

Irradiated benzene ice provides clues to meteoritic organic chemistry



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ABSTRACT

Aromatic hydrocarbons account for a significant portion of the organic matter in carbonaceous chondrite meteorites, as a component of both the low molecular weight, solvent-extractable compounds and the insoluble organic macromolecular material. Previous work has suggested that the aromatic compounds in carbonaceous chondrites may have originated in the radiation-processed icy mantles of interstellar dust grains. Here we report new studies of the organic residue made from benzene irradiated at 19 K by 0.8 MeV protons. Polyphenyls with up to four rings were unambiguously identified in the residue by gas chromatography–mass spectrometry. Atmospheric pressure photoionization Fourier transform mass spectrometry was used to determine molecular composition, and accurate mass measurements suggested the presence of polyphenyls, partially hydrogenated polyphenyls, and other complex aromatic compounds. The profile of low molecular weight compounds in the residue compared well with extracts from the Murchison and Orgueil meteorites. These results are consistent with the possibility that solid phase radiation chemistry of benzene produced some of the complex aromatics found in meteorites.

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1. Introduction

Meteorites preserve a record of the chemistry that occurred in the early Solar System before the planets fully accreted. Carbonaceous chondrites are among the most primitive of meteorites, but they are also the most chemically complex (Schmitt-Kopplin et al., 2010). They contain a plethora of organic molecules, including many that are essential in contemporary biology (Callahan et al., 2011; Cooper et al., 2001, 2011; Cronin and Pizzarello, 1997; Kvenvolden et al., 1970; Meierhenrich et al., 2004; Yuen and Kvenvolden, 1973), and their delivery to the early Earth could have been an important source of prebiotic compounds for the emergence of life (Chyba and Sagan, 1992; Oró, 1961).

Aromatic hydrocarbons account for a significant portion (~5%) of the free (solvent-extracted) organic matter in carbonaceous chondrites (Mullie and Reisse, 1987), and are related to the insoluble macromolecular material, which composes 70–99% of the organic matter in these same meteorites (Sephton et al., 1998). The aromatics in the Murchison meteorite are enriched in deuterium (Kerridge et al., 1987), which suggests their low temperature chemical synthesis. Sephton and Gilmour used gas chromatography–isotope ratio mass spectrometry to measure $\delta^{13}\text{C}$ values for

individual free aromatic compounds in the Cold Bokkeveld and Murchison meteorites, and they concluded that these compounds were synthesized from radiation induced reactions, most likely in the icy organic mantles of interstellar grains (Sephton and Gilmour, 2000; Sephton et al., 2000). Furthermore, theoretical modeling has shown that warming, in addition to irradiation, would be natural consequences of the dynamical evolution of ice grains in the solar nebula, which would facilitate the production of complex organics (Ciesla and Sandford, 2012).

Among all aromatic molecules, benzene (C_6H_6) is the simplest neutral cyclic hydrocarbon (Fig. 1), and it has been identified in a diverse range of extraterrestrial materials and environments. For example, benzene has been found in carbonaceous chondrites (Sephton, 2002), in the circumstellar medium of the protoplanetary nebula CRL618 (Cernicharo et al., 2001), and also in Titan's atmosphere (Coustenis et al., 2003; Flasar et al., 2005; Waite et al., 2005). Ionizing radiation in circumstellar and interstellar environments will alter benzene and all other organics, and it has been postulated that Titan's atmospheric benzene could be processed by Saturn's magnetosphere to form higher molecular weight products (Delitsky and McKay, 2010). Moreover, benzene has been suggested as an intermediate in the formation of polycyclic aromatic hydrocarbons (PAHs, Fig. 1) and other organics (Frenklach and Feigelson, 1989).

Given such a rich set of applications involving benzene, it is surprising that so little work has been done on the radiation chemistry of solid C_6H_6 . Strazzulla and Baratta (1991) showed that more

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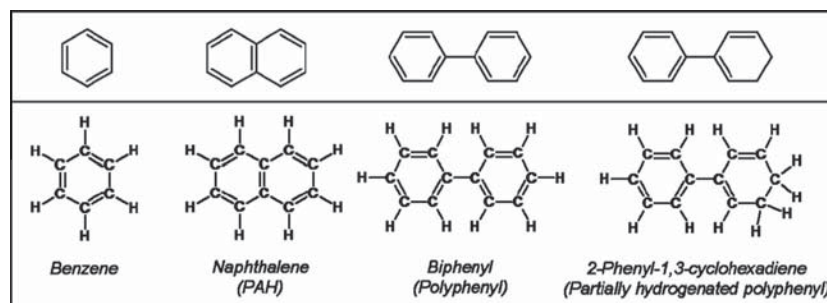


Fig. 1. The general structures of benzene, polycyclic aromatic hydrocarbons or PAHs (such as naphthalene, $C_{10}H_8$), polyphenyls (such as biphenyl, $C_{12}H_{10}$), and partially hydrogenated polyphenyls (such as 2-phenyl-1,3-cyclohexadiene, $C_{12}H_{12}$). The top structures are the same molecules but with carbon and hydrogen labels omitted for clarity.

complex molecules were formed after frozen benzene was irradiated with a 3-keV He^+ beam; however, their analysis of the post-irradiation organic residue was limited to infrared (IR) spectroscopy. Later experiments in our laboratory by [Ruiterkamp et al. \(2005\)](#) determined the stability of solid, matrix-isolated, and H_2O ice-embedded benzene exposed to 0.8-MeV H^+ , and showed that C_6H_6 could survive in interstellar dense clouds on the surfaces of icy grains and in circumstellar envelopes if sufficient shielding existed. Still, the organic residue after irradiation was not examined in detail.

Because of this contrast between multiple applications of benzene chemistry and the paucity of associated laboratory work, we recently have investigated the radiation processing of C_6H_6 at low temperatures (<20 K). Here, we report a significant extension of our previous studies ([Ruiterkamp et al., 2005](#)), now emphasizing the composition of the refractory residue recovered from irradiated frozen benzene. We have applied the highly sensitive analytical techniques of gas chromatography–mass spectrometry (GC–MS) and atmospheric pressure photoionization Fourier transform mass spectrometry (APPI–FTMS) for molecular characterization of this residue. We also have analyzed solvent extracts from three different meteorites for comparison to possible radiation induced aromatic chemistry on meteorite parent bodies. While the present paper is restricted to connections of our experiments to meteorites, our results may also be relevant to Titan and interstellar chemistry. We note that benzene serves as a model compound for aromatic chemistry as we expect that the products and processes described here are relevant for other aromatic molecules.

2. Experimental methods

2.1. Radiation experiments

Proton irradiation experiments were performed in the Cosmic Ice Laboratory at the NASA Goddard Space Flight Center. The system used consisted of a stainless steel high vacuum chamber containing a polished aluminum substrate attached to the cold finger of a closed-cycle helium cryostat (ARS model DE-204). This rotatable substrate can face a deposition tube, a beam of 0.8-MeV protons from a Van de Graaff accelerator, or an FT-IR spectrometer ([Hudson and Moore, 2003, 2004](#)). By leaking benzene vapor into the vacuum chamber, a C_6H_6 ice (thickness ≈ 11 μm) was grown on the substrate, which was held at 19 K. Contaminants (mainly H_2O) made up no more than 1% of the final ice, based on our estimates of the background gases present and the rate at which the sample was grown.

After deposition, the benzene ice was exposed to a 0.8-MeV proton beam with a current of 150 nA until a fluence of 3×10^{15} protons cm^{-2} was achieved. The average energy dose (energy absorbed) was 119 eV per initial benzene molecule deposited,

assuming a proton stopping power for solid C_6H_6 of 307.1 MeV cm^2 g^{-1} proton $^{-1}$. Two experiments at low temperature (~ 20 K) and irradiation were conducted as well as another experiment at higher temperature (150 K). For descriptions of the IR spectra of proton-irradiated frozen benzene, see [Strazzulla and Baratta \(1991\)](#) and [Ruiterkamp et al. \(2005\)](#).

2.2. Gas chromatography–mass spectrometry measurements

After irradiation, the benzene ice sample was kept under vacuum and allowed to slowly warm to room temperature overnight, permitting any volatile products and unreacted benzene to be pumped away. The remaining material, which we refer to as a refractory organic residue, was removed from the substrate by washing with 1 mL of HPLC grade (99.9%) dichloromethane (CH_2Cl_2). The sample extract was dried under vacuum then re-dissolved in 100 μL of dichloromethane to concentrate the extract.

A Finnigan TraceGC ultra gas chromatograph was used for this study, equipped with a Restek Rxi-5 ms column (30 m, 0.25 mm ID, 0.5 μm film thickness) and coupled to a Finnigan TraceDSQ quadrupole mass spectrometer. A sample injection volume of 1 μL , injector temperature of 275 $^{\circ}C$, transfer line temperature of 280 $^{\circ}C$, and a flow of 1.2 mL min^{-1} helium were used. The column temperature was held at 75 $^{\circ}C$ for 30 s, increased to 245 $^{\circ}C$ at 25 $^{\circ}C$ min^{-1} , increased again to 330 $^{\circ}C$ at 4 $^{\circ}C$ min^{-1} , and then held at 330 $^{\circ}C$ for 15 min. The ionization source used 70 eV electron energies and was kept at 200 $^{\circ}C$. Mass spectra were recorded from $m/z = 50$ –650 Da, and a solvent delay time of 4 min was employed. Compound identifications were made by comparing chromatographic retention times and electron ionization mass spectra with commercial reference standards obtained from Sigma Aldrich. In addition, a mass spectral library (Wiley Registry 8th Edition/NIST 2005) was searched for possible compound identification.

2.3. Atmospheric pressure photoionization–mass spectrometry (APPI–MS) measurements

APPI–MS analyses were conducted with an Accela 1250 ultra-high precision liquid chromatography pump and autosampler (Thermo Scientific) coupled to a LTQ Orbitrap XL hybrid mass spectrometer (Thermo Scientific) fitted with an atmospheric pressure photoionization (APPI) source. In APPI, a sample solution is vaporized and then ionized by photons. The APPI source uses a krypton lamp that emits photons at 10.0 and 10.6 eV, and was chosen because it can ionize, with minimal fragmentation, both polar and nonpolar molecules ([Hanold et al., 2004](#); [Robb et al., 2000](#)). The analyte molecule can be ionized directly (direct photoionization) or ionized indirectly with the help of solvent molecules or inclusion of a dopant. In our analyses, protonation of neutral analytes likely occurred via photoionization–induced chemical ionization

where photoionization of the methanol mobile phase produced protonated methanol clusters which then led to chemical ionization of an analyte (Short et al., 2007).

For the flow-injection analyses, 10 μL of sample were injected at a flow rate of 50 $\mu\text{L min}^{-1}$ using methanol as the mobile phase. For APPI, the vaporizer temperature was 375 $^{\circ}\text{C}$, the sheath gas flow was 25 (arbitrary units), the auxiliary gas flow was 5 (arbitrary units), and the sweep gas flow was 1 (arbitrary units). The sheath, auxiliary, and sweep gases were all nitrogen, and these settings assisted in the vaporization of the sample solution. The APPI lamp was positioned 1–2 mm from the orifice of the ion transfer capillary. The ion transfer capillary voltage and ion transfer capillary temperature were 18 V and 200 $^{\circ}\text{C}$, respectively. The tube lens was set at 45 V. The mass spectrometer was operated in positive ion mode and the mass resolution was set to 100,000 (full-width at half-maximum for $m/z = 400$). A high resolution mass spectrum captures a “molecular snapshot” of all the organic compounds in the sample attainable from dichloromethane extraction and APPI. In addition, the instrument’s high mass accuracy enables the assignment of elemental composition to mass peaks, which can be used for molecular characterization.

The mass spectrometer was externally calibrated using a mixture of caffeine, MRFA (L-methionyl-arginyl-phenylalanyl-alanine acetate hydrate) peptide, and Ultramark 1621 in an acetonitrile-methanol-water solution containing 1% acetic acid. Electrospray ionization was used because this method of ionization does not affect the calibration. After external mass calibration, the electrospray ionization probe was replaced by the APPI probe and lamp. A background compound ($m/z = 87.08044$, $[\text{C}_5\text{H}_{10}\text{O}+\text{H}]^+$) was used for internal calibration, which resulted in a typical relative mass error under 2 parts-per-million (ppm). For the benzene residue, each molecular component detected was assumed to be composed of only the elements C, H, and O, where residual water in the irradiation setup could be a source of oxygen contamination.

2.4. Meteorite extractions

Sample handling tools, ceramics, and glassware were rinsed with ultrapure water (18.2 M Ω cm, <5 ppb total organic carbon from a Millipore Milli-Q Integral 10 system), then wrapped in aluminum foil, and then heated under air at 500 $^{\circ}\text{C}$ for 24 h to remove

any organic contaminants. Meteorites were crushed to a powder using a porcelain mortar and pestle in a Class-100 laminar flow hood under HEPA-filtered positive pressure. The powdered meteorite samples (14.8 mg for Murchison meteorite, 11.6 mg for Orgueil, and 12.6 mg for Roberts Massif (RBT) 04262) were transferred to borosilicate centrifuge vials and 300 μL dichloromethane was added to each before sealing with a PTFE-lined screw cap. The vials were put into a water bath-shaker maintained at 35 $^{\circ}\text{C}$, and then agitated overnight in order to extract the soluble organic matter from the meteorite powder. Finally, the vials were centrifuged to isolate the meteorite extracts, which were transferred to autosampler vials and analyzed by APPI mass spectrometry.

3. Results

3.1. Aromatic products in the residue from proton-irradiated benzene

Fig. 2 shows the GC–MS total ion chromatogram of the dichloromethane extract of the room temperature benzene residue. The compounds corresponding to the most intense peaks in the chromatogram were identified as biphenyl ($(\text{C}_6\text{H}_5)_2$, sometimes called diphenyl) followed in intensity by *o*-terphenyl, *m*-terphenyl, and *p*-terphenyl. Several quaterphenyls likely were present based on strong molecular ion peaks and late retention times (between 12 and 22 min), although due to a lack of reference standards only 1,2,3-triphenylbenzene, and 1,3,5-triphenylbenzene could be identified. All of the molecules identified above belong to the class of compounds known as polyphenyls (Fig. 1), which are composed of benzene rings (phenyl groups) linked only by C–C bonds.

The GC–MS chromatogram of Fig. 2 also contains numerous smaller peaks, which suggested that the benzene residue contained other complex organic compounds. Some of these peaks are consistent with substituted aromatic compounds, which may have resulted from ring opening of one of the aromatic rings in biphenyl; however no firm identifications can be made based on our mass spectral library. Larger polyphenyls (five rings and greater) were not detected, but may also be present because GC–MS analysis is often unable to detect organic compounds with low volatility, low thermal stability, and/or large size. Finally, we used our GC–MS method to search for the following PAHs in the benzene residue: naphthalene, anthracene, phenanthrene, pyrene,

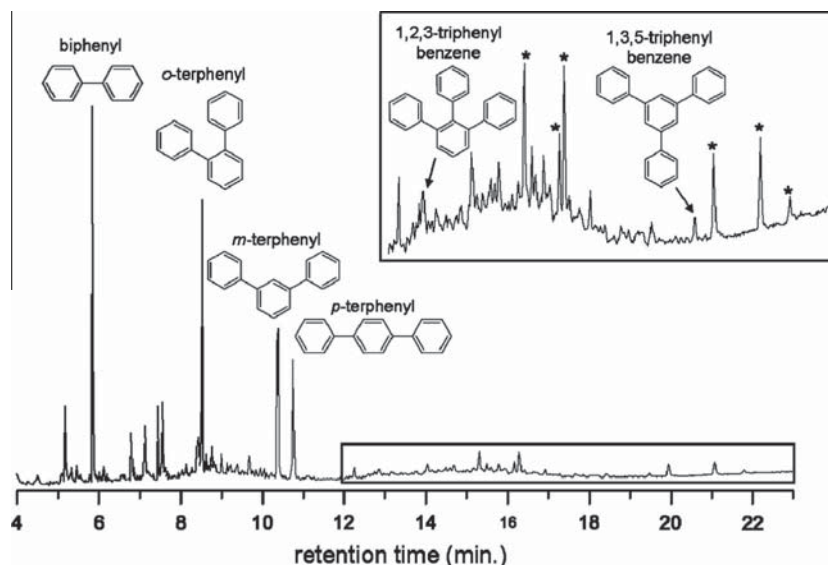


Fig. 2. The GC–MS chromatogram of the residue made from benzene irradiated at 19 K by 0.8 MeV protons. The boxed inset shows a close-up view of the region from 12 to 23 min. Peaks labeled with an asterisk are assigned to other quaterphenyl isomers based on their mass spectra.

1,2-benzanthracene, perylene, benzo[g,h,i]perylene, and coronene. None of these PAHs were detected above our detection limits (~ 10 pmol). Some of the smaller peaks in the GC–MS chromatogram may be substituted PAHs, but definitive assignments were impossible using only our mass spectral library because substituted polyphenyls also have very similar mass spectra.

Fig. 3 shows the residue's APPI mass spectrum, which is complex with over a thousand peaks. The high mass accuracy of the Orbitrap analyzer, along with the utilization of the natural isotope pattern, enabled the assignment of elemental formulae for small molecules. It is worth noting that a single elemental formula could represent numerous structural isomers. The high resolution mass spectrometry techniques employed here may represent a more accurate picture of the sample's chemical diversity compared to the GC–MS results.

Mass envelopes with prominent peaks separated by 76 Da were observed, which indicated a phenyl group addition and hydrogen elimination. Elemental formulae from accurate mass measurements confirmed the presence of polyphenyls as protonated species from APPI. Proton irradiation of benzene also resulted in partially hydrogenated polyphenyls (Fig. 1) and other partially hydrogenated aromatic hydrocarbons based on the repeated addition of two hydrogen atoms observed in the mass spectrum (Fig. 3 and Table 1). Additionally, larger molecular weight compounds display a greater extent of hydrogenation because there are more opportunities to include partially hydrogenated aromatic rings into the structure as the polyphenyl chain increases in size. Hydrogen atom addition to aromatic rings has been reported as partially hydrogenated aromatic hydrocarbons were formed during the UV irradiation of PAHs in low temperature ices (Bernstein et al., 1999, 2002; Gudipati and Yang, 2012) and from the gamma radiolysis of liquid benzene (Gordon et al., 1958). Superhydrogenated derivatives of the PAH coronene through H-atom addition reactions also have been demonstrated at high temperatures (Thrower et al., 2012). These modifications transform some of the aromatic rings into cyclic aliphatic hydrocarbon structures, which reduce the overall degree of aromaticity in the molecule and change their spectroscopic signature (e.g., a 3.4- μm band, due to the presence of aliphatic carbon, may appear next to the aromatic 3.3- μm band).

High molecular weight species ($m/z \sim 800$ Da), which were inaccessible by our GC–MS methods, were observed in the APPI mass spectrum (Fig. 3). Assignments using accurate mass measurements are less certain for high molecular weight species because the list of potential elemental formulae becomes very large despite constant mass accuracy. However, if we assume that polyphenyl

synthesis could extend to higher masses, we observe elemental formulae consistent with large polyphenyls containing up to ten rings, although for large compounds containing eight rings or more, all products were partially hydrogenated. Our assumption is verified via carbon-normalized double bond equivalents (DBE/C) analysis, previously used in ultrahigh resolution mass spectrometry studies (Hockaday et al., 2006), to provide additional insight on the aromaticity of a given molecule. A $\text{DBE/C} \geq 0.7$ suggests fused aromatic ring structures (such as PAHs). For peaks with $S/N > 10$, only 3% of the mass peaks have a $\text{DBE/C} \geq 0.7$, which suggests the majority of the peaks are “polyphenyl-like” as opposed to “PAH-like”. It is worth pointing out that there is a very weak peak in the APPI mass spectrum that corresponds to protonated naphthalene; however, additional information (e.g., chromatographic retention time, product ion spectrum) would be needed for unambiguous identification.

Finally, oxygenated species are present throughout the APPI mass spectrum (Fig. 3). Despite the fact that proton irradiation was performed under vacuum, some residual water was likely trapped within the sample and could have reacted with benzene to form oxygenated species. Some oxygenation may also have occurred during exposure to the atmosphere after warm-up, extraction, or during analysis.

3.2. Meteorite results and comparison to the benzene residue

The high-resolution mass spectrum of the benzene residue (Fig. 3) shows a large number of mass peaks. The peak intensity reaches a maximum for the 4-ring group; however, this group may not represent the most abundant compounds because peak intensity depends on multiple factors (such as ionization efficiency). Thus, APPI mass spectral data should be considered qualitative only. This point is further illustrated when this data is compared with GC–MS data of the benzene residue, which shows that peak intensity decreases as molecular size increases (i.e., 2-ring > 3-ring > 4-ring, etc.), which likely resembles its true distribution. While assigning every peak in such a spectrum is nearly impossible, in some cases such complexity can be beneficial. Along those lines, we selected a set of 69 of the strongest peaks from $m/z = 120$ – 320 to use as a “fingerprint” of the radiation chemistry of frozen benzene. This set of intense peaks represented diagnostic hydrocarbon ions, and were selected because they most likely correspond to polyphenyls, partially hydrogenated polyphenyls, and other complex aromatic compounds. Table 1 lists the selected ions,

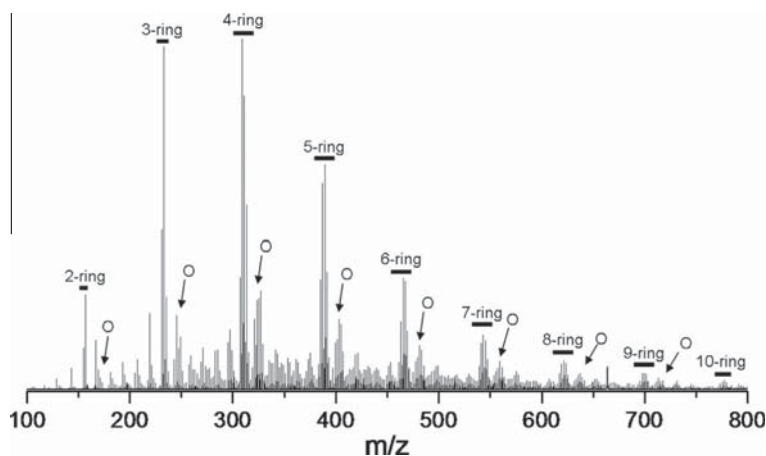


Fig. 3. APPI mass spectrum of the residue made from benzene irradiated at 19 K by 0.8 MeV protons. Polyphenyls and partially hydrogenated polyphenyls up to 10-ring compounds are indicated by the horizontal lines. Mass envelopes of oxygenated species also are present, and are marked by “O”.

Table 1

Benzene residue diagnostic ions in meteorites.

Measured <i>m/z</i>	Theoretical <i>m/z</i>	Mass error (ppm)	Formula	Murchison (CM2)	Orgueil (CI)	RBT 04262 (SNC)
129.0699	129.0699	−0.19	C ₁₀ H ₉	+	+	—
131.0855	131.0855	−0.22	C ₁₀ H ₁₁	+	+	—
141.0700	141.0699	1.01	C ₁₁ H ₉	+	+	—
143.0856	143.0855	0.45	C ₁₁ H ₁₁	+	+	—
<i>155.0854</i>	<i>155.0855</i>	−0.88	<i>C₁₂H₁₁</i>	+	+	—
<i>157.1011</i>	<i>157.1012</i>	−0.54	<i>C₁₂H₁₃</i>	+	+	—
167.0854	167.0855	−0.73	C ₁₃ H ₁₁	+	+	—
169.1010	169.1012	−1.17	C ₁₃ H ₁₃	+	+	—
171.1167	171.1168	−0.98	C ₁₃ H ₁₅	+	+	+
179.0856	179.0855	0.61	C ₁₄ H ₁₁	+	+	—
181.1011	181.1012	−0.45	C ₁₄ H ₁₃	+	+	—
183.1167	183.1168	−0.79	C ₁₄ H ₁₅	+	+	—
185.1323	185.1325	−0.82	C ₁₄ H ₁₇	+	+	—
191.0853	191.0855	−0.99	C ₁₅ H ₁₁	+	+	—
193.1011	193.1012	−0.60	C ₁₅ H ₁₃	+	+	—
195.1167	195.1168	−0.53	C ₁₅ H ₁₅	+	+	—
197.1324	197.1325	−0.40	C ₁₅ H ₁₇	+	+	—
199.1481	199.1481	−0.37	C ₁₅ H ₁₉	+	+	—
205.1011	205.1012	−0.51	C ₁₆ H ₁₃	+	+	—
207.1168	207.1168	−0.10	C ₁₆ H ₁₅	+	+	—
209.1323	209.1325	−0.73	C ₁₆ H ₁₇	+	+	—
211.1481	211.1481	0.09	C ₁₆ H ₁₉	+	+	—
213.1638	213.1638	0.19	C ₁₆ H ₂₁	+	+	—
217.1010	217.1012	−0.92	C ₁₇ H ₁₃	+	+	—
219.1168	219.1168	−0.27	C ₁₇ H ₁₅	+	+	—
221.1324	221.1325	−0.47	C ₁₇ H ₁₇	+	+	—
223.1480	223.1481	−0.77	C ₁₇ H ₁₉	+	+	—
225.1637	225.1638	−0.21	C ₁₇ H ₂₁	+	+	—
227.1795	227.1794	0.15	C ₁₇ H ₂₃	+	+	—
229.1013	229.1012	0.35	C ₁₈ H ₁₃	+	+	—
<i>231.1167</i>	<i>231.1168</i>	−0.35	<i>C₁₈H₁₅</i>	+	+	—
<i>233.1325</i>	<i>233.1325</i>	−0.09	<i>C₁₈H₁₇</i>	+	+	—
<i>235.1481</i>	<i>235.1481</i>	−0.13	<i>C₁₈H₁₉</i>	+	+	—
<i>237.1637</i>	<i>237.1638</i>	−0.25	<i>C₁₈H₂₁</i>	+	+	—
<i>239.1795</i>	<i>239.1794</i>	0.34	<i>C₁₈H₂₃</i>	+	+	—
243.1168	243.1168	−0.26	C ₁₉ H ₁₅	+	+	—
245.1325	245.1325	0.02	C ₁₉ H ₁₇	+	+	—
247.1481	247.1481	−0.21	C ₁₉ H ₁₉	+	+	—
249.1637	249.1638	−0.43	C ₁₉ H ₂₁	+	+	—
251.1795	251.1794	0.29	C ₁₉ H ₂₃	+	+	—
255.1167	255.1168	−0.34	C ₂₀ H ₁₅	—	+	—
257.1324	257.1325	−0.41	C ₂₀ H ₁₇	—	+	—
259.1481	259.1481	−0.30	C ₂₀ H ₁₉	+	+	—
261.1638	261.1638	0.20	C ₂₀ H ₂₁	+	+	—
263.1793	263.1794	−0.50	C ₂₀ H ₂₃	+	+	—
267.1174	267.1168	1.98	C ₂₁ H ₁₅	—	+	—
269.1328	269.1325	1.10	C ₂₁ H ₁₇	+	+	—
271.1485	271.1481	1.20	C ₂₁ H ₁₉	+	+	—
273.1641	273.1638	1.06	C ₂₁ H ₂₁	+	+	—
275.1796	275.1794	0.56	C ₂₁ H ₂₃	+	+	—
281.1328	281.1325	1.08	C ₂₂ H ₁₇	+	—	—
283.1485	283.1481	1.19	C ₂₂ H ₁₉	+	+	—
285.1642	285.1638	1.45	C ₂₂ H ₂₁	+	+	—
287.1798	287.1794	1.15	C ₂₂ H ₂₃	+	+	—
289.1954	289.1951	1.00	C ₂₂ H ₂₅	+	+	—
293.1330	293.1325	1.70	C ₂₃ H ₁₇	—	+	—
295.1484	295.1481	0.93	C ₂₃ H ₁₉	+	+	—
297.1642	297.1638	1.43	C ₂₃ H ₂₁	—	+	—
299.1798	299.1794	1.12	C ₂₃ H ₂₃	+	+	—
301.1955	301.1951	1.27	C ₂₃ H ₂₅	—	+	—
303.2112	303.2107	1.63	C ₂₃ H ₂₇	—	+	—
305.1324	305.1325	−0.11	C ₂₄ H ₁₇	+	—	—
<i>307.1480</i>	<i>307.1481</i>	−0.36	<i>C₂₄H₁₉</i>	—	+	—
<i>309.1638</i>	<i>309.1638</i>	−0.07	<i>C₂₄H₂₁</i>	+	+	—
<i>311.1794</i>	<i>311.1794</i>	−0.05	<i>C₂₄H₂₃</i>	+	+	—
<i>313.1951</i>	<i>313.1951</i>	−0.07	<i>C₂₄H₂₅</i>	+	+	—
<i>315.2106</i>	<i>315.2107</i>	−0.45	<i>C₂₄H₂₇</i>	+	+	—
317.2264	317.2264	0.14	C ₂₄ H ₂₉	—	+	—
<i>319.2421</i>	<i>319.2420</i>	0.15	<i>C₂₄H₃₁</i>	+	+	—

Notes. Summary of accurate mass measurements for the residue made from benzene irradiated at 19 K by 0.8 MeV protons. Molecular formulae correspond to protonated molecules. Sections highlighted in italics represent formulae that correspond to polyphenyls (e.g., biphenyl, terphenyl, and quaterphenyl) and partially hydrogenated polyphenyls. Additionally, the presence (+) or absence (−) of these compounds in three different meteorites (two carbonaceous chondrites and one martian SNC meteorite) are also noted. A signal-to-noise ratio greater than three and a relative mass error of <5 ppm were used to define a “+” designation in meteorites, although signal-to-noise ratios of 10–100, or higher, usually were observed. The relative mass error, in ppm, is calculated as $10^6 \times (mass_{\text{experimental}} - mass_{\text{theoretical}})/(mass_{\text{theoretical}})$.

their formulas as assigned by accurate mass measurement, and the associated relative mass error.

An important purpose of our work was to compare the products of proton-irradiated benzene with organics found in meteorites. To do this, we extracted samples from Murchison (CM2 carbonaceous chondrite) and Orgueil (CI1 carbonaceous chondrite) powders in a method identical to that described above for the analysis of the benzene residue. Of the 69 diagnostic ions listed in Table 1 for the fingerprint of irradiated benzene ice, we found that Murchison showed 60 of them and Orgueil showed 67. Masses corresponding to biphenyl, terphenyl, quaterphenyl, and their partially hydrogenated derivatives were found in both meteorites. Both biphenyl and terphenyl were reported previously in carbonaceous chondrites (Naraoka et al., 2000; Pizzarello et al., 2008). This strong overlap of organic compounds is suggestive of, although not conclusive evidence for, a connection between the radiation chemistry of frozen benzene and the numerous aromatic compounds observed in carbonaceous chondrites. Fig. 4 shows the APPI mass spectrum of the Murchison meteorite dichloromethane extract along with close-up regions of selected mass ranges (where protonated terphenyls appear). The benzene residue masses that are detected in Murchison (as well as Orgueil) are all low intensity peaks, which suggest that these compounds are likely low abundance products.

To probe the extent of our conclusions, we also analyzed a sample from RBT 04262 – a martian shergottite. RBT 04262 has undergone high temperature igneous processing rather than aqueous alteration (Usui et al., 2010). Only one of the 69 diagnostic ions of Table 1 was present in this martian meteorite, and it is unknown whether this ion is from either the same molecule(s) or (a) structural isomer(s) measured in the benzene residue. Nonetheless, these results suggest that these organics are not all shared by extraterrestrial materials and that the synthesis and preservation of these organics may require an environment such as icy organic mantles of interstellar grains that eventually get incorporated into the meteorite parent body.

4. Discussion

4.1. Radiation chemistry of benzene

The analyses shown in Figs. 2 and 3 provide compositional “snapshots” of the organics made from C_6H_6 at the radiation dose employed. Although only one such dose (average energy: $119\text{ eV molecule}^{-1}$) was used for the samples that were analyzed, it can be considered a fair compromise between the much smaller radiation doses expected for the middle of dense interstellar clouds and the much larger ones for diffuse interstellar clouds. In any case, the IR spectra of irradiated benzene showed little, if any, changes as our final dose was reached, suggesting that an equilibrium state had been achieved. Smaller doses might give somewhat less product, but larger ones are not expected to give more.

The formation of polyphenyls from benzene, which we report here for the solid state, has been known for over 50 years for liquid- and gas-phase experiments. Such syntheses have been conducted with a variety of energy sources (1H , 4He , and ^{12}C ions, γ -rays, radio frequency (spark) discharge), but not in the solid phase nor at the low temperatures used here (Gordon et al., 1958; LaVerne and Araos, 2002; Lee et al., 2007a,b).

Beyond our identification of polyphenyls and other products from irradiated benzene ice, one of our more striking conclusions is that there is no evidence for significant yields of PAHs in any of our experiments. As before, Fig. 1 illustrates that polyphenyls are composed of benzene rings (phenyl groups) linked only by C–C bonds, whereas PAHs are made of rings that are fused (Fig. 1, naphthalene for example). Our results suggest that PAHs in meteorites are not constructed by radiation processes involving smaller rings, but perhaps by the accumulation of atoms or molecular fragments. Once rings are formed; however, it appears to be relatively easy to make more complex molecules.

In astrophysical environments, PAHs have not been identified in interstellar ices; however, significant hydrogenation of PAHs in interstellar ices may preclude their spectroscopic detection. Therefore, a low temperature synthesis for PAHs cannot be ruled out. For

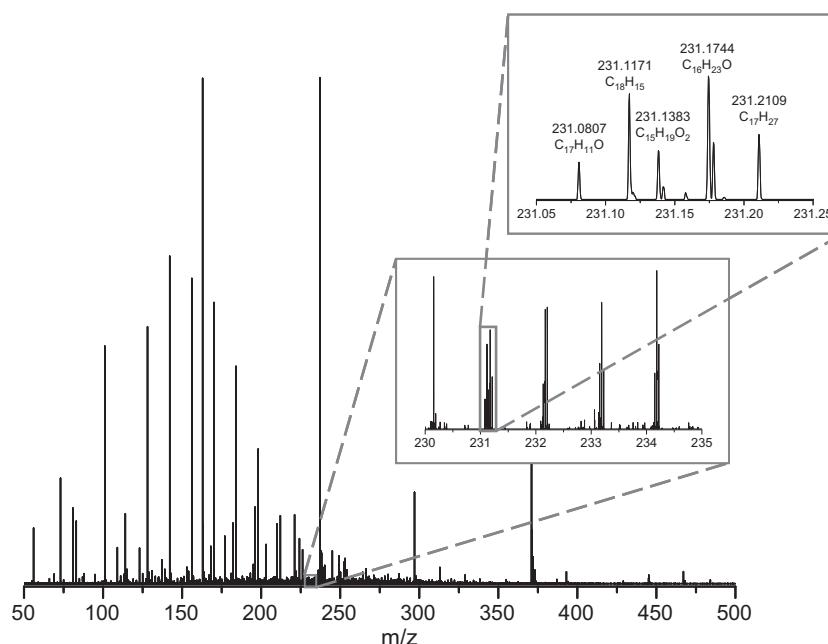


Fig. 4. APPI mass spectrum of Murchison meteorite dichloromethane extract with insets displaying selected mass ranges. The mass peak labeled $C_{18}H_{15}$ likely corresponds to protonated terphenyl.

example, experiments (along with electronic structure calculations) have shown that naphthalene (the simplest PAH) can be synthesized from vinylacetylene and phenyl radical in a low temperature environment (Parker et al., 2012), the latter precursor molecule produced possibly from irradiation and/or photolysis of benzene. Thus, benzene may still play a role in the synthesis of PAHs if other reagents are present.

The published results on chemical products from irradiated benzene stand in sharp contrast to the mechanistic details that are available – an undesirable situation. As a MeV ion passes through an ice it will produce a chain of ionizations and excitations that effect most of the resulting chemistry, with the dominant agent of change being secondary electrons with energies below 100 eV. An expected result with benzene will be the formation of phenyl radicals ($\cdot\text{C}_6\text{H}_5$) either through single step C–H bond breakage or a multi-step process perhaps involving solid phase ion–molecule reactions. In either case, dimerization of the resulting $\cdot\text{C}_6\text{H}_5$ radicals will produce $(\text{C}_6\text{H}_5)_2$, the biphenyl that we and others have observed. Dimerization is also a key step in the formation of other astronomical molecules, such as ethane (C_2H_6) (Moore and Hudson, 1998), hydrogen peroxide (H_2O_2) (Moore and Hudson, 2000), and ethylene glycol ($\text{C}_2\text{H}_6\text{O}_2$) (Hudson and Moore, 2000). We note, however, that this straightforward formation mechanism has been shown to be incomplete through work by LaVerne and colleagues (LaVerne and Araos, 2002). When radical scavengers are added to benzene before irradiation, to react with the $\cdot\text{C}_6\text{H}_5$ radicals produced, some biphenyl formation is still observed. Excited states of benzene or the benzene radical cation may play a role, but in both cases details remain to be determined (Baidak et al., 2011).

4.2. Comparisons to meteorite chemistry

We have compared our benzene residue “fingerprint” results to the APPI mass spectra of different meteorite extracts to investigate possible similarities to the radiation chemistry of frozen benzene and to determine if this type of cold, radiation induced aromatic chemistry may have influenced meteoritic and hence early Solar System chemistry. Table 1 shows that there are compositional similarities between the mass spectra of our benzene residue and the meteorites, but important differences exist. Fig. 5 compares our Orgueil meteorite and benzene residue results for three separate mass regions, and clearly demonstrates that the mass spectrum for Orgueil is more complex than that of the residue. However, due to the broad ionization of APPI and the elemental complexity, the peaks in the meteorite spectra that are not matched by those in the residue’s spectra likely correspond to compounds other than aromatic hydrocarbons. At the measured relative mass error

(<2 ppm) these other peaks are likely due to molecules containing nitrogen, oxygen, or both.

Furthermore, higher molecular weight products detected in the benzene residue were not observed in meteorite extracts, for which we can offer four possible explanations. First, larger molecules are produced more readily in the pure benzene ice than in the dilute ices likely involved in the formation of the meteorites. Second, benzene in astrophysical ices would likely be a minor component (in both absolute and relative abundances compared with H_2O , CO , CO_2 , CH_3OH , etc.), and it would probably react with other species rather than itself to form polyphenyls. Third, the extraction method we employed is less effective for our meteorites than for our benzene residue. Finally, the abundances of these compounds in the meteorites decrease as the molecular weight increases to the point of being undetectable in our analysis. In any case, our results demonstrate that the irradiation of a single molecule, benzene, can lead to the production of numerous complex organic molecules and that much of their mass spectral signature is shared by at least two carbonaceous chondrites.

These types of experiments can be extended to other aromatic molecules such as nitrogen heterocycles (e.g., pyridine, pyrimidine, purine, and triazine). For instance, the nucleobases uracil and cytosine have been synthesized from pyrimidine–water ices under low temperature conditions and UV photolysis (Nuevo et al., 2009, 2012). We speculate that similar syntheses of nucleobases (and other complex products) can also occur *via* proton irradiation (cosmic rays) of pyrimidine–water ices. Similar comparisons using high-resolution mass spectral fingerprinting of these mixed-molecular ice residues and meteorite extracts would also be possible.

4.3. Potential relevance to Titan

We also carried out proton irradiation experiments of benzene at 150 K and analyzed the residue by APPI-MS. The APPI mass spectra for the residues of the 19 K and 150 K experiments were identical (results not shown). A portion of this temperature range (130–150 K) overlaps relevant Titan temperatures where benzene was detected by the Cassini spacecraft (Waite et al., 2007). Although benzene has been detected only in the gas phase (the Cassini/Huygens instrumentation was far more sensitive to gases), the presence of condensed benzene remains likely, since benzene in Titan’s upper atmosphere is close to its saturation vapor pressure (Waite et al., 2007). Furthermore, Cassini measurements of Titan’s upper atmosphere revealed evidence of heavy positively charged (100–350 Da) and negatively charged (20–8000 Da) ions (Waite et al., 2007). Thus, biphenyl may be a feasible candidate in Titan’s atmosphere as well as larger molecular weight polyphenyls,

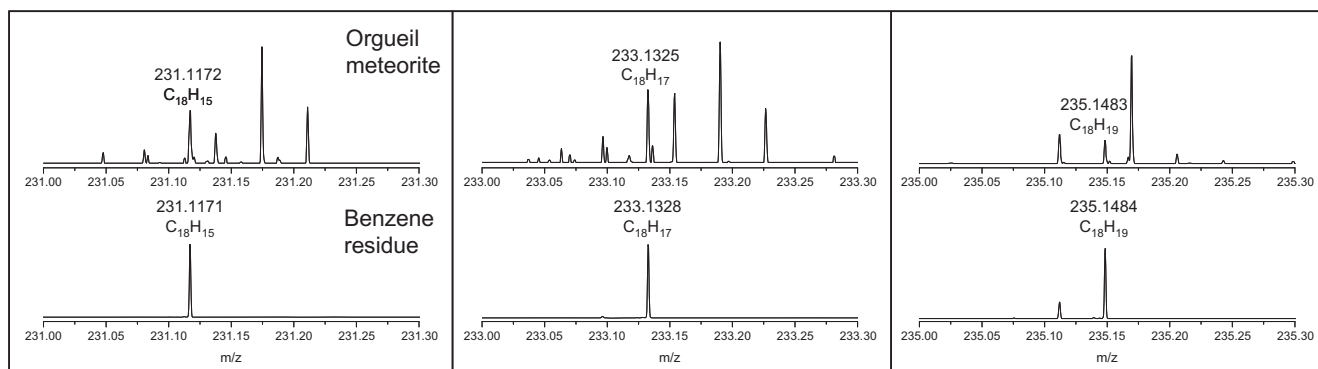


Fig. 5. Comparison of three regions in the APPI mass spectra of the Orgueil carbonaceous chondrite (top traces) and the residue made from benzene irradiated at 19 K by 0.8 MeV protons (bottom traces).

especially if they can accumulate into aerosol particles. Furthermore, polyphenyls (biphenyl and terphenyls) are known to have good radiation resistance and thermal stability (Delitsky and McKay, 2010), which would aid their survival in Titan's atmosphere. However, additional experiments that simulate more realistic Titan conditions (e.g., EUV radiation, benzene-nitrogen-methane mixtures, benzene-tholin mixtures, and gas phase reactions) are required to establish if polyphenyls are good candidates to account for the high molecular masses detected in Titan's atmosphere.

5. Summary and conclusions

By means of GC–MS and APPI-FTMS, we measured a highly complex suite of organic compounds in the residue made from benzene irradiated at 19 K by 0.8 MeV protons. Our analysis unambiguously identified numerous polyphenyls and also suggested the presence of partially hydrogenated polyphenyls and other complex aromatic compounds. The strong overlap of low molecular weight organic compounds suggests a connection between the radiation chemistry of benzene and the numerous aromatic compounds observed in (at least two) carbonaceous meteorites. Furthermore, radiation-induced reactions provide a facile mechanism for the extensive hydrogenation (likely) observed in meteoritic organics. Our results concur with a low temperature origin for meteoritic aromatic compounds, most likely on icy organic mantles of interstellar grains. Alternative routes for the synthesis of the organics involving the meteorite parent body, such as synthesis during periods of aqueous alteration, may be difficult because benzene is relatively non-reactive, the formation of new C–C bonds have high energetic barriers, and cosmic rays will have limited penetration depth. On the other hand, gamma radiation produced from the decay of radionuclides within the meteorite parent body over an extended timescale may have facilitated similar chemical reactions possibly though radiation-induced “circle” reactions (Sephton and Gilmour, 2000) involving simultaneous bond synthesis and breaking. This possibility may explain why Murchison and Orgueil meteorites had similar profiles of low molecular weight hydrocarbons despite experiencing different degrees of aqueous alteration.

Finally, applications of the radiation chemistry of low temperature benzene may extend beyond asteroids and meteoritics. The radiation chemistry (and photochemistry) of benzene in Titan's atmosphere is likely to produce complex products, and so polyphenyls also may be present in Titan's atmosphere and precursors to larger haze particles. Interstellar applications of low temperature polyphenyl synthesis from benzene also are possible.

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