



ULTRAVIOLET IRRADIATION OF THE POLYCYCLIC AROMATIC HYDROCARBON (PAH) NAPHTHALENE IN H₂O. IMPLICATIONS FOR METEORITES AND BIOGENESIS

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ABSTRACT

The polycyclic aromatic hydrocarbon (PAH) naphthalene was exposed to ultraviolet radiation in H₂O ice under astrophysical conditions, and the products were analyzed using high performance liquid chromatography. As we found in our earlier studies on the photoprocessing of coronene in H₂O ice, aromatic alcohols and ketones (quinones) were formed. The regiochemistry reported here leads to specific predictions of the relative abundances of oxidized naphthalenes that should exist in meteorites. Since oxidized PAHs are present in meteorites and interplanetary dust particles, 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. © 2002 COSPAR. Published by Elsevier Science Ltd. All rights reserved.

INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) are common in carbonaceous chondrites (Cronin *et al.*, 1988; Hahn *et al.*, 1988; Cronin and Chang, 1993), and 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). 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).

Kerridge *et al.* (1987) and Krishnamurthy *et al.* (1992) have shown PAHs the meteorites carry D-enrichments indicative of an interstellar heritage. There is also evidence that suggests that PAHs may be one of the carriers of deuterium excess in IDPs (Messenger *et al.*, 1995, 1996). These observations all suggest that at least a portion of the PAHs in meteorites have an interstellar origin. We have been investigating the UV processing of PAHs in H₂O ice with an emphasis on exploring the possible connections between interstellar and meteoritic PAHs. We have shown that the PAH coronene undergoes oxidation and reduction reactions in ice producing species similar to those seen in carbonaceous chondrites and IDPs (Bernstein *et al.*, 1999), and that these same processes may produce the deuterium enrichments in the aromatics (Sandford *et al.*, 2000). Here we describe related studies on the PAH naphthalene (C₁₀H₈) with an emphasis on understanding the regiochemistry of the process.

EXPERIMENTAL TECHNIQUES

The UV irradiation of H₂O-naphthalene ices were performed in an evacuated sample chamber containing a rotatable ~15 K CsI or Ni foil substrate described in detail elsewhere (Bernstein *et al.*, 1995; Hudgins and Allamandola, 1995). The naphthalene and H₂O were simultaneously vapor deposited from a finger containing freeze/pump/thawed liquid water and solid naphthalene onto the substrate at a rate that produced an ice layer ~ 0.1 μm thick after 30 minutes of deposition (as measured from interference fringes in the infrared spectrum of the sample). Analysis of the areas of the resulting infrared absorption bands of both the H₂O and naphthalene indicates that our sample ice layers typically had H₂O/naphthalene ratios of >100. This vapor deposition technique produces intimately mixed ices with the H₂O in a high density amorphous form that is only observed at low temperatures and pressures, a form that is believed to be representative of H₂O-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 ~2×10¹⁵ photons cm⁻²sec⁻¹, the flux being nearly evenly divided between the Lyman α line at 121.6 nm and a roughly 20 nm wide molecular transition centered at 160 nm. Cycles of deposition and photolysis were repeated up to a total of 5 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 CaF₂ filter in front of the hydrogen lamp during irradiation to block the highest energy photons (λ < 160 nm), or we employed a high-pressure xenon arc lamp and water filter, both with and without a glass filter (to remove λ < 320 nm) to assess the wavelength dependency of the photolysis.

Following final photolysis, samples were warmed to 160 K at ~ 1 K per minute 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 parallel diode array UV/Vis and fluorescence using a Vydac C-18 4.6 x 250 mm 5 μm resin analytical column and a mobile phase of 10% A (methanol) and 90% B (pH 5.5 50mM sodium acetate + 8% methanol) to 40% B in 15 minutes. 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 peak of the unknown with that of the standard, both taken *in situ* on the HPLC.

Experiments in which we examined the yield for a variety of single-layer irradiation times (0.17, 1, 3, 5, and 12 hours) indicate that the ices co-deposited with simultaneous photolysis were exposed to UV doses equivalent to individual ice layers subjected to ~30 minutes of UV per ~0.1 μm ice layer. Experiments involving multiple layers gave identical results. These doses fall within the range expected for ices in dense molecular clouds (Prasad and Tarafdar, 1983; Bernstein *et al.*, 1995).

Control experiments performed either in the absence of naphthalene or with *unirradiated* H₂O-naphthalene mixtures did not produce any detectable products. These experiments indicate that the oxidized naphthalene products described below were formed only when H₂O 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 H₂O-naphthalene ices results in a mixture of unprocessed naphthalene and oxidized naphthalene compounds (Figure 1). The oxidized photoproducts include both alcohols and ketones. The main products are the two isomers of naphthalene bearing a hydroxy group (naphthols), and an isomer of naphthalene bearing two carbonyls (1,4-naphthoquinone). The structures of these compounds are shown in Equation 1.

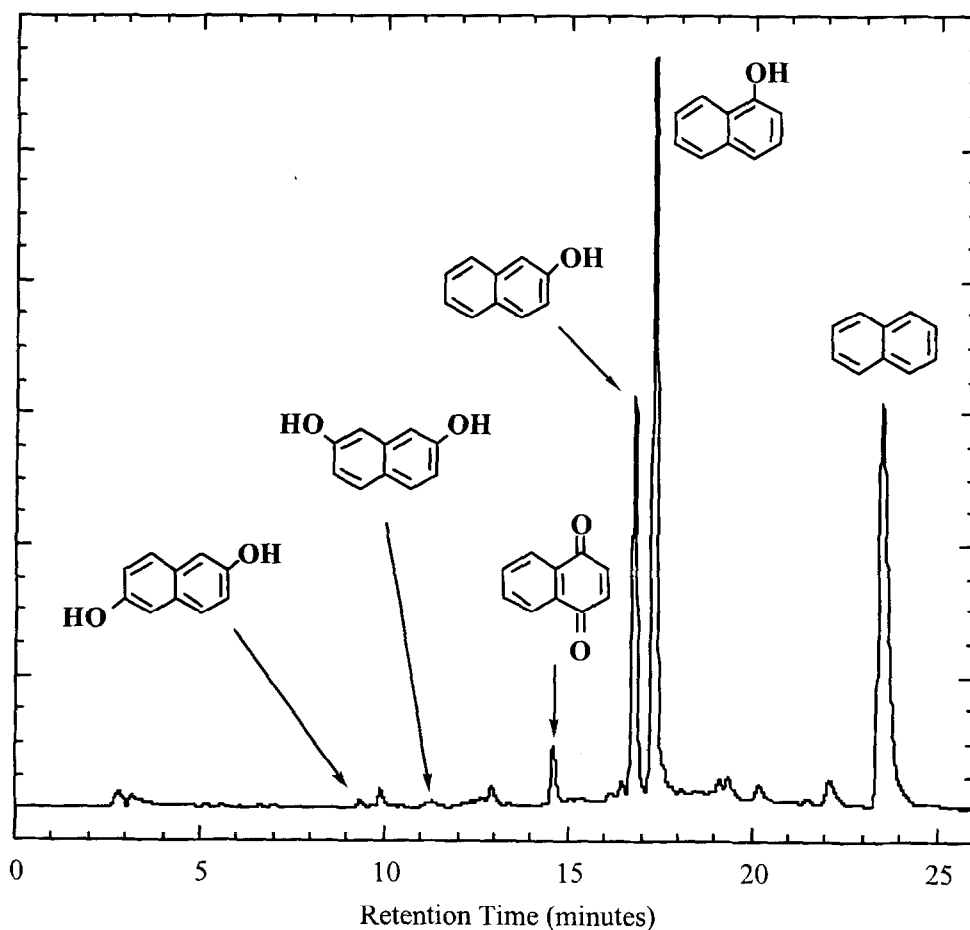
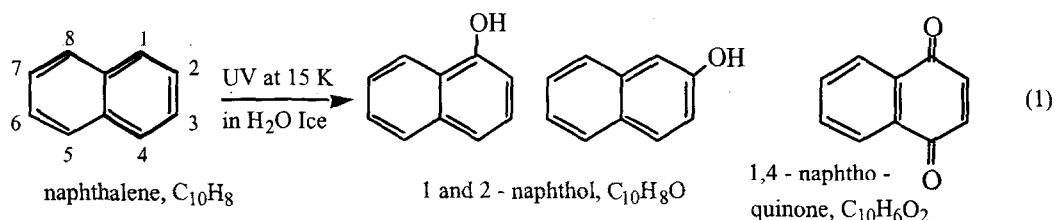


Fig. 1. The HPLC separation of the material resulting from the UV photolysis of an H₂O:naphthalene ice at 15 K. The peaks associated with the original naphthalene and the photoproducts 1-naphthol, 2-naphthol, 1,4-naphthoquinone, 2,6-dihydroxy naphthalene, and 2,7-dihydroxy naphthalene are labeled with the corresponding molecular structures.

In typical experiments (30 minutes 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-naphthoquinone, 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 Equation 1 make up >97% of all the products of H_2O -naphthalene ice photolysis at ~ 15 K. At lower doses the yield decreased, but the ratio of 1- to 2-naphthol stayed near 2 (10 minutes 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 (Figure 1). There are a number of small peaks observed in the HPLC trace that we were unable to identify however, it is reasonable to conjecture that these unidentified species include other dihydroxy naphthalenes, naphthoquinones.

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 vacuum UV photons. However, when a glass filter was employed to remove $\lambda < 320$ nm, the light was unable to drive these reactions to any significant degree (< 10^{-3} % yield of naphthols).

DISCUSSION: REGIOCHEMISTRY AND MECHANISM

In our previous studies of the photochemistry of 11 larger PAHs (Bernstein *et al.*, 1999) we concentrated on the PAH coronene ($\text{C}_{24}\text{H}_{12}$); its symmetry is such that it has only one possible mono-alcohol and one mono-ketone isomer. The structure of naphthalene allows for the possibility of two different naphthol, and ten diol, structures (see Equation 1). Thus, while the results presented here are in agreement with our earlier work, the regiochemistry is somewhat 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 two more abundant than the 2-naphthol. The dominance of the 1-naphthol is probably consistent with several production mechanisms but it could be a reflection of the stability of the cation intermediate leading to this isomer. However, theoretical calculations (Ricca and Bauschlicher, 2000), the direct observation of the naphthalene in UV irradiated H_2O ices at 15 K (Gudipati *et al.*, 2001) are consistent with them arising from a common 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.

DISCUSSION: POSSIBLE IMPLICATIONS FOR METEORITIC AROMATICS

Oxidized Aromatics

It has long been known that the organic fraction of meteorites contains a major aromatic component (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 (Pering and Ponnampertuma, 1971; Basile *et al.*, 1984; Hahn *et al.*, 1988; 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, the study by Krishnamurthy *et al.* (1992) of the Murchison meteorite does address members of this class of compounds; they list three aromatic ketones: fluorenone,

anthracenone, and anthracenequinone. While the chromatograms presented by Krishnamurthy *et al.* contain unidentified peaks with retention times consistent with naphthols and naphthoquinones, we are unaware of anyone pursuing this by specifically searching for oxidized naphthalenes in meteorites. Any future study that reports 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 of the meteorites in which aromatic compounds have been detected have experienced aqueous alteration on their parent body (Zolensky and McSween, 1988). One could imagine that this process might also contribute to the oxidation of PAHs to make aromatic alcohols and ketones. 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 timescales 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 the product 1-naphthol is favored, these papers report that the major product of naphthalene photo-oxidation under terrestrial conditions is the 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.

Deuterium Enrichments in Meteoritic Aromatics

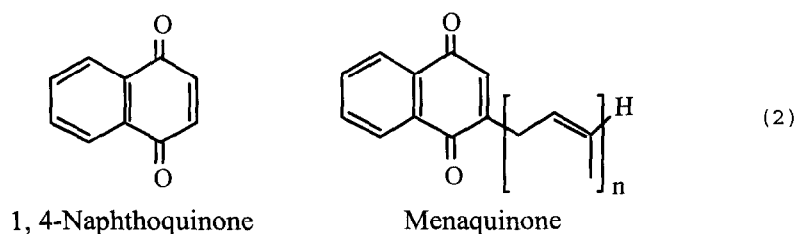
There are a number of processes by which interstellar PAHs can become deuterium enriched, including gas phase ion-molecule reactions (Dalgarno and Lepp 1984; Tielens, 1997), gas-grain reactions (Tielens, 1983, 1997), and unimolecular photodissociation (Allamandola *et al.*, 1987, 1989). In addition, 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 D enrichment in the PAH population.

Ion-molecule reactions would be expected to preferentially deuterate the *larger* PAHs (Tielens, 1997; Charnley, personal communication), while unimolecular photodissociation should D-enrich only the *smallest* ones (Allamandola *et al.*, 1989). In contrast, in D-enriched interstellar ices (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 H₂O-rich ices (Sandford *et al.*, 2000).

Thus, the regiochemistry of PAH D-enrichment in meteoritic materials, and correlation (or lack thereof) with the presence of specific classes of aromatic compounds could potentially place strong constraints on the relative contributions of a number of different interstellar chemical processes that could have 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 D-enrichment with PAH size and oxidation state in meteoritic organics would be of particular interest.

Astrobiological Implications

The UV photolysis of naphthalene in H₂O ice produces 1,4-naphthoquinone as the third most abundant product in our ice experiments. 1,4-naphthoquinones, further functionalized, often with a methyl group and a long isoprene chain, play essential roles in biochemistry. The structures of these compounds are shown in Equation 2. While best known as K vitamins and for their role as blood clotting co-factors, naphthoquinones, 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 H₂S as their main energy source (Thurl *et al.*, 1985).



It is possible that the ease of production of 1,4-naphthoquinone and the ubiquity of 1,4-naphthoquinone-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. We also note that the presentation given by Dr. Wynn-Williams at this conference centered on the antiquity of naphthoquinones as chromophores (ref). Perhaps protection was their first function on an early Earth where there was no ozone to protect proto organisms from ultraviolet radiation, and only later did they become involved in electron transport and proton pumping.

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