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ULTRAVIOLET PHOTOPROCESSING OF INTERSTELLAR DUST MANTLES AS A SOURCE OF POLYCYCLIC AROMATIC HYDROCARBONS AND OTHER CONJUGATED MOLECULES

J. Mayo Greenberg,[1] J. Seb Gillette,[2] Guillermo M. Muñoz Caro,[1] Tania B. Mahajan,[2] Richard N. Zare,[2]
Aigen Li,[1] Willem A. Schutte,[1] Menno de Groot,[1] and Celia Mendoza-Gómez[1]
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ABSTRACT

By co-depositing a gas mixture of simple carbon- and nitrogen-containing molecules with water on a 10 K surface and exposing it to ultraviolet radiation, we were able to form a residue. This residue was then placed aboard the *EURECA* satellite behind a magnesium fluoride window and exposed to solar radiation for 4 months before it was returned and analyzed. The resulting residue is believed to simulate the photoprocessing of organic dust mantles in the interstellar medium. Mass spectrometry indicated that the photoprocessing created a rich mixture of polycyclic aromatic hydrocarbons (PAHs) and other conjugated organic molecules, which may explain how PAHs are replenished in space.

Subject headings: dust, extinction — Galaxy: evolution — ISM: molecules

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been a topic of intense interest since the mid-1980s when it was proposed that such species are widespread in the interstellar medium (ISM; Leger & Puget 1984; Allamandola, Tielens, & Barker 1985). The earliest suggestion that aromatic hydrocarbons might exist in the ISM dates back even further (Donn 1968). Current estimates (Allamandola 1995; Dwek et al. 1997; Li & Greenberg 1997) suggest that about 20% of the cosmic carbon in the Galaxy is contained in PAHs. It is as yet unclear how PAHs are formed in such abundance, given that their production by evolved stars does not keep up with their proposed destruction rate (Giard et al. 1994). Several mechanisms for the formation of PAHs in the ISM have been advanced, including the splitting of graphite grains (Tielens et al. 1987), the accretion of carbon cations (Puget & Leger 1989), the gas-phase formation by ion-molecule reactions (Herbst 1991), and the processing of simple gas-phase molecules by sparks or ultraviolet light (Sagan & Khare 1979). The presence of molecules such as CO, NH_3, CH_3OH, and CH_4 in the ISM has been established through the assignment of infrared bands in astronomical spectra of distant objects (d'Hendecourt & de Muizon 1989; van Dishoeck, Bearda, & van Hemert 1996; Knacke et al. 1982; Whittet & Duley 1991). Here we report on the formation of PAHs by the ultraviolet photoprocessing of these simple organic precursors under conditions similar to those found in the ISM.

The ISM is composed of a number of distinct phases in which the associated gas temperatures and densities range from 10 K and approximately 300 or more H atoms cm^{-3} in molecular clouds to 100 K and approximately 25–50 H atoms cm^{-3} in diffuse clouds. Dust temperatures do not change as much, varying from 5 K in molecular clouds to approximately 15 K in diffuse clouds. Figure 1 in Greenberg & Li (1999) presents a possible scenario for the evolution of various organic components of interstellar dust. As the density of the cloud increases from the diffuse cloud phase to the molecular cloud phase, simple molecules such as CO and NH_3 as well as some carbonaceous and PAH particles condense on the dust particles, thus forming an icy mantle (Greenberg 1984; Schutte 1998; Whittet 1992). The photoprocessing of the ice by ultraviolet radiation leads to the production of complex organic molecules (Bernstein et al. 1995; Jenniskens et al. 1993) that we refer to as "first-generation organics." The transition back to the diffuse cloud phase occurs with a substantial increase in ultraviolet radiation (Greenberg 1978). This transition, in which ultraviolet fluxes are 1000–10,000 times greater than in the molecular cloud, may result in the major processing of the ices before they are evaporated or sputtered away. While the ices are destroyed in the diffuse cloud, the icy mantles release the organics, and they regain their diffuse cloud character (Mennella et al. 1998). The same intense ultraviolet light modifies the outer first-generation organic mantle, resulting in a highly processed organic refractory diffuse cloud dust mantle. Thus, the PAHs and other organic molecules on the dust are continuously recycled.

2. THE LABORATORY ANALOG

The laboratory analog of the cyclically ultraviolet-processed interstellar dust that occurs in molecular and diffuse clouds was created in two stages. Gas-phase mixtures containing different combinations of H_2O, CO, NH_3, CH_3OH, CH_4, and C_2H_2 were deposited on small blocks of aluminum at 10 K at a deposition rate of 10^{16} molecules s^{-1}. Although the commonly observed molecular abundances (Schutte 1998; Whittet 1992) served as a guide, the initial abundances were selected to represent the depleted elemental ratios characteristic of diffuse clouds. During and after deposition, the mixtures were irradiated for times of 22–68 hr with a microwave-stimulated hydrogen discharge ultraviolet lamp providing a flux of approximately 10^{15} photons cm^{-2} s^{-1}. The radiation was dominated by light at the Lyα wavelength (121.5 nm) and a 20 nm–wide transition centered at 160 nm. The irradiated sample was then warmed to room temperature, leaving a yellow-colored residue. This residue is presumed to resemble first-generation organic dust mantles formed in molecular clouds. The blocks containing the yellow residues were then sealed in a sample carrier behind a magnesium fluoride window with a slight overpressure of N_2. The sample carrier was flown into space on the Exobiology Radiation Assembly (ERA) platform of the *EURECA* satellite, which remained at an altitude of 500 km for about 11 months. While in orbit, the samples were subjected to irradiation by

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[1] Raymond and Beverly Sackler Laboratory for Astrophysics, University of Leiden, Postbus 9504, Leiden, 2300 RA, Netherlands.

[2] Department of Chemistry, Stanford University, Stanford, CA 94305-5080.

the full solar spectrum for a total of 4 months. Upon return to Earth, the sample carrier was resealed in an argon atmosphere. The samples were then transported to Leiden University for analysis. The infrared spectra of these photoprocessed residues provided an excellent match to the 3.4 μm absorption feature seen in the infrared spectra of diffuse cloud interstellar dust as reported elsewhere (Greenberg et al. 1995). This result provides us with confidence that a realistic surrogate for interstellar refractories has been achieved. A photograph of the organic residues in the sample carrier was taken before and after solar irradiation. A change in color from yellow to brown was seen. Otherwise, the samples retained the same morphological structure and appeared unchanged.

3. RESULTS

After remaining in storage under an argon atmosphere, several samples were transferred to Stanford University for mass spectrometric analysis. Figure 1 displays the microprobe laser desorption/laser ionization mass spectrometry (μL^2MS) spectra of two *EURECA* residues produced from the photoprocessing of H_2O, CO, NH_3, and CH_3OH in a 5 : 5 : 1 : 1 mixture (R1) and H_2O, CO, NH_3, and CH_4 in a 5 : 2 : 2 : 2 mixture (R2). The μL^2MS instrument uses 266 nm light from a frequency-quadrupled Nd:YAG laser to ionize gas-phase molecules before injection into the time-of-flight apparatus. Only molecules with multiple aromatic rings or an extended conjugation system are appreciably ionized owing to their low-ionization potentials and resonant absorbances at 266 nm (Clemett & Zare 1997). Although the μL^2MS system is quite selective, the spectra are comprised of many aromatic molecules. Because so many compounds are detected, identification of each individual species becomes difficult, although some trends are apparent. Both spectra in Figure 1 contain large peaks representative of parent PAHs having 2-ring (128 amu), 3-ring (178 amu), 4-ring (202 and 228 amu), 5-ring (252 amu), and 6-ring (276 and 300 amu) systems. It must be noted that an aluminum block with vapor-deposited coronene was included in the sample carrier. Although it was concluded that cross contamination was negligible, the peak at 300 amu in these spectra may have a minor contribution from contamination. Peaks resulting from the addition of methylene groups (CH_2, 14 amu) to the parent PAH skeletons to form alkyl side chains are also present. Interesting features not seen in meteorite spectra are the mass envelopes containing peaks separated by 2 amu, with the lowest mass in the envelope being that of a parent PAH skeleton. These mass envelopes likely result from a partially hydrogenated parent PAH skeleton. The resonant ionization method employed by the μL^2MS instrument allows detection of partially hydrogenated PAHs with minimal fragmentation. Additional even-mass peaks are attributed to side chains, in varying degrees of unsaturation, attached to the parent PAH skeletons. A number of peaks with odd masses indicate the presence of nitrogen-containing molecules. Because μL^2MS is substantially less sensitive to heterocyclic compounds, it is thought that the nitrogen is present in functional groups, such as NH_2 or CN, attached to the PAH skeleton or an alkyl side chain on the PAH skeleton. The complexity of aromatic molecules seen in these spectra is much greater than that in chondritic meteorites. It is, however, remarkably similar to the μL^2MS spectra obtained from interplanetary dust particles (Clemett et al. 1993).

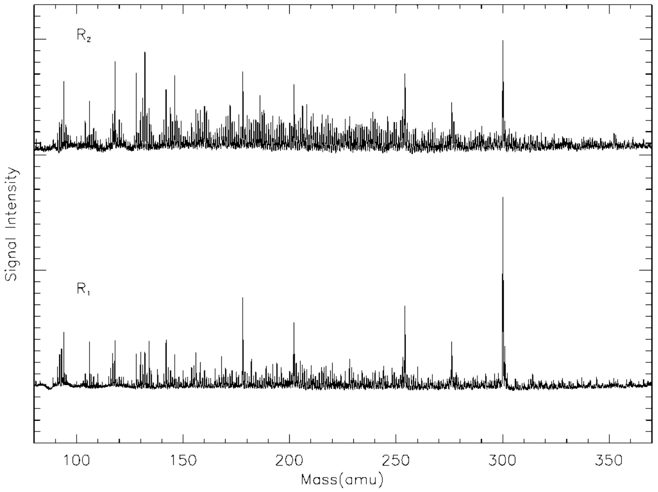

FIG. 1.—The μL^2MS spectra of two separate residues that resulted from the photoprocessing of simple precursors. R_1 began as a 5 : 5 : 1 : 1 mixture of H_2O, CO, NH_3, and CH_3OH. R_2 began as a 5 : 2 : 2 : 2 mixture of H_2O, CO, NH_3, and CH_4. Some mass-to-charge peaks are identified as phenanthrene ($m/z = 178$), pyrene ($m/z = 202$), benzopyrene ($m/z = 252$), benzoperylene ($m/z = 276$), and coronene ($m/z = 300$).

The μL^2MS analysis was also performed on the first-generation organics corresponding to the mixture used in residue R1. Some aromatic compounds are detected, but they are neither as abundant nor as varied as those seen in the further processed residues. Placing the first-generation organic residues aboard the ERA platform allowed us to simulate the intense increase of ultraviolet light associated with the transition from a molecular cloud to the diffuse ISM. The μL^2MS spectra clearly indicate that this photoprocessing results in the production of complex molecules from simple precursors.

4. CONCLUSIONS

These experiments suggest that a source (possibly the major one) of the PAHs seen as gas-phase molecules results from the destruction of photoprocessed interstellar dust organic mantles. The case for this is supported by the fact that the formation in carbon stars appears to be very restrictive. Given a PAH survival time of $\leq 10^8$ yr (Draine & Salpeter 1979; Omont 1986; McKee 1989; Mendoza-Gómez, de Groot, & Greenberg 1995; Allain, Leach, & Sedlmayer 1996; Tielens 1998), the injection rate from C-rich giants (Clausen et al. 1987; Knapp & Wilcots 1987; Gehrz 1989; Frenklach 1990; Tielens 1990) would have to be increased by at least a factor of 10 to obtain the observed abundance. Carbon stars can account for at most 5%–10% of the observed PAHs (Greenberg & Li 1999).

Based on the observed extinction and strength of the 3.4 μm feature in interstellar spectra, no more than about 20% of the total carbon in the dust mantles can be in aliphatics (Tielens et al. 1996; Schutte et al. 1998). It has also been proposed that 50% of cosmically available carbon is contained in the dust mantles (Li & Greenberg 1997). These percentages imply that the fraction of cosmically available carbon trapped in the PAH component of the grain mantle is about 40%, more than enough to account for the current estimate of 20% (Allamandola 1995; Dwek et al. 1997; Li & Greenberg 1997). Our experiments suggest that the major source of PAHs seen as gas-phase molecules is the destruction of photoprocessed interstellar dust organic mantles. While the organic mantles are diminished in the diffuse ISM by sputtering and grain-grain collisions (McKee 1989; Tielens 1998), they appear to be replenished in the molecular cloud phase by accretion and photoprocessing. These competing mechanisms enable a steady state to be maintained in the diffuse cloud/molecular cloud cycle. Because the mean cycle time is 10^8 yr with approximately equal time being spent in each phase, the PAHs are continuously recycled. The current laboratory experiments also indicate that interstellar dust mantles act as chemical factories for PAHs and other conjugated organic molecules. In this way, PAHs can be replenished at a rate comparable to their rate of destruction.

5. CONCLUDING REMARKS

This work has many implications, not only for additional laboratory analog studies of the evolution of organics in the ISM but also for new observational missions such as the analysis of comet organics. For some clouds of dust, the diffuse cloud/molecular cloud cycle is broken by a molecular cloud collapse leading to formation of stars, planetary systems, and comets. In situ mass spectrometry of comet Halley dust confirmed that most of the carbon in comets is contained in organic molecules (Kissel et al. 1986; Kissel & Krueger 1987; Krueger & Kissel 1987). Although the exact composition of the comet dust was difficult to construct, some aromatic species were inferred (Kissel & Krueger 1987). Direct evidence presently exists for at least one PAH, phenanthrene (178 amu), in comet Halley's coma (Moreels et al. 1994). Additionally, the similarity between the PAHs found in the residues and those found in interplanetary dust particles, which are proposed by Bradley (1998) to come from comets, further supports this idea. The ultimate proof of these ideas must await the recovery and analysis of the most pristine material of the solar system, namely, comets. It is important to realize that not only the chemistry but also the morphological structure of the cometary material is critical in relating the formation of the solar system to its origin.

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