3^+	$HCO + Ar$	43	-329.3
	$CH_2CH_2^+$	$O + Ar$	4	-151.8
	HCO^+	$CH_3 + Ar$	38	-494.7
	H_2CO^+	$CH_2 + Ar$	5	-149.4
	$C_2OH_2^{+\,a}$	$H_2 + Ar$	4	-627.2
	$C_2OH_3^{+\,b}$	$H + Ar$	3	?[c]
N_2^+	CH_3^+	$HCO + N_2$	45	-312.1
	HCO^+	$CH_3 + N_2$	45	-477.5
	H_2CO^+	$CH_2 + N_2$	4	-132.2
	$C_2OH_2^{+\,a}$	$H_2 + N_2$	3	-610
	$C_2OH_3^{+\,b}$	$H + N_2$	3	?[c]
NH^+	$CH_2(OH)CH_2^+$-c	N	100	-425.5
NH_2^+	$CH_2(OH)CH_2^+$-c	NH	100	-131.6
NH_3^+	NH_4^+	H_2COCH	100	-89.5
NH_4^+	H_2COCH_2-c*NH_4^+	-	100	?[c]
$HCNH^+$	$CH_2(OH)CH_2^+$-c	HCN^{α}	100	-164.7

CH_2CHCHO

Primary ion	Ion Product	Neutral Products	%	ΔH_r ($kJmol^{-1}$)
Ar^+	CH_2C^+	$CH_2O + Ar$	11	-237.7
	CH_2CH^+	$HCO + Ar$	50	-305
	HCO^+	$CH_2CH + Ar$	30	-322
	CH_2CHCO^+	$H + Ar$	6	-336.7
	CH_2CHCHO^+	Ar	3	-545
N_2^+	CH_2CH^+	$HCO + N_2$	70	-287.8
	HCO^+	$CH_2CH + N_2$	20	-304.8
	CH_2CHCO^+	$H + N_2$	5	-319.5
	CH_2CHCHO^+	N_2	5	-527.9
NH^+	$CH_2CHCH(OH)^+$	N	100	-448.3
NH_2^+	$CH_2CHCH(OH)^+$	NH	100	-154.4
NH_3^+	NH_4^+	CH_2CHCO^{e}	100	-170.1
NH_4^+	CH_2CHCHO*NH_4^+	-	100	?[c]
$HCNH^+$	$CH_2CHCH(OH)^+$	HCN^{α}	100	-187.51

Table 4.3 Shown are the k_b values (cm^3s^{-1}) for the binary switching reactions, (3) and (4), of the horizontally listed $NH_4^+X_{1,2}$ associations with the vertically listed neutrals (Y) whose proton affinities (PA) are also listed. Several reactions were omitted either because they were not possible via quadrupole mass spectrometry (exchanges of X with X) or were not necessary to complete the desired analysis. Values presently determined in the present study are in bold. Other k_b values were taken from a previous paper [15] to aid comparison.

a The rate coefficients for the double associations are for a single X exchange (4).

b The dimerization of CH_3COOH was accounted for in determining the k values.

		Reactant Ions, $NH_4^+X_{1,2}$								
		CH_3CHO	CH_2OCH_2-c	$(CH_2OCH_2\text{-c})_2$[a]	CH_3COOH	$(CH_3COOH)_2$[a]	$(CH_3)_2O$	CH_2CHCHO	$(CH_2CHCHO)_2$	$(CH_3)_2CO$
Reactant Neutrals (Y)	**PA ($kJmol^{-1}$)**	769	774	774	783	783	792	797	797	811
CH_3CHO	769	-	-	-	4.0(-10)	-	-	-	-	-
CH_2OCH_2-c	774	-	-	-	**1.3(-10)**	**1.0(-10)**	-	-	-	-
CH_3COOH[b]	783	**1.0(-9)**	**2.2(-10)**	**1.7(-10)**	-	-	7.5(-10)	**3.9(-10)**	**1.7(-11)**	< 1.0(-13)
$(CH_3)_2O$	792	-	-	-	3.5(-11)	-	-	-	-	-
CH_2CHCHO	797	-	-	-	**7.2(-10)**	**9.0(-10)**	-	-	-	-
$(CH_3)_2CO$	811	-	-	-	2.6(-10)	-	-	-	-	-

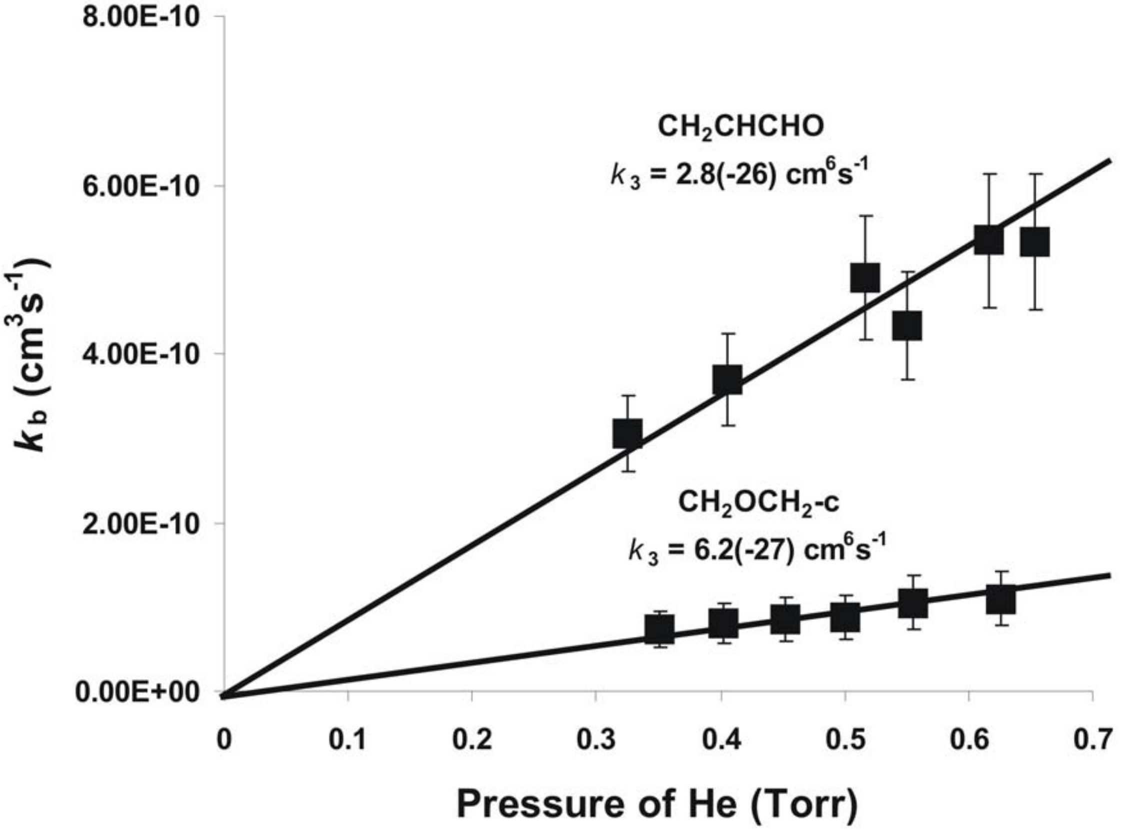

Figure 4.2 The k_b values of the association reaction (1) of NH_4^+ with propenal and ethylene oxide at a series of pressures of He are plotted for comparison. Note the regression lines used to determine the k_3 values extrapolate well to (0,0) within experimental error.

CHAPTER 5

CONCLUSIONS

The current efforts to synthesize amino acids in the gas phase using conventional molecules have had limited success. Many pathways that seem plausible result in proton transfer or fragmentation stifling a progressive synthesis of more complex organics. Using amines as neutral reactant gases will not effectively synthesize larger organic molecules; the amines prefer to fragment into the major product $H_2CNH_2^+$ or proton transfer when energetically possible. Also, the fragment ions of amines and $NH_{1,2}^+$ ions do not react with carboxylic acids or similar neutrals to form C-N bonds but rather via proton transfer. Ions of high recombination energy, such as Ar^+ and N_2^+, fragment carboxylic acids, RCOOH, cleaving the R-COOH bond or the RCO-OH bond, and fragment methyl formate yielding CH_3O^+ as the major product with significant contributions from HCO^+ and CH_3^+ as minor products. The unique neutrals, ethylene oxide and propenal, which contain a 3-member ring or electron conjugation, react similarly via fragmentation to yield CH_3^+ and HCO^+ for ethylene oxide and CH_2CH^+ and HCO^+ for propenal.

Though many plausible gas phase routes to amino acids through ion-molecule reactions have not yielded amino acids, there has been some success, and a great deal of data useful to astrochemical models and mechanistic studies have been collected. The success of Blagojevic et al. with ion-molecule reactions of $NH_{2,3}OH^+$ type species with certain neutrals to form amino acids indicates one possible mechanism which must be investigated further to determine this pathway's relevance to astrochemistry. Also, as indicated by the reactions of NH_3^+ with the various neutrals studied, abstraction of H produces complex radicals whose reactions have not been investigated to this point, but which may react with other radicals or ions to produce more complex species. Additionally, the electron-ion recombination of species such as acetic acid associated with NH_4^+ may also yield a product of interest if during this process rearrangement can occur. Little is known about the structure and bonding of these associated products beyond what has been investigated here, and further study in both theory and experiment is needed. Few plausible routes to amino acids using gas phase ion-molecule reactions remain using currently available laboratory species, yet methods must be developed which can carefully investigate the remaining options in the realm of radical neutrals, electron-ion recombination, or perhaps even combined gas and surface chemistry to verify the possible existence of glycine and other amino acids in the interstellar and circumstellar regions.

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