FORMATION OF CARBON-CARBON BONDS IN THE PHOTOCHEMICAL ALKYLATION OF POLYCYCLIC AROMATIC HYDROCARBONS

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(Received 16 April 2002; accepted in revised form 17 July 2002)

Abstract. The reaction of polycyclic aromatic hydrocarbons (PAHs) with alkanes was examined in the presence of ultraviolet (UV) light under model prebiotic Earth and interstellar medium (ISM) conditions. We observed the formation of alkylated PAHs from a variety of PAHs and alkanes, which was caused by the absorption of UV light by the PAH molecule. Photoalkylation occurred in PAHs and alkanes in solution, in thin films in contact with simulated ocean water, and in matrices simulating ISM conditions. Photoalkylation occurred readily, with significant product yields within 5 h of irradiation. Because alkanes and PAHs are presumed to be part of the organic inventory in the ISM and on the early Earth, we propose that this photoalkylation reaction is a plausible pathway for the formation of carbon-carbon bonds in both these environments.

Keywords: alkanes, early Earth, ISM, PAHs, photochemistry, UV irradiation

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are of considerable interest today because they are ubiquitous on Earth and in the interstellar medium (ISM). These molecules, composed of two or more fused aromatic rings, have been identified in the air (Odabasi *et al*., 1997), water (Piperidou *et al*., 1996), soils (Blumer and Youngblood, 1975), sediments (Ghosh *et al*., 2000), terrestrial rocks (Mahajan *et al*., 2001), meteorites (Clemett, 1996; Clemett *et al*., 1992), interplanetary dust particles (Clemett *et al*., 1993), graphite grains believed to be interstellar in origin (Clemett *et al*., 1995) and the ISM (Allamondola *et al*., 1985; Leger and Puget, 1984). In fact, about 20% of carbon in the galaxy is estimated to be in the form of PAHs (Allamondola, 1995; Dwek *et al*., 1997; Li and Greenberg, 1997). On Earth, PAHs are formed from both anthropogenic and natural sources including incomplete combustion of organic matter (Blumer, 1976; Hoffman and Wyder, 1968; Wang and Frenklach, 1997) and long-term degradation of biological material (Brown *et al*., 1972; Orr and Grady, 1967). Laboratory simulations suggest that the synthesis of PAHs in the ISM involves the processing of simple gas-phase

Origins of Life and Evolution of the Biosphere **33:** 17–35, 2003.

molecules (Sagan and Khare, 1979) and interstellar dust mantles (Greenberg *et al.*, 2000) by ultraviolet (UV) light. PAHs may also be formed in circumstellar outflows of asymptotic giant branch (AGB) stars (see Tielens and Charnley, 1997 for a review). Splitting of graphite grains (Tielens *et al.*, 1987), accretion of carbon cations (Puget and Leger, 1989), and ion-molecule reactions (Herbst, 1991) have also been proposed as synthetic pathways.

In this study we explored the photochemistry of PAHs in the presence of alkanes. In general, PAHs are stable compounds because the π electrons in PAHs are delocalized over the aromatic rings and these molecules have large resonance energies. In spite of the intrinsically low chemical reactivities of PAHs, they absorb light in the near UV and undergo numerous photochemical reactions. The most extensively studied class of reactions is that of PAHs and oxygen (Fox and Olive, 1979) or ozone (Greenberg and Darack, 1987) in the presence of sunlight. Bernstein and co-workers have reported the formation of a variety of compounds such as hydrogenated PAHs, quinones, alcohols, and ethers from the photoreaction of PAHs in ices under simulated interstellar conditions (Bernstein *et al.*, 1999). Little information exists, however, about possible photochemistry of PAHs with alkanes, a topic that might have importance in understanding organics on the early Earth or in the ISM.

The reaction of PAHs and alkanes in interesting because these compounds are abundant in certain environments, and photoreactions between these molecules may provide a facile mechanism for linking them to each other through the formation of new carbon-carbon (C-C) bonds. C-C bonds are strong, with average bond energies of 348 kJ mol^{-1}, and elaborate conditions are used to produce them in the laboratory today. Because the bonds connect PAHs with other molecules, this step is integral in the synthesis of large and complex aromatic compounds, such as what constitutes kerogen.

We explored the photochemistry of PAHs and alkanes under conditions relevant to the prebiotic Earth and the ISM. Alkanes are abundant in the ISM (Lacy *et al.*, 1991), interplanetary dust particles, comets, and meteorites (Cronin and Pizzarello, 1990; Cronin *et al.*, 1988). Moreover, it is likely that they were plentiful components of the organic inventory deposited on Earth during the heavy bombardment period (Chyba and Sagan, 1992; Chyba *et al.*, 1990). UV light was the primary source of energy in the early solar system (see Deamer, 1997 for a review), and would have impinged on surfaces of planets and on dust particles of the molecular cloud. In the absence of the ozone layer 4 billion years ago, the shorter and more energetic wavelengths of UV light should have reached the Earth's surface, making photochemical reactions possible.

UV radiation is also an important energy source in the diffuse ISM and, to a lesser extent, in dense molecular clouds. In the cold temperatures (10–20 K) in molecular clouds, PAHs, alkanes, and other gas-phase species condense onto refractory dust grains to form icy mantles, which can then be further processed by UV radiation (Bernstein *et al.*, 1995; Greenberg *et al.*, 2000; McDonald *et al.*, 1996; Sandford and Allamandola, 1993). The extent of processing depends on the location of the ice grain, as the interiors of molecular clouds are more shielded from the UV flux. On the other hand, ices that drift into the diffuse ISM may experience enough UV flux to not only drive synthetic reactions but also cause destruction of PAHs and other organic species. The UV dosages used in our work represent $\sim$ 500 yr at the edge of a dense cloud, and $\sim 1 \times 10^5$ yr at an optical depth of 5 within a dense molecular cloud, based on the interstellar radiation field and ignoring internal sources (Prasad and Tarafder, 1983).

In the work reported here, we addressed three specific questions:

(1) Does photochemistry between PAHs and alkanes yield new C-C bonds?
(2) Were these reactions possible on the early Earth?
(3) Could these reactions occur in the ISM?

The results of our study suggest that photoalkylation of PAHs is a robust reaction that occurs for a variety of alkanes and PAHs. Moreover, C-C bond formation by this means might have occurred under plausible prebiotic early Earth and interstellar conditions.

2. Experimental

2.1. CHEMICALS

All reagents were purchased in the highest grade available from Sigma-Aldrich, Milwaukee, WI, and were used as received. Table I lists the structures of the PAHs and alkanes investigated in this study. Argon (99.995% purity) and CO_2 (99.9%) gases were purchased from Praxair, Santa Clara, CA. Methane was purchased from Matheson Tri-Gas, Newark, CA (99.0%). The CO_2 was passed through a purge to remove O_2 gas before use.

2.2. PHOTOREACTIONS OF PAH:ALKANE SOLUTIONS

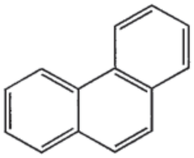
The experiments were carried out in a commercial microscale immersion well reactor (Ace Glass Inc, KY) (Penn and Orr, 1989). The source of UV energy was a mercury lamp (Model-11-SC-1) run from a power supply (SCT-1), both purchased from UVP Inc., CA. It mostly emits 254 nm light, with smaller amounts of 296-, 313-, and 365 nm light.

Standard solutions were prepared by dissolving 0.001 moles of a particular PAH in 0.1 moles of alkane. For each reaction, 2 mL aliquots of the PAH:alkane solution were placed in the outer jacket of the reactor and argon was passed through for an hour to remove any O_2 that may have been present. CO_2 was then bubbled through the solution while irradiation occurred for varying periods of time, ranging from 5–200 h. The bubbling ensured that the solution was uniformly mixed during irradiation and that the amount of O_2 present was minimized.

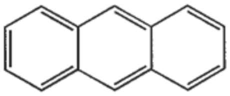
TABLE I

Structures and molecular weights of compounds investigated

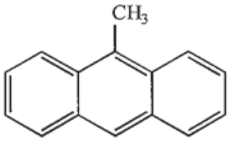
POLYCYCLIC AROMATIC HYDROCARBONS



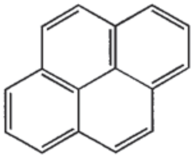
Phenanthrene (178 Da)



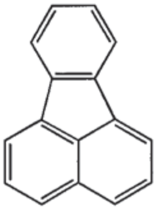
Anthracene (178 Da)



9-methyl anthracene
(192 Da)



Pyrene (202 Da)



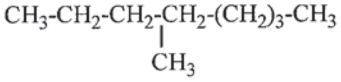
Fluoranthene (202 Da)

ALKANES

CH_4
methane (16 Da)

$CH_3(CH_2)_6CH_3$
n-octane (114 Da)

$CH_3(CH_2)_7CH_3$
n-nonane (128 Da)

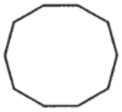


$CH_3\text{-}CH_2\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH_2}}\text{-}(CH_2)_3\text{-}CH_3$

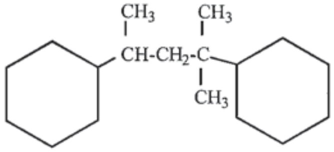
4-methyl nonane (142 Da)

$CH_3(CH_2)_8CH_3$
n-decane (142 Da)

$CH_3(CH_2)_{14}CH_3$
n-hexadecane (226 Da)



Cyclodecane (140 Da)



1-1′-(1,1,3-trimethyl-1,3-propanediyl)
biscyclohexane (250 Da)

2.3. PHOTOREACTIONS UNDER PLAUSIBLE PREBIOTIC EARTH CONDITIONS

Simulated early ocean water was prepared by adding four salts to Milli-Q water and then saturating the solution with CO_2. The composition of ocean water on the early Earth is unknown; it is generally believed to have been similar to modern ocean water with a higher ferrous ion concentration (Keefe and Miller, 1996; Morse and Mackenzie, 1998). The final solution had salt concentrations of 0.5 M sodium chloride, 0.05 M magnesium chloride, 0.01 M calcium chloride, and 0.01 M ferrous chloride. Mixtures of 0.2 mL of PAH:alkane solution (1:100) and 2 mL of the ocean water were studied in two forms, a dispersion and a thin film. The dispersion was constantly agitated by bubbling gas to reduce phase separation of the PAH:alkane mixture, which otherwise forms a separate oil phase on the surface of the water. To simulate a thin film of the PAH:alkane solution on ocean water, CO_2 was bubbled at a slower rate to minimize mixing effects. Irradiation was carried out for a period of 5 h using the same immersion well and mercury lamp as were used for the PAH:alkane solutions.

2.4. PHOTOREACTIONS UNDER MODEL INTERSTELLAR MEDIUM CONDITIONS

These experiments were performed at NASA Ames Research Center, Mountain View, CA. The irradiation apparatus consists of an evacuated sample chamber containing a rotatable 10 K substrate (Bernstein *et al.*, 1999). Phenanthrene and an Ar:alkane mixture (50:1 for methane and 400:1 for octane) were simultaneously vapor deposited onto the substrate. The argon is used to isolate the alkane molecules from each other and thereby minimize alkane polymerization. The sample was then UV irradiated for a period of 30 min with a microwave-powered, flowing hydrogen, discharge lamp (Bowey *et al.*, 1998) that produces $\sim 2 \times 10^{15}$ photons $cm^{-2}\ s^{-1}$, the flux being nearly evenly divided between the hydrogen Lyman α line and a roughly 20 nm wide molecular transition centered at 160 nm. When irradiation was complete, the sample was slowly warmed to room temperature and removed from the vacuum chamber for analysis.

2.5. μL^2MS ANALYSES

All the samples were analyzed by microprobe two-step laser desorption/laser ionization mass spectrometry (μL^2MS), which has been used to detect PAHs in a variety of ancient terrestrial rocks (Mahajan *et al.*, 2001), contaminated soils and sediments (Ghosh *et al.*, 2000; Gillette *et al.*, 1999), and meteorites (McKay *et al.*, 1996; Zenobi *et al.*, 1989). In most cases, samples consisted of 10 μL of a PAH:alkane solution evaporated on a glass plate. For the simulated ISM experiments, a piece of the foil substrate was analyzed. The samples were then placed on a brass sample platter that was introduced in the μL^2MS chamber through a vacuum interlock. A detailed description of the instrument is given elsewhere

(Clemett and Zare, 1997). In the first step, constituent sample molecules are desorbed by a pulsed IR laser beam that is focused to a 40 μm spot using a microscope objective. In the second step the desorbed molecules are selectively ionized with a pulsed ultraviolet laser (266 nm), and the resulting ions are analyzed in a reflectron time-of-flight mass spectrometer. The mass spectra consist primarily of the PAHs and their derivatives.

3. Results and Discussion

3.1. Photoreaction of phenanthrene and hexadecane in the presence of UV light

Phenanthrene [$C_{14}H_{10}$] and hexadecane [$CH_3(CH_2)_{14}CH_3$] were chosen as model test compounds for PAH and alkane respectively. Figure 1 shows the mass spectra that result from a phenanthrene:hexadecane sample exposed to UV light (Figure 1a) and from a similar sample that was not exposed to UV radiation (Figure 1b). Both reactions were conducted for a period of 5 h and CO_2 was bubbled throughout.

In the presence of UV light (Figure 1a), the solution forms a prominent peak at 402 Da that corresponds to the substitution of the hexadecane chain (226 Da) onto the phenanthrene ring (178 Da). The hexadecyl group is likely to be substituted at the 9 position, which is known to be the most reactive site of phenanthrene (Jeanes and Adams, 1937). Alkylated products resulting from the addition of methyl, ethyl, or propyl groups to the phenanthrene rings were also observed. These products have been labeled as C_n-PAH, with n indicating the number of carbon atoms that have added to the PAH. In addition, products resulting from the addition of an oxygen atom (O) or a hydroxyl group to the phenanthrene ring were detected at 194 Da (Phn + O) and at 418 Da (C_{16}-Phn + O). The oxidation products likely result from the reaction of phenanthrene with trace amounts of O_2 gas in the reaction mixture. The solubility of O_2 in n-alkanes is known to be high (Battino *et al.*, 1981), and some O_2 probably remains dissolved in the alkane. Another possible source is residual O_2 from the gas bottle used to bubble CO_2 during the course of the reaction.

It should be noted that the μL^2MS technique is unable to provide information on positional or functional isomers; for example, the peak at 206 Da could be either dimethyl or ethyl phenanthrene, while the oxidation products could result from the addition of either a doubly bonded oxygen atom or an OH group. Nonetheless, the data clearly indicate that new C-C and C=O/C-OH bonds are being formed.

No products were formed in the dark control (Figure 1b), indicating that UV radiation is driving the alkylation reaction. A control sample of UV-irradiated hexadecane without phenanthrene present also yielded no products (spectrum not shown). The UV absorption of hexadecane is negligible, so absorption of light

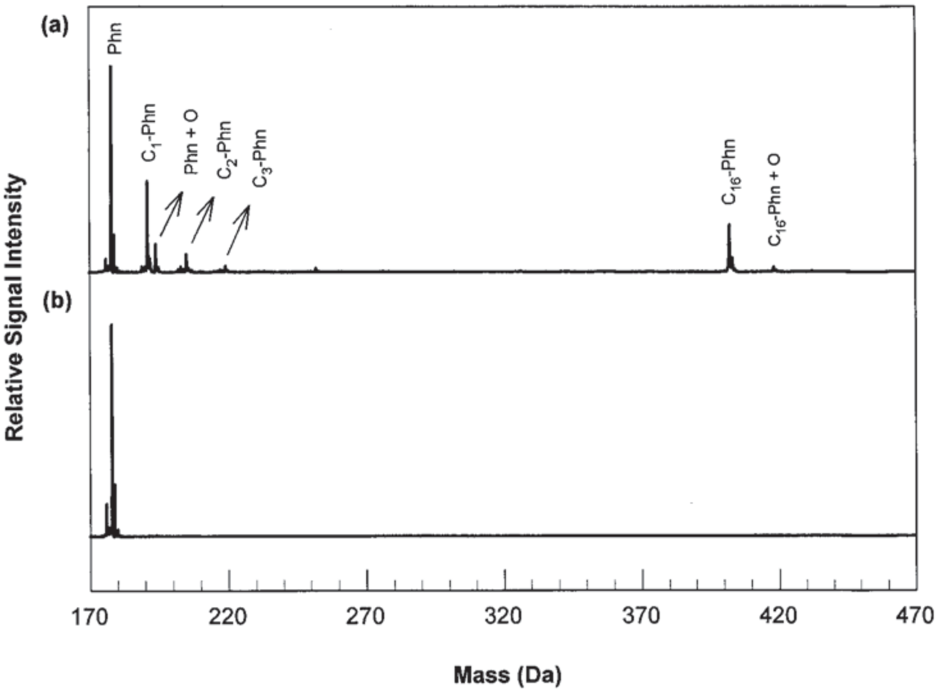


Figure 1. μL^2MS spectra of products formed during the reaction of solutions of phenanthrene and hexadecane (1:100) (a) in the presence of UV light, and (b) in the absence of UV light. Both the reactions were carried out for 5 h in a microscale immersion well reactor, and CO_2 was bubbled throughout. The peaks are assigned as Phn (phenanthrene), C_1-Phn (methylphenanthrene), C_2-Phn (dimethyl/ethyl phenenthrene), C_3-Phn (phenanthrene + C_3H_7), and C_{16}-Phn (phenanthrene + $C_{16}H_{33}$). The oxidized products are indicated by (Phn + O) and (C_{16}-Phn + O) where O stands for an oxygen atom or a hydroxyl group.

by phenanthrene is the key factor. The excited phenanthrene may then transfer energy to the hexadecane, driving the substitution reaction. The presence of methyl, ethyl, and propyl product species suggests that the excited state PAH has sufficient energy to activate fragmentation of the hexadecane chain, and the alkyl fragments also undergo substitution reactions where they replace hydrogen atoms on the PAH rings.

The products formed from the photoreaction of phenanthrene with hexadecane were extremely stable, and did not degrade over a period of several months. The reaction was carried out under a series of different conditions. N_2 was bubbled through the PAH-alkane mixture instead of CO_2, and the same alkylated products were formed upon irradiation with UV light. This result confirms that the only role of the gas is to ensure intimate mixing of PAH and alkane molecules. Addition of oxygen was still observed with N_2 bubbling, although to a lesser extent than with CO_2 bubbling, suggesting that the reaction mixture may be exposed to O_2 both from the CO_2 bottle and from the laboratory environment. No reaction occurs between PAH and CO_2. When a ratio of 1:50 PAH:alkane was used instead of 1:100 the products were formed in the same relative amounts, presumably because most of the PAH molecules are surrounded by alkane molecules at both ratios. Ratios smaller than 1:100 were not tested because the amount of PAH would be insufficient for detection of products, while ratios greater than 1:50 were not used because of solubility problems. The reaction was also carried out in the solid state by immersing the whole reaction setup in dry ice. No gas was bubbled in this case. Under these conditions, in addition to the alkylated PAHs expected, dimerized phenanthrene was formed at 354 Da.

This study of the photoreaction of phenanthrene and hexadecane indicates that the UV irradiation of PAH solutions in alkane solvents is a facile way to make C-C bonds and yield alkylated PAHs. The ratio of PAH:alkane (as long as the alkane is present in excess) and the physical state of the reactants do not measurably affect the alkylation reaction. Alkylated PAHs are formed whether or not N_2 or CO_2 is bubbled through the solution.

3.2. PHOTOREACTIONS OF VARIOUS PAHS AND ALKANES

A number of different PAHs and alkanes were examined to test the robustness the photoalkylation process. Anthracene, 9-methyl anthracene, pyrene, and fluoranthene were dissolved in hexadecane and irradiated with UV light under the same conditions as the phenanthrene experiments in the previous section. The products formed in each case are given in Table II.

All the PAHs underwent alkylation, and the most prominent alkylated products were found to be the methylated or the hexadecylated species of the particular PAH. In all cases there are peaks for dimethylated/ethylated products as well, but their peak intensities in the μL^2MS spectra were considerably lower. In addition to the alkylated products, small amounts of oxidation products appear from the addition of one or two oxygen atoms or hydroxyl groups to the starting PAH.

Photoreactions of phenanthrene were also carried out with five other alkanes, and the μL^2MS results are presented in Table III. The alkanes studied were chosen based on their availability, physical state, and solubility of PAHs in them. Solid-state alkanes were not used because of the difficulty of making homogeneous solid solutions and irradiating them uniformly. In all cases studied alkylated products were detected.

The fact that a wide variety of PAHs and alkanes reacted to give alkylated PAHs confirms that the photoalkylation reaction is very robust. Irrespective of the structure of the PAH, length of the alkane chain, and cyclic structure of two of the alkanes investigated, new carbon-carbon bonds were produced. It should be noted that controls were run for all the PAH-alkane mixtures investigated. In the absence of light no products were observed.

TABLE II

Products and percent yields for photoreactions of different PAHs in hexadecane (1:100). The solutions were UV-irradiated for 5 h in a microscale well reactor

PAH	Alkylated products[a]	Yields at the end of the reaction[b]		
		% Alkylated	% Oxidized	% Unreacted
Phenanthrene	C_1-phenanthrene, 192 Da C_2-phenanthrene, 206 Da C_3-phenanthrene, 220 Da C_{16}-phenanthrene, 402 Da	47	7	46
Anthracene	C_1-anthracene, 192 Da C_2-anthracene, 206 Da C_{16}-anthracene, 402	19	4	77
9-methyl anthracene	C_2-anthracene, 206 Da C_{17}-anthracene, 416 Da	18	3	79
Pyrene	C_1-pyrene, 216 Da C_2-pyrene, 216 Da C_{16}-pyrene, 426 Da	23	6	71
Fluoranthene	C_1-fluoranthene, 216 Da C_2-fluoranthene, 230 Da C_{16}-fluoranthene, 426 Da	22	5	73

[a] Alkylated products have been labeled as C_n-PAH, with n indicating the number of carbon atoms that have added to the PAH.

[b] Percent yields are semi-quantitative estimates from the peak intensities of the μL^2MS spectra.

3.3. PHOTOREACTION OF PHENANTHRENE AND HEXADECANE IN A DISPERSION AND A FILM

A significant source of organics on the Earth during the late Hadean to early Archean period is believed to have been extraterrestrial material (Anders, 1989; Chyba *et al*., 1990) that would enter the ocean and be released by hydrolytic processes over time, creating oil slicks at the surface of the ocean. Both PAHs and alkanes are known to be abundant components of carbonaceous meteorites (Cronin and Chang, 1993) and would presumably have been important constituents of the organic inventory delivered in this manner. Once on the Earth, these organics would have been exposed to an atmosphere consisting mostly of CO_2 and N_2 (Kasting, 1993; Kasting *et al*., 1993) and to the sun's UV radiation. Because PAHs absorb in the near UV, it is likely that PAH molecules acted as primitive pigments, which took part in photochemical reactions on the prebiotic ocean surface. To study this possibility, the reaction of phenanthrene and hexadecane was studied under model prebiotic conditions, and Figure 2 presents the resulting mass spectrum.

TABLE III

Products and percent yields for photoreactions of phenanthrene in different alkanes (1:100). The solutions were UV-irradiated for 5 h in a microscale immersion well reactor

Alkane	Alkylated products[a]	Yields at the end of the reaction[b]		
		% Alkylated	% Oxidized	% Unreacted
n-nonane	C_1-phenanthrene, 192 Da C_2-phenanthrene, 206 Da C_9-phenanthrene, 304 Da	23	9	68
n-decane	C_1-phenanthrene, 192 Da C_2-phenanthrene, 206 Da C_{10}-phenanthrene, 318 Da	31	6	63
n-hexadecane	C_1-phenanthrene, 192 Da C_2-phenanthrene, 206 Da C_{16}-phenanthrene, 402 Da	47	7	46
4-methyl nonane	C_1-phenanthrene, 192 Da C_7-phenanthrene, 276 Da C_{10}-phenanthrene, 318 Da	9	8	83
cyclodecane	C_1-phenanthrene, 192 Da cyclodecane-phenanthrene, 316 Da	7	23	70
1,1′-(1,1,3-trimethyl-1,3-propanediyl) biscyclohexane	C_1-phenanthrene, 192 Da compound-phenanthrene, 426 Da	N.D[c]	N.D.	28

[a] Alkylated products have been labeled as C_n-PAH, with n indicating the number of carbon atoms that have added to the PAH.

[b] Percent yields are semi-quantitative estimates from the peak intensities of the μL^2MS spectra.

[c] N.D.: not determined. Some of the peaks in the μL^2MS spectrum were not identified, and the percentage yields were not calculated.

From Figure 2a it is clear that when the phenanthrene and alkane are in a thin oil film on the surface of model ocean water both alkylated and oxidized products are formed. The ratio of oxidized products to alkylated products, as indicated by the relative intensity of the μL^2MS peaks, is higher than that obtained for the photoreaction of a pure phenanthrene:hexadecane solution (Figure 1). Because the film is in close contact with the water it is likely that some of the phenanthrene present reacts with the water, providing an additional source of oxidized products and explaining the higher relative oxidation yield. The photooxygenation of PAHs in water has been previously observed (Zepp and Schlotzhauer, 1979). Oxidation from residual O_2 from the CO_2 gas bottle is also a possibility; CO_2 was used for bubbling rather than N_2 or Ar, however, to simulate the prebiotic atmosphere.

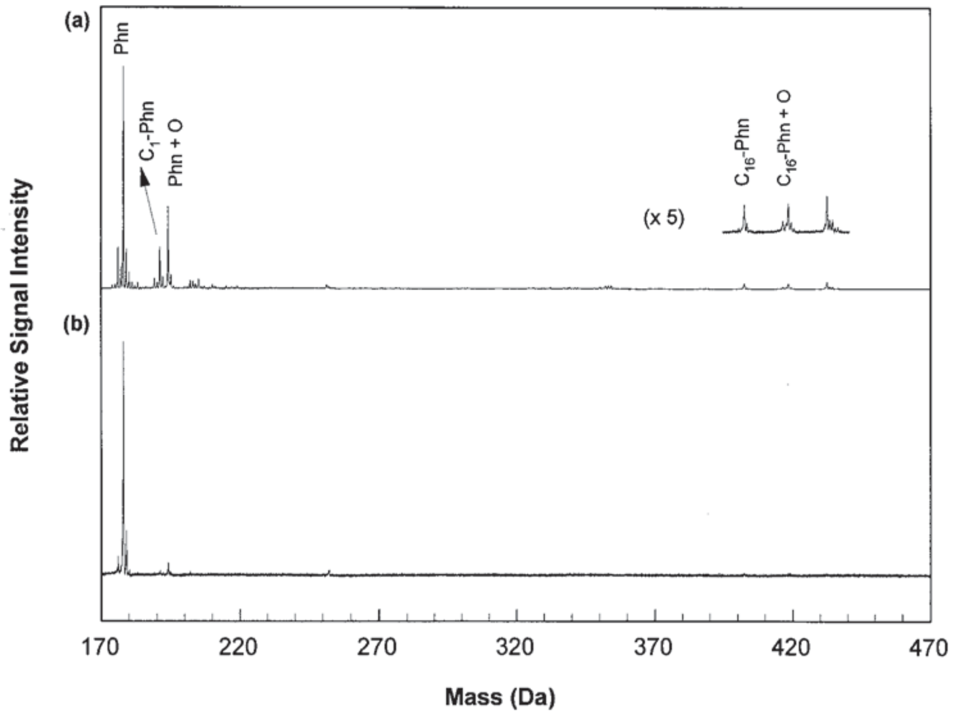


Figure 2. μL^2MS spectra of products formed in the (a) oil layer and (b) water layer during the photoreaction of a thin film of phenanthrene and hexadecane (1:100). The film floated on ocean water (sodium chloride + magnesium chloride + calcium chloride + ferrous chloride) to simulate early Earth oil slick conditions. The sample was irradiated with UV light, for 5 h. The peaks are assigned as Phn (phenanthrene), C_1-Phn (methylphenanthrene), and C_{16}-Phn (phenanthrene + $C_{16}H_{33}$). The oxidized products are indicated by (Phn + O) and (C_{16}-Phn + O) where O stands for an oxygen atom or a hydroxyl group.

The simulated ocean water that we used did not include all the elements that would likely have been present in the prebiotic ocean. The sodium, magnesium, calcium, and ferrous salts added should, however, be sufficient for us to determine the effect of inorganic compounds on the PAH:alkane photoreaction. The data indicate that the presence of inorganic salts does not affect the photoalkylation reaction. The water beneath the film was analyzed as well (Figure 2b). Other than a very weak peak from oxidized PAHs, no products were detected, as would be expected.

The reaction was also studied in the form of a dispersion of the phenanthrene:hexadecane mixture throughout the ocean water. Vigorous bubbling of CO_2 gas during the reaction time helped to maintain a uniform dispersion. When the gas bubbling was stopped, the dispersion separated into an organic layer floating on the aqueous phase. The organic layer contained both alkylated and oxidized products (spectrum not shown). The water layer had very low amounts of PAHs, as indicated by the absolute signal intensity during μL^2MS analysis. The peaks present are mostly from unreacted phenanthrene, and a small amount of alkylated and oxidized products.

The mass spectra shown in Figure 2 are from an irradiation period of five hours. Longer irradiation times were also used to determine if the alkylated and oxidized products were still observed with approximately the same relative peak intensities as at five hours. The most noticeable change with long irradiation times was the increased intensity of the peak at 626 Da, corresponding to addition of two hexadecyl units to the phenanthrene ring. These results indicate that not only could the alkylated and oxidized products survive long periods of irradiation under early Earth conditions, but also that PAHs could become highly alkylated given enough time and UV radiation. In a recent study Cleaves and Miller (Cleaves and Miller, 1998) demonstrated that organic polymers, solubilized elemental sulfur, and inorganics, such as Cl^-, Br^-, $MgCl^{2+}$, and Fe^{2+}, present in the prebiotic ocean would have been sufficiently effective UV absorbers to protect oceanic organic molecules from UV degradation. This report as well as our experimental data makes us believe that alkylated PAHs produced during plausible photoreactions would survive extended periods of UV exposure.

Hexadecane was chosen as a model alkane for this work, although normal alkanes were not likely to be present among the organics delivered through extraterrestrial infall. Cronin and co-workers (Cronin and Pizzarello, 1990) have shown that the alkanes present in meteorites are cyclic (mon-, di- and tri-), branched, alkyl-substituted, and range from C_{15} to C_{30}. It was not possible for us to study such alkanes because of limitations associated with their availability and physical state. The data from the previous section indicate that the photoalkylation of PAHs occurs with a wide range of alkanes, and suggest that under prebiotic conditions this reaction may have occurred with any alkane present. It should also be noted that the PAH:alkane ratio of 1:100 used in this study is lower than the ratio of 1:4 seen in the Murchison meteorite. It was not possible to use a PAH:alkane ratio of 1:4 because of the limited solubility of PAHs in the alkanes.

The illumination provided by the mercury lamp to the solutions in the immersion well was approximately 4.5 mJ $cm^{-2}s^{-1}$ at 254 nm. Phenanthrene has a strong UV absorption in the range of 220 to 270 nm. On the surface of the early Earth, before photosynthetic production of oxygen, the UV flux in this wavelength range was approximately 0.4 mJ $cm^{-2}s^{-1}$ (Kasting, 1987). Although the power of the mercury lamp was higher than that reaching the early Earth's surface, the amount of time the solution was irradiated in our experiments was much shorter, of course, than the millions of years that PAHs would be expected to be exposed to UV light on the early Earth. The experimental results of this section imply that some of the PAHs and alkanes present in an oil slick on the early ocean were likely to become linked to each other in the presence of UV radiation. The photochemical reaction would have yielded new carbon-carbon bonds between PAH and alkane molecules and may have been an important step in producing complex organics from simple precursors. It is likely that the alkylated PAHs would become part of the rich and complex organic inventory that was believed to be present on the early Earth.

3.4. PHOTOREACTION OF PHENANTHRENE AND ALKANE UNDER MODEL INTERSTELLAR CONDITIONS

It is known that in cold regions of space, gas-phase species condense to form icy mantles on small cooled silicate grains (Sandford and Allamandola, 1993). The species in these ices may include PAHs, which have been observed to be abundant in the interstellar medium (Allamandola *et al.*, 1985; Leger and Puget, 1984). Simple alkanes such as methane and ethane have been identified in both the gas phase and in interstellar ices (Lacy *et al.*, 1991). The ices can be photochemically processed by UV radiation from the galactic UV field or from stellar objects to produce more complex compounds (Bernstein *et al.*, 1995; Greenberg *et al.*, 2000; McDonald *et al.*, 1996). To model interstellar ices in our work, phenanthrene and either a 50:1 Ar:methane or a 400:1 Ar:octane mixture were co-deposited on pieces of nickel foil and UV-irradiated under conditions of very low temperature (~ 10 K) and pressure ($\sim 10^{-8}$ Torr). After warming to room temperature, the residues were analyzed by μL^2MS and the results are shown in Figure 3.

The results in Figure 3 indicate that when phenanthrene and alkanes are irradiated in a condensed matrix under vacuum conditions and at very low temperatures, alkylation and oxidation products are formed. The presence of oxidation products at 194 and 210 Da indicates that there was some oxygen-donating compound in the ice. The source was most likely water, which is difficult to remove completely from the irradiation chamber. Nevertheless, Figure 3 clearly shows the photoalkylation of phenanthrene in both the methane- and octane-containing ices. Product peaks corresponding to methylated phenanthrene are observed in both cases. The octane ice (Figure 3b) also shows peaks at 206 (C_2-Phn), 276 (C_7-Phn), and 290 (C_8-Phn) Da, which result from addition of ethyl, heptyl, and octyl groups to phenanthrene. A number of controls were run for the phenanthrene:methane and phenanthrene:octane mixtures. In the absence of UV light, no products were observed.

The conditions used for the experimental ice formation and irradiation are somewhat representative of those expected in the ISM. In both cases, the ices are formed by condensation of gases at very low pressures on to a cold substrate, either a piece of nickel foil in the laboratory or a cooled silicate grain in the ISM. Hydrogen emission is the source of UV light in both instances. It should be noted that the phenanthrene:alkane ratios investigated in this work are not related to the interstellar ratios. While PAHs are known to be very abundant in the gas phase in the ISM, their abundance in the solid phase is not well characterized. Interstellar ices tend to be dominated by water, and methane has been observed to have an abundance of 1–4% relative to water (Lacy *et al.*, 1991).

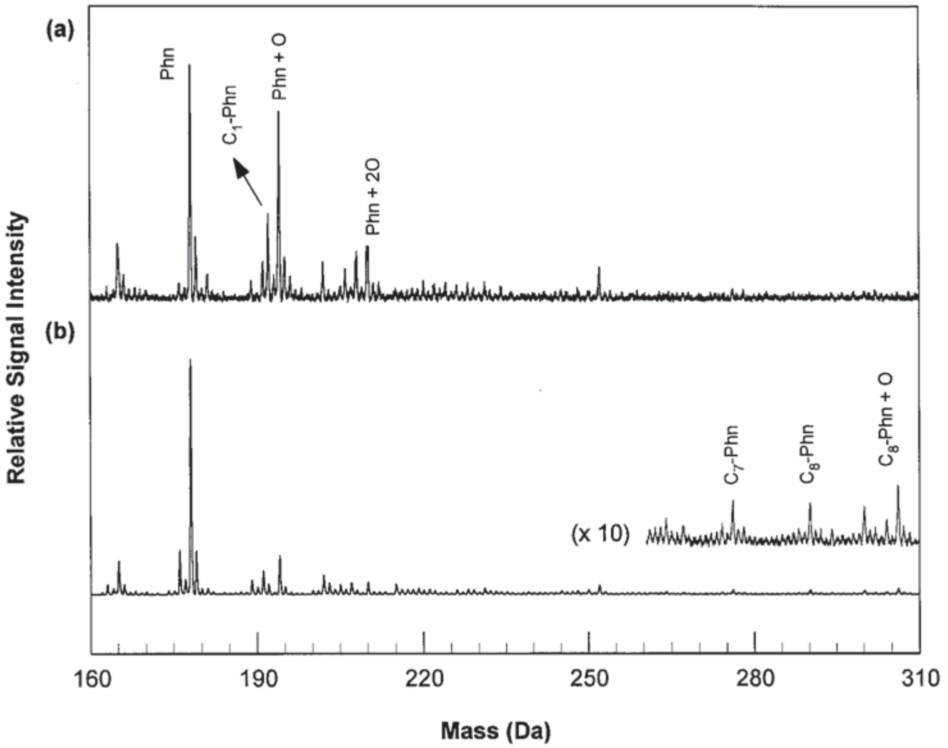


Figure 3. μL^2MS spectra of products formed during the photoreactions of frozen mixtures of (a) phenanthrene, methane, and argon and (b) phenanthrene, octane, and argon. Mixtures were deposited on nickel substrates at 10K in an evacuated chamber to simulate ISM conditions. In both cases samples were irradiated with UV light for 30 min. The peaks are assigned as Phn (phenanthrene), C_1-Phn (methylphenanthrene), C_7-Phn (phenanthrene + C_7H_{15}) and C_8-Phn (phenanthrene + C_8H_{17}). The oxidized products are indicated by (Phn + O), (Phn + 2O), and (C_8-Phn + O), where O stands for an oxygen atom or a hydroxyl group.

The presence of large amounts of other compounds, particularly water, in interstellar ices is likely to have some effect on the photoalkylation reaction. The photochemical reactions of PAHs in water-dominated ices have been studied and are known to produce partially oxidized aromatics (Bernstein *et al.*, 1999). These oxidation reactions will probably compete with the photoalkylation and decrease overall yields of alkylated products in the ISM. The ices used in our experiments comprise a simple non-interfering matrix that should provide fundamental insight into the photochemistry of the organic species. We do not believe that these ices are likely to represent exactly the conditions present in the ISM, but we suggest that they serve as a good model for the type of behavior that might be expected.

The interstellar ices modeled in this work are believed to be present in dense interstellar clouds, which are also the site of planetary system formation, and the UV irradiation dose corresponds to ~ 500 yr on the edge of a molecular cloud or

10^5 yr in its interior. While some of the alkylated PAHs produced may be destroyed by prolonged UV irradiation in the ISM, ice grains within a dense molecular cloud may be shielded from damaging amounts of radiation. The products seen in this work are the result of a balance between photoproduction and destruction caused by the 30 min experimental UV irradiation time. The compounds produced in interstellar ice reactions shielded in molecular clouds may therefore be included in forming planetesimals, eventually becoming part of the complex organic suite present in meteorites. Alkylated and oxidized PAHs such as those produced in our work have been identified in meteorites (Cronin *et al*., 1988; Krishnamurthy *et al*., 1992; Sephton and Gilmour, 2001). Studies of meteoritic organics have shown deuterium enrichment similar to that expected from low-temperature ice photochemistry, suggesting that molecules produced in interstellar ices can be incorporated into meteorites (Kerridge *et al*., 1987; Sandford *et al*., 2000). Although this is not the only way in which such compounds could be produced, it is reasonable to suggest that some fraction of these meteoritic compounds were produced through UV-driven photoreactions between PAHs and alkanes in ice grains.

The results of our work indicate that the photochemical reactions of PAHs and alkanes under interstellar conditions may provide a plausible mechanism for forming C-C bonds between molecules present. Complex molecules can thus be built up from simpler ones, and perhaps contribute to the suite of organic molecules present in meteorites.

4. Conclusions

This study indicates that alkylated PAHs are readily produced when a mixture of PAH and alkane is exposed to UV irradiation. Experiments were performed under model early Earth and ISM conditions in an attempt to determine plausible prebiotic and interstellar photochemistry. We conclude that photoalkylation of PAHs was likely to have occurred on the prebiotic Earth and is also possible in the ISM. Furthermore, the photochemical linking of PAHs and alkanes in both these environments, via the formation of new carbon-carbon bonds, may have served as a preliminary step in creating complex organics from much simpler molecules.

The detailed investigation of pure PAH-alkane solutions reported here demonstrates that PAHs and alkanes readily undergo photochemical processing to form a variety of alkylated PAH derivatives. Although PAHs and alkanes are known to be relatively unreactive compounds, the alkylation reaction occurs for a number of PAHs and a wide range of starting materials including cyclic, normal, long-chain, short-chain, substituted, and unsubstituted alkanes. Different experimental conditions such as the physical state of the sample irradiated, the presence or absence of gas, the identity of the gas bubbled, and the ratio of PAH:alkane do not affect photoalkylation.

The exact conditions prevalent on the early Earth are unknown, and our experiments were designed to simulate a range of prebiotic environments described in the literature. The robustness of the photoalkylation reaction as well as the ease with which it occurs strongly suggests that any PAH molecule exposed to UV light on the prebiotic ocean was likely to undergo alkylation in the presence of alkanes. Because C-C bonds are strong, the photoreactions on early Earth would be a remarkably facile way of linking at least some of the carbon atoms in PAHs and alkanes present. It is likely that the alkylated products in the prebiotic environment underwent subsequent reactions to create even more complex organic species.

In the experiments performed under model ISM conditions, alkylated PAHs are again produced. The results suggest a pathway for the formation of complex interstellar aromatic compounds, which may have been incorporated into meteorites over time.

To the best of our knowledge, this work is the first report of photochemical formation of alkylated PAHs under prebiotic and interstellar conditions. The photoreaction of PAHs is proven to be a feasible, robust, and facile way to produce C-C bonds, one of the key requirements in the synthesis of complex compounds, in reasonably high yields.

Acknowledgments

We thank Louis Allamandola, Scott Sandford, Max Bernstein, and Jason Dworkin, Astrochemistry Laboratory, NASA Ames Research Center, for preparing the ISM samples and for useful discussions. Fiona Plows at Stanford University provided us with valuable comments and suggestions. This research was funded by the National Aeronautics and Space Administration's program in cosmochemistry, Grant # NAG5-7208.

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