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International Journal of Mass Spectrometry 247 (2005) 55–60

www.elsevier.com/locate/ijms

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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Received 6 July 2005; received in revised form 1 September 2005; accepted 8 September 2005

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 [D.M. Jackson, N.J. Stibrich, N.G. Adams, L.M. Babcock, Int. J. Mass Spectrom. 243 (2005) 115–120]. 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^3 s^{-1}.

Keywords: SIFT; Ion–molecule reaction; Rate coefficient; Interstellar medium; Amino acids

1. Introduction

Astrochemical models and laboratory measurements have aided the understanding of the formation of organic matter in interstellar clouds where planetary systems form [2,3]. 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 [4–7]. In fact, meteorites impacting Earth have been shown to carry many amino acids [8]. Indeed, it has been reported that the amino acid glycine may have been detected in the gas phase in the interstellar medium [9], but this report has been recently contested [10]. One possible ion–molecule reaction pathway to interstellar amino acid synthesis has already been proposed [11], 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 [1].

The present study has been conducted in a selected ion flow tube (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 [12,13]. $HCNH^+$ 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 [1], the latter of which has been detected in the interstellar medium [13], and $HCNH^+$ is also believed to play an important role in the atmosphere of Titan [14,15]. 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.

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doi:10.1016/j.ijms.2005.09.001

2. Experimental

The selected ion flow tube technique has been used to introduce a single primary ion species into a flowing He carrier gas. The SIFT technique has been described previously [16,17] and will not be described in detail here. A microwave cavity (MC) ionization source of the type used in Flowing Afterglow studies [17] 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 [1]. 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 [18] 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 [19,20] (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 [16,17,21] 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%.

3. Results

The experimental reaction rate coefficients, k_{exp}, are given in Table 1 along with the theoretical collisional rate coefficients, k_{theor}, calculated using Variational Transition State Theory [22] and comparative literature values, k_{lit}, are included where available [23–25]. The decay of the primary ion versus the flow of neutral gas in a typical reaction is shown in Fig. 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

Table 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 [22] with polarizabilities and dipole moments from literature [27] and literature rate coefficients, $k_{lit,}$ are given where available [23–25]

Primary ion	k_{exp} (10^{-9} cm^3 s^{-1})	k_{theor} (10^{-9} cm^3 s^{-1})	k_{lit} (10^{-9} cm^3 s^{-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

The reaction efficiency, k_{exp}/k_{theor}, is also included. All rate coefficients are expressed in units of 10^{-9} cm^3 s^{-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 five SIFT literature values [23].

[c] Previous data obtained using a FA [24,25].

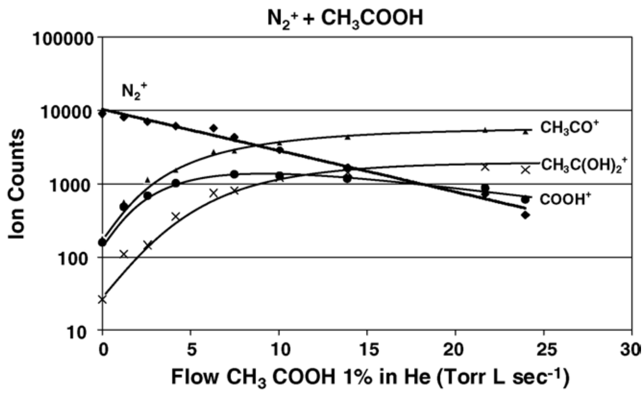

Fig. 1. Decay of N_2^+ in a typical charge transfer reaction with CH_3COOH is shown above. Note the linear decay of the reactant ion over approximately 1.5 orders of magnitude and that the secondary reaction of $COOH^+$ with the neutral produces protonated CH_3COOH.

apparatus. As can be seen in Table 1, our measurement of the rate coefficient with this reaction is in close agreement with literature [23]. 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, $k_{\mathrm{exp}}/k_{\mathrm{theor}}$, are given in Table 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 [18,26–29] are included in Table 2 along with the very limited literature data [23–25]. 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 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

Table 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 [24,25]

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[d]	100	–	−173

Reaction enthalpies, ΔH_r, in kJ mol^{-1} are also listed showing each proposed product channel is exothermic. Thermochemical data were obtained from the literature [18,26–29].

[a] Reaction may also form radical via extraction of the carboxylic H although these are reported to be less thermodynamically and structurally stable [28,31].

[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 [31].

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

with several other species containing hydrogen including H_2CO and CH_3OH [30].

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 [22]. 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 [24,25]. 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 kJ mol^{-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 [31]. 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 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 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 ($\Delta H_r = \sim 27$ kJ mol^{-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 kJ mol^{-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 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 [32]. 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 kJ mol^{-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 [30]. For species with no H atoms to abstract, such as CO_2 and CO, no reaction occurs at all with NH_3^+ ($k \leq 5(-13)\,\mathrm{cm^3\,s^{-1}}$) [30]. 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 [30], 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 [31], and the CH_3COO radical has been reported to decompose into CH_3 and CO_2 at 200 Torr in N_2 [28]. 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 [28,31] 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 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 [34]. 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.

Acknowledgements

Funding from National Science Foundation Grant No. 0212368 is gratefully acknowledged. D.M.J. acknowledges the continued support of the University of Georgia Center for Undergraduate Research Opportunities.

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