

# A selected ion flow tube study of the reactions of a sequence of ions with amines

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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 acids and methyl formate ions. The rate coefficients of these reactions have also been determined showing that they are nearly all gas kinetic with the ethylamine reaction rate coefficients tending to be slightly less than their methylamine counterparts.

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**Keywords:** SIFT; Ion–molecule reaction; Rate coefficient; Interstellar medium; Protonated acid

## 1. Introduction

Astrochemical models together with laboratory measurements of reaction rate coefficients and product ion distributions have provided insight into the earliest routes to the synthesis of the organic matter detected in interstellar clouds [1,2], 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 [3–6]. In fact, meteorites impacting Earth have been shown to carry many complex organics including many amino acids [7]. 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 [9], 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 routes to 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 [10,11].  $CH_3COOH$ ,  $HCOOCH_3$ ,  $HCOOH$ , and  $CH_3NH_2$  have all been detected in the interstellar medium [12,13], 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.

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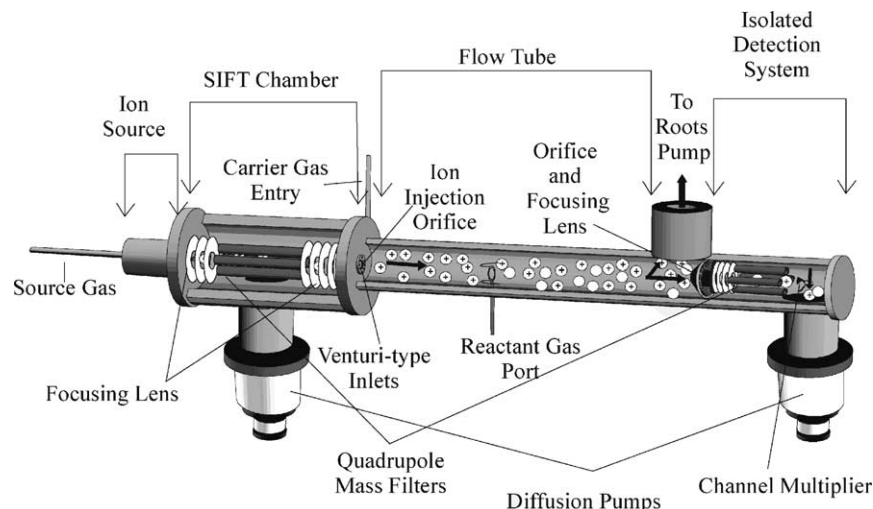


Fig. 1. A schematic diagram of the University of Georgia SIFT apparatus. Ions are focused from the ion source into a quadrupole mass filter, mass selected, refocused, and injected into the flow tube through the ion injection orifice. These ions are entrained in the He carrier gas flow to which reactant 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.

## 2. Experimental

The selected ion flow tube (SIFT) technique (see Fig. 1) has been used to introduce a single primary ion species into a flowing He carrier gas. The SIFT technique has been described previously [14,15] 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  $\text{N}^+$ ,  $\text{N}_2^+$ ,  $\text{Ar}^+$ ,  $\text{CO}^+$ , and  $\text{CO}_2^+$  from  $\text{N}_2$ , Ar, and  $\text{CO}_2$ . 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 absence of such excitation is evident from the fact that no endothermic reaction channels were observed and that the primary ion decays were linear (except for the reactions where a different explanation is apparent; see Section 3.1). 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  $\text{HCOOH}$  was first introduced into this source.  $\text{HC}(\text{OH})_2^+$  was detected in the SIFT and injected into the flow tube, however, the filament corroded and burned out after only about 30 min of exposure. The same would occur for any attempt at injecting  $\text{O}_2^+$  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 [15]. 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  $\text{H}_3\text{O}^+$  from the SIFT (with  $\text{H}_2\text{O}$  in the source) and into the flow tube and using it to proton transfer to  $\text{CH}_3\text{COOH}$ ,  $\text{HCOOCH}_3$ , and  $\text{HCOOH}$ . As the flow of a neutral carboxylic acid was increased,  $\text{H}_3\text{O}^+$  was completely depleted by proton transfer. At the point  $\text{H}_3\text{O}^+$  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 in addition to the protonated acids. However, it has been shown by Mackay et al. that the three body stabilized dimerization reaction does not totally deplete the desired primary ion at the flow rate used to study the reaction [16]. The reactions were carried out in a He carrier gas introduced into the flow tube to a total pressure of  $\sim 0.5$  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  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{CH}_2\text{NH}_2$  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 [15,17,18]. Rate coefficients are accurate to  $\pm 15\%$  and product ions to  $\pm 5$  in the percentage.

## 3. Results and discussion

The experimental rate coefficients along with literature values [11] where available and the gas kinetic rate coeffi-

Table 1

Experimental rate coefficients,  $k_{\text{exp}}$ , of a series of ions (indicated) with  $\text{CH}_3\text{NH}_2$  and  $\text{CH}_3\text{CH}_2\text{NH}_2$  are listed followed by literature rate coefficients,  $k_{\text{lit}}$ , [11] where available and theoretical collisional rate coefficients,  $k_{\text{theor}}$ , determined using Variational Transition State Theory [19] with polarizabilities and dipole moments from literature [20]

Ion	$k_{\text{exp}}$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k_{\text{lit}}$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	$k_{\text{theor}}$ ( $10^{-9} \text{ cm}^3 \text{ s}^{-1}$ )	Efficiency
<b><math>\text{CH}_3\text{NH}_2</math></b>				
$\text{Ar}^+$	1.92	–	1.99	0.965
$\text{N}_2^+$	1.22	1.20	2.17	0.562
$\text{N}^+$	2.56	2.00	2.68	0.955
$\text{CO}^+$	2.12	–	2.17	0.977
$\text{CO}_2^+$	2.13	–	1.95	1.09 <sup>a</sup>
$\text{O}_2^+$	2.50 <sup>b</sup>	1.00	2.10	1.19 <sup>a</sup>
$\text{HC(OH)}_2^+$	1.78	–	1.93	0.922
$\text{CH}_3\text{C(OH)}_2^+$	2.86	–	1.84	1.55 <sup>a</sup>
$\text{HC(OH)OCH}_3^+$	2.45	–	1.84	1.33 <sup>c</sup>
<b><math>\text{CH}_3\text{CH}_2\text{NH}_2</math></b>				
$\text{Ar}^+$	0.926	–	1.87	0.495
$\text{N}_2^+$	1.54	–	2.07	0.744
$\text{N}^+$	2.14	–	2.64	0.811
$\text{CO}^+$	1.53	–	2.07	0.739
$\text{CO}_2^+$	1.22	–	1.83	0.667
$\text{O}_2^+$	1.52	–	1.99	0.763
$\text{HC(OH)}_2^+$	1.58	–	1.80	0.878
$\text{CH}_3\text{C(OH)}_2^+$	2.35	–	1.69	1.39 <sup>c</sup>
$\text{HC(OH)OCH}_3^+$	2.11	–	1.69	1.25 <sup>c</sup>

The reaction efficiency,  $k_{\text{exp}}/k_{\text{theor}}$ , is also given. All rate coefficients are expressed in units of  $10^{-9} \text{ cm}^3/\text{s}$ .

<sup>a</sup> Within error of the gas kinetic rate.

<sup>b</sup> Obtained by modeling the data in Fig. 3.

<sup>c</sup> The high efficiencies are noted in Section 3.2.

coefficients calculated using Variational Transition State Theory [19] with polarizabilities and dipole moments obtained from literature [20] are displayed in Table 1. All rate coefficients for the  $\text{CH}_3\text{NH}_2$  reactions with the simple ions were near the gas kinetic values, and the  $\text{CH}_3\text{CH}_2\text{NH}_2$  reactions with the simple ions had rate coefficients just below the equivalent gas kinetic values. The reactions with  $\text{HC(OH)}_2^+$  were near the gas kinetic rate; whereas, the reactions of the amines with  $\text{CH}_3\text{C(OH)}_2^+$  and  $\text{HC(OH)OCH}_3^+$  gave rate coefficients above the gas kinetic value. In general, the efficiencies for reactions involving a particular ion and  $\text{CH}_3\text{NH}_2$  were higher than for  $\text{CH}_3\text{CH}_2\text{NH}_2$ . Table 2 displays the experimental products and percentage product distributions along with literature values [11] 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. Reactions of the amines with  $\text{HC(OH)}_2^+$ ,  $\text{CH}_3\text{C(OH)}_2^+$ , and  $\text{HC(OH)OCH}_3^+$ , like the previously mentioned secondary reactions, exclusively result in proton transfer to the neutral amine. The analyses of the reactions with the ions  $\text{N}^+$ ,  $\text{Ar}^+$ ,  $\text{CO}_2^+$ ,  $\text{CH}_3\text{C(OH)}_2^+$ ,  $\text{HC(OH)OCH}_3^+$ , and  $\text{HC(OH)}_2^+$  were straight-forward; however, the ions  $\text{N}_2^+$ ,  $\text{CO}^+$ , and  $\text{O}_2^+$  posed problems since there were possible prod-

ucts with molecular masses equivalent to those of the primary ions.

### 3.1. $\text{O}_2^+$ , $\text{N}_2^+$ , and $\text{CO}^+$ reactions with $\text{CH}_3\text{NH}_2$

$\text{O}_2^+$ ,  $\text{N}_2^+$ , and  $\text{CO}^+$  when reacted with  $\text{CH}_3\text{NH}_2$  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

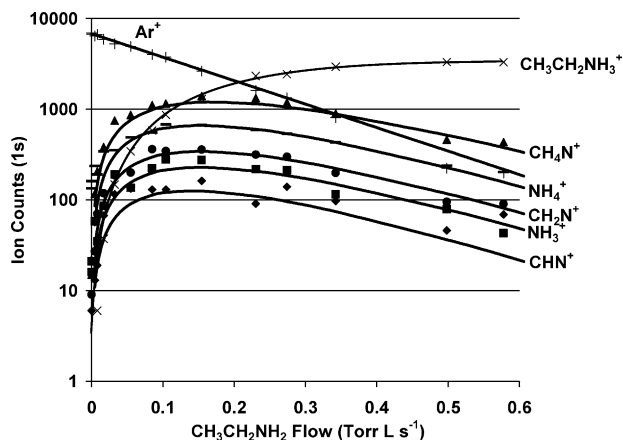


Fig. 2. Decay of  $\text{Ar}^+$  in a typical charge transfer reaction with  $\text{CH}_3\text{CH}_2\text{NH}_2$ . Note the linear decay of the reactant ion over approximately two orders of magnitude and that the secondary reactions all produce protonated  $\text{CH}_3\text{CH}_2\text{NH}_2$ .

Table 2

Product ion distributions (%) for the reactions of CH<sub>3</sub>NH<sub>2</sub> and CH<sub>3</sub>CH<sub>2</sub>NH<sub>2</sub> with the ions indicated are listed along with literature product ion percentages [11] (in parentheses) where available

Source ion	CH <sub>3</sub> NH <sub>2</sub> reactions			CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> reactions		
	Ion product	Neutral products	%	Ion product	Neutral products	%
<b>Fragmentation reactions</b>						
Ar <sup>+</sup> (15.76 eV)	CH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> + Ar	8	NH <sub>3</sub> <sup>+</sup>	C <sub>2</sub> H <sub>4</sub> + Ar	10
	CH <sub>2</sub> N <sup>+</sup>	H <sub>2</sub> + H + Ar	59	NH <sub>4</sub> <sup>+</sup>	C <sub>2</sub> H <sub>3</sub> + Ar	25
	CH <sub>3</sub> N <sup>+</sup>	H <sub>2</sub> + Ar	3	CHN <sup>+</sup>	CH <sub>4</sub> + H <sub>2</sub> + Ar	6
	CH <sub>4</sub> N <sup>+</sup>	H + Ar	30	CH <sub>2</sub> N <sup>+</sup>	CH <sub>4</sub> + H + Ar	12
N <sub>2</sub> <sup>+</sup> (15.58 eV)	CH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> + N <sub>2</sub>	7 (21)	CH <sub>3</sub> N <sup>+</sup>	CH <sub>4</sub> + N <sub>2</sub>	24
	CH <sub>3</sub> N <sup>+</sup>	H <sub>2</sub> + N <sub>2</sub>	21 (0)	CH <sub>4</sub> N <sup>+</sup>	CH <sub>3</sub> + N <sub>2</sub>	76
	CH <sub>4</sub> N <sup>+</sup>	H + N <sub>2</sub>	67 (73)			
	CH <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	N <sub>2</sub>	5 (6)			
N <sup>+</sup> (14.53 eV)	CH <sub>3</sub> <sup>+</sup>	NH <sub>2</sub> + N	7 (6)	CH <sub>4</sub> N <sup>+</sup>	CH <sub>3</sub> + N	100
	CH <sub>2</sub> N <sup>+</sup>	H <sub>2</sub> + H + N	18 (10)			
	CH <sub>3</sub> N <sup>+</sup>	H <sub>2</sub> + N	7 (7)			
	CH <sub>4</sub> N <sup>+</sup>	H + N	62 (70)			
	CH <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	N	6 (7)			
CO <sup>+</sup> (13.99 eV)	CH <sub>3</sub> N <sup>+</sup>	H <sub>2</sub> CO	18	CH <sub>3</sub> N <sup>+</sup>	CH <sub>4</sub> + CO	12
	CH <sub>4</sub> N <sup>+</sup>	HCO	79	CH <sub>4</sub> N <sup>+</sup>	CH <sub>3</sub> + CO	68
	CH <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	CO	3	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup>	HCO	20
CO <sub>2</sub> <sup>+</sup> (13.75 eV)	CH <sub>2</sub> N <sup>+</sup>	HCO <sub>2</sub> + H <sub>2</sub>	4	CH <sub>4</sub> N <sup>+</sup>	CH <sub>3</sub> + CO <sub>2</sub>	86
	CH <sub>3</sub> N <sup>+</sup>	CO <sub>2</sub> + H <sub>2</sub>	10	CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	CO <sub>2</sub>	14
	CH <sub>4</sub> N <sup>+</sup>	HCO <sub>2</sub>	72			
	CH <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	CO <sub>2</sub>	14			
O <sub>2</sub> <sup>+</sup> (12.07 eV)	CH <sub>4</sub> N <sup>+</sup>	HO <sub>2</sub>	40 (35)	CH <sub>4</sub> N <sup>+</sup>	CH <sub>3</sub> + O <sub>2</sub>	86
	CH <sub>3</sub> NH <sub>2</sub> <sup>+</sup>	O <sub>2</sub>	60 (65)	C <sub>2</sub> H <sub>6</sub> N <sup>+</sup>	HO <sub>2</sub>	4
				CH <sub>3</sub> CH <sub>2</sub> NH <sub>2</sub> <sup>+</sup>	O <sub>2</sub>	10
<b>Proton transfer reactions</b>						
HC(OH) <sub>2</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	HCOOH	100	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	HCOOH	100
CH <sub>3</sub> C(OH) <sub>2</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> COOH	100	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> COOH	100
HC(OH)OCH <sub>3</sub> <sup>+</sup>	CH <sub>3</sub> NH <sub>3</sub> <sup>+</sup>	HCOOCH <sub>3</sub>	100	CH <sub>3</sub> CH <sub>2</sub> NH <sub>3</sub> <sup>+</sup>	HCOOCH <sub>3</sub>	100

Each proposed product channel was exothermic with reaction enthalpies,  $\Delta H_r$ , ranging from approximately  $-47$  kJ/mol to approximately  $-840$  kJ/mol. Thermochemical data were obtained from the literature [23]. The reactant ions are arranged in order of decreasing recombination energy.

primary ions with CH<sub>3</sub>NH<sub>2</sub> were modeled kinetically to determine whether or not an additional product was present. Though no extra primary product was present for the O<sub>2</sub><sup>+</sup> reaction, its decay was affected by the rise of the secondary product, CH<sub>3</sub>NH<sub>3</sub><sup>+</sup>, 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. 3:

$$[P^+] = [P^+]_0 \exp(-k_1[M]t) \quad (1)$$

$$[A^+] = \frac{k_1 f_a [P^+]_0}{k_{2a} - k_1} (\exp(-k_1[M]t) - \exp(-k_{2a}[M]t)) \quad (2)$$

$$[MH^+] = \frac{k_1 f_a [P^+]_0}{k_{2a} - k_1} \exp(-k_{2a}[M]t) + \frac{k_1 f_b [P^+]_0}{k_{2b} - k_1} \exp(-k_{2b}[M]t)$$

$$- \frac{k_{2a} f_a [P^+]_0}{k_{2a} - k_1} \exp(-k_1[M]t) - \frac{k_{2b} f_b [P^+]_0}{k_{2b} - k_1} \exp(-k_1[M]t) \quad (3)$$

[ ] indicates the concentrations of the primary ion (P<sup>+</sup>), CH<sub>3</sub>NH<sub>2</sub> (M), a primary product (A<sup>+</sup>), and the secondary product (MH<sup>+</sup>). The rate coefficient of the primary reaction is given by  $k_1$ , and  $k_{2a,b,\dots,n}$  and  $f_{a,b,\dots,n}$  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<sub>2</sub><sup>+</sup> reaction with CH<sub>3</sub>NH<sub>2</sub> but not the reactions of other primary ions which may produce different numbers of products. From this fit, a rate coefficient was obtained for the primary O<sub>2</sub><sup>+</sup> reaction and is listed in Table 1.

Several trends in the data indicate that N<sub>2</sub><sup>+</sup> could have CH<sub>2</sub>N<sup>+</sup> as a product. Firstly, the other ions of higher recombination energy cause fragmentation into smaller molecules, CH<sub>2</sub>N<sup>+</sup> being a common product in these cases. Also, the

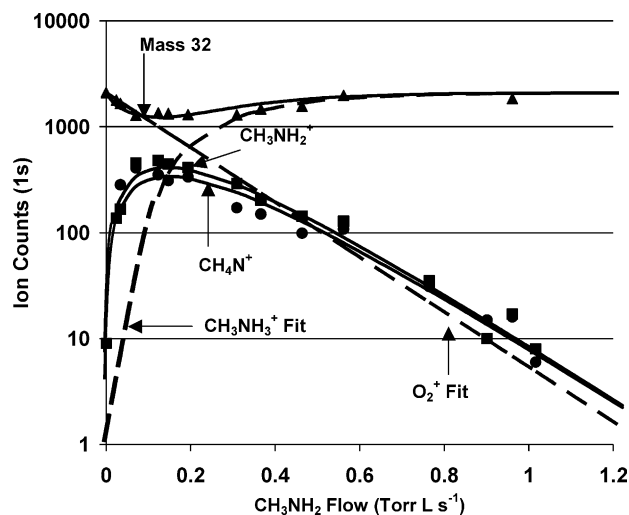


Fig. 3. Variation of  $O_2^+$  and product ion counts in reaction with  $CH_3NH_2$ . The decay of  $O_2^+$  is soon obscured by the rise of the secondary product,  $CH_3NH_3^+$ . The line through the mass 32 data points is the sum of the modeled decay of  $O_2^+$  and modeled rise of  $CH_3NH_3^+$  as 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.

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 1). However, the kinetic models according to Eqs. (1) and (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 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 that 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  $3.85 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for the reactions of each ion with  $CH_3NH_2$  and  $3.13 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  for the reactions with  $CH_3CH_2NH_2$  [21] which are both larger than the experimental values. Note that the reactions with  $CH_3CH_2NH_2$  are less efficient than those with  $CH_3NH_2$  ( $\sim 0.65$  to  $\sim 0.75$ , if the dipole is fully locked). Since when proton transfer is energetically possible, it generally occurs at the collisional rate [22], this implies that the protonated acetic acid reactions are actually gas kinetic which would give a locking constant of  $\sim 0.65$ .

### 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 these ions 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  $\text{CH}_n\text{N}^+$  counterparts [23]. Furthermore, the limited literature data available [10] shows that the members of the amine series,  $\text{CH}_3(\text{CH}_2)_n\text{NH}_2$  ( $n = 3, 4, 5$ ), when reacted with  $\text{O}_2^+$  each show  $\text{CH}_4\text{N}^+$  (the observed major product in all simple ion reactions with  $\text{CH}_3\text{CH}_2\text{NH}_2$  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: $\text{CH}_3^+$ , $\text{NH}_3^+$ , and $\text{NH}_4^+$

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.  $\text{CH}_3^+$  would be expected to be formed in  $\text{CH}_3\text{NH}_2$  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  $\text{CH}_3^+$  product since the orientation of the collision would most often be toward the non-bonding pair about the N. The observed  $\text{NH}_3^+$  and  $\text{NH}_4^+$  would be expected to form when a high energy primary ion approaches near the C atom of the C–N bond of  $\text{CH}_3\text{CH}_2\text{NH}_2$ .

### 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,  $\text{CH}_3\text{C}(\text{OH})_2^+$ ,  $\text{HC}(\text{OH})\text{OCH}_3^+$ , and  $\text{HC}(\text{OH})_2^+$ , also proceed by proton transfer. This is consistent with the general trend that proton transfer is efficient when exothermic [22]. 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. This 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 neutral amines abstract a proton but otherwise 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.

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## References

- [1] E. Herbst, W. Klemperer, *Ap. J.* 185 (1973) 505.
- [2] P.M. Solomon, W. Klemperer, *Ap. J.* 178 (1972) 389.
- [3] C.F. Chyba, C. Sagan, *Nature* 355 (1992) 125.
- [4] A.H. Delsemme, *Icarus* 146 (2000) 313.
- [5] A.H. Delsemme, *Am. Scientist* 89 (2001) 432.
- [6] C.F. Chyba, P.J. Thomas, L. Brookshaw, C. Sagan, *Science* 249 (1990) 366.
- [7] C.F. Chyba, *Nature* 348 (1990) 113.
- [8] Y.-J. Kuan, S.B. Charnley, H.-C. Huang, W.-L. Tseng, Z. Kisiel, *Astrophys. J.* 593 (2003) 848.
- [9] V. Blagojevic, S. Petrie, D.K. Bohme, *Mon. Not. R. Astron. Soc.* 339 (2003) L7.
- [10] V. Anicich, *An Index of the Literature for Bimolecular Gas Phase Cation–Molecule Reaction Kinetics*, Jet Propulsion Laboratory, Pasadena, 2003.
- [11] D. Smith, N.G. Adams, T.M. Miller, *J. Chem. Phys.* 69 (1978) 308.
- [12] M.C. McCarthy, P. Thaddeus, *Chem. Soc. Rev.* 30 (2001) 177.
- [13] H.A., Wooten, 2002, [www.cv.nrao.edu/~awooten/allmols.html](http://www.cv.nrao.edu/~awooten/allmols.html).
- [14] N.G. Adams, D. Smith, *Int. J. Mass Spectrom. Ion Phys.* 21 (1976) 349.
- [15] N.G. Adams, D. Smith, in: J.M. Farrar, J.W.H. Saunders (Eds.), *Techniques for the Study of Ion–Molecule Reactions*, Wiley-Interscience, New York, 1988, p. 165.
- [16] G.I. Mackay, A.C. Hopkins, D.K. Bohme, *J. Am. Chem. Soc.* 100 (1978) 7460.
- [17] N.G. Adams, D. Smith, *J. Phys. B* 9 (1976) 1439.
- [18] N.G. Adams, D. Smith, *Int. J. Mass Spectrom. Ion Phys.* 21 (1976) 349.
- [19] T. Su, W.J. Chesnavich, *J. Chem. Phys.* 76 (1982) 5183.
- [20] NIST Computational Chemistry Comparison and Benchmark DataBase, NIST Standard Reference Database 101, <http://srdata.nist.gov/cccbdb/>, Release 10, May 2004.
- [21] T. Su, M.T. Bowers, in: M.T. Bowers (Ed.), *Gas Phase Ion Chemistry*, Academic Press, New York, 1979, p. 83.
- [22] D.K. Bohme, in: P. Ausloos (Ed.), *Interaction Between Ions and Molecules*, Plenum Press, New York, 1975, p. 489.
- [23] NIST Chemistry WebBook, NIST Standard Database 69, <http://webbook.nist.gov/chemistry/>, March 2003.