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Gas-phase syntheses for interstellar carboxylic and amino acids

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ABSTRACT

We report experimental results that demonstrate gas-phase, ionic syntheses of glycine and β-alanine, as well as acetic and propanoic acid, from smaller molecules found in space; in doing so, we infer the formation of these acids in the interstellar environment. We show that ionized glycine and β-alanine are produced in the reactions of hydroxylamine ions, NH_2OH^+, with acetic and propanoic acid respectively. Even more promising in the context of interstellar synthesis are our results that demonstrate the corresponding production of the protonated amino acids from analogous reactions with protonated hydroxylamine. The striking specificity of these syntheses for the β-isomer of alanine suggests that the amino acids of CI (Carbonaceous Ivona) chondrite meteorites are products of interstellar chemistry and supports the hypothesis that these meteorites are of cometary origin.

Key words: astrobiology – astrochemistry – comets: general – ISM: molecules.

1 INTRODUCTION

The formation of biomolecules in interstellar environments presents intriguing possibilities for the origin of life. Interstellar amino acid formation may precede the syntheses of larger, more complex biomolecules in space (Wincel, Fokkens & Nibbering 2000). However, synthetic routes to any amino acid in the interstellar medium remain elusive. One possible source of amino acids is gas-phase ion chemistry initiated by cosmic and ultraviolet radiation, since such chemistry is known to be crucial to the formation of many other complex molecules in the interstellar medium (Herbst 2001). Glycine, the simplest amino acid and a key ‘building block’ for proteins and peptides (Wincel et al. 2000), has achieved special biomolecular importance in both interstellar chemistry and the origin of life on Earth (Anders 1989; Chyba et al. 1990). Indirect evidence for the existence of extraterrestrial glycine, and many other amino acids, appears to have come from the analysis of interplanetary dust particles and of carbonaceous meteorites of asteroidal and cometary origin (Cronin 1976). The search for interstellar glycine by radio astronomers is ongoing (Combes, Nguyen-Q-Rieu & Wlodarczak 1996; Snyder 1997). Possible molecular precursors of glycine, such as CH_4, CO, H_2O and NH_3, are now known to be present in various regions of the interstellar medium (Smith 1992, and references therein). Production of amino acids from such precursors, both from the gas phase (Kobayashi et al. 2001) and from ice mixtures (Bernstein et al. 2002; Munoz Caro et al. 2002), has been achieved in the laboratory, although the discrete chemical steps involved in these conversions remain unclear. Research exploring the interstellar synthesis of amino acids has focused on the α-amino acids essential for life; nevertheless, analyses of carbonaceous meteorites show significant contributions of β- and γ-amino acids, especially β-alanine (Ehrenfreund et al. 2001a; Sephton 2002).

2 METHODS

The flow reactor/tandem mass spectrometer used to study the formation of glycine is a selected ion flow tube (SIFT) instrument that consists of two quadrupole mass filters separated by a steel flow tube (Mackay et al. 1980). Helium flows through the tube at a constant pressure of 0.35 torr and room temperature. Ions generated in the ion source are separated by the first quadrupole mass filter before they enter the flow tube upstream, and ions downstream are sampled through a nose cone and analysed by the second quadrupole mass filter. Collisions with the buffer gas thermalize the ions derived from the ion source or generated upstream by chemical reaction before they enter the reaction region downstream. CO, methane and ethylene were added as pure gases, water was added as a 2 per cent mixture of vapour in helium, and the acids and hydroxylamine were added as pure vapours of the corresponding solids or liquids. Bond connectivities within the ions sampled can be explored by changing the nose cone potential (Baranov & Bohme 1996) and thereby inducing multi-collisional dissociation. It is important to note that, even though the measurements were made at 0.35 torr and room temperature, the results should apply to low- pressure, low-temperature environments. The rates of fast bimolecular ion–molecule reactions are pressure-independent and usually do not exhibit activation energies because of the electrostatic interaction between ions and molecules.

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3 EXPERIMENTAL RESULTS

3.1 Syntheses of amino acids

Ion–molecule reactions can be especially effective in the synthesis of complex interstellar molecules because the long-range electrostatic interaction between the reactants ensures high reaction efficiency, even at interstellar temperatures (typically 10–100 K in molecular environments). In the approach reported here, we have achieved a synthesis of glycine through ion chemistry using a flow reactor/tandem mass spectrometer instrument that allows the measurement of individual chemical steps in reactions of ions with molecules and concomitantly provides insight into molecular structure. Earlier searches in our laboratory for routes leading to the direct formation of glycine from plausible ionized and molecular fragments were hampered by the preferential attack of electronegative sites by positive ions. The reactions of $CH_3NH_2^+$ with HCOOH, CO_2 or CO + H_2O, NH_3^+ with CH_3COOH and CH_2COOH^+ with NH_3 all failed to produce glycine. For example, our experiments showed that the reaction of NH_3^+ with CH_3COOH does not produce glycine$^+$ but the acetohydroximic acid cation, $CH_3CONHOH^+$, instead. The latter results from nitrogen insertion into the C–OH bond. In fact, all our attempts to form glycine from its apparent fragments were unsuccessful because N–O bond formation was preferred over the desired C–C or C–N bond formation. So the most obvious direct approach toward glycine synthesis failed.

The reactions we have identified that produce ionized and protonated glycine are the reactions of acetic acid with ionized and protonated hydroxylamine produced by electron transfer to CO^+ and proton transfer from CH_5^+, respectively. Two major products were observed under our experimental conditions:

$$NH_{2,3}OH^+ + CH_3COOH \rightarrow NH_{2,3}CH_2COOH^+ + H_2O \qquad (1a)$$

$$\rightarrow NH_{2,3}OH^+(CH_3COOH) \qquad (1b)$$

The rate coefficients of these two reactions are estimated to be $>10^{-12}$ cm^3 molecule^{-1} s^{-1}. The quoted lower limit of 10^{-12} cm^3 molecule^{-1} s^{-1} is derived from an estimate of the amount of carboxylic acid added to the flow tube. (The precise control of the amount of acid added was not possible because the acid, owing to its corrosive nature, interfered with our gas handling and pressure control systems.) Elimination of H_2O to form ionized or protonated glycine was observed in about 30 per cent of the reactive collisions, with the remainder leading to collision-stabilized solvation at the He buffer-gas pressure (0.35 torr) of our experiments. Channel (1a) is expected to predominate under interstellar conditions of much lower gas densities at which collisional stabilization becomes negligible. The identities of the product ions in channel (1a) as ionized and protonated glycine were established in multi-collision induced dissociation (CID) experiments in which the observed dissociation of these ions was compared with that observed with commercial glycine ionized by electron transfer to CO^+ or protonated by proton transfer from CH_5^+. Fig. 1 shows CID profiles obtained for ionized and protonated glycine.

We see excellent agreement not only between the natures of the CID fragment ions but also, more importantly, between the collision energies at which they arise. Formation of ionized glycine from ionized hydroxylamine in channel (1a) is exothermic by 66.5 kcal mol^{-1}, while formation of protonated glycine from protonated hydroxylamine in channel (1a) is exothermic by 55.7 kcal mol^{-1} (Lias et al. 1988).

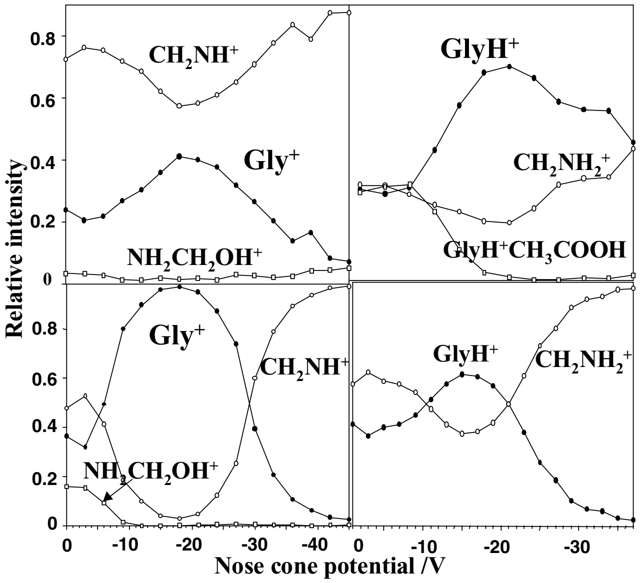

Figure 1. Comparison of multi-collision CID profiles of ionized and protonated glycine synthesized in the reactions of $NH_{2,3}OH^+$ with CH_3COOH (top left and right), with ionized and protonated glycine produced from pure glycine vapour (bottom left and right respectively). Glycine was ionized by electron transfer to CO^+ created in the electron impact (EI) ion source and protonated by proton transfer from CH_5^+ ions created in the EI ion source from methane. Some $NH_{1,2}CH_2^+$ ions are present initially owing to fragmentation of glycine either during ionization and protonation or during vaporization.

The same chemical approach was successful for the synthesis of alanine, using propanoic acid in place of acetic acid:

$$NH_{2,3}OH^+ + CH_3CH_2COOH \rightarrow NH_{2,3}CH_2CH_2COOH^+ + H_2O \qquad (2a)$$

$$\rightarrow NH_{2,3}OH^+(CH_3CH_2COOH) \qquad (2b)$$

The rate coefficients of these two reactions also are estimated to be $>10^{-12}$ molecule cm^{-3} s^{-1}. We have seen that this reaction (2a) produces ionized or protonated alanine in more than 40 per cent of the reactive collisions under our experimental conditions. CID experiments performed show that the β-isomer is produced in reaction (2a) rather than the α-isomer. This is illustrated in Fig. 2 for ionized alanine: the CID pattern of β-alanine$^+$, $NH_2CH_2CH_2COOH^+$, is distinctly different from that of α-alanine$^+$, $CH_3CH(NH_2)COOH^+$, and is the one that matches the CID pattern of the ionized product ion in reaction (2a). Similarly, there was a match between the CID profiles of the protonated product ion in reaction (2a) and commercial β-alanine protonated with CH_5^+. Formation of ionized β-alanine from ionized hydroxylamine in channel (2a) is exothermic by 70.8 kcal mol^{-1} (Lias et al. 1988). It is likely that formation of protonated β-alanine from protonated hydroxylamine is also exothermic. The proton affinity of β-alanine [PA(β-alanine)] is not known but should be similar to PA(α-alanine) = 214.8 kcal mol^{-1} (Lias et al. 1988) which would make formation of protonated β-alanine exothermic by *ca.* 63 kcal mol^{-1}.

Plausible interstellar pathways to the neutral amino acids glycine and β-alanine from the ions produced in reactions (1a) and (2a) involve dissociative recombination, e.g. reaction (3), and electron transfer, e.g. reaction (4), where M is a species of lower ionization energy (such as a metal atom) than that of the amino acid itself

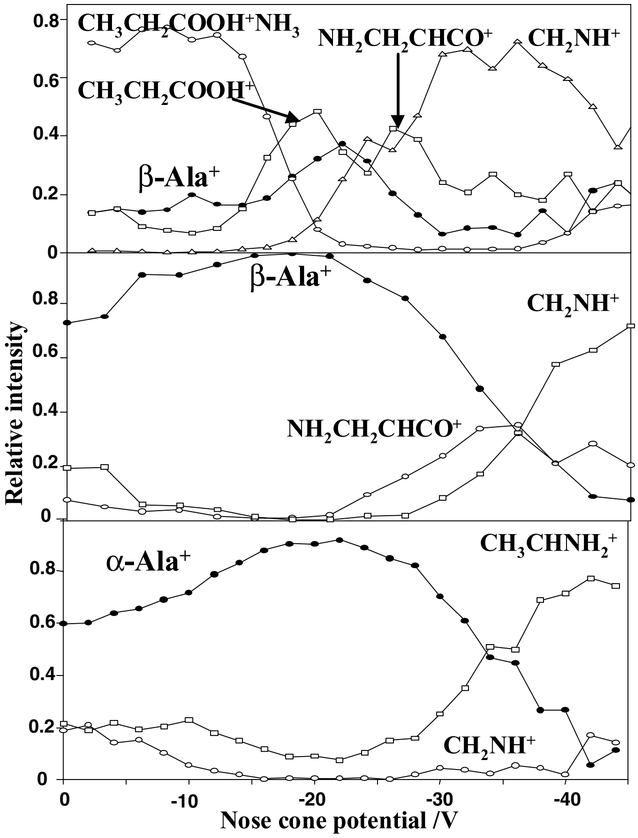

Figure 2. Comparison of multi-collision CID profiles of β-alanine cation synthesized in the reaction of NH_2OH^+ with CH_3CH_2COOH (top), ionized β-alanine (middle) and ionized α-alanine (bottom). The latter two ions were produced from β- or α-alanine vapour by electron transfer to CO^+. Some CH_2NH^+ and $NH_2CH_2CHCO^+$ ions are present initially owing to fragmentation of β-alanine cations in the process of their formation. The large $CH_3CH_2COOH^+NH_3$ signal present initially arises from the ionization of residual CH_3CH_2COOH reactant by CO^+ (used to ionize NH_2OH) followed by addition of NH_3 (produced in the vaporization of the hydroxylamine hydrochloride). The NH_3 is detached at low nose cone potentials. The rise of β-alanine$^+$ at ~ -15 V is due to fragmentation of various weak adducts of β-alanine$^+$ formed with neutral molecules present in the flow tube reactor. These are not shown for clarity. The $NH_2CH_2CHCO^+$ arises from the dissociation of β-alanine$^+$ (there is some mass overlap with $CH_3CH_2COOH^+$ at the resolution employed in the experiments).

[for example, IE(gly) = 8.9 eV] (Lias et al. 1988):

$$NH_3CH_2COOH^+ + e^- \rightarrow NH_2CH_2COOH + H \qquad (3)$$

$$NH_2CH_2COOH^+ + M \rightarrow NH_2CH_2COOH + M^+ \qquad (4)$$

Of these processes, the dissociative recombination pathway (3) is expected to be of greater interstellar significance than (4), since the very high proton affinity of glycine (PA $=211.6$ kcal mol^{-1}) strongly suggests that no major competing neutralization processes (such as proton transfer to other interstellar molecules) exist for loss of protonated glycine, while the metal atoms thought necessary for (4) are generally considered to be of very low abundance in the interstellar regions in which amino acid synthesis is feasible. Although the prediction of dissociative recombination product channels is an inexact science at best, the small set of protonated molecules for which precise experimental dissociative recombination branching ratios have been reported (H_3O^+, CH_5^+, $C_2H_3^+$, $HCNH^+$) all show that single H-atom loss [such as in (3)] is a significant product channel

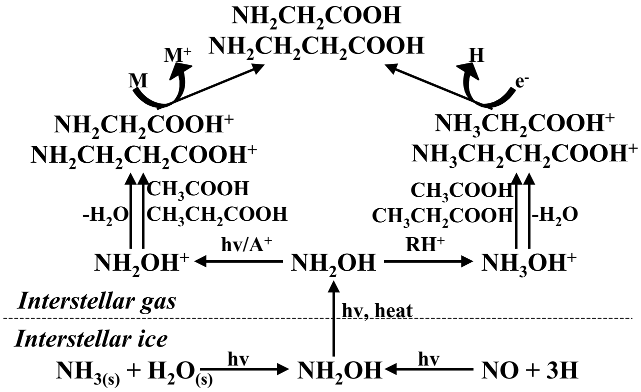

Figure 3. Proposed route for the synthesis of amino acids in interstellar environments. M and A represent any neutral atom/molecule with a suitable ionization energy (see text). RH^+ represents a proton carrier with PA(R) < PA(NH_2OH) (see text).

(Adams et al. 1991). Our proposal for the overall interstellar synthesis of the amino acids glycine and β-alanine is shown schematically in Fig. 3.

3.2 Synthesis of carboxylic acids

The immediate precursors to amino acids in our proposed interstellar synthesis are acetic and propanoic acid and ionized or protonated hydroxylamine. Acetic acid has been detected in the interstellar environment (Mehringer, Snyder & Miao 1997), hydroxylamine has been proposed as an important constituent of interstellar dust grain mantles (Charnley, Rodgers & Ehrenfreund 2001), and propanoic acid is currently an undetected, but very plausible, species in regions where acetic acid is found. We report here also a possible route for the interstellar syntheses of carboxylic acids that we have identified in our experiments. The laboratory syntheses involve gas-phase reactions of CH_2^+ and $C_2H_4^+$ with CO in the presence of H_2O. They produce acetic and propanoic acid, respectively, in the following reaction sequences:

$$CH_2^+/C_2H_4^+ + CO \rightarrow CH_2CO^+/C_2H_4CO^+ \qquad (5)$$

$$CH_2CO^+/C_2H_4CO^+ + H_2O \rightarrow CH_2CO^+H_2O/C_2H_4CO^+H_2O \qquad (6)$$

$$\begin{aligned} &CH_2CO^+H_2O/C_2H_4CO^+H_2O + H_2O \\ &\quad \rightarrow CH_3COOH^+/CH_3CH_2COOH^+ + H_2O \end{aligned} \qquad (7)$$

The products of reaction (5) have been identified from the match of their CID profiles with the CID profiles of commercial ionized acetic and propanoic acid. The second water molecule acts as a catalyst for addition of water across the C=C bond in the ketene ions by reducing the activation barrier. Reduction of activation energy for the equivalent neutral/neutral reaction has been calculated to be around 20 kcal mol^{-1} (Nguyen & Raspoet 1999).

3.3 Synthesis of hydroxylamine

A route for the synthesis of the hydroxylamine has been proposed by Nishi et al. (1984). These authors found that the ultraviolet laser irradiation of ice mixtures of water and ammonia that simulate interstellar ice grains produces NH_2OH possibly by radical recombination above the surface of the ice, reaction (8):

$$NH_2 + H + H_2O \rightarrow NH_2OH + H_2 \qquad (8)$$

In the interstellar medium the NH_2OH (IE = 10.06 eV) (Lias et al. 1988) can be ionized by photons or electron transfer. We have attempted to produce NH_2OH^+ by several different gas-phase reactions such as reaction (9), but under our experimental conditions no product ion was observed ($k_9 < 10^{-14}$ cm^3 molecule^{-1} s^{-1}):

$$HNO^+ + H_2 \rightarrow NH_2OH^+ + h\nu\left(\Delta H^{o}_{298} = -35\,\mathrm{kcal\,mol^{-1}}\right) \qquad (9)$$

(Lias et al. 1988). Hydroxylamine can easily be protonated in the gas phase of the interstellar medium because of its high proton affinity, PA(NH_2OH) = 193.5 kcal mol^{-1} (Boulet et al. 1999), Possible proton donors include H_3^+, HCO^+, CH_5^+ and H_3O^+, since PA(H_2) = 101.2, PA(CO) = 142, PA(CH_4) = 131.6 and PA(H_2O) = 166.5 kcal mol^{-1} (Lias et al. 1988). The high proton affinity of hydroxylamine, higher than those of the carboxylic acids CH_3COOH (PA =190.2 kcal mol^{-1}) and C_2H_5COOH (PA = 191.8 kcal mol^{-1}) (Lias et al. 1988), is advantageous for complex molecule formation, insofar as the viable bimolecular product channels are restricted to bond-forming reactions and not merely proton transfer.

4 DISCUSSION AND CONCLUSIONS

Having demonstrated these syntheses, we need now ask in which regions of the interstellar environment are these molecules likely to be formed and, once formed, will they survive exposure to ambient energetic radiation? The stabilities of glycine and β-alanine against ultraviolet (UV) radiation have very recently been tested by Ehrenfreund et al. (2001b) in laboratory experiments under conditions that simulate interstellar gas and interstellar grains. The results of these experiments were interpreted to indicate that 'amino acids in the gas phase will likely be destroyed during the lifetime of a typical interstellar cloud'. However, survival is more likely in UV-shielded environments such as dense molecular clouds and hot cores (star-forming regions). Hot cores are rich in ammonia and water (Ehrenfreund & Charnley 2000) which are required to initiate our proposed syntheses. Acetic acid has been detected in one core, known as the 'Large Molecule Heimat' (LMH) source within the giant molecular cloud complex Sagittarius B2 (Mehringer et al. 1997); formation of acetic acid and other complex oxygenated molecules in this source is explicable by gas-phase chemistry involving evaporation of dust grain mantles (Rodgers & Charnley 2001). This is even more likely since formic acid has been detected in the interstellar ice (Schutte et al. 1999). Glycine production in the LMH source would be fully consistent with such a model, especially given the proposed presence of NH_2OH on these (evaporating) dust grain mantles (Charnley et al. 2001), and this is also the most probable source for interstellar detection of propanoic acid and therefore, we suggest, β-alanine. Radio astronomical detection of the NH_2OH molecule, the microwave spectrum of which has recently become available (Luckhaus 1997; Morino et al. 2000), would provide additional valuable evidence on promising sources for interstellar amino acids.

The gas-phase synthesis of alanine demonstrated by our experiments leads to the preferential formation of β-alanine. Interestingly, β-alanine is the most abundant of all the amino acids, including glycine, detected in CI chondrites (see Table 1) that are believed to originate from extinct comets (Campins & Swindle 1998; Lodders & Osborne 1999). Since cometary nuclei may be low-density aggregates of interstellar dust (Lodders & Osborne 1999), the observed 10:1 preference of β-alanine over α-alanine in CI chondrite meteorites may be a manifestation of the gas-phase synthesis that we have proposed.

Table 1. Amino acid content in CI (Orgueil and Ivuna) chondrite meteorites as reported by Ehrenfreund et al. (2001a). Here we show the average percentage of each amino acid in both meteorites [nstead of the amounts of amino acids in p.p.b. given by Ehrenfreund et al. (2001a)]. CI chondrites are the class of carbonaceous chondrite meteorites with a composition similar to the composition of the meteorite Ivuna (which fell in Tanzania in 1938). The letters CI stand for C-carbonaceous and I-Ivuna.

Amino acid	(per cent)
Glycine	17
β-alanine	40
α-alanine	4.4
α-ABA	0.3*
β, γ-ABA	23
α-AIB	1*
β-AIB	2.8
Isovaline	4*
Other α-a. acids	7.5
Total:	
α-amino acids	17
β, γ-amino acids	66
Glycine	17

*Numbers shown are close to the detection limit.

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