CHEMICAL PROPERTIES OF INTERSTELLAR POLYCYCLIC AROMATIC MOLECULES

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There is substantial evidence of the presence of polycyclic aromatic molecules, mainly hydrocarbons (PAH's) in the interstellar medium (Léger and Puget, 1984, Allamandola et al. 1985, Léger and d'Hendecourt in these proceedings). They should contain typically N = 20-100 carbon atoms, and they can contain perhaps 1-10 % of the total interstellar carbon. I have recently discussed in detail their physical and chemical properties (Omont, 1986), which should be intermediate between that of conventional interstellar molecules and grains.

Depending on the UV radiation and the electron density their charge can be either 0 or \pm e : in the vicinity of strong UV sources, such as in reflection nebulae, they are positively charged ; in the normal diffuse medium they are probably mostly neutral with a significant fraction positively charged ; in dense molecular clouds, when they are protected from photodetachment (attachment energy \sim 1-1.5 eV), they are mostly negatively charged, and they can bear a significant fraction of the negative charge.

For $N_{2} > 20$ they are relatively stable against photodissociation. However, frequent absorption of UV photons or other mechanisms favours internal reorganization or possibly photolysis of H atoms. A minimum rate for the last process is given by the RRKM theory of unimolecular reactions assuming a complete redistribution in the vibration modes of the PAH of the energy of the UV photons absorbed. It is inefficient for $N_{c} \gtrsim 25$ in the normal diffuse interstellar medium ($N_{c} \gtrsim 30-40$ by twophoton processes in regions of very strong UV radiation). However, it is not impossible that the probability of direct photolysis after the absorption of the photon is appreciable, and thus maintains a significant proportion of radical sites on the periphery of heavy PAH's. Atoms (and radicals) of the gas probably accrete efficiently on such radical sites, opening the possibility that a significant proportion of heteroatoms, such as 0, is present at the periphery of the interstellar PAH's. Growth by accretion of C atoms, or sputtering by reactions with O atoms (Duley and Williams 1986) can result in such processes which remain very uncertain.

Because of the large uncertainty on the values of the adsorption energy of atoms (H in particular) on graphite surfaces, it is very dif-

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M. S. Vardya and S. P. Tarafdar (eds.), Astrochemistry, 545–546. © 1987 by the IAU. ficult to appreciate the possible importance of catalytic reactions (e.g. H_2 formation) on non radical PAH's. However, as the total surface per unit volume of interstellar PAH's is comparable to that of grains, the potential role of PAH's on the chemistry of the interstellar gas should be considered seriously.

In particular, ions of the gas react with neutral or negatively charged PAH's either by simple charge exchange, or by more complicated processes including association and formation of small fragments, as demonstrated by the laboratory studies of the reaction of C^+ with C_6H_6 (Smith and De Corpo 1976, Bohme et al. 1982). Reaction rates of gas ions are very fast with negatively charged PAH's, and even with neutral ones because of their large polarizability. Accordingly, PAH's are probably a major sink for atomic ions of the gas.

Besides photodissociation and possible chemical sputtering, the main destruction processes are (temporary) accretion onto grains in molecular clouds, and sputtering in the hot medium and in shocks. Contrary to grains, because of their small mass, their velocity remains generally comparable to the thermal velocity (a few 10^3 cm/s), except in magnetic shocks. In dense clouds their accretion onto grains is slowed down by their negative charge ; the time constant for this accretion is probably comparable to that of grain coagulation. It is likely that the accreted PAH's are efficiently desorbed in moderate velocity shocks. Their overall lifetime in the interstellar medium, because of periodic passages in strong shocks and in the hot medium, is probably comparable to that of small grains (a few 10^8 years).

Some formation of PAH's is likely in cold stars, but it is too slow to account for their observed abundance in the interstellar medium. Because of the small interplane binding energy in graphite compounds, PAH's are likely products of cleaving of carbon grains in grain-grain collisions in moderate velocity shocks. The other possible formation mechanism is synthesis from smaller carbon chains, if the association reactions are efficient enough. In any case, growth of PAH's by accretion of C^+ or of other carbon species can be very fast ; and the time constant for doubling their mass in extended molecular clouds can be as small as a few 10⁴ years.

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