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Recent Selected Ion Flow Tube (SIFT) Studies Concerning the Formation of Amino Acids in the Gas Phase

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ABSTRACT

Recently the simplest amino acid, glycine, has been detected in interstellar clouds, ISC, although this has since been contested. In order to substantiate either of these claims, plausible routes to amino acids need to be investigated. For gas phase synthesis, the SIFT technique has been employed to study simple amino acids via ion-molecule reactions of several ions of interstellar interest with methylamine, ethylamine, formic acid, acetic acid, and methyl formate. Carboxylic acid type ions were considered in the reactions involving the amines. In reactions where the carboxylic acid and methyl formate neutrals were studied, the reactant ions were primarily amine ion fragments. It was observed that the amines and acids preferentially fragment or accept a proton whenever energetically possible. NH_3^+, however, uniquely reacted with the neutrals via atom abstraction to form NH_4^+. These studies yielded a body of data relevant to astrochemistry, supplementing the available literature. However, the search for gas phase routes to amino acids using conventional molecules has been frustrated. Our most recent research investigates the fragmentation patterns of several amino acids and several possible routes have been suggested for future study.

1. Introduction

Astrochemical models have given insight into the formation of ions and molecules in interstellar clouds (ISC)(Chyba & Sagan 1992; Delsemme 2000) and are of much importance today in the interpretation of data from several NASA missions. Deep Impact and Stardust are directly interested in the composition of comets and what their composition might mean concerning interstellar molecules. Amino acids may very well be detected in either mission and have been detected on meteorites in the past (Chyba 1990); they are a class of molecules which may be essential to the formation of life. The origin of amino acids on meteorites is not entirely understood. One explanation is that asteroids and comets collect amino acids and other organic molecules from the ISC as they travel through space (Chyba et al. 1990;

Delsemme 2000). If this is the case, astrochemical models may play an important role in determining the origin of amino acids in these ISC. Recently the simplest amino acid, glycine, has been detected in ISC (Kuan et al. 2003) although this report has since been contested (Snyder et al. 2005). In order to substantiate either of these possibilities, plausible routes to amino acids need to be investigated in the laboratory. Indeed such studies, coupled with detailed modeling, may be the only way that the gas phase existence of prebiotic molecules can be established. For gas phase synthesis, the SIFT technique is useful to study possible routes to simple amino acids via ion-molecule reactions. Neutral molecules, which have been detected in the ISC, include methylamine, formic acid, acetic acid, and methyl formate (Wooten 2002). This paper reports attempts to investigate reactions of these and similar molecules with ions, many of which have been observed in the ISC as well. Carboxylic acid type ions were studied in the reactions involving the amines (Jackson et al. 2005a). In reactions where the carboxylic acid and methyl formate neutrals were studied, the reactant ions were primarily amine ion fragments (Jackson et al. 2005b). Reaction rate coefficients and product distributions of the reactions studied supplement theoretical models of the ISC.

2. Experimental

An overview of the SIFT technique, described in detail elsewhere (Adams & Smith 1976), will be given as it pertains to this particular study. A source gas is introduced into a microwave cavity, MC, ionization source. Ions are drawn into a quadrupole mass filter where the primary reactant ion is selected from the various possible ions via its mass to charge ratio. The primary ion is then introduced into a He carrier gas flow at a total pressure of ~ 0.5 Torr. A neutral reactant gas is added to the flow at one of three ports allowing for varying reaction times. The detection system is composed of a nose cone sampling orifice at a small negative potential followed by a series of focusing lens elements and a second quadrupole mass filter with an electron multiplier. For the introduction of sticky gases such as carboxylic acid vapors, which dimerize, a special procedure was employed (Jackson, et al. 2005b).

3. Results and Discussion

For a complete listing of all reactions studied including data for product distributions and rate coefficients refer to Jackson et al. 2005a, 2005b. Many of the reactions studied resulted in dissociative charge transfer fragmentation of the neutral. These reactions though not necessarily intended to produce amino acids, e.g. Ar^+ reactions, do reveal which fragments form in greatest abundance and thus the connectivity on the reaction potential surface. The preferred fragment for each amine is $H_2CNH_2^+$, and the acids (RCOOH) fragment into RCO^+ and $COOH^+$ solely with RCO^+ in greatest abundance. Methyl formate fragments into H_3CO^+, HCO^+, and CH_3^+ in descending order of abundance. Reactions which result in proton transfer can be predicted by observing relative proton affinities; however, the reaction of NH_3^+ with the neutrals results in H atom abstraction to form NH_4^+ since proton transfer is endothermic. The reactions of NH_3^+ with the neutrals may play a role in the ISC since NH_3^+ reacts slowly with molecular hydrogen.(Smith & Adams 1980) If this is the case, the abstraction reactions of NH_3^+ with the neutrals may form radical species, which could possibly participate in a further reaction especially if assisted catalytically by molecular dust grains to form more complex species. NH_4^+ does not react with molecular hydrogen and is therefore available for further reaction. Previous studies have indicated that NH_4^+ tends to associate with molecules such as acetic acid. Upon electron-ion recombination, it is possible that glycine could be formed. Blagojevic et al. report ion-molecule reactions that produce glycine and β-alanine using the primary ions $NH_{2,3}OH^+$ (Blagojevic, Petrie, & Bohme 2003). These reactions reportedly undergo "condensation" ejecting water and attaching the amine group to the proper carbon of acetic acid and propanoic acid. However, the interstellar importance of $NH_{2,3}OH^+$ is not known. These molecules have not been observed in the ISC nor has their reactivity with molecular hydrogen been investigated (Blagojevic et al. 2003). Even so, the chemistry indicates that similar reaction pathways involving "condensation" reactions may be possible. For example, reactions of certain neutrals with NH_4^+ may undergo a similar process condensing molecular hydrogen.

4. Conclusion

The present studies reveal that current efforts to synthesize amino acids in the gas phase using conventional molecules have limited success. Many plausible pathways result in proton transfer or fragmentation stifling a progressive synthesis of more complex organics. Though many possible 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 useful data has been collected. The success of Blagojevic et al. indicates that so-called condensation reactions with NH_4^+ type species with certain neutrals are successful to some degree. Also, as indicated by the reactions of NH_3^+, abstraction of H produces complex neutral radicals, which may react with other radicals or ions to produce more complex species. These kinds of reactions are difficult to study and have not been investigated. Finally, the electron-ion recombination of species such as acetic acid associated with NH_4^+ may yield a product of interest. Little is known about the structure and bonding of these associated products, and further investigation in both theory and experiment is needed. As we have shown, there are many possible routes to amino acids in the ISC that have not been investigated yet. These must be examined to verify the possible existence of glycine and other amino acids in the ISC.

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