Laboratory Studies of PAH Cations of Interest for Studies of the Diffuse Interstellar Medium

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We describe laboratory studies of the chemical properties of small PAH cations which have been suggested as possible carriers of the unidentified diffuse interstellar bands. Our measurements, carried out through the use of a tandem-flowing afterglow-selected ion flow tube (FA-SIFT), show that PAH cations and dehydrogenated PAH cations will quickly migrate to their protonated forms in the diffuse ISM, through the addition of atomic or molecular hydrogen. To date we have made these measurements for ionized benzene ($C_6H_6{}^+$), napthalene ($C_{10}H_8{}^+$), and pyrene ($C_{16}H_{10}{}^+$), as well as their dehydrogenated forms, with similar results in each case. The reaction rates with hydrogen are greater than those for other neutral collision partners (including small molecules); this, combined with the overwhelming abundance superiority of hydrogen, means that protonation is the dominant chemical process. Physical processes such as recombination with electrons and dehydrogenation via UV absorption may be competitive, so full models are needed in order to determine the ultimate fate of small PAH cations in the diffuse ISM. For now we can say that small PAH cations are probably not good candidates as diffuse band carriers, but large PAHs, large PAH ions, and various forms of radical PAH fragments are not ruled out. In addition to summarizing results already obtained, we describe plans for future laboratory work on this problem.

Evidence that large molecular species are important in the diffuse interstellar medium comes from the ultraviolet, the optical, and the infrared regions of the spectrum. In the UV we have continuous and selective extinction which is attributed by some to a suite of large organic molecules, particularly the polycyclic aromatic hydrocarbons (PAHs; see, for example, reviews by Allamandola *et al.* 1989, or Puget and Léger 1989). In the visible there are about 200 unidentified diffuse interstellar bands (DIBs), which appear likely to be formed by large organic molecules or molecular ions (e.g. see reviews in Tielens and Snow 1995). And in the infrared there are the so-called unidentified infrared emission features (UIRs), which can be explained as due to large organics, again specifically PAHs (e.g. Puget and Léger 1989; reviews cited above) or more likely, their positive ions (e.g. Hudgins *et al.* 1998).

The classes of molecules invoked to explain these observational phenomena include primarily the PAHs and their ionic counterparts, as well as heterocyclic variants, and also carbon chain molecules. The carbon chains suggest themselves due to their preponderance among the larger species identified in dark clouds through their rotational emission spectra (e.g. Thaddeus 1995), and also because they appear capable of producing visible-wavelength spectra similar qualitatively (and perhaps quantitatively) to the DIBs (e.g. the work of John Maier's group, especially Lockwood *et al.* 1998).

In view of the growing evidence that large organic molecules or molecular ions may be abundant in the diffuse interstellar medium, we have embarked on a laboratory study of the chemistry (and eventually the optical spectroscopy) of large organic molecules that may be important in the diffuse interstellar medium. Our experiments have been carried out in a tandem flowing afterglow-selected ion flow tube (FA-SIFT; Van Doren *et al.* 1987), which is ideally suited to the study of ion-atom reactions. The $C_6H_6{}^+$, $C_{10}H_8{}^+$ and $C_{16}H_{10}{}^+$ ions were formed by Penning ionization of the neutral parent species with metastable argon atoms which are generated in a cold cathode discharge (Howorka 1978); this relatively gentle ionization process cleanly generates the parent cation. The dehydrogenated ions were formed by chemical ionization with helium ions that were produced by electron impact ionization. In both cases the reactant ions were extracted from the source region, mass-selected, and injected into the reaction flow tube where they were thermalized by collisions with helium. We studied the dehydrogenated forms $C_{10}H_7{}^+$ and $C_{16}H_9{}^+$ because in the diffuse ISM such species are likely to be present as a result of photodissociation of the parent PAH cations.

The selection of neutral reactants was guided by the expected abundances in the diffuse interstellar medium (e.g. Savage and Sembach 1996). The DIBs appear to form most efficiently in H I clouds, which are dominated by atomic hydrogen but which also contain substantial quantities of molecular hydrogen, atomic nitrogen, and atomic oxygen (other cosmically abundant elements such as carbon are predominantly ionized in H I clouds and will not react with PAH cations).

In our experiments H_2 was added through a manifold of inlets, and kinetics were measured as a function of reaction distance. Atomic hydrogen was generated by passing ultra-high purity H_2 through a microwave discharge tube; calibration reactions were used to measure the resulting atomic hydrogen density (Petrie *et al.* 1992; Scott *et al.* 1997; Tosi *et al.* 1984) and indicated that dissociation ratios were about 30 percent. Atomic nitrogen was formed by passing N_2 through the microwave discharge, and atomic oxygen was formed by titration of atomic nitrogen with nitric oxide (Setser *et al.* 1979) $N + NO \rightarrow N_2 + O$. Dissociation ratios of N_2 were about 2 percent. Small corrections to the rate constants were made to account for wall recombination and mixing of the atomic reagents. Corrections for three-body relaxation via collisions with helium atoms in our apparatus were facilitated by the work of our colleague Y. Keheyan, who measured purely radiative rates for some of the same reactions, using a Fourier transform-ion cyclotron resonance instrument.

Our initial studies (reported in Snow *et al.* 1998) have focused on PAH cations, which appear to be viable candidates as the carriers of the DIBs (Van der Zwet and Allamandola 1985; Léger and d'Hendecourt 1985; Crawford *et al.* 1985), an idea that has been supported by laboratory spectroscopy of PAH cations in inert matrices (Salama and Allamandola 1992a,b; Léger *et al.* 1995). Beginning with cations of the simplest aromatic (benzene; C_6H_6) and moving progressively to cations of larger species (naphthalene, $C_{10}H_8$; pyrene, $C_{16}H_{10}$; and most recently chrysene, $C_{18}H_{12}$ and coronene $C_{24}H_{12}$), we have been able to derive rate coefficients for reactions with neutral species that are abundant in the diffuse interstellar medium. Our principal results have been as follows:

First, we found that the reactions of atomic hydrogen dominate over those of other abundant neutrals, for two reasons: (1) hydrogen has larger reaction rate coefficients with PAH^+ than do other neutrals such as N and O; and (2) hydrogen is far more abundant than other potential reaction partners (by about a factor of 10^4 in the cases of N and O and more for other atoms or simple molecules).

Second, we found that the parent PAH cations quickly migrate to their protonated forms (i.e. the cationic form having one additional hydrogen atom), on timescales more rapid than those for other processes such as electron recombination (but note that the electron recombination rate coefficients are not well known). The transition to the protonated form also occurs for PAH cations that are initially dehydrogenated, either by the addition of an H_2 molecule (also measured in our experiments) or successive additions of hydrogen atoms. Once in the hydrogenated form, the PAH cations have closed shells and become relatively inert, with very slow reaction rate coefficients for further interaction with the reagents studied.

Table 1 summarizes our measurements of reaction rate coefficients for the cations of benzene, naphthalene, and pyrene (including dehydrogenated and protonated forms).

Table 1. Measured reaction rate coefficients

Reactants	H_2	H	O	N
benzene				
$C_6H_5{}^+$	5.0×10^{-11}			
$C_6H_6{}^+$	no rxn	2.2×10^{-10}	9.5×10^{-11}	1.2×10^{-10}
$C_6H_7{}^+$	no rxn	$\approx3\times10^{-12}$		
naphthalene				
$C_{10}H_7{}^+$	5.2×10^{-11}			
$C_{10}H_8{}^+$	no rxn	1.9×10^{-10}	1.0×10^{-10}	2.3×10^{-11}
$C_{10}H_9{}^+$	no rxn	$\approx4\times10^{-12}$		
pyrene				
$C_{16}H_9{}^+$	no rxn	$\approx1.6\times10^{-10}$	$\approx2\times10^{-10}$	$\approx3\times10^{-11}$
$C_{16}H_{10}{}^+$	no rxn	1.4×10^{-10}	9.5×10^{-11}	1.5×10^{-12}
$C_{16}H_{11}{}^+$	no rxn	$\approx4\times10^{-12}$		

It is important to compare our measured chemical destruction rates for PAH cations with other processes such as electron recombination. We can compare the timescales for hydrogenation ($\tau_H = 1/\mathrm{k}n_H$) and electron recombination ($\tau_e = 1/\alpha n_e$). Here α is the electron recombination rate coefficient and n_e is the electron density. The ratio of the two timescales is $\tau_H/\tau_e = \alpha n_e/\mathrm{k}n_H$. It is typically assumed that all of the electrons in the diffuse interstellar medium come from the (complete) ionization of carbon, so that the ratio n_e/n_H equals the cosmic ratio of carbon to hydrogen, which we take (Snow and Witt 1995) to be 1.4×10^{-4}; for diffuse clouds this ratio is independent of the overall cloud density. Thus the ratio of timescales becomes $\tau_H/\tau_e = 1.4\times10^{-4}(\alpha/\mathrm{k})$. The electron recombination rate coefficient (α) has been measured only for the benzene and naphthalene cations (Abouelaziz *et al.*

1993). Here, for illustrative purposes, we consider the latter ($C_{10}H_8{}^+$). Using the value k = 4.2×10^{-10} cm^{3}s^{-1} as discussed above, and taking $\alpha(T) = 3.0\times10^{-7}(T/300)^{-1/2}$ (Abouelaziz *et al.* 1993; Salama *et al.* 1996), we find that at T = 100 K the ratio of timescales is τ_H/τ_e = 0.17. Thus in a typical diffuse cloud hydrogenation dominates (by a factor of 6) over recombination, and we can expect PAH cations to migrate to their protonated form before recombining.

Thus we conclude that small PAH cations in the diffuse ISM will migrate to their protonated forms and remain there until destroyed by some non-chemical process. This would seem to rule out small PAH cations as carriers of the DIBs, but it is not certain whether this conclusion extends to large PAH cations, to a host of heterocyclic PAH cations, or to those with various kinds of end groups such as aliphatic chains. These possibilities require further study, which is a part of our planned research program for the coming months.

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