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NOVEL CHEMICAL ROLE FOR POLYCYCLIC AROMATIC HYDROCARBONS IN THE SYNTHESIS OF INTERSTELLAR MOLECULES

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ABSTRACT

With naphthalene as a model polycyclic aromatic hydrocarbon (PAH) molecule, results of laboratory measurements are presented for chemistry initiated by atomic silicon ions which indicate a novel chemical role for PAH molecules in the synthesis of interstellar molecules containing silicon and, by inference, of interstellar molecules generally.

Subject headings: interstellar molecules — molecular processes

I. INTRODUCTION

The possible interstellar presence of polycyclic aromatic hydrocarbon (PAH) molecules has sparked considerable interest in the manner in which PAH molecules may influence the gas-phase chemistry of different interstellar environments (Duley and Williams 1986; Omont 1986; Lepp and Dalgarno 1988; Lepp *et al.* 1988). For example, it has been suggested that PAH molecules may attach electrons, ions, or atoms and molecules, and that ensuing chemistry may provide new routes for neutralization and the synthesis of simple and complex molecules. Such processes have been adopted in recent detailed models of the chemistry of dense and diffuse interstellar clouds (Lepp and Dalgarno 1988; Lepp *et al.* 1988). But much of this chemistry is still speculative as very few, if any, laboratory measurements or quantum chemical calculations are available for corroboration. Here we report the results of a laboratory study of the chemistry initiated by atomic silicon ions in the presence of naphthalene, the simplest model PAH molecule, which will begin to provide an experimental data base. PAH molecules are expected to be a particularly important sink for atomic silicon ions in interstellar environments because Si^+ does not efficiently recombine with electrons or react with hydrogen (Wlodek, Fox, and Bohme 1987). The laboratory measurements provide experimental evidence for the occurrence of ion attachment and identify a novel chemical role for PAH molecules in the synthesis of complex molecules. They may also be useful in understanding chemistry catalyzed by grain surfaces, particularly on grains made of graphitic material (Tielens and Allamandola 1987).

II. EXPERIMENTAL RESULTS

The experiments were performed with the Selected-Ion Flow Tube (SIFT) instrument in the Ion Chemistry Laboratory at York University. The instrument and its operation have been described in detail (Mackay *et al.* 1980; Raksit and Bohme 1983; Wlodek, Fox, and Bohme 1987). When naphthalene vapor was introduced into the flow tube upstream into helium carrier gas in which ground-state Si^+ cations were established as the dominant ions, the mass spectrum observed downstream provided evidence both for the capture of Si^+ by the naphthalene molecules and for the transfer of an electron which leaves naphthalene ionized. Under the adopted experimental operating conditions these two events occurred in a proportion of about 7 to 1, respectively, and can be described by reaction (1):

$$Si^+ + C_{10}H_8 \rightarrow (SiC_{10}H_8)^+ \qquad (1a)$$

$$\rightarrow C_{10}H_8{}^+ + Si\,. \qquad (1b)$$

The electron transfer channel is nearly energy-resonant in view of the ionization energies for Si, 8.151 eV, and naphthalene, 8.136 eV. The helium pressure in these experiments was 0.35 torr (1.1×10^{16} atoms cm^{-3}), and the gas temperature was 296 ± 3 K. Under these conditions the attachment of Si^+ to naphthalene, reaction (1a), presumably occurs in a termolecular fashion, but radiative bimolecular association is also possible although its contribution is unknown.

Downstream addition of molecules, M, was observed to lead to a reactive decay of the adduct ion $(SiC_{10}H_8)^+$ with the concomitant production of $C_{10}H_8{}^+$ in a reaction of type (2):

$$(SiC_{10}H_8)^+ + M \rightarrow C_{10}H_8{}^+ + (SiM)\,. \qquad (2)$$

We observed fast reactions of type (2) with acetylene and diacetylene, only a very slow reaction with O_2, and no reactions with deuterium, nitrogen and benzene. The experimental results are summarized in Table 1.

III. DISCUSSION

The range in reaction rate from very fast to immeasurably slow observed for the six molecules chosen as reactants indicates that the formation of $C_{10}H_8{}^+$ is due to chemical interaction of type (2) and not collision-induced dissociation of $(SiC_{10}H_8)^+$. The driving force for the reactions of type (2) observed with O_2, acetylene and diacetylene must be formation of stable neutral molecules containing silicon, viz., SiO_2, SiC_2H_2, and SiC_4H_2, although these could not be monitored with the downstream mass spectrometer. The production of $C_{10}H_8{}^+$ and a free silicon atom by collision-induced dissociation is precluded by its endothermicity which is equal to the binding energy of Si to ionized naphthalene.

Reaction (2) provides a novel pathway for the synthesis of SiC_4H_2, SiC_2H_2 and SiO_2. The most stable isomer of SiC_2H_2 has been predicted from ab initio calculations to be

TABLE 1

SUMMARY OF KINETIC DATA OBTAINED FOR THERMAL REACTIONS OF $(SiC_{10}H_8)^+$ CATIONS IN HELIUM CARRIER GAS AT 296 ± 3 K

REACTANT	PRODUCTS	BRANCHING RATIO[a]	RATE CONSTANT	
			Experiment[b]	Theory[c]
D_2	No reaction	...	<0.0035	11
N_2	No reaction	...	<0.004	6.3
C_6H_6	No reaction	...	<0.006	10
O_2	$C_{10}H_8{}^+ + (SiO_2)$	1.0	0.0037	5.8
C_2H_2	$C_{10}H_8{}^+ + (SiC_2H_2)$	0.9	0.63	9.1
	$(SiC_{12}H_{10})^+$	0.1	...	...
C_4H_2	$C_{10}H_8{}^+ + (SiC_4H_2)$	1.0	10.0	9.3

[a] Branching ratios are estimated from experimental repetition to have a relative accuracy of within ±30%.

[b] Effective bimolecular rate constant in units of 10^{-10} cm^3 molecules^{-1} s^{-1} at a total helium pressure of 0.35 torr and density of 1.1×10^{16} atoms cm^{-3}. The accuracy is estimated to be better than ±30%.

[c] Collision rate constant in units of 10^{-10} cm^3 molecules^{-1} s^{-1} derived from a combined variational transition-state theory/classical trajectory study (Su and Chesnavich 1982).

3-silacyclopropenylidene (Frenking, Remington, and Schaefer 1986). It is reasonable to expect the formation of this isomer during the interaction of $(SiC_{10}H_8)^+$ with a C_2H_2 molecule because no significant rearrangement is required and other isomers are higher in energy: vinylidenesilene, CH_2CSi:, and silylenylacetylene, $HSiC_2H$, are higher in energy by approximately 17 and 22 kcal mol^{-1}, respectively (Frenking, Remington, and Schaefer 1986). It is interesting to note that gas-phase experiments have recorded a rapid reaction of ground-state silicon atoms with acetylene which was presumed to result from efficient addition with ring insertion (Husain and Norris 1978). Cyclic attachment of the silicon atom to a triple bond is also expected for the analogous reaction of $(SiC_{10}H_8)^+$ with diacetylene. The extremely slow reaction of $(SiC_{10}H_8)^+$ with oxygen is probably due to an energy barrier against insertion into the O—O bond which is required for the formation of SiO_2.

Given that naphthalene has a slightly lower ionization energy than Si, we propose that intramolecular charge transfer in the $(SiC_{10}H_8)^+$ adduct ion will leave a neutral Si atom situated above (and not part of) a positively charged carbon lattice. Mechanistically, reaction (2) then may be viewed as a neutral reaction between Si and the incoming reactant molecule M proceeding on a positively charged naphthalene "surface." The exothermicity of chemical bond formation between Si and M will be sufficient to release the product SiM molecule from this "surface." We can also expect the $(SiC_{10}H_8)^+$ adduct ion to be formed from the attachment of free silicon atoms to ionized naphthalene and for it also to trigger reactions of type (2).

Attempts to observe the carbon analog of reaction (2) indicated a much less favorable formation of the adduct ion $(C_{11}H_8)^+$ by the analog of reaction (1a). The higher electron recombination energy of C^+, 11.260 eV, leads predominantly to electron transfer in this case. Preliminary measurements suggest a ratio of 0.4 to 1 for the association and electron transfer channels as opposed to the ratio of 7 to 1 obtained for the reaction with Si^+ under similar operating conditions. Neutral reactions of type (3) analogous to reaction (1a) have been invoked by Lepp *et al.* (1988) to form adducts which react further with atomic species to produce new routes for the synthesis of complex molecules in diffuse clouds (Lepp *et al.* 1988):

$$\mathrm{PAH} + \mathrm{C} \rightarrow \mathrm{CPAH}\ . \tag{3}$$

The C atom in these adducts is also assumed to occupy a special site which is not part of the PAH lattice (Lepp *et al.* 1988). We suggest that when reaction (3) is followed by a reaction with acetylene analogous to reaction (2), a novel synthetic route is achieved for the synthesis of cyclopropenylidene, $c{-}C_3H_2$, the C analog of $c{-}SiC_2H_2$, and a known interstellar molecular (Mathews and Irvine 1985; Thaddeus, Vrtilek, and Gottlieb 1985). The occurrence of reactions of type (2) points toward analogous reactions of type (4) involving higher PAH molecules or ions and reactions of type (5) involving other ions, X^+, or neutrals, X:

$$(\mathrm{SiPAH})^+ + \mathrm{M} \rightarrow \mathrm{PAH}^+ + \mathrm{SiM} \tag{4}$$

and

$$(\mathrm{XPAH})^+ + \mathrm{M} \rightarrow \mathrm{PAH}^+ + \mathrm{XM}\ . \tag{5}$$

Adduct formation can be expected to be more favorable when electron transfer is endothermic. Given that the ionization energies of PAH molecules higher than naphthalene are about equal to 7 eV (Omont 1986), an inspection of the ionization energies of some interstellar atoms, viz., S (10.360), Zn (9.394), Fe (7.870), Mg (7.646), Ca (6.113), and Al (5.986), would suggest preferential depletion of Ca^+ and Al^+ in the presence of PAH molecules or S, Zn, Fe, and Mg in the presence of PAH^+ ions. Our laboratory experience with Si^+ suggests that such depletions occurring in interstellar clouds in the presence of other interstellar gases, such as acetylenes and other hydrocarbon molecules, might well be accompanied by the formation of interesting and novel molecules, such as organometallic molecules, for example. Some of these predictions will now be tested in our laboratory.

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