Meteoritics & Planetary Science 36, 351–358 (2001)
Available online at http://www.uark.edu/meteor

Ultraviolet irradiation of naphthalene in H_2O ice: Implications for meteorites and biogenesis

MAX P. BERNSTEIN†, JASON P. DWORKIN†, SCOTT A. SANDFORD*
AND LOUIS J. ALLAMANDOLA

NASA Ames Research Center, Mail Stop 245-6, Moffett Field, California 94035-1000, USA
†Also of the SETI Institute, Mountain View, California 94043, USA
*Correspondence author's e-mail address: ssandford@mail.arc.nasa.gov

(Received 2000 August 29; accepted in revised form 2000 November 15)

Abstract–The polycyclic aromatic hydrocarbon (PAH) naphthalene was exposed to ultraviolet radiation in H_2O ice under astrophysical conditions, and the products were analyzed using infrared spectroscopy and high-performance liquid chromatography. As we found in our earlier studies on the photoprocessing of coronene in H_2O ice, aromatic alcohols and ketones (quinones) were formed. The regiochemistry of the reactions is described and leads to specific predictions of the relative abundances of various oxidized naphthalenes that should exist in meteorites if interstellar ice photochemistry influenced their aromatic inventory. Since oxidized PAHs are present in carbon-rich meteorites and interplanetary dust particles (IDPs), and ubiquitous in and fundamental to biochemistry, the delivery of such extraterrestrial molecules to the early Earth may have played a role in the origin and evolution of life.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are common in carbonaceous chondrites (cf., Cronin *et al.*, 1988; Hahn *et al.*, 1988; Cronin and Chang, 1993), and interplanetary dust particles (IDPs) (Allamandola *et al.*, 1987; Clemett *et al.*, 1993), and are probably the most abundant and widespread class of organic compounds in the universe (Puget and Leger 1989; Allamandola *et al.*, 1989, 1999). These PAHs are observed to be in the gas phase in a wide variety of interstellar environments, for example, protoplanetary and planetary nebulae, reflection nebulae, HII regions, and the diffuse interstellar medium. However, in dense molecular clouds where temperatures are low ($T < 50$ K) PAHs, along with most other species, condense onto refractory dust grains (Sandford and Allamandola, 1993). The resulting ice mantles can have a variety of compositions, but H_2O is the dominant species in the ices along most lines-of-sight through dense interstellar clouds (see Sandford, 1996). The presence of PAHs in interstellar ices has been demonstrated by recent astronomical detection of their C-H stretching and out-of-plane bending mode bands in absorption in the spectra of stars embedded within dense clouds (Sellgren *et al.*, 1995; Brooke *et al.*, 1999; Chiar *et al.*, 2000; Bregman *et al.*, 2000). In addition, emission from PAHs has been reported in the coma of comet P/Halley (Moreels *et al.*, 1994).

Kerridge *et al.* (1987) determined that the organic population in the Murchison meteorite contains three or four isotopically distinct components, suggesting a complex history. At least three of these components carry deuterium-enrichment signatures indicative of an interstellar heritage, and PAHs were found to be a major carrier of the deuterium (Kerridge *et al.*'s component C(II)H(II)). The suite of meteoritic organics examined by Krishnamurthy *et al.* (1992) were observed to have δD values that ranged from about +100 to +1000, with the aromatic fractions having higher values than the aliphatic fractions. There is also evidence that suggests that PAHs may be one of the carriers of deuterium excess in IDPs (Messenger *et al.*, 1995, 1996; Keller *et al.*, 2000). These observations all suggest that at least a portion of the PAHs in meteorites have an interstellar origin.

Based on the evidence that PAHs are abundant in interstellar space and in meteorites, and that at least some of the meteoritic aromatics have an interstellar heritage, we have been investigating the ultraviolet (UV) processing of PAHs in H_2O ice with an emphasis on exploring the possible connections between interstellar and meteoritic PAHs. We have previously shown that PAHs undergo both oxidation and reduction photoreactions in ices that result in the production of aromatic hydrocarbon species similar to some of those seen in carbonaceous chondrites and IDPs (Bernstein *et al.*, 1999), and that these same processes can produce large deuterium enrichments in the aromatics (Sandford *et al.*, 2000; 2001, unpubl. data). Here we describe related studies on the PAH naphthalene ($C_{10}H_8$) with an emphasis on understanding the regiochemistry of the process.

© Meteoritical Society, 2001. Printed in USA.

EXPERIMENTAL TECHNIQUES

The UV irradiation of H_2O-naphthalene ices were performed in an evacuated sample chamber containing a rotatable ~15 K CsI or Ni foil substrate coupled to an infrared spectrometer that is described in detail elsewhere (Bernstein *et al.*, 1995; Hudgins and Allamandola, 1995). In these experiments, the naphthalene and H_2O were simultaneously vapor deposited from a finger containing liquid water and solid naphthalene onto the substrate at a rate that produced an ice layer ~0.1 μm thick after 30 min of deposition (as measured from interference fringes in the infrared spectrum of the sample). After deposition onto the CsI, the 4000–500 cm^{-1} (2.5–20 μm) infrared spectrum of the H_2O-naphthalene ice was measured at a resolution of 0.9 cm^{-1} (the observed width of an unresolved line). Analysis of the areas of the resulting infrared absorption bands of both the H_2O and naphthalene indicates that our sample ice layers typically had H_2O/naphthalene ratios of >100. This vapor deposition technique produces intimately mixed ices with the H_2O in a high density amorphous form that is only observed at low temperatures and pressures, a form that is believed to be representative of H_2O-rich ices in interstellar molecular clouds (Allamandola and Sandford, 1988; Jenniskens and Blake, 1994; Jenniskens *et al.*, 1995).

After deposition, samples were usually UV irradiated using a microwave-powered, flowing hydrogen, discharge lamp (Warneck, 1962), which produces ~2×10^{15} photons cm^{-2} s^{-1} with a wavelength distribution that is representative of the UV radiation expected in dense interstellar clouds (cf., Prasad and Tarafdar, 1983). Cycles of deposition and photolysis were repeated up to a total of five times, depending on sample requirements. Analogous experiments were also carried out in which the samples were continuously co-deposited simultaneous with UV photolysis for up to a week. In a few experiments, we inserted a CaF_2 filter in front of the hydrogen lamp during irradiation to block the highest energy photons ($\lambda < 160$ nm), or we employed a high-pressure xenon arc lamp and water filter, both with and without a glass filter (to remove $\lambda < 320$ nm) to assess the wavelength dependency of the photolysis. For further details of the various lamp/filter configurations, see Table 1. This was done to delineate the wavelength dependence of the photochemistry and simulate radiation at the surfaces of icy solar system bodies.

Following photolysis, samples were warmed to 160 K at ~1 K/min under dynamic vacuum. The foil onto which the ice was deposited was then removed from the vacuum system under air, placed in a glass vial, and the ice was quickly dissolved in 250 μL of HPLC grade methanol. The sample solution was then separated using high-performance liquid chromatography (HPLC). Chromatography was performed on a Hewlett Packard 1100 series HPLC with tandem diode array UV/Vis and fluorescence detectors and a manual injector with a 5 μL loop. Separation was achieved using a Vydac C-18 4.6 × 250 mm 5 μm resin analytical column and a mobile phase of 10% A (methanol) and 90% B (pH 5.5 50 mM sodium acetate + 8% methanol) to 40% B in 15 min. Elution was monitored by simultaneously measuring both the absorption at 220, 290, and 320 nm and the emission at 325 nm when excited at 220 nm. Observed peaks were identified by co-injection with standards and by comparison of the UV spectrum of the unknown with that of the standard. Abundances were quantified by calculating the average of the ratio of the area of a given peak at each wavelength to that of a linear fit through zero of the standard at three concentrations.

TABLE 1. Summary of experiments.

UV irradiation	Lamp	UV fluence*	Filter	Naphthalene (%)	1-Naphthol (%)	2-Naphthol (%)	1,4-Naphthoquinone (%)
None	N/A	0	N/A	100	0[†]	0[†]	0[†]
10 min/layer	Hydrogen	1×10^{18}[‡]	MgF_2	99	0.6	0.4	[§]
5 h/layer	Hydrogen	3×10^{19}[‡]	MgF_2	47	28	25	[§]
12 h/layer	Hydrogen	7×10^{19}[‡]	MgF_2	39	34	27	[§]
Simultaneous[#]	Hydrogen	4×10^{18}[‡]	MgF_2	96	2.4	1.3	0.3
Simultaneous[#]	Hydrogen	2×10^{18}[$]	CaF_2	97	2.4	0.4	0.2
Simultaneous[#]	Xenon	0[@]	Glass + Water	100	0[†]	0[†]	0[†]
Simultaneous[#]	Xenon	~1×10^{20}[¥]	MgF_2 + Water	81	15	4	[§]

*Photons per 0.1 μm layer per cm^2.

[†] Undetected.

[‡] Photons having $\lambda > 110$ nm evenly divided between the Lyman α line at 121.6 nm and a roughly 20 nm wide molecular transition centered at 160 nm.

[§] Identification considered to be tentative because of low concentration and poor signal-to-noise.

[#] Deposition and irradiation were done simultaneously, equivalent to ~30 min of UV irradiation per 0.1 μm layer of ice.

[$] Photons having $\lambda > 160$ nm with the majority of the flux falling between 140 and 160 nm.

[@] The glass/water filter combination only passes photons with $\lambda > 320$ nm.

[¥] Photons having $\lambda > 200$ nm, with most of the flux falling in a continuum spanning the range from 300 nm into the visible.

We also performed gas chromatography with mass spectral detection (GC-MS) on one of our samples. The GC-MS was performed on a Thermoquest-Finnigan GCQ ion trap with an injector temperature of 240 °C and a DB-17ms-60m (J&W Scientific) column at an initial temperature of 70 °C increasing at 5 °C/min to 240 °C. A naphthalene sample was extracted with methanol, an aliquot was analyzed *via* HPLC, and the remainder was dried, then derivatized by adding Bissilyl-trifluoroacetamide containing 1% trimethyl chlorosilane (from Alltech) and anhydrous pyridine in a ratio of 1:3. This was sonicated and stirred for 30 min, after which 1 μL was injected into the GC-MS. A sample was also injected without derivatization. However, for the compounds of interest, the GC-MS was 100 to 1000× less sensitive than the HPLC and the GC-MS results were of limited utility.

A comparison of the results from different experiments demonstrates that samples prepared by ice deposition followed by irradiation produces the same products as by simultaneously depositing with irradiation. However, simultaneous deposition with irradiation gave higher product yields, probably because the ices were considerably thicker and were more uniformly irradiated. Experiments in which we examined the yield for a variety of single-layer irradiation times (0.17, 1, 3, 5, and 12 h) indicate that the ices co-deposited with simultaneous photolysis were exposed to UV doses equivalent to individual (~0.1 μm thick) ice layers subjected to ~30 min of UV. These doses fall within the range expected for ices in dense molecular clouds (cf., Prasad and Tarafdar, 1983; Bernstein *et al.*, 1995).

The naphthalene and oxidized naphthalene standards used in our studies were purchased from the Aldrich chemical company: naphthalene, 1-naphthol, 2-naphthol, 1,4-naphthoquinone, 1,2-naphthoquinone, 1,2-dihydroxy naphthalene, 1,3-dihydroxy naphthalene, 1,5-dihydroxy naphthalene, 1,6-dihydroxy naphthalene, 2,3-dihydroxy naphthalene, 2,6-dihydroxy naphthalene, 2,7-dihydroxy naphthalene, 2-hydroxy-1,4-naphthoquinone, and 5-hydroxy-1,4-naphthoquinone. We also used 1,4-dihydroxy naphthalene from the Fluka Chemical Company. No naphthols were detected *via* HPLC as contaminants in the 99% pure naphthalene. The HPLC grade methanol, sodium hydroxide, and acetic acid for the HPLC buffer were all obtained from Fisher. The water was purified *via* a Millipore Milli-Q water system to 18.2 MΩ and then triply freeze/pump/thawed to remove dissolved gases.

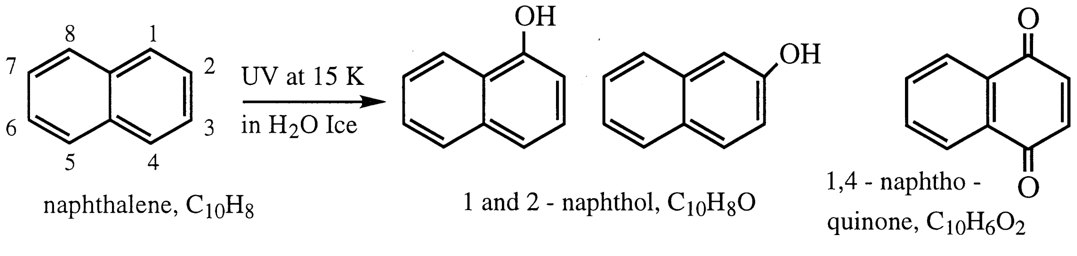
Control experiments performed either in the absence of naphthalene or with *un*irradiated H_2O-naphthalene mixtures did not produce any detectable products. These experiments indicate that the oxidized naphthalene products described below were formed only when H_2O and naphthalene are exposed together to UV irradiation. Thus, they are not the result of contamination or other nonphotolytic reaction processes.

RESULTS

Our HPLC analyses demonstrate that the UV photolysis of H_2O-naphthalene ices results in a mixture of unprocessed naphthalene and oxidized naphthalene compounds (Fig. 1). The oxidized photoproducts include both alcohols and ketones. The main products are the two isomers of naphthalene bearing one hydroxy group (naphthols), and an isomer of naphthalene bearing two carbonyls (1,4-napthoquinone). The structures of these compounds are shown in Eq. (1) below.

In typical simultaneous deposition/irradiation experiments (equivalent to 30 min UV per 0.1 μm ice layer), 1-naphthol and 2-naphthol were observed to be produced with approximately 2.5% and 1.4% yields, respectively, relative to naphthalene. 1,4-Napthoquinone, the next most abundant product, is produced with roughly a 0.4% yield relative to naphthalene. The three compounds, represented on the right side of Eq. (1), make up >97% of all the products of H_2O-naphthalene ice photolysis at ~15 K. However, as the UV dose was increased, the yield increased and the ratios of the mono-naphthols approached 1 (at 12 h of photolysis, the yield was 34% for the 1-naphthol and 27% for the 2-naphthol). At lower doses the yield decreased, but the ratio of 1- to 2-naphthol stayed near 2 (10 min of photolysis produced yields of 0.63% for 1-naphthol and 0.37% for 2-naphthol).

Other naphthalenes with multiple oxygen atoms, as well as other unidentified products, are also present, but at lower levels (<0.1%). We have identified the 2,6- and 2,7-dihydroxy naphthalenes, based on both their retention times and their UV absorption spectra. We have also tentatively identified the 1,3- and 1,5-dihydroxy naphthalenes and 5-hydroxy-1,4-naphthoquinone (juglone) at 12.9, 9.9, and 16.1 min, respectively (Fig. 1). We have less confidence in these latter three identifications because of the poor quality of their UV spectra due to contaminating peaks, low abundances, and inconclusive co-injections. We searched for, but were unable to detect, the other oxidized naphthalenes listed in the experimental section. There are a number of small peaks observed in the HPLC trace that we were unable to identify because we were not able to obtain standard samples of all the



(1)

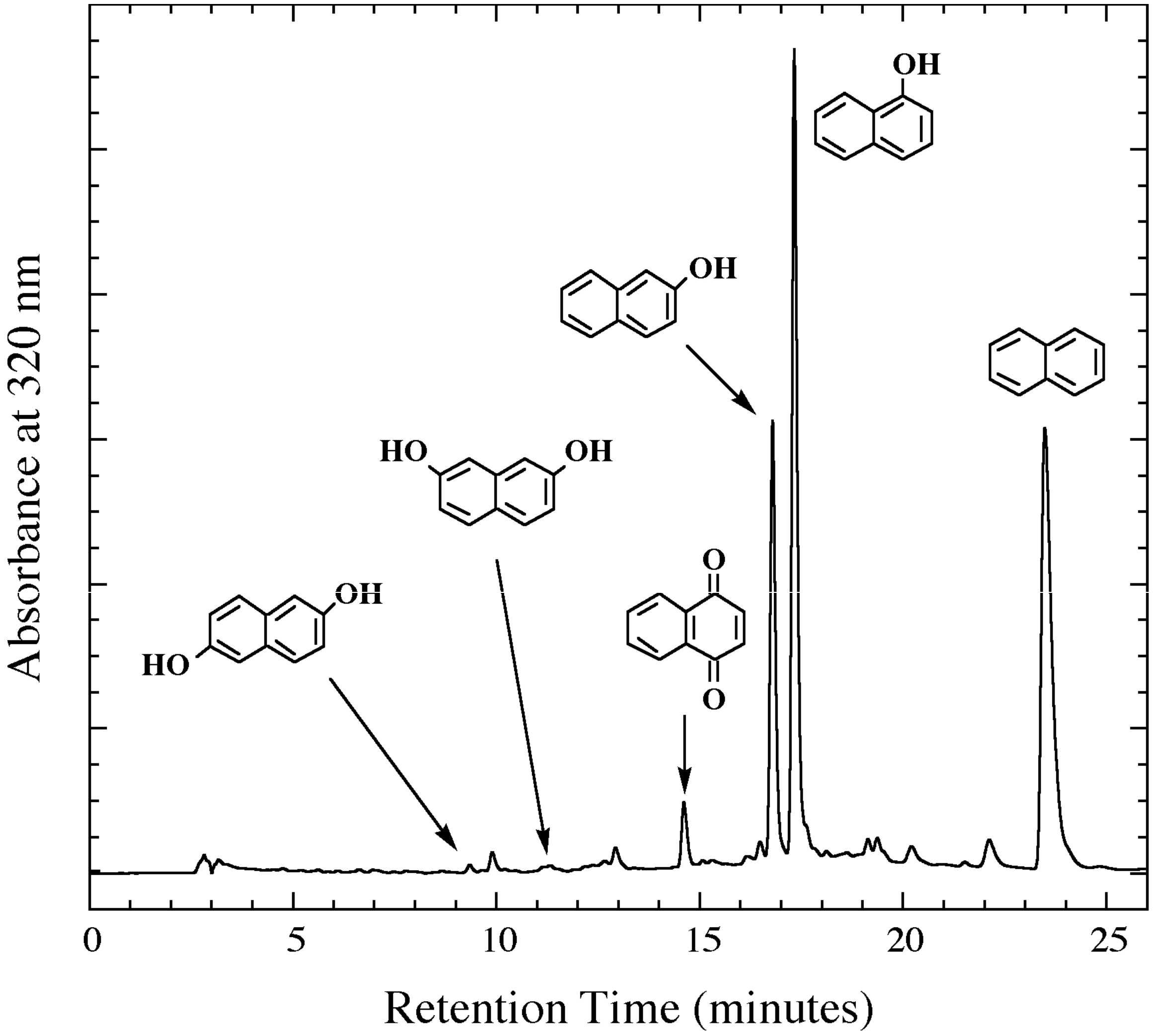


FIG. 1. The HPLC separation of the material resulting from the UV photolysis of an H_2O:naphthalene ice at 15 K. The peaks associated with the original naphthalene and the photoproducts 1-naphthol, 2-naphthol, 1,4-naphthoquinone, 2,6-dihydroxy naphthalene, and 2,7-dihydroxy naphthalene are labeled with the corresponding molecular structures.

possible oxidized and reduced naphthalene variants. However, it is reasonable to conjecture that these unidentified species include other dihydroxy naphthalenes, naphthoquinones, and possibly partially hydrogenated hydroxy naphthalenes.

Because of its lower sensitivity for these compounds, the GC-MS results obtained from our largest sample after derivatization were inconclusive. They provide a tentative confirmation of the presence of 1-naphthol and show a series of very weak peaks that elute together that are consistent with the presence of a number of oxides of naphthalene. However, the signal was not good enough to identify the individual species.

Experiments in which we used a CaF_2 filter to block the highest energy photons ($\lambda < 160$ nm) from the H_2 lamp, and those using a high-pressure Xe lamp, produced similar results to the unfiltered H_2 lamp. This indicates that the formation of these photoproducts does not require Lyman α or even vacuum UV photons. However, when a glass filter was employed to remove photons with $\lambda < 320$ nm, the light was unable to drive these reactions to any detectable degree ($<10^{-3}$% yield of naphthols).

In addition, experiments in which we photolyzed the H_2O-naphthalene samples at 150 K produced similar results to those of our 15 K samples; the alcohols were still the dominant products and 1-naphthol was produced more abundantly than the 2-naphthol. Finally, in experiments in which we photolyzed H_2O ices containing either of the mono-naphthols, rather than naphthalene, we observed the formation of the other mono-naphthol and unoxidized naphthalene.

Details of the various experiments and the relative yields of the main products are summarized in Table 1. The photon doses and yields reported in Table 1 should be viewed with some caution because the wavelength-dependent UV cross-sections of naphthalene and intermediates in H_2O are unknown (naphthalene's principle UV absorption falls between 180 and 300 nm when in Ar; Salama and Allamandola, 1993). The reaction process may also involve multiple serial photons. Thus, the yield of photoproducts is dependent on the spectrum of the lamp, total photolysis time, *etc*. and the yields reported in Table 1 are only relevant for the conditions probed by our experiments.

DISCUSSION

Regiochemistry and Mechanism

In our previous studies of the photochemistry of 11 larger PAHs we concentrated on the fully condensed PAH molecule coronene ($C_{24}H_{12}$). Because of its high symmetry, coronene has only one possible mono-alcohol and one mono-ketone isomer (Bernstein *et al.*, 1999). The structure of naphthalene allows for the possibility of two different naphthol, and ten diol, structures (see Eq. (1)). Thus, while the results presented here are qualitatively in agreement with our earlier work, the regiochemistry is more complex.

The naphthols were the most abundant products in all our experiments. For realistic doses the 1-naphthol was measured to be consistently about a factor of 2 more abundant than the 2-naphthol. The dominance of the 1-naphthol is probably consistent with several production mechanisms, but it may be a reflection of the stability of the intermediate leading to this isomer. Theoretical calculations (Ricca and Bauschlicher, 2000), the observation of the naphthalene cation when naphthalene is UV irradiated in H_2O ice at 15 K (Gudipati *et al.*, 2001, unpubl. data), and the invariance in the ratio of produced naphthols with temperature are all consistent with a naphthalene radical cation intermediate, as previously postulated for other aromatics (Bernstein *et al.*, 1999). Our observation that oxidation shuts down when $\lambda < 320$ nm light is excluded may correspond to the point at which there is insufficient energy to generate the radical cation, but this has yet to be demonstrated.

The UV photolysis of either mono-naphthol in H_2O ice produced the other mono-naphthol and unoxidized naphthalene. Such a reversible interconversion could provide a path to 2-naphthol (the thermodynamic product), even if the 1-naphthol were formed initially.

Possible Implications for Meteoritic Aromatics

Oxidized Aromatics–It has long been known that the organic fraction of meteorites contains a major aromatic component (cf., Studier *et al.*, 1972; Hayatsu *et al.*, 1977), and various studies over the years have identified the presence of a host of aromatic molecules, including the molecule naphthalene (cf., Pering and Ponnamperuma, 1971; Basile *et al.*, 1984; Tingle *et al.*, 1991; Kovalenko *et al.*, 1992; Zenobi *et al.*, 1992). To date, relatively little attention has been paid to oxidized aromatics in meteorites. However, studies of the Murchison meteorite by Basile *et al.* (1984), Hahn *et al.* (1988), and Krishnamurthy *et al.* (1992) have identified a number of aromatic ketones like fluorenone, anthracenenone, anthracenedione, and benzoanthracenone. While the chromatograms presented by Krishnamurthy *et al.* contain unidentified peaks with retention times consistent with naphthols and naphthoquinones, we are unaware of anyone specifically searching for oxidized naphthalenes in meteorites and hydroxy-aromatics have not been reported in meteorites. Whether the lack of detection of hydroxy-aromatics is due to their absence, the result of selection effects associated with their extraction from meteorites, or the fact that they have not been specifically searched for is not yet clear. Targeted searches for aromatics with -OH edge groups are needed to address this issue. Since two of our three most abundant products are hydroxy-naphthalenes, any future studies of the relative abundances of the naphthols and naphthoquinones in carbonaceous chondrites could be instructive regarding the possible role of ice photochemistry as a source of such species.

Regiochemistry–Ice Photolysis *versus* Aqueous Alteration–Many meteorites in which aromatic compounds have been detected experienced aqueous alteration on their parent body (cf., Zolensky and McSween, 1988). One could imagine that this process might also contribute to the oxidation of PAHs. Unfortunately, the oxidation of PAHs in liquid water (in the absence of radiation or air) has received very little study. Thus, it is not currently possible to say whether PAH oxidation would be appreciable under the conditions and time scales of aqueous alteration on asteroidal parent bodies, let alone identifying isomers that would be indicative of this process. However, a project is currently underway in our laboratory to study the rates and products of PAH oxidation in liquid water to determine if there are product isomers or ratios that might distinguish between the oxidized aromatic products of aqueous alteration and ice photochemistry.

Although little is known about the thermal oxidation of naphthalene in liquid water, studies on the photo-oxidation of PAHs in liquid water have been reported in the environmental literature (Keyeyan and Perez, 1991; Beltran *et al.,* 1995). In contrast to our ice photochemistry results, where 1-naphthol is favored, these papers report that the major product of naphthalene photo-oxidation under terrestrial conditions is 2-naphthol. Thus, it is possible that the relative proportion of 1-naphthol and 2-naphthol in meteorites may provide an indicator of the relative contributions of aqueous alteration and ice photolysis to oxidized meteoritic aromatics.

Of course, meteorites have had long and complex histories and the organics found in them were undoubtedly created by the combination of a variety of processes. A fuller understanding of the complex chemistry that led to the organics observed in carbonaceous chondrites will undoubtedly only come about through continued meteoritic and laboratory studies.

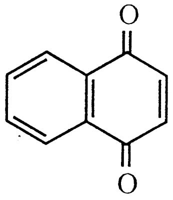
Deuterium Enrichments in Meteoritic Aromatics–There are a number of processes by which interstellar PAHs can become deuterium enriched, including gas phase ion-molecule reactions (cf., Dalgarno and Lepp, 1984; Tielens, 1997), gas-grain reactions (Tielens, 1983, 1997), and unimolecular photodissociation (Allamandola *et al.*, 1987, 1989). In addition, we have recently shown that, in interstellar ices, PAHs can become enriched in deuterium by the same ice photolysis processes that make the oxidized aromatics (Sandford *et al.*, 2000). Each of these various processes is expected to leave a distinctly different signature in the distribution of deuterium enrichment in the PAH population (Sandford *et al.*, 2001, unpubl. data).

Ion-molecule reactions would be expected to preferentially deuterate the *larger* PAHs (Tielens, 1997; Charnley, pers. comm.), while unimolecular photodissociation should deuterium-enrich only the *smallest* ones (Allamandola *et al.*, 1989). In contrast, in deuterium-enriched interstellar ices (cf., Sandford, 1996; Teixeira *et al.*, 1999), ice photochemistry should produce aromatic deuterium enrichments that are *independent* of PAH molecular size, but which should correlate with specific functional groups, namely the alcohols, ketones, and aliphatic rings produced when PAHs are UV irradiated in H_2O-rich ices (Sandford *et al.*, 2000).

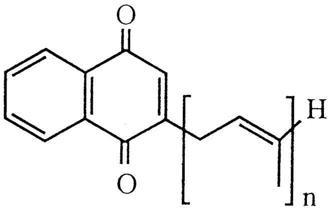
Thus, the regiochemistry of PAH deuterium-enrichment in meteoritic materials, and correlation (or lack thereof) with the presence of specific functionalized aromatic compounds could place constraints on the relative contributions of different interstellar processes that acted on presolar PAHs. In light of the recent work of Sandford *et al.* (2000) and the work reported above, searches for a correlation of deuterium-enrichment with PAH size and oxidation state in meteoritic organics would be of particular interest.

Astrobiological Implications

The UV photolysis of naphthalene in H_2O ice produces 1,4-napthoquinone as the third most abundant product in our ice experiments. 1,4-naphthoquinone, further functionalized, often with a methyl group and a long isoprene chain, play essential roles in biochemistry. While best known as K vitamins and for their role as blood clotting co-factors, napthoquinones, such as the menaquinones, also perform key biochemical functions in organisms all across the tree of life (Suttie, 1979). Menaquinones often augment or replace ubiquinone or plastoquinone as electron transporters and oxidative phosphorylation co-enzymes. Electron transport and oxidative phosphorylation are absolutely essential processes that are integral to terrestrial metabolism. As one example, the Archaea *Thermoproteus tenax* use menaquinones in the reduction of elemental sulfur to H_2S as their main energy source (Thurl *et al.*, 1985).



1, 4-Naphthoquinone



Menaquinone

It is possible that the ease of production of 1,4-napthoquinone and the ubiquity of 1,4-napthoquinone-based compounds in biochemistry is not a coincidence. Our lab simulations of ice photochemistry suggest a possible connection between the interstellar molecular clouds from which protostellar nebulae form, and meteoritic materials such as quinones and aromatic alcohols. The possibility that these aromatic compounds were delivered to the early Earth by meteorites and IDPs suggests that this connection could have influenced the selection of this class of coenzymes during the origin of life and/or its early evolution.

CONCLUSIONS

The main products of the UV irradiation of the PAH naphthalene in H_2O at 15 K are 1- and 2-naphthol, and 1,4-napthoquinone. For astrophysically relevant irradiations, the yields of these compounds were found to be 2.5%, 1.4%, and 0.4%, respectively. At lower abundance ($<0.1\%$ yield) we have also identified the 2,6- and 2,7-dihydroxy naphthalenes, and possibly the 1,3- and 1,5-dihydroxy naphthalenes and 5-hydroxy-1,4-naphthoquinone (Juglone). A number of other minor photoproducts ($<0.1\%$) remain unidentified.

The regiochemistry of the UV photoproducts of H_2O-naphthalene ices is distinctive and can be used to make predictions of the relative abundances of various oxidized naphthalenes that should exist in meteorites if interstellar PAHs contributed to their aromatic inventory. This same interstellar photolysis process is expected to lead to deuterium-enrichment of the aromatics. Thus, if a significant fraction of the aromatics in meteorites have been processed in this manner, one would predict that the deuterium enrichment in meteoritic PAHs should correlate with the presence of reduced PAHs (H_n-PAHs) and oxidized PAHs (aromatic alcohols and ketones).

While a few oxidized aromatic compounds have been detected in meteorites, this class of molecules has yet to be carefully characterized in meteoritic organics. Thus, a systematic examination of the abundance, deuterium-enrichment, and regiochemistry of oxidized PAHs in meteorites could lead to significant constraints on the interstellar source(s) of meteoritic PAHs and the processes by which they formed and evolved.

Finally, the presence of oxidized aromatic materials in meteorites would be of special interest since these species exhibit interesting biochemical activity and their delivery to the early Earth by extraterrestrial sources could have played a role in the origin and evolution of life.

Acknowledgements–This work was supported by NASA grants 344-37-44-01 (Origins of Solar Systems), 344-38-12-04 (Exobiology), and 344-50-92-02 (Astrobiology). The authors grateful acknowledge useful discussions with C. Bauschlicher, O. Botta, S. Charnley, J. Cronin, D. Deamer, T. Mahajan, and A. Ricca. They are also grateful for excellent technical support from R. Walker, assistance with the GC-MS measurements from G. Cooper, and very helpful reviews from G. McDonald and an anonymous referee.

Editorial handling: D. W. G. Sears

REFERENCES

ALLAMANDOLA L. J. AND SANDFORD S. A. (1988) Laboratory simulation of dust spectra. In *Dust in the Universe* (eds. M. Bailey and D. Williams), pp. 229–263. Cambridge Univ. Press, Cambridge, U.K.

ALLAMANDOLA L. J., SANDFORD S. A. AND WOPENKA B. (1987) Interstellar polycyclic aromatic hydrocarbons and carbon in interplanetary dust particles and meteorites. *Science* **237**, 56–59.

ALLAMANDOLA L. J., TIELENS A. G. G. M. AND BARKER, J. R. (1989) Interstellar polycyclic aromatic hydrocarbons: The infrared emission bands, the excitation-emission mechanism and the astrophysical implications. *Astrophys. J. Suppl. Ser.* **71**, 733–755.

ALLAMANDOLA L. J., HUDGINS D. M. AND SANDFORD S. A. (1999) Modeling the unidentified infrared emission with combinations of polycyclic aromatic hydrocarbons. *Astrophys. J.* **511**, L115–L119.

BASILE B. P., MIDDLEDITCH B. S. AND ORÓ J. (1984) Polycyclic aromatic hydrocarbons in the Murchison meteorite. *Geochim. Cosmochim. Acta* **5**, 211–216.

BELTRAN F. J., OVEJERO G., GARCIA-ARAYA J. F. AND RIVAS J. (1995) Oxidation of polynuclear aromatic hydrocarbons in water. 2. UV radiation and ozonation in the presence of UV radiation. *Ind. Eng. Chem. Res.* **34**, 1607–1615.

BERNSTEIN M. P., SANDFORD S. A., ALLAMANDOLA L. J., CHANG S. AND SCHARBERG M. A. (1995) Organic compounds produced by photolysis of realistic interstellar and cometary ice analogs containing methanol. *Astrophys. J.* **454**, 327–344.

BERNSTEIN M. P., SANDFORD S. A., ALLAMANDOLA L. J., GILLETTE J. S., CLEMETT S. J. AND ZARE R. N. (1999) Ultraviolet irradiation of polycyclic aromatic hydrocarbons (PAHs) in ices: Production of alcohols, quinones, and ethers. *Science* **283**, 1135–1138.

BREGMAN J. D., HAYWARD T. L. AND SLOAN G. C. (2000) Discovery of the 11.2 micron polycyclic aromatic hydrocarbon band in absorption toward Monoceros R2 IRS3. *Astrophys. J.* **544**, L75–L78.

BROOKE T. Y., SELLGREN K. AND GEBALLE T. R. (1999) New 3 micron spectra of young stellar objects with H_2O ice bands. *Astrophys. J.* **517**, 883–900.

CHIAR J. E., TIELENS A. G. G. M., WHITTET D. C. B., SCHUTTE W. A., BOOGERT A. C. A., LUTZ D., VAN DISHOECK E. F. AND BERNSTEIN M. P. (2000) The composition and distribution of dust along the line of sight towards the Galactic Center. *Astrophys. J.* **537**, 749–762.

CLEMETT S., MAECHLING C., ZARE R., SWAN P. AND WALKER R. (1993) Identification of complex aromatic molecules in individual interplanetary dust particles. *Science* **262**, 721–725.

CRONIN J. R. AND CHANG S. (1993) Organic matter in meteorites: Molecular and isotopic analyses of the Murchison meteorite. In *The Chemistry of Life's Origins* (eds. J. Greenberg, C. Mendoza-Gómez and V. Pirronello), pp. 209–258. Kluwer Academic Publishers, The Netherlands.

CRONIN J. R., PIZZARELLO S. AND CRUIKSHANK D. P. (1988) Organic matter in carbonaceous chondrites, planetary satellites, asteroids, and comets. In *Meteorites and the Early Solar System* (eds. J. F. Kerridge and M. S. Matthews), pp. 819–857. Univ. Arizona Press, Tucson, Arizona, USA.

DALGARNO A. AND LEPP S. (1984) Deuterium fractionation mechanisms in interstellar clouds. *Astrophys. J.* **287**, L47–L50.

HAHN J. H., ZENOBI R., BADA J. L. AND ZARE R. N. (1988) Application of two-step laser mass spectrometry to cosmochemistry: Direct analysis of meteorites. *Science* **239**, 1523–1525.

HAYATSU R., MATSUOKA S., SCOTT R. G., STUDIER M. H. AND ANDERS E. (1977) Origin of organic matter in the early solar system. VII. The organic polymer in carbonaceous chondrites. *Geochim. Cosmochim. Acta* **41**, 1325–1339.

HUDGINS D. M. AND ALLAMANDOLA L. J. (1995) Infrared spectroscopy of matrix-isolated polycyclic aromatic hydrocarbon cations 2: The members of the thermodynamically most favorable series through coronene. *J. Phys. Chem.* **99**, 3033–3046.

JENNISKENS P. AND BLAKE D. F. (1994) Structural transitions in amorphous water ice and astrophysical implications. *Science* **265**, 753–756.

JENNISKENS P., BLAKE D. F., WILSON M. A. AND POHORILLE A. (1995) High-density amorphous ice, the frost on interstellar grains. *Astrophys. J.* **455**, 389–401.

KELLER L. P., MESSENGER S., FLYNN G. J., JACOBSEN C. AND WIRICK S. (2000) Chemical and petrographic studies of molecular cloud materials preserved in interplanetary dust (abstract). *Meteorit. Planet. Sci.* **35 (Suppl.)**, A86–A87.

KERRIDGE J. F., CHANG S. AND SHIPP R. (1987) Isotopic characterization of kerogen-like material in the Murchison carbonaceous chondrite. *Geochim. Cosmochim. Acta* **51**, 2527–2540.

KEYEYAN Y. AND PEREZ G. (1991) Radiation induced gas phase naphthalene hydroxylation. *Chemosphere* **23**, 627–632.

KOVALENKO L. J., MAECHLING C. R., CLEMETT S. J., PHILIPPOZ J. M., ZARE R. N. AND ALEXANDER C. M. O'D. (1992) Microscopic organic analysis using two-step laser mass spectrometry: Application to meteoritic acid residues. *Anal. Chem.* **64**, 682–690.

KRISHNAMURTHY R., EPSTEIN S., CRONIN J., PIZZARELLO S. AND YUEN G. (1992) Isotopic and molecular analyses of hydrocarbons and monocarboxylic acids of the Murchison meteorite. *Geochim. Cosmochim. Acta* **56**, 4045–4058.

MESSENGER S., CLEMETT S. J., KELLER L. P., THOMAS K. L., CHILLIER X. D. F. AND ZARE R. N. (1995) Chemical and mineralogical studies of an extremely deuterium-rich IDP (abstract). *Meteoritics* **30**, 546.

MESSENGER S., WALKER R. M., CLEMETT S. J. AND ZARE R. N. (1996) Deuterium enrichments in cluster IDPs (abstract). *Lunar Planet. Sci.* **27**, 867.

MOREELS G., CLAIREMIDI J., HERMINE P., BRECHIGNAC P. AND ROUSSELOT P. (1994) Detection of a polycyclic aromatic molecule in Comet P/Halley. *Astron. Astrophys.* **282**, 643–656.

PERING K. L. AND PONNAMPERUMA C. (1971) Aromatic hydrocarbons in the Murchison meteorite. *Science* **173**, 237–239.

PRASAD S. S. AND TARAFDAR S. P. (1983) UV radiation field inside dense clouds: Its possible existence and chemical implications. *Astrophys. J.* **267**, 603–609.

PUGET J. L. AND LEGER A. (1989) A new component of the interstellar matter: Small grains and large aromatic molecules. *Ann. Rev. Astr. Ap.* **27**, 161–198.

RICCA A. AND BAUSCHLICHER C. W., JR. (2000) The reactions of polycyclic aromatic hydrocarbons with OH. *Chem. Phys. Lett.* **328**, 396.

SALAMA F. AND ALLAMANDOLA L. J. (1993) Neutral and ionized polycyclic aromatic hydrocarbons, diffuse interstellar bands and the ultraviolet extinction curve. *J. Chem. Soc. Farad. Trans.* **89**, 2277–2284.

SANDFORD S. A. (1996) The inventory of interstellar materials available for the formation of the solar system. *Meteorit. Planet. Sci.* **31**, 449–476.

SANDFORD S. A. AND ALLAMANDOLA L. J. (1993) Condensation and vaporization studies of CH_3OH and NH_3 ices: Major implications for astrochemistry. *Astrophys. J.* **417**, 815–825.

SANDFORD S. A., BERNSTEIN M. P., ALLAMANDOLA L. J., GILLETTE J. S. AND ZARE R. N. (2000) Deuterium enrichment of PAHs by photochemically induced exchange with deuterium-rich cosmic ices. *Astrophys. J.* **538**, 691–697.

SELLGREN K., BROOKE T. Y., SMITH R. G. AND GEBALLE T. R. (1995) A new 3.25 micron absorption feature towards Mon R2/IRS-3. *Astrophys. J.* **449**, L69–L72.

STUDIER M. H., HAYATSU R. AND ANDERS E. (1972) Origin of organic matter in early solar system – V. Further studies of meteoritic hydrocarbons and a discussion of their origin. *Geochim. Cosmochim. Acta* **36**, 189–215.

SUTTIE J. W., ED. (1979) *Vitamin K Metabolism and Vitamin K Dependent Proteins*. Univ. Park Press, Baltimore, Maryland, USA. 592 pp.

TEIXEIRA T. C., DEVLIN J. P., BUCH V. AND EMERSON J. P. (1999) Discovery of solid HDO in grain mantles. *Astron. Astrophys.* **347**, L19–L22.

TIELENS A. (1983) Surface chemistry of deuterated molecules. *Astron. Astrophys.* **119**, 177–184.

TIELENS A. (1997) Deuterium and interstellar chemical processes. In *Astrophysical Implications of the Laboratory Study of Presolar Materials*, (eds. T. J. Bernatowicz and E. K. Zinner), pp. 523–544. AIP Press, Woodbury, New York, USA.

TINGLE T. N., BECKER C. H. AND MALHOTRA R. (1991) Organic compounds in the Murchison and Allende carbonaceous chondrites studied by photoionization mass spectrometry. *Meteoritics* **26**, 117–127.

THURL S., BUHROW I. AND SCHAFER W. (1985) Quinones from Archaebacteria, I. New types of menaquinones from the thermophilic archaebacterium *Thermoproteus tenax*. *Biol. Chem. Hoppe Seyler* **366**, 1079–1083.

WARNECK P. (1962) A microwave-powered hydrogen lamp for vacuum ultraviolet photochemical research. *Applied Optics* **1**, 721–726.

ZENOBI R., PHILIPPOZ J-M., ZARE R. N., WING M. R., BADA J. L. AND MARTI K. (1992) Organic compounds in the Forest Vale, H4 ordinary chondrite. *Geochim. Cosmochim. Acta* **56**, 2899–2905.

ZOLENSKY M. AND MCSWEEN H. Y., JR. (1988) Aqueous Alteration. In *Meteorites and the Early Solar System*, (eds. J. F. Kerridge and M. S. Matthews), pp. 114–143. Univ. Arizona Press, Tucson, Arizona, USA.

Forward

Back

Table of Contents