Ion-Molecule Reactions of Several Ions with Ethylene Oxide and Propenal in a Selected Ion Flow Tube

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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, CH₂OCH₂-c, and propenal, CH₂CHCHO. Both molecules have been identified in hot-core star forming regions [1, 2]@nd 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 are 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 CH₃⁺ and HCO⁺ for ethylene oxide and CH₂CH⁺ 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⁺, NH₂⁺, and HCNH⁺ reacted via proton transfer. NH₃⁺ reacted with each molecule via H-atom abstraction to produce NH₄⁺, and NH₄⁺ 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 Ikeda et al. and Hollis et al. (J Am Soc Mass Spectrom 2007, 18, 445–452) © 2007 American Society for Mass Spectrometry

The use of various telescopes for analytical spectroscopy of stellar and interstellar regions have 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@nolecules@nave@been@dentified@3]@nd@he@ist@f 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 the heterogeneous region Sagittarius B2 have led to the discovery of many organic@ompounds@ncluding@nethylamine@4],@cetic acid@5],@nethyl@ormate@6],@ormic@cid@7],@thylene oxide \$\Pi\$1, and \$\Pi\$ropenal \$\Pi\$2]. One \$\Pi\$tudy \$\Pi\$ven \$\Pi\$roposed the@letection@f@he@pectral@ingerprint@f@lycine@8], the simplest amino acid, in these hot-core regions, but this@claim@was@ater@disputed@[9].@Regardless@of@the authenticity of the glycine detection, it may be possible to synthesize glycine or other amino acids via ionmolecule reactions from various ions and neutrals found in these or other regions of space. If synthesized,

Published online November 30, 2006

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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@he@eeds@f@fe@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 @ncrease @rom @bout @10 @X @o @~100 @200 @X @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 $\sim 10^6 - 10^{7}$ ° cm⁻³° [14], ©which ©are © ~ 3 ©to ©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 $(1.6 \times 10^{16} \text{ cm}^{-3})$, 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@ependent@ernary@ssociation@eactions@15]. Such collisionally stabilized reactions cannot occur in the cloud environments, but their radiatively stabilized analogs can, and the ternary reactions provide data to estimate@uch@inary@ate@oefficients@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 dead do the formation of a mino 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 [17,@18],@and@t@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 Chree-membered Ging 19]. Propenal CH₂CHCHO), 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 \$\Pi\$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 N₂⁺ 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_{2,3OH} with@cetic@cid@20];@owever,@he@nterstellar 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 NH₃ reacts slowly with molecular hydrogen in forming NH₄⁺, and this is a terminal ion in the presence of@molecular@hydrogen@as@is@HCNH+[©][21].@NH₄ is known to associate with various neutrals via a ternary reaction@n@ne@f@everal@possible@nechanisms@15]. 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.

Experimental

The SIFT technique has been described in detail elsewhere \$\pi22,\tilde{\tilde{Q}}2\) and \$\tilde{\tilde{Q}}\) ind \$\tilde{\tilde{Q}}\) eviewed \$\tilde{\tilde{Q}}\) noting to the experimental procedure will be mentioned. A detailed figure of the University of Georgia \$\tilde{S}\) IFT apparatus \$\tilde{\tilde{Q}}\) and and arlier \$\tilde{\tilde{Q}}\) are 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, prepurified, Matheson Gas Products, Parsippany, NJ) and N_2 (nitrogen, BOC grade 5.0). Each of the two electron impact sources was equipped with 0.005 in diameter tungsten wire filaments. The LPIS was used to produce the ions NH⁺, NH₂⁺, and NH₃⁺ from NH₃ (Ammonia, Matheson, anhydrous) and HCNH⁺ from CH₃NH₂ (Methylamine, anhydrous, Aldrich, Milwaukee, WI). The HPIS was used to produce NH₄ from NH₃. After production and mass selection, the ions were then focused by a series of lens elements through a 1 mm 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 (prepurified, National Welders, Durham, NC) 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 (99% Messer, Malvern, PA) is susceptible to polymerization and must be kept at room temperature or slightly lower temperature environments and has a limited life \sim 1 y. 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@18]@in@reporting@rate coefficients for the switching reactions. The ternary reactions with NH₄⁺ proceeded by successively associating one then two neutrals, X,

$$NH_4^+ + X + He \rightarrow NH_4^+ X + He$$
 (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 eq 1 and eq 2 as the primary reactant ions.

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

$$NH_4^+X_2 + Y \to NH_4^+XY + X$$
 (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

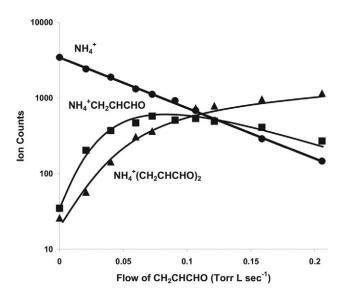


Figure 1. NH₄⁺ ion counts versus the flow of reactant gas propenal. Note the linear decay of the primary ion NH₄⁺, the rise of the primary association product, NH₄⁺CH₂CHCHO, and its subsequent reaction with propenal to form the secondary product, NH₄⁺(CH₂CHCHO)₂.

desired ionic products of eq 1 and eq 2 were available in greatest abundance as primary reactant ions in eq 3 and eq 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 eq 1 or eq 2 were maintained and eq 3 or eq 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@lecay@f@he@rimary@on@22-24]@nd@re accurate to $\pm 30\%$ for these sticky vapors.

Results

Figure@@isplays@he@ata@btained@n@@ypical@eaction 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.

Rate Coefficients

The binary rate coefficients, $k_{\rm b}$ (cm³s⁻¹), for the reactions of the primary ions, Ar⁺, N₂⁺, NH_n⁺ (n=1–3), and HCNH⁺ with ethylene oxide and propenal may be viewed@in©Table©I©followed©by©the©theoretical©rate coefficients, $k_{\rm theor}$ (cm³s⁻¹), calculated using the parameterized@rajectory@model©[25].@Molecular@dipole@moments and polarizabilities were obtained from the literature@26,@7].@he@eaction@fficiency,@which@s@he@atio of $k_{\rm b}$ to $k_{\rm theor}$, is also listed. Most of the $k_{\rm b}$ values are within experimental error (±30%) of the $k_{\rm theor}$ values,

indicating that the reactions usually proceed at the gas kinetic rate for true binary reactions. The atom abstraction reactions with NH₃⁺ occur slightly slower and are slightly less than 100% efficient for various organic molecules \$\Pi18\]. Ot Should Decoted that \$\PiH_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 Figure Q. Additionally, The Qb value for these reactions varies as a function of He pressure indicating that ternary reactions, eq 1 and eq 2, were occurring. The values of the effective binary rate coefficient at a series of He pressures of the ternary association reactions of NH₄ with ethylene oxide and propenal were determined experimentally and three body rate coefficients, $k_3 = k_b/[\text{He}] \text{ (cm}^6\text{s}^{-1})$, were calculated yielding values of 2.8(-26) cm⁶s⁻¹ and 6.2(-27) cm⁶s⁻¹ for propenal and ethylene oxide respectively where the notation A(B) represents A \times 10^B.

Product Ion Distributions

The ionic product distributions of the reactions of all primary@ons@with@he@neutrals@are@given@n@Table@followed by the estimated neutral products and the percentages of the product channels. The enthalpy of reaction, $\Delta H_{\rm r}$, is given for each reaction channel, and all channels are exothermic. The $\Delta H_{\rm r}$ 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. With such a wealth of products

Table 1. Binary reaction rate coefficients

Primary ion	$k_b (cm^3 sec^{-1})$	k_{theor} (cm 3 sec $^{-1}$)	Efficiency
CH ₂ OCH 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 ₂ CHCHO			
Ār ⁺	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
$NH_3^{\overline{+}}$	2.5 (-9)	4.4 (-9)	0.57
HCNH ⁺	2.7 (-9)	3.7 (-9)	0.73

The experimental binary reaction rate coefficients, $k_{\rm b}$, are listed for each reaction of a primary ion with a given neutral molecule followed by the theoretical reaction rate coefficients, $k_{\rm theor}$, calculated using the parameterized trajectory model [25] with dipole moments and polarizabilities obtained from the literature [26, 27]. The reaction efficiency is given by the ratio $k_{\rm b}/k_{\rm theor}$. Note that the $k_{\rm b}$ values are within experimental error ($\pm 30\%$) of the $k_{\rm theor}$ values indicating that the reactions proceed at or close to the gas kinetic rate for these true binary reactions.

Table 2. Reaction product distributions

Primary ion	lon product	Neutral products	%	$\Delta H_{\rm r}$ (kJmol ⁻¹)
CH ₂ OCH ₂				
$Ar^{\scriptscriptstyle +}$	CH ₂ ⁺	$CH_2O + Ar$	3	-194.3
	CH ₃ ⁺	HCO + Ar	43	-329.3
	CH ₂ CH ₂ ⁺	O + Ar	4	-151.8
	HCO ⁺	$CH_3 + Ar$	38	-494.7
	H ₂ CO ⁺	$CH_2 + Ar$	5	-149.4
	C ₂ OH ₂ ^{+a}	$H_2 + Ar$	4	-627.2
	$C_2^-OH_3^{+b}$	H + Ar	3	?°
N_2^+	CH ₃ ⁺	$HCO + N_2$	45	-312.1
	HCO ⁺	$CH_3 + N_2$	45	-477.5
	H ₂ CO ⁺	$CH_2 + N_2$	4	-132.2
	$C_2^-OH_2^{+a}$	$H_2 + N_2$	3	-610
	C ₂ OH ₃ ^{+b}	$H + N_2$	3	?°
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 ⁺	H₂COCH	100	-89.5
NH ₄ ⁺	H ₂ COCH ₂ -c ⁺ NH ₄ ⁺	-	100	?°
HCNH ⁺	CH ₂ (OH)CH ₂ +-c	HCN ^d	100	-164.7
CH ₂ CHCHO	<u> </u>			
$\operatorname{Ar^+}$	CH ₂ C ⁺	CH ₂ O + Ar	11	-237.7
	CH ₂ CH ⁺	HCO + Ar	50	-305
	HCO ⁺	CH₂CH + Ar	30	-322
	CH ₂ CHCO ⁺	H + Ar	6	-336.7
	CH ₂ CHCHO ⁺	Ar	3	-545
N_{2}^{+}	CH ₂ CH ⁺	$HCO + N_2$	70	-287.8
-	HCO ⁺	$CH_2CH + N_2$	20	-304.8
	CH ₂ CHCO ⁺	$H + N_2$	5	-319.5
	CH ₂ CHCHO ⁺	N_2	5	-527.9
NH^+	CH ₂ CHCH(OH) ⁺	N	100	-448.3
NH_2^+	CH ₂ CHCH(OH)+	NH	100	-154.4
$NH_3^{\frac{1}{+}}$	NH ₄ ⁺	CH ₂ CHCO ^e	100	-170.1
$NH_4^{\overset{\circ}{+}}$	CH ₂ CHCHO ⁺ NH ₄ ⁺	-	100	? ^c
HCNH ⁺	CH ₂ CHCH(OH)+	HCN ^d	100	-187.51

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 [26, 27]. Note all channels proposed are exothermic.

likely multiple potential curves are accessed. 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 [28], @o@urther@iscussion@@ecessary@f@hese reactions. For NH₃⁺, however, proton transfer is endothermic, and the ion instead reacts with each neutral via H-atom abstraction to form NH₄⁺. This is a common mechanism for NH₃⁺ reactions with H containing molecules. Switching reactions, eq 3 and eq 4, of the type discussed@reviously@15]@vere@erformed@y@eacting the neutral gas, acetic acid, with the association products of reactions eq1 and eq 2 to investigate mechanisms and @tructures. @Table @Ghows @he@eaction @ate@oeffi-line and @tructures. @Table @Ghows @he@eaction @tructures. @Table @Ghows @he@eaction @tructures. @Table @Ghows @he@eaction @tructures. @Table @Ghows @he@eaction @tructures. @Table @Ghows @tructures. @Table @Table @Ghows @tructures. @Table @Ghows @tructucients 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@ata@re@ncluded@n@able@@rom@@revious

study \$\Pi\$15] Concerning NH₄ association reactions to aid comparison.

Discussion

Products and Product Structures

Two@najor@onic@roducts@ppear@n@able@@or@ach@f the dissociative charge-transfer reactions in relatively high product percentages. These ionic products are HCO⁺ and CH₃⁺ for the dissociation of ethylene oxide and HCO+ and CH2CH+ 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, [CH2-CH2-O]⁺, where the positive charge can lie on either end of the molecule but not the central C atom. The appear-

 $^{^{}b}$ 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.

 $^{^{\}text{c}}\text{lt}$ was not possible to give the ΔH_{r} for these reactions due to the lack of thermodynamic data.

dHNC is also thermodynamically possible for reactions with both propenal/ethylene oxide with $\Delta H_r = -25/-2.2$ kJmol⁻¹ respectively.

^eThe structures CH=CH—CH=O or CH₂=C—CH=O are also energetically possible.

reactions
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					Rea	Reactant lons, NH ₄ ⁺ X _{1,2}	2			
Reactant Neutrals (Y)	Reactant PA ———————————————————————————————————	СН3СНО	CH ₂ OCH ₂ -c	(CH ₂ OCH ₂ -c) ₂ ^a	нооо:но	(CH ₃ COOH) ₂ ^a	(CH ₃) ₂ 0	СН2СНСНО	CH ₃ COOH (CH ₃ COOH) ₂ ⁸ (CH ₃) ₂ O CH ₂ CHCHO (CH ₂ CHCHO) ₂ (CH ₃) ₂ CO	(CH ₃) ₂ CO
		769	774	774	783	783	792	797	797	811
СН3СНО	692	ı	ı	1	4.0(-10)	ı	ı	ı	ı	ı
CH,OCH,-c	774	ı	1	1	1.3 (-10)	1.0 (-10)	ı	1	ı	ı
CH ₃ COO _H _b	783	1.0 (-9)	2.2 (-10)	1.7 (-10)	ı	ı	7.5	3.9 (-10)	1.7 (-11)	< 1.0
							(-10)			(-13)
(CH ₃) ₂ 0	792	ı	1	1	3.5 (-11)	I	ı	1	ı	ı
СН2СНСНО	797	ı	I	ı	7.2 (-10)	9.0 (-10)	ı	I	ı	ı
$(CH_3)_2CO$	811	I	I	I	2.6 (-10)	I	I	I	I	I

rctions, (3) and (4), of the horizontally listed NH $_{u}^{+}X_{1,2}$ associations with the vertically listed neutrals (Y) whose proton affinities (PA) are also listed. possible via quadrupole mass spectrometry (exchanges of X with X) or were not necessary to complete the desired analysis. Values presently swere taken from a previous paper [15] to aid comparison. ingle X exchange (4). for a single X exchange switching react they were not p ther k_b values v mined in the present study are in bold. Other $k_{\rm b}$ rate coefficients for the double something in values (cm³s⁻¹) for the binary accounted Shown are the $k_{\rm b}$ values (cm 3 s $^-$ ' Several reactions were omitted ğ determined in the dimerization

ance of the product CH₃⁺ 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 CH₃⁺ along with neutral HCO is then formed via an intermediate. In the case that the charge of [CH2-CH2-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 CH₃ 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 [CH₃-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, CH₃OCHO@18].

The observed ionic products and neutral products listed @in @Table @G for @the @dissociative @charge-transferreactions 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 CH₂CH₂⁺ 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 were available to determine the ΔH_r of the reactions producing this ion, CH₂-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 H₂ 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, CH₂=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@mplied@n@Table@.

The neutral products of certain reactions warrant brief discussion of their astrochemical implications. The reactions of NH₃⁺ with various saturated compounds such as CH₄ and CH₃OH and unsaturated species such as CH₂CH₂@nd©H₃COOH©16,@8]@ave@een@hown@o 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 CH₂OCH 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 because of the difficulty of the experiments. Much more work is needed to investigate the chemical possibilities.

NH₄⁺ Association

The $k_{\rm b}$ values at a series of He pressures of the association reactions of NH₄⁺ with ethylene oxide and propenal@lotted@n@igure@@re@ignificantly@ower@han@he 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 Cregression Clines Cseen Cin CFigure C2. CThe Capproach toward the limiting gas kinetic rate can become relevant at relatively high pressures, causing the measured $k_{\rm b}$ values to level off giving a less accurate k_3 [value \mathbb{Q} 29]; however, little indication of this effect over the range of pressures@studied@s@seen@n@Figure@.@The@ine@itted through the Cata points in Figure Callustrates the Cinear portion, which extrapolates near $k_{\rm b}=0$ within experimental error (±30%) at 0 Torr. A wider pressure range

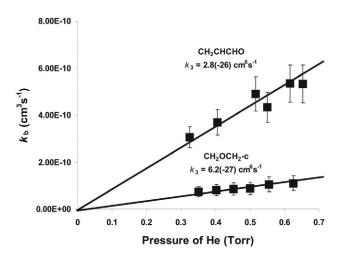


Figure 2. The k_b values of the association reaction (1) of NH⁺₄ with propenal and ethylene oxide at a series of pressures of He are plotted for comparison. Note the regression lines used to determine the k_3 values extrapolate well to (0, 0) within experimental error

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 that 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.

Association Reaction Mechanism

Previously a mechanism, M₁, was proposed for the association reactions eq 1 by analyzing the results of the switching reactions. It was suggested that a mechanism involving an intermediate complex occurs in which the NH₄ 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 = $CHCH_2$ -O- NH_3^+ . The ion formed is likely analogous in reactivity to the NH₃OH⁺ ion in the Blagojevic mechanism. A second mechanism, M₂, was reported by Blagojevic et al., involving the ion-molecule reactions of NH_{2,3OH} with acetic acid to form charged glycine and protonated glycine respectively. M2 proceeds by the NH_{2.3OH} ion reacting with acetic acid to attach NH_{2.3} group to the acid apparently at the -CH₃ end and eject H_2O . Considering the NH_3OH^+ pathway with M_2 ,

likely 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 H₂O 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 NH₃OH⁺ and CH₂=CHCH₂-O-NH₃⁺ are in fact analogous, then the switching reaction of the association product of propenal and NH₄ in the present study with CH₃COOH should not switch but rather attach an NH₃ group to CH₃COOH and eject a neutral alcohol, CH₂=CHCH₂OH. 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 NH₄⁺CH₂=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 \$\Pi\$15] Cor@ny Of Che Ceactions Cisted. Assuming that M₂ 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 CH₃OH, 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 NH₄⁺ would allow the mechanism to proceed via a ring-opening reaction to form CH₃CH₂-O-NH₃⁺. Temporarily assuming that the mechanism proceeds as such according to M₁ for both unsaturated carbonyl containing species as well as epoxides, applying the mechanism to acetaldehyde, CH₃CHO, the association product would be CH₃CH₂-O-NH₃⁺, which is identical to that of the proposed association product of the isomeric ethylene oxide. If M₁ does proceed for both of these molecules, then the switching reactions of these two ions should proceed@t@dentical@ates.@As@hown@n@Table@@he@th value for eq 3 between the association product of NH₄⁺ with ethylene oxide and acetic acid, 2.2(-10) cm³s⁻¹, is significantly different than the k_b value for eq 3 with the association product of NH₄ with acetaldehyde and acetic acid, 1.0(-9) cm³s⁻¹, indicating that the ring of ethylene oxide does not open. This casts doubt on the covalence of a bond of the molecule to the N atom of the

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@f@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 NH₄⁺. The bond 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 NH₄ affinity. In Table (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 M₁ in saturated species. The reactivity of ethylene oxide is of particular relevance to this problem since the steric hindrance present in (CH₃)₂O is eliminated by the three-member ring, which effectively bares the O atom. Note that NH₄+CH₃COOH switches with ethylene oxide at a rate of 1.3(-10) cm³s⁻¹, and the same ion switches with $(CH_3)_2O$ at a rate of 3.5(-11) cm³s⁻¹, which is indeed significantly lower even though the proton affinity of (CH₃)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

The k_b -values of the switching reactions given the Table 3 red sted such that comparison 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 3 s $^{-1}$). On the other hand, the k_b value for the reaction of singly associated propenal with acetic acid is 3.9(-10) cm 3 s $^{-1}$, and is 1.70(-11) cm 3 s $^{-1}$ 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 3 s $^{-1}$ and 9.0(-10) cm 3 s $^{-1}$, respectively. The data seem to indicate that for neutrals with similar NH $_4^+$

affinities, Capparently Csuch Cas Cacetic Cacid Cand Cethylene oxide, the $k_{\rm h}$ values will be similar for all combinations of reaction of association and neutral, and for neutrals with very different NH₄⁺ affinity the reactions will have markedly different $k_{\rm b}$ values that will tend to be low when trying to switch out a reactant with a relatively high NH₄⁺ affinity, and relatively high when trying to switch out neutral with a relatively low NH₄⁺ 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.

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 that must be investigated further to determine this pathway's relevance to astrochemistry. Also, as indicated by the reactions of NH₃⁺ 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 NH₄⁺ may also yield a product of interest if during this process rearrangement can occur. In addition C₄H⁻ has recently been@etected@30]@nd@on-ion@ecombination@ould@lso contribute to the neutral products (note that this produces less fragmentation than electron-ion recombination). 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 utilizing 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.

Acknowledgments

The authors gratefully acknowledge funding by NSF grant no. 0212368. DMJ also recognizes the continued support of the UGA CURO and Foundation Fellows programs.

References

- 1. Ikeda, M.; Ohishi, M.; Nummelin, A.; Dickens, J. E.; Bergman, P.; Hjalmarson, A.; Irvine, W. M. Survey Observations of c-C₂H₄O and CH₃CHO Toward Massive Star-Forming Regions. Astrophys. J. 2001, 560, 792-805.
- 2. Hollis, J. M.; Jewell, P. R.; Lovas, F. J.; Remijan, A.; Mollendal, H. Green Bank Telescope Detection of New Interstellar Aldehydes: Propenal and Propanal. Astrophys. J. 2004, 610, L21–L24.
- 3. Wooten, H. A. The 129 Reported Interstellar and Circumstellar Molecules,@www.cv.nrao.edu/~awootten/allmols.html.@ational@adio@Astronomy Observatory. 2005.
- 4. Kaifu, N.; Morimoto, M.; Nagane, K.; Akabane, K.; Iguchi, T.; Takagi, K. Detection of Interstellar Methylamine. Astrophys. J. 1974, 191, L135
- 5. Mehringer, D. M.; Snyder, L. E.; Miao, Y. Detection and Confirmation of Interstellar Acetic Acid. Astrophys. J. 1997, 480, L71-L74.
- 6. Hollis, J. M.; Vogel, S. N.; Snyder, L. E.; Jewell, P. R.; Lovas, F. J. The Spatial Scale of Glycoaldehyde in the Galactic Center. Astrophys. J. 2001, 554L81.
- 7. Liu, S.-Y.; Mehringer, D. M.; Snyder, L. E. Observations of Formic Acid in Hot Molecular Cores. Astrophys. J. 2001, 552, 654-663.
- Kuan, Y.-J.; Charnley, S. B.; Huang, H.-C.; Tseng, W.-L.; Kisiel, Z. Interstellar Glycine. Astrophys. J. 2003, 593, 848–867.
- 9. Snyder, L. E.; Lovas, F. J.; Hollis, J. M.; Friedel, D. N.; Jewell, P. R.; Remijan, A.; Ilyushin, V. V.; Alekseev, E. A.; Dyubko, S. F. A Rigorous Attempt to Verify Interstellar Glycine. Astrophys. J. 2004, 619, 914–930.
- 10. Chyba, C. F.; Thomas, P. J.; Brookshaw, L.; Sagan, C. Cometary Delivery of Organic Molecules to the Early Earth. Science 1990, 249, 366-373.
- 11. Chyba, C. F.; Sagan, C. Endogenous Production, Exogenous Delivery, and Impact Shock Synthesis of Organic Molecules: An Inventory for the Origins of Life. Nature 1992, 355, 125-132.
- 12. Delsemme, A. H. Cometary Origin of the Biosphere. Icarus 2000, 146, 313-325
- 13. Delsemme, A. H. An Argument for the Cometary Origin of the
- Biosphere. *Am. Sci.* **2001**, *89*, 432–442. 14. Williams, D. A.; Herbst, E. It's a Dusty Universe: Surface Science in Space. Surf. Sci. 2002, 500, 823-837.
- 15. Adams, N. G.; Babcock, L. M.; Mosteafoui, T.; Kerns, M. S. Selected Ion Flow Tube Study of NH₄⁺ Association and Product Switching Reactions with a Series of Organic Molecules. Int. J. Mass Spectrom. 2003, 223,224, 459 - 471
- 16. Anicich, V. An Index of the Literature for Bimolecular Gas Phase Cation-Molecule Reaction Kinetics; Jet Propulsion Laboratory: Pasadena, CA,
- 17. Jackson, D. M.; Stibrich, N. J.; Adams, N. G.; Babcock, L. M. A Selected Ion Flow Tube Study of the Reactions of a Sequence of Ions with Amines. Int. J. Mass Spectrom. 2005, 243, 115-120.
- 18. Jackson, D. M.; Stibrich, N. J.; McLain, J. L.; Fondren, L. D.; Adams, N. G.; Babcock, L. M. A Selected Ion Flow Tube Study of the Reactions of Various Nitrogen Containing Ions with Formic Acid, Acetic Acid, and Methyl Formate. Int. J. Mass Spectrom. 2005, 247, 55-60.
- 19. McMurry, J. Ring-Opening Reactions of Epoxides. In Organic Chemistry; Brooks/Cole: 2000; pp 720-724.
- 20. Blagojevic, V.; Petrie, S.; Bohme, D. K. Gas-Phase Synthesis for Interstellar Carboxylic and Amino Acids. Mon. Not. R. Astron. Soc. 2003, 339,
- 21. Smith, D.; Adams, N. G. Molecular Synthesis in Interstellar Clouds: Some Relevant Laboratory Measurements. Astrophys. J. 1977, 217, 741-
- 22. Adams, N. G.; Smith, D. The Selected Ion Flow Tube (SIFT); a Technique for Studying Ion-Neutral Reactions. Int. J. Mass Spectrom. Ion Phys. 1976,
- 23. Adams, N. G.; Smith, A. D., Flowing Afterglow and SIFT. In Techniques for the Study of Ion-Molecule Reactions; Farrar, J. M.; Saunders, J. W. H., Eds.; John Wiley and Sons: NY, 1988; pp 165-220.
- 24. Adams, N. G.; Smith, D. Product-Ion Distributions for Some Ion-Molecule Reactions. *J. Phys. Chem. B* **1976**, *9*, 1439–1451.

 25. Su, T.; Chesnavich, W. J. Parametrization of the Ion-Polar Molecule
- Collision Rate Constant by Trajectory Calculations. Chem. Phys. 1982, 76, 5183-5185.
- 26. NIST Computational Chemistry Comparison and Benchmark Database, NIST©tandard@eference@atabase@01@ttp://srdata.nist.gov/cccbdb. Release 10, May 2004.
- 27. CRC Handbook of Chemistry and Physics, 69th ed.; Weast, R. C., Ed.; CRC Press, Inc.: Boca Raton, FL, 1989; pp 5-4-5-60, 69-42-73, 10-199-110-213.

 28. Bohme, D. K., The Kinetics and Energetics of Proton Transfer. In
- Interaction Between Ions and Molecules; Ausloos, P., Ed.; Plenum Press: New York, 1975; pp 489-504.
- 29. Adams, N. G.; Smith, D.; Lister, D. G.; Rakshit, A. B.; Tichy, M.; Twiddy, N. D. Ternary Association Reactions of CH₃⁺ Ions in the Temperature Range 100 to 300K. Chem. Phys. Lett. 1979, 63, 166-170.
- 30. McCarthy, M. C., Gottlieb, C. A., Gupta, H., Thaddeus, P. Laboratory and Astronomical Identification of the Negative Molecular Ion C₆H⁻. Astrophys J. Lett. 2006, preprint.