

## Laboratory Studies of Stabilities of Heterocyclic Aromatic Molecules: Suggested Gas Phase Ion-Molecule Routes to Production in Interstellar Gas Clouds

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### ABSTRACT

Several ring compounds have been detected in interstellar gas clouds, ISC, including the aromatic, benzene. Polycyclic aromatic hydrocarbons, PAHs, have been implicated as carriers of diffuse interstellar bands (DIBs) and unidentified infrared (UIR) bands. Heterocyclic aromatic rings of intermediate size containing nitrogen, possibly PreLife molecules, were included in early searches but were not detected and a recent search for Pyrimidine was unsuccessful. Our laboratory investigations of routes to such molecules could establish their existence in ISC and suggest conditions under which their concentrations would be maximized thus aiding the searches. The stability of such ring compounds ( $C_5H_5N$ ,  $C_4H_4N_2$ ,  $C_5H_{11}N$  and  $C_4H_8O_2$ ) has been tested in the laboratory using charge transfer excitation in ion-molecule reactions. The fragmentation paths, including production of  $C_4H_4^+$ ,  $C_3H_3N^+$  and HCN, suggest reverse routes to the parent molecules, which are presently under laboratory investigation as production sources.

### 1. Introduction

A series of small ring molecules ( $SiC_2$ ,  $C_3H$ ,  $SiC_3$ ,  $C_3H_2$ ,  $CH_2OCH_2$ ,  $C_2H_3N$ ,  $C_2H_5N$ ,  $C_4H_4NH$ ; Dickins et al. 2001; Kuan et al. 2004) has been detected in interstellar clouds, ISC (Wooten 2002; Kuan et al 2004). In addition, the larger ring, benzene, ( $C_6H_6$ ) has been detected (Wooten 2002). Benzene has also been tentatively detected in the Titan atmosphere and (although this may be a contaminant; Waite et al. 2005) it has been included in recent models of this atmosphere (Wilson & Atreya 2004). Multiple rings, PAHs, are thought to be responsible for at least some of the DIBs and UIR lines (van der Zwet & Allamandola 1985; Leger & dHendecourt 1985; Salama, & Allamandola 1993), although this is still in contention. Other ring molecules ( $C_5H_5N$  Pyridine,  $C_4H_4N_2$  Pyrimidine,  $C_4H_5N$  Pyrrole,  $C_3H_4N_2$  Imidazole) were included in early searches (1973-1981), but were not detected (Simon & Simon 1973; Myers, Thaddeus, & Linke, 1980; Irvine, W., et al. 1981). There has also

been one recent unsuccessful search for  $C_4H_4N_2$  (Kuan et al. 2003, 2004). These larger rings are of interest since substituted versions are prebiotic molecules (e.g., the nucleotide bases of DNA (thymine, cytosine, uracil) are substituted pyrimidines). The lack of detections is not surprising since as molecules get larger and more floppy, the emissions are divided amongst more lines and are thus weaker. An example is the disputed detection of glycine (Kuan et al. 2003; Snyder et al. 2005). Here, ion chemical modeling with laboratory data can help by showing where detection is most likely. Indeed, ion chemical modeling may be the only way to establish the presence of some molecules. Thus, based on all this information, it can be concluded that there is little doubt that heterocyclic aromatic rings are present in ISC and in the Titan atmosphere. But what is the stability of such aromatic rings and how long can they survive in these hostile environments? We have investigated this by studying charge transfer reactions with ions having recombination energies from 21.6 to 4.8 eV (the recombination energies of  $NH_4^+$  and  $H_3O^+$  are 4.8 and 6.4 eV respectively to  $NH_3 + H$  and  $H_2O + H$ ).

## 2. Experimental

Measurements were made using the Selected Ion Flow Tube (SIFT) technique, which has been discussed in detail in the literature (Adams & Smith 1976a, b). Reactant ions were generated in a remote ion source, mass selected and injected into flowing He at  $\sim 0.5$  Torr. Reactant gases were added to the flow, and the primary and secondary ions detected by a downstream mass spectrometer with ion counting. All the measurements were made at 300K, although there is the ability to make measurements over the temperature range 80 to 600 K. Rate coefficients are accurate to within 20% (for the sticky gases used in this study) and products to within  $\pm 5$  in the percentage.

## 3. Results

Data were obtained for the reactions of  $Ne^+$ ,  $Ar^+$ ,  $N_2^+$ ,  $N^+$ ,  $Kr^+$ ,  $O^+$ ,  $O_2^+$ ,  $NH_3^+$ ,  $H_3O^+$  and  $NH_4^+$  with  $C_5H_5N$ ,  $C_4H_4N_2$ ,  $C_5H_{11}N$  (Piperidine) and  $C_4H_8O_2$  (Dioxane). Comparisons were also made with literature data for  $C_6H_6$  (Arnold et al. 1999). All reactions occur with close to unit efficiency when compared with the theoretical collisional rate (Su, & Chesnavich 1982). For ions with recombination energies below  $\sim 12$  eV ( $O_2^+$ ,  $NH_3^+$ ,  $H_3O^+$  and  $NH_4^+$ ), there is no fragmentation of  $C_5H_5N$  or  $C_4H_4N_2$ , but the fragmentation increases as the recombination energy gets larger. In particular, initially there is one important type of fragmentation channel,  $C_4H_4^+ + HCN$  for  $C_5H_5N$  and  $C_3H_3N^+ + HCN$  for  $C_4H_4N_2$  charge transfer reactions. Note that these ions have the same masses as  $C_3H_2N^+$  and  $C_2N_2H^+$ , however, so far the identity of the ion as  $C_4H_4^+$  has been established by deuterium labeling. Such reactions may be significant since HCN is important in both the Titan atmosphere (the

reactions with  $\text{N}^+$  and  $\text{N}_2^+$  are particularly important since these are major precursor ions in the Titan chemistry) and dense ISC (Tanguy et al. 1990; Snyder, L. E. & Buhl 1971). Other fragmentation channels become important at the higher exothermicities. For  $\text{C}_6\text{H}_6$ , there is less fragmentation at recombination energies of 12 to 13 eV. This is consistent with the observations of Peeters et al. (2005), which showed benzene to be the more stable against uv radiation than the substituted rings. For the low recombination energy protonated ions ( $\text{H}_3\text{O}^+$  and  $\text{NH}_4^+$ ), only proton transfer is observed.

#### 4. Conclusion

It has been shown from charge transfer reactions, that although quite stable and able to exist quite well in dense ISC,  $\text{C}_5\text{H}_5\text{N}$  and  $\text{C}_4\text{H}_4\text{N}_2$  are not as stable as  $\text{C}_6\text{H}_6$ . In particular, at energies at which the ionized species begin to fragment, the fragmentation channels are to  $\text{C}_4\text{H}_4^+ + \text{HCN}$  and  $\text{C}_3\text{H}_3\text{N}^+ + \text{HCN}$  respectively. This shows connectivity on the potential surfaces from the fragments to the undissociated ions. By microscopic reversibility, association of these product species could, in principle, produce rings. It is intended to study these and analogous reactions as a source of heterocyclic rings.

NSF funding of Grant 0212368 is gratefully acknowledged.

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