

SIDE GROUP ADDITION TO THE POLYCYCLIC AROMATIC HYDROCARBON CORONENE BY PROTON IRRADIATION IN COSMIC ICE ANALOGS

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ABSTRACT

Ices at ~ 15 K consisting of the polycyclic aromatic hydrocarbon coronene ($C_{24}H_{12}$) condensed either with H_2O , CO_2 , or CO in the ratio of 1 : 100 or greater have been subjected to MeV proton bombardment from a Van de Graaff generator. The resulting reaction products have been examined by infrared transmission-reflection-transmission spectroscopy and by microprobe laser-desorption laser-ionization mass spectrometry. Just as in the case of UV photolysis, oxygen atoms are added to coronene, yielding, in the case of H_2O ices, the addition of one or more alcohol ($-OH$) and ketone ($>C=O$) side chains to the coronene scaffolding. There are, however, significant differences between the products formed by proton irradiation and the products formed by UV photolysis of coronene containing CO and CO_2 ices. The formation of a coronene carboxylic acid ($-COOH$) by proton irradiation is facile in solid CO but not in CO_2 , the reverse of what was previously observed for UV photolysis under otherwise identical conditions. This work presents evidence that cosmic-ray irradiation of interstellar or cometary ices should have contributed to the formation of aromatics bearing ketone and carboxylic acid functional groups in primitive meteorites and interplanetary dust particles.

Subject headings: astrobiology — astrochemistry — comets: general — cosmic rays — ISM: molecules — molecular processes

1. INTRODUCTION

Polycyclic aromatic hydrocarbons (PAHs) have been seen in absorption along lines of sight that include cold (10–50 K) dense cloud material (Sellgren et al. 1995; Brooke, Sellgren, & Geballe 1999; Chiar et al. 2000; Bregman, Hayward, & Sloan 2000; Bregman & Temi 2001). In dense clouds, PAHs should be condensed into ice mantles where they come in contact with H_2O , CO_2 , and CO (Sandford et al. 1988; Tielens et al. 1991; Ehrenfreund & Charnley 2000 and references therein). Emission from PAHs has been tentatively reported in the coma of comet P/Halley (Moreels et al. 1994), so PAHs are also probably present in cometary ices. PAHs would be exposed to cosmic rays while in both interstellar and cometary ices.

Aromatic compounds are common in carbonaceous chondrites (Basile, Middleditch, & Oró 1984; Cronin, Pizzarello, & Cruikshank 1988; Cronin & Chang 1993) and interplanetary (cometary/asteroidal) dust particles (IDPs; Allamandola, Sandford, & Wopenka 1987; Clemett et al. 1993). The aromatics in the Murchison meteorite are enriched in deuterium (D; Kerridge, Chang, & Shipp 1987), and there is evidence that they may be one of the carriers of D excess in IDPs (Messenger et al. 1995).

Given that the D enrichment of PAHs present in meteoritic materials suggests low-temperature chemistry (Sandford et al. 2000; Sephton & Gilmour 2000; Sandford, Bernstein, & Dworkin 2001) and is consistent with the telescopic observation of dense clouds, we have studied the UV photochemistry of PAHs under dense cloud conditions (Bernstein et al. 1999, 2001). Meteoritic D enrichments, recent lab reports of phenanthrene

photo-oxidation and alkylation (Mahajan et al. 2002), and the UV photolytic formation of nitrogen-, carbon-, and oxygen-substituted aromatics (Bernstein et al. 2002) similar to those in meteorites (Krishnamurthy et al. 1992; Sephton, Pillinger, & Gilmour 1998, 2001; Cody, Alexander, & Tera 2002) suggested a link between the energetic processing of ices and meteoritic kerogen.

We report here an extension of our previous work to include the proton irradiation of the PAH coronene ($C_{24}H_{12}$) frozen in H_2O , CO , and CO_2 ices at 15 K. H_2O , CO , and CO_2 are seen along essentially all lines of sight passing through interstellar dense clouds and are among the most abundant molecules in interstellar ices. For example, CO and CO_2 have abundances of $\sim 21\%$ and $\sim 15\%$, respectively, relative to H_2O around the high-mass protostar RAFGL 7009S (d’Hendecourt et al. 1999), and similar abundances are observed around other objects (Gibb et al. 2000; Ehrenfreund & Charnley 2000 and references therein). In addition, H_2O , CO , and CO_2 are commonly observed in the tails and comae of comets (Mumma 1997), so these experiments may be of relevance to cometary ices as well as cold interstellar grains.

2. EXPERIMENTAL

The irradiation of coronene-containing (15 K) ices was performed on substrates mounted on a rotatable cryostat in a vacuum chamber at $\sim 10^{-8}$ torr, connected to a Van de Graaff generator as described in detail elsewhere (Moore & Hudson 1998). In these experiments, the PAH coronene was vapor-deposited from a borosilicate tube while H_2O , CO_2 , or CO was simultaneously deposited through a separate inlet. This resulted in ices of H_2O , CO_2 , or CO within which the PAH was isolated (Hudgins & Allamandola 1995). A Ni substrate was used for mass spectrometry, while a mirror was used for transmission-reflection-transmission IR spectroscopy. The rate of deposition was estimated from the growth rate of fringes and absorption features in the IR spectra of samples deposited on the mirrored substrate. This indicated that ice mixtures were generally de-

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posited at a rate that produced an ice layer $\sim 10 \mu\text{m}$ thick after 15 minutes and that they typically had ice/coronene ratios of greater than 100. This resulted in ices in which the coronene molecules were largely isolated from one another. 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 and is believed to be representative of H_2O -rich ices in interstellar molecular clouds (Jenniskens et al. 1995).

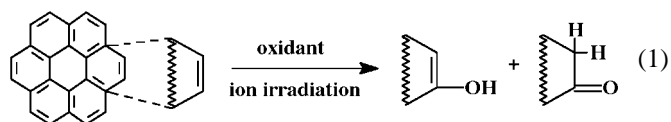
After deposition, samples were proton-irradiated with 0.8 MeV protons at a flux of 1×10^{11} protons $\text{cm}^{-2} \text{s}^{-1}$. A total fluence of 2×10^{14} protons cm^{-2} resulted in ~ 2 eV molecule $^{-1}$ deposited in the ice over ~ 30 minutes. This is a reasonable dose representing $\sim 1 \times 10^6$ yr in a dense cloud, based on the estimates of the interstellar Galactic MeV cosmic-ray flux (Moore, Hudson, & Gerakines 2001).

After the deposition and irradiation were completed, the ices were warmed at ~ 1 K minute $^{-1}$ under a dynamic vacuum at $\sim 10^{-8}$ torr to room temperature. Under these experimental conditions, the ice sublimates during warm-up, leaving behind unreacted coronene and its irradiation products. At no point during this procedure does the ice melt, nor is the residual organic material exposed to any liquid. For cases in which the samples were prepared on a Ni substrate, the sample was removed from the vacuum system after it had reached room temperature. The substrate-bearing residual organic material was then placed in the sample chamber of the microprobe laser-desorption laser-ionization mass spectrometer ($\mu\text{L}^2\text{MS}$; located in the Chemistry Department, Stanford University; Clemett & Zare 1996), and mass spectra were recorded of nonvolatile, PAH-related, radiation products remaining on the metal substrate.

The coronene was purchased from the Aldrich chemical company; control experiments indicate that it contains benzo[ghi]perylene ($\text{C}_{22}\text{H}_{12}$) as a minor impurity. The water was purified with a Millipore Milli-Q water system to 18.2 M Ω . The gases CO (Matheson, 99.99%) and CO_2 (Matheson, 99.995%) were transferred under vacuum into the glass bulb holding the matrix gases without any further purification. The Ni substrate (99.9%) was a 0.03 mm thick foil (Goodfellow).

3. RESULTS

Figure 1 shows the $\mu\text{L}^2\text{MS}$ of the residual organic material resulting from the ion irradiation of coronene in pure solid H_2O , CO_2 , and CO ice compared with a control experiment in which the entire deposition and warming sequence was performed but in which the sample was not irradiated. The clusters of peaks of declining intensity with increasing mass at $M/Z = 316, 332,$ and 348 amu correspond to the addition of one, two, and three oxygen atoms, respectively, to the coronene molecule. Thus, the MeV proton irradiation of coronene isolated in pure, solid H_2O , CO_2 , or CO at 15 K results in the oxidation of edge carbon atoms in the coronene molecule, as indicated by the mass spectra in Figure 1 and represented structurally in equation (1):



The observation of a new absorption at $\sim 1665 \text{ cm}^{-1}$ in the IR

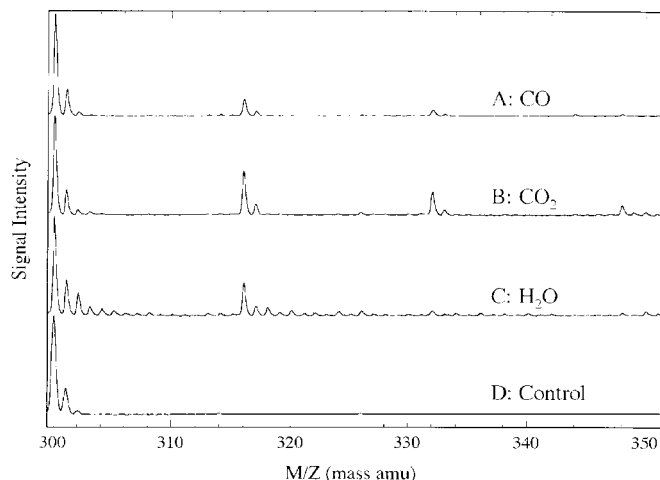
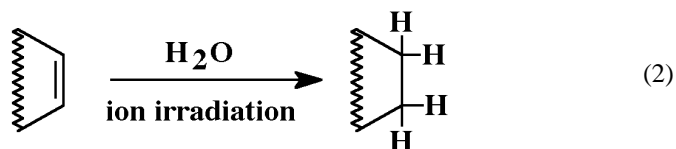


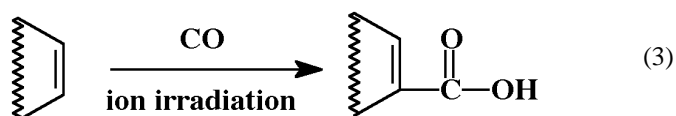
FIG. 1.—The $\mu\text{L}^2\text{MS}$ spectra of organic material resulting from (A) the proton irradiation of coronene ($\text{C}_{22}\text{H}_{12}$, 300 amu) isolated in CO ice at 15 K, (B) the proton irradiation of coronene isolated in CO_2 ice at 15 K, (C) the proton irradiation of coronene isolated in H_2O ice at 15 K, and (D) a control experiment with coronene and H_2O but no radiation. The groups of peaks at $M/Z = 316, 332,$ and 348 amu correspond to the addition of one, two, and three oxygen atoms, respectively, to the coronene molecule (see eq. [1]). The enhanced peak at 302 amu in trace C corresponds to the addition of two hydrogen atoms to coronene. The total doses were ~ 2 eV molecule $^{-1}$.

spectra taken in situ is consistent with the ketone ($\text{C}=\text{O}$) assignment. In H_2O ice experiments, hydrogen atom addition reactions also occur, producing aliphatic ($-\text{CH}_2-\text{CH}_2-$) bridges as indicated by the peaks in the $M/Z = 302-308$ and $318-322$ amu ranges in Figure 1 trace C and represented structurally in equation (2):



Even in CO and CO_2 ice experiments, some hydrogen atom addition is seen (e.g., in Fig. 2, the peak at $M/Z = 350$ amu indicates the addition of two H atoms to the triply oxidized coronene). These hydrogen atoms presumably derive from trace H_2O in the vacuum chamber, and this is consistent with small H_2O peaks seen in the IR spectra. All of these new results for MeV proton irradiation parallel our previously presented data on the UV photolysis of PAHs under otherwise identical conditions (Bernstein et al. 1999).

However, the top spectrum in Figure 2 (the irradiation of coronene in CO ice) also includes an obvious peak at 344 amu that is not seen in the previously reported UV photolysis experiments. This is consistent with the addition of a single molecule of CO_2 to coronene to form a carboxylic acid group:



The mass peak at $M/Z = 344$ amu has an area $\sim 1\%$ of the

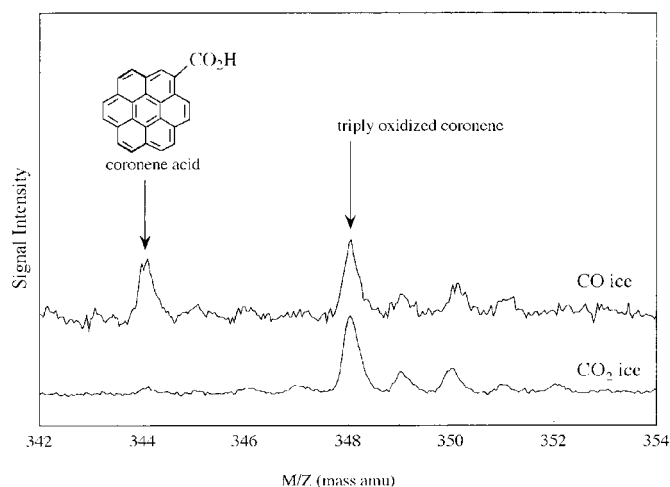


FIG. 2.—Expansion of the 342–354 amu region of the $\mu\text{L}^2\text{MS}$ spectra of the organic material resulting from the proton irradiation of coronene isolated in CO and CO_2 ice (traces A and B from Fig. 1). The peak at approximately $M/Z = 344$ amu is consistent with the addition of CO_2 to the coronene molecule resulting in a coronene monocarboxylic acid (see eq. [3]). The peak at 348 amu is consistent with coronene bearing three oxygen atoms, and that at 350 amu the addition of two hydrogen atoms to that species. The total dose was ~ 2 eV molecule $^{-1}$ in both cases.

unreacted coronene-starting material and thus represents a minor product (compare relative heights of the peak at 344 amu in trace A with the other peaks in Fig. 1). A very small peak at 344 amu also appears in the mass spectrum of the material derived from the irradiation of coronene in CO_2 ice (bottom spectrum in Fig. 2), but if this is the acid, it is very much less efficiently formed than that from the irradiation in CO.

Control experiments performed either in the absence of coronene or in the absence of irradiation did not produce any coronene-related products. These experiments indicate that the products described here are formed only when ice and coronene are exposed together to proton irradiation. Thus, they are not the result of contamination or other, nonradiative, reaction processes. We did not see any clear evidence of ring (carbon–carbon bond) breaking.

4. DISCUSSION AND IMPLICATIONS

Exposure of mixed molecular ices containing coronene to moderate MeV proton bombardment produces new PAH–hydrogen, PAH–carbon, and PAH–oxygen bonds, while control experiments in the absence of radiation (or coronene) do not. This demonstrates that the MeV proton irradiation of PAHs in ices can lead to new and varied aromatic molecules and suggests that cosmic rays should cause this kind of chemistry in ices containing PAHs.

4.1. UV Photochemistry versus Proton Irradiation

It has been noted that in many cases, the ice chemistry induced by UV photolysis is very similar to that induced by ion irradiation (Cottin, Szopa, & Moore 2001; Gerakines, Moore, & Hudson 2001). The same appears to be true for PAH–ice irradiation chemistry. We note that the major reactions (oxygen and hydrogen atom addition; eqs. [1] and [2]) produced by MeV proton irradiation are the same as those that result from UV photolysis. Furthermore, similar doses of energy deposited into the ice sample seem to result in comparable conversion of the coronene.

However, there are some notable differences between UV photolysis and proton irradiation. Specifically, while the MeV proton irradiation of coronene in solid CO results in an acid group (eq. [3]), this reaction is very much less efficient in solid CO_2 . The previously reported UV photolysis of coronene in CO resulted only in oxygen addition (eq. [1]), *not* acid formation, while in CO_2 , UV photolysis of coronene does produce some acid (Bernstein et al. 2002). Thus, with regard to acid formation only, the results from UV photolysis and proton irradiation are the reverse of one another under otherwise identical conditions.

The observation of efficient organic acid formation in pure CO ices (but not CO_2 ices) is very similar to that previously noted by Gerakines & Moore (2001) in their study of carbon suboxide formation by UV photolysis and MeV proton irradiation. They observed that carbon suboxide formation was hundreds of times more efficient from the irradiation of CO_2 and that irradiation of suboxides in H_2O yields CO_2 and CO. Perhaps there is a common reactive intermediate generated from the MeV proton irradiation of CO (but not CO_2) that both forms carbon suboxide and reacts with coronene to produce an aromatic acid, as seen in equation (3). Why the conditions for acid formation by UV photolysis are the reverse remains enigmatic, but an investigation of this phenomenon is beyond the scope of this Letter.

4.2. Implications for Extraterrestrial Ices

We have observed the formation of new carbon–oxygen, carbon–hydrogen, and carbon–carbon bonds, in descending order of efficiency. Since PAHs are ubiquitous and H_2O extremely common, this suggests that in cold regions where these species condense, aromatics bearing oxygen (ketones, alcohols) and some PAHs with extra hydrogen atoms (H_n -PAHs; Bernstein, Sandford, & Allamandola 1996) will form. In ices where a substantial amount of solid CO is present (as is the case in many interstellar ices), we expect some aromatic acids may form as well.

Since the signal intensity of the mass spectra depends on efficiencies of sublimation and ionization and since, unfortunately, no authentic standards exist for these coronene compounds, we cannot quantitatively measure the product yields. However, one can get relative rates from the data displayed in Figure 1. For example, the relative heights of the peaks at 300 amu compared with those at 316, 332, and 348 amu indicate that oxidation is most efficient in CO_2 , and under otherwise identical conditions, the reaction has proceeded one-half as fast in solid H_2O and one-third as fast in solid CO.

Having irradiated our ices in the lab at 15 K, these experiments are most representative of cold interstellar environments, such as dense molecular clouds. However, since UV photolysis experiments in H_2O ice gave similar results over a wide range of temperatures, the same is likely to be true for ion irradiation. Thus, these results may also apply to a wide range of cold solar system environments, such as polar caps on the Earth and other planets, the H_2O -rich icy surfaces of outer solar system satellites, and comets.

4.3. Ice-processed Aromatics in Meteorites

Since planetary systems form out of dense interstellar clouds, the kinds of molecules that we have reported here should have been in the solar nebula even before nebular and parent-body

processes began to enrich its chemical inventory. Furthermore, icy planetesimals and comets, from which meteorites and IDPs come, are also environments where PAHs and ice are exposed to cosmic rays. Thus, whether in the interstellar medium (ISM) or the outer solar system, it seems reasonable that the suite of organic molecules seen in meteorites and IDPs should include aromatics that experienced irradiation in ice.

Indeed, the kinds of molecules seen in meteorites are consistent with this proposed ice chemistry. For example, it has been shown that meteorites contain extractable aromatic molecules functionalized with ketone ($>C=O$; Krishnamurthy et al. 1992), aliphatic ($-CH_2-CH_2-$; Cronin & Pizzarello 1990), and acid ($-COOH$; Sephton et al. 2001) groups. Furthermore, evidence from degradation (Hayatsu et al. 1980; Komiya, Shimoyama, & Harada 1993; Sephton et al. 1998, 2001) and nuclear magnetic resonance studies (Gardinier et al. 2000; Cody et al. 2002) suggests that meteoritic macromolecular material also contains such functional groups.

While such side groups presumably could have added to the aromatics during a high-temperature solar system process, the results presented here demonstrate that some chemical modification or augmentation of the basic PAH skeleton could have occurred in a low-temperature environment. This very low temperature modification of PAHs described here is consistent with D enrichments of many meteoritic molecules (Sandford et al. 2001). For example, polar hydrocarbon fractions in primitive meteorites (where oxidized aromatics are found) are considerably D-enriched (Kerridge et al. 1987).

Although energetic processing of ices containing PAHs can create compounds that are consistent with analyses of extraterrestrial materials, these are not the only way to make such molecules. Other circumstellar, interstellar, and nebular processes could account for them as well. Even if, as we suggest, energetic processing of ices forms the functional groups described here, this does not obviate subsequent modification by a higher temperature process, such as aqueous alteration on the asteroidal or cometary parent body.

4.4. Astrobiological Implications

The presence of functionalized aromatic materials in meteorites may be of astrobiological interest since some of these molecules are essential for important processes in living systems. Naphthoquinone (oxidized naphthalene bearing two ketones), which is formed when the PAH naphthalene is UV-photolyzed in H_2O -rich ices, is an example (Bernstein et al. 2001). Naphthoquinones, such as menaquinone or the K vitamins, are essential to the metabolism of organisms

across all three domains of life. Menaquinone can augment or replace ubiquinone or plastoquinone as electron transport and oxidative phosphorylation coenzymes. The presumably ancient Archaea *Thermoproteus tenax* uses menaquinone in the metabolic reduction of elemental sulfur H_2S (Thurl, Buhrow, & Schafer 1985). The kinds of oxidation chemistry that we have described here are analogous to those seen previously for UV photolysis and thus represent a broadening of the conditions under which such prebiological compounds can be formed. Moreover, the facile formation of an acid ($-COOH$) group is also of relevance as aromatic acids also play important roles in biochemistry. For example, 1,4-dihydroxy-2-naphthoic acid is known to be a biosynthetic precursor of menaquinone (Newman & Kolter 2000).

5. CONCLUSIONS

PAHs with oxygen, hydrogen, and acid side groups should form in the ISM and on the surface of icy solar system bodies and planetary polar caps where aromatics in ices are exposed to ionizing radiation. This assertion is based on the observation that MeV proton irradiation of the PAH coronene in ice at 15 K causes oxygen atom addition [presumably as both alcohol ($-OH$) and ketone ($C=O$) groups, by analogy with our previously published work on UV photolysis], hydrogen atom addition (forming H_n -PAHs), and, in some cases, acid ($-COOH$) group formation.

The efficiency of addition of these functional groups depends on the radiation dose and ice composition, but all reactions were observed even after lab doses equivalent to reasonably dense molecular cloud exposures (~ 2 eV molecule $^{-1}$, or an exposure of $\sim 1 \times 10^6$ yr in a dense cloud based on interstellar Galactic MeV cosmic-ray flux estimates). Coronene acid formation by proton irradiation is facile in solid CO but not in CO_2 , the reverse of what was previously observed for UV photolysis under otherwise identical conditions.

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