**Detection of nitrated and oxygenated polycyclic aromatic hydrocarbons using atmospheric
pressure chemical ionization high resolution mass spectrometry**

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Abstract

Polycyclic aromatic hydrocarbons (PAHs) are common pollutants in the atmosphere and have long been recognized to be toxic to humans. These PAHs can be oxidized into more toxic products in both the gas and condensed (on the surface of suspended particulate matter) phases. In this work, we report fragmentation patterns observed atmospheric pressure chemical ionization with high resolution mass spectrometry (APCI-HRMS) for PAH oxidation products. A representative group of 18 PAH derivatives containing carbonyl (oxo-PAHs), hydroxyl (hydroxy-PAHs), carboxyl (carboxy-PAHs), and/or nitro (nitro-PAHs) groups was studied. Ionization of carboxy-PAHs in negative mode yielded common fragments of $[M-H]^-$, $[M-H-CO]^-$, and $[M-H-CO_2]^-$. Oxo-PAHs provided common fragments of $[M+H]^+$, $[M+H-CO]^+$ and $[M+H-2CO]^+$ in positive mode and $[M+e]^-$ in negative mode. Mass spectra of aldehydes exhibited common fragments of $[M+H]^+$, $[M+H-CO]^+$, and $[M+H-O]^+$ in positive mode and $[M+e]^-$ and $[M-H+O]^-$ in negative mode. For all nitro-PAHs, $[M+H]^+$, $[M+H-O]^+$ and $[M+3H-O_2]^+$ ions were observed in positive mode. On the basis of the APCI-HRMS analysis of standards, eight reaction products of pyrene oxidation under heterogeneous conditions were characterized. HRMS data, specific fragments and common ions such as that of 205 m/z , characteristic for carbonyl phenanthrene, enabled the identification of the oxidation products.

Keywords

Polycyclic Aromatic Hydrocarbon Derivatives

High Resolution Mass Spectrometry

Ionization/Fragmentation Patterns

Identification of Unknowns

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are currently recognized for their adverse effect on human health [1]. PAH derivatives produced during incomplete combustion or as a result of atmospheric reactions were previously shown to be even more toxic than their native PAHs [2]. The major PAH derivatives previously reported are those functionalized with carbonyl (oxo-PAHs), nitro (nitro-PAHs), hydroxyl (hydroxy-PAHs), and carboxyl (carboxy-PAHs) groups [3–16]. Nevertheless, due to the difficulty in their analysis, PAH derivatives have been reported to a lesser extent than their PAH precursors, with studies targeting either selected classes of compounds or specific chemicals [12,17–22]. The identification of specific compounds, particularly isomers, may provide further insights into the mechanisms of atmospheric processes and help measure the contribution of primary and secondary emissions [23]. For example, 1-nitropyrene and 3-nitrofluoranthene are formed through incomplete combustion of diesel fuel, while 2-nitropyrene and 2-nitrofluoranthene are produced during gas-phase reactions in the atmosphere [9,21,24–26].

In addition to identifying unknown PAH oxidation products, the determination of their concentrations in the atmosphere is also of importance. In order to obtain reliable concentration

measurements, versatile and robust analytical methods enabling their effective separation and identification are required. Owing to its high resolution, gas chromatography-mass spectrometry (GC-MS) often turns out to be the method of choice. However, higher molecular weight PAHs with five or more rings typically exhibit poor GC sensitivity due to their low volatility [27]. Similarly, species that are either thermally labile or contain highly polar functional groups (i.e., hydroxy- and carboxy-PAHs) are not easily detected. In addition, polar analytes require derivatization prior to analysis [28,29].

For these compounds, high performance liquid chromatography (HPLC) coupled to MS has been successfully applied as an alternative method with optimized HPLC conditions for known standards [17–20,30,31]. From the two commonly used ionization sources, atmospheric pressure chemical ionization (APCI) and electrospray ionization (ESI), the former was demonstrated to be more sensitive for the analysis of PAH derivatives [18]. Major MS ions of several PAH derivatives analyzed in the present work were described in previous HPLC-APCI-MS studies [18–20]; however, fragmentation pathways were reported for only a few of these species [11,30]. Furthermore, these studies did not focus on confirming if the observed ions were either molecular ions or fragments.

Using low resolution MS methods, limited data on the fragmentation of PAH derivatives with HPLC-APCI have been reported for only a small number of targeted species. For hydroxy-PAHs, the main ions observed in negative mode are the molecular anion $[M]^{-}$ and the deprotonated molecule $[M-H]^{-}$ [29]. In positive mode, protonation as well as protonation followed by the loss of H_2O were the main ionization and fragmentation processes previously observed [29]. Additionally, $[M+15]^{+}$ adducts have been detected and tentatively identified as $[M+CH_3]^{+}$.

Letzel et al. analyzed two carboxy-PAH species, 2-naphthoic acid and 2-anthraquinone acid, using HPLC-APCI with low resolution MS detection [31]. In negative APCI mode, the most common ions resulted from deprotonation ($[M-H]^-$ ions) followed by decarboxylation ($[M-H-CO_2]^-$ anions) [31]. In addition, a fragment $[M-H-28-28]^-$ was observed and proposed to form by either two CO (28 Da) losses or consecutive losses of CO and C_2H_4 (28 Da). When using higher fragmentor voltages (prompting collision induced dissociation and focusing the ion beam into the MS analyzer), fragments $[M-H-44-18]^-$ and $[M-H-44-28]^-$ were also observed. Their formation was explained as the losses of CO_2 followed by H_2O and CO, respectively. As for hydroxy-PAHs, the identities of these fragments have not been confirmed using high resolution data. Fragmentations of carboxy-PAHs in positive mode were not observed, mainly due to their low proton affinities and, therefore, a limited degree of protonation [31].

Many research groups utilized HPLC-APCI-MS for detecting oxo-PAHs [17–20,30]. However, in the majority of these studies, only the most abundant ion was used during method optimization, with common fragments reported to a limited extent. In positive mode, the losses of CO ($[M+H-CO]^+$) and C_2O_2 ($[M+H-CO-CO]^+$) from the protonated ion molecule were reported [20]. In negative mode, C_2O_2 loss from the deprotonated molecule (giving the $[M-H-CO-CO]^-$ ion) along with electron capture (giving the $[M+e]^-$ ion) were the most common pathways [18,19]. In these studies, only single isomers of oxo-PAH derivatives were subjected to MS analysis, thus fragmentation processes specific for each constitutional isomer have yet to be identified. Another important information reported by Delhomme et al. was increased sensitivity for diketones in negative mode and for monoketones in positive mode [18].

HPLC-APCI-MS methods for analysis of nitro-PAHs were utilized in several studies; however, as with oxo-PAHs, most of the reports were focused only on the quantification using the major

ions. The most frequently observed pattern for nitro-PAHs in spectra obtained in positive APCI mode was the neutral loss of 30 Da. The identity of this neutral fragment has been up for debate, being attributed to either the loss of NO[32] or nitro group reduction (i.e., losing 2O and gaining 2H, giving a net loss of 30 Da) [33]. Using deuterium oxide in place of water for the eluent solvent mixture, Karancsi & Slegel (1999) showed that the fragment of $[M-30]^+$ was formed for singly substituted one- or two-ring containing nitroaromatic species as a result of nitro group reduction [33]. For three-ring nitro-PAHs, the identity of the $[M-30]^+$ fragment has not been confirmed. In negative mode, the most common ionization pathway was also the loss of 30 Da proposed as the loss of NO based on low resolution data [11,30,34,35]. Also, the $[M-H+16]^-$ adduct was observed and interpreted as the gain of oxygen [11,35]. The identities of these species using high resolution mass spectrometry (HRMS) are yet to be confirmed.

In the present study, ionization and fragmentations that occur during APCI of common atmospheric oxidation products of PAHs, namely derivatives containing either nitro, amino, carbonyl, carboxyl, or hydroxyl groups, or a combination thereof, were evaluated using HRMS. APCI was coupled with HPLC, which has been reported to be more suitable for some classes of PAH derivatives than GC. For each class of PAH derivatives, fragmentation pathways were proposed based on the ions and fragments detected. The ionization and fragmentation trends observed for standards were then employed to identify unknown pyrene oxidation products formed in flow reactor experiments involving the ozonation and nitration of PAHs.

2. Materials and Methods

2.1. Chemicals

The PAH derivatives including 9-nitroanthracene, 1-nitropyrene, 1,6-dinitropyrene, anthrone, 9,10-anthracenedione, 9,10-phenanthrenedione, 1,4-phenanthrenedione, pyrene-4,5-dione, 9-

phenanthrenecarboxaldehyde, and 4-carboxy-5-phenanthrenecarboxaldehyde were obtained from Sigma Aldrich (Atlanta, GA, USA). 9-Nitrophenanthrene, 3-nitrophenanthrene and 9,10-dinitroanthracene were obtained from Accustandard Inc. (New Haven, CT, USA). See Fig. 1 for the structures of all PAH derivatives investigated in this work. LC-MS Optima grade methanol (MeOH) and LC-MS Optima grade acetonitrile were purchased from Fisher Scientific (Chicago, IL, USA). Formic acid (LC-MS grade) was obtained from Fluka (Atlanta, GA, USA). MilliQ water (Millipore) was used during HPLC experiments.

2.2. HPLC-APCI-MS Analysis

HPLC-MS analyses were carried out with an Agilent 1100 HPLC system coupled to a high resolution Agilent 1969 Time-of-flight MS (ToF-MS) equipped with an APCI source (Agilent Technologies, Santa Clara, CA, USA).

All HPLC separations were performed using a Restek C₁₈ 200 mm × 3.2 mm reverse phase HPLC column with 5 µm particle size (Restek, Bellefonte, PA, USA). A binary solvent system consisting of water (A) and methanol (B) was used. A gradient program at a flow rate of 0.2 mL min⁻¹ started with 20% B for 5 min, followed with a linear increase to 90% B at 20 min, and hold at 90% until 27 min, and then was linearly decreased to 20% at 30 min and held at 20% B for 5 min to allow for equilibration. The column oven temperature was set at 30 °C and injection volume was 50 µL.

APCI was performed in both positive and negative modes with each sample containing 5 mM formic acid. Drying gas (N₂) was set at 300 °C at a flow of 3 L min⁻¹. For all experiments the capillary voltage was set to 4500 V. In order to minimize the contribution of post-source fragmentation, the fragmentor voltage was set to 120 V for all experiments. All HPLC-APCI-ToF-MS analyses were performed with the corona discharge current set at 10 µA. For

experiments evaluating the contribution of the corona current to gas-phase ion fragmentation, the corona discharge current was varied within the range of 4–25 μ A.

2.3. Reaction Experiments

The flow reactor used for the ozonation of pyrene consisted of three main parts: a gas injection/dilution system, mixing chamber, and reaction chamber (Fig. S1). The gas injection/dilution system delivered breathing quality air to a mixing chamber composed entirely of Teflon (31.5 cm length $\times$ 9 cm I.D.) through $\frac{1}{4}$ " stainless steel tubing. Two-way stainless steel valves were used for selecting the gases used in each experiment. All gas flows through the reactor system were regulated with mass flow controllers (Alicat Scientific, Tucson, AZ, USA) to achieve the desired dilution of gases. After passing the mixing chamber, the gas flow was split using stainless steel tees, leading to the reaction chamber, an O₃ gas analyzer, and an exhaust vent. During ozonation experiments, ozone levels at the outlet of the mixing chamber were measured using a photometric O₃ gas analyzer (Model 400E, Teledyne, Thousand Oaks, CA, USA). The gas mixtures from the mixing chamber were supplied to the Teflon reaction chamber (43 cm in length $\times$ 9 cm I.D.) through an inlet located on top of the chamber. A quartz tissue filter (90 mm I.D., PALL Corporation, Port Washington, NY) was spiked with pyrene solution and placed onto a Teflon-coated aluminum mesh at the bottom of the reaction chamber. The outlet of the reactor chamber was located after the filter support. The total flow through the reaction chamber was controlled using an oil-less pump with a mass flow controller positioned between the reaction chamber and the pump. The flow drawn by the pump was always kept lower than the gas flow exiting the mixing chamber in order to ensure that ambient air was not drawn through the flow splitter (installed to prevent over-pressurization of the reaction chamber).

An allotted amount of a PAH stock solution (40 μL) at 100 $\mu\text{g mL}^{-1}$ per compound was spiked over the quartz tissue filter and allowed to evaporate at room temperature for 60 s (resulting in a final amount of 4 μg on the filter). All quartz filters were pre-baked at 500 $^{\circ}\text{C}$ for 12 h, then placed in the flow reactor and exposed to O_3 at 1.25 ppm for 90 min.

Upon the completion of each reaction experiment, the filter was extracted using sonication with 10 mL of DCM for 30 min and the resulting extract collected. The vial and filter were washed twice with 10 mL of DCM each time. Ultimately all DCM extract fractions obtained were combined, filtered over deactivated glass wool, and evaporated under a gentle stream of nitrogen to ~ 0.5 mL. The samples were then submitted to HPLC-APCI-ToF-MS analysis.

Identification was based on a match of retention times of the overlayed extracted ion chromatogram (EIC) peaks (± 0.03 Da), on the relative intensities as well as high resolution MS data.

3. Results and Discussion

3.1. Carboxy- & Hydroxy-PAHs

The four carboxy-PAHs and one hydroxy-PAH investigated in this study are presented in Table 1 and Fig. 1, top row. Three of them, 9-phenanthrene-, 4-phenanthrene-, 4-anthracenecarboxylic acids, are constitutional isomers that differ either in the ring arrangement or the location of the carboxyl group. The fourth compound, 4-carboxy-5-phenanthrenecarboxaldehyde, contains both carboxyl and carbonyl groups.

As previously reported,[31] the APCI in negative mode was more sensitive and resulted in more uniform fragmentation patterns (Table 1; spectra shown in Fig. S2). The fragmentation proposed in Scheme 1 corresponds to neutral losses previously observed by others [31]. The spectra of four analyzed carboxy-PAH derivatives exhibited the base peak of the deprotonated molecule

[M-H]⁻ as well as the signals corresponding to the loss of CO₂ and CO from the deprotonated molecule. In contrast to the previous work [31], no ion corresponding to two subsequent losses of CO (giving the [M-H-CO-CO]⁻ ion) was observed detected. For 4-carboxy-5-phenanthrenecarboxaldehyde, no CO loss from the deprotonated molecule was observed, but rather the successive losses of CO from the aldehyde group and CO₂ from the carboxyl group following deprotonation (Scheme 2).

While the analysis of carboxy-PAHs with APCI in positive mode resulted in lower response, the compounds studied still exhibited common ionization/fragmentation trends but with significantly varied ion abundances. The differences in abundance for three isomeric compounds (9-anthracene-, 9-phenanthrene- and 4-phenanthrenecarboxylic acids) may be essential for their accurate identification. The protonated molecule [M+H]⁺ for 4- and 9-phenanthrenecarboxylic acids showed responses at 45% and 20% relative to the base peak, respectively, and was not observed for 9-anthracenecarboxylic acid. For 4-carboxy-5-phenanthrenecarboxaldehyde, a higher relative response of the [M+H]⁺ ion was detected, most likely due to protonation of the aldehyde group (see Scheme 2). The protonation followed by the loss of H₂O was observed for all carboxy-PAHs, although in varied relative intensities. For 9-phenanthrenecarboxylic acid, the [M+H-H₂O]⁺ species assigned to the carbonyl phenanthrene ion [C₁₅H₁₉O]⁺, was the least prevalent (10% relative intensity to the base peak), while for the other three species this ion of 205 *m/z* was much more abundant (60–80%). Three compounds, 9-phenanthrenecarboxylic acid, 9-anthracenecarboxylic acid and 4-carboxy-5-phenanthrenecarboxaldehyde, exhibited the [M+H+CH₂]⁺ ion at 25, 30, and 85% abundances relative to the base peak, respectively. This ion is possibly a result of gas-phase esterification by methanol.

In this study only one hydroxy-PAH, 1-hydroxypyrene, was considered. This compound is one of the most abundant hydroxy-PAHs in atmospheric samples [28]. In positive mode, ionization via protonation as well as electron abstraction $[M+H]^+$ and $[M-e]^{+}$ ions were observed in 100% and 85% relative abundance, respectively. Additionally, an oxygen adduct $[M-H+O]^+$ was detected in 75% relative abundance to the base peak. In negative mode, 1-hydroxypyrene was mainly ionized via deprotonation, yielding the $[M-H]^{-}$ ion. In the spectra obtained using positive mode, the signal of the oxygen adduct $[M-2H+O]^{-}$ was again found.

3.2. Oxo-PAHs

To our knowledge, HRMS data of several major fragment ions for seven oxo-PAHs (Table 2, structures are shown in Fig. 1 2nd and 3rd rows) are being reported for the first time in this work.

In positive mode, several common trends were observed among the oxo-PAHs investigated. The major ionization pathway for most of the mono- and diketones studied was protonation (spectra shown in Fig. S3), mirroring observations made in previous studies [18–20,30]. The loss of CO from the protonated molecule was observed for each of these compounds but varying in abundance. Successive losses of CO giving the $[M+H-C_2O_2]^+$ ion were observed for only two compounds, 9,10-phenanthrenedione and pyrene-4,5-dione (Fig. S3). This seems to be a highly regioselective process since spectra of the other two three-ring diketone PAHs did not exhibit this fragment ion. We suggest that this fragmentation is likely to occur via ring opening (Schemes 3a and b). For 9,10-phenanthrenedione, the structure of the $[M+H-C_2O_2]^+$ ion is similar to that of a deprotonated biphenyl cation (Scheme 3a). In contrast, for pyrene-4,5-dione, an analogous ring-opening process could result in a structure that resembles a deprotonated phenanthrene molecule. The ring-opening pathway would explain the absence of both the $[M+H-CO]^+$ and $[M+H-C_2O_2]^+$ ions for 9,10-anthracenedione, whose specific ring fusion

pattern makes this process unlikely. Similarly, these fragments were not detected in the spectrum of 1,4-phenanthrenedione, a compound with two carbonyl groups not adjacent to each other. Dimerization was observed only for two studied compounds, anthrone and 9,10-anthracenedione. Anthrone exhibited a small degree of dimerization, most likely into a structure similar to a protonated bianthrone ion observed at m/z of 385 (Fig. S3). The same ion (m/z 385) was also discernible for 9,10-anthracenedione, suggesting the loss of CO prior to the dimerization. For anthrone, a fragment of 165 m/z was assigned to $C_{13}H_9$, formed possibly by the loss of CH_2O from the $[M+H]^+$ ion; however, the mechanism of this process is unclear. Using APCI in positive mode, two monocarboxaldehydes showed similar ionization pathways as the mono- and diketone PAHs. The major ionization pathway was protonation (Fig. S3). The loss of CO from the protonated molecule was also observed for both aldehydes. It appears that the loss of CO for these aldehydes and diketones proceeds via different pathways. Instead of the expected ion at m/z 177 as a result of the protonation of the aldehydic oxygen followed by the loss of formaldehyde CH_2O , the ion at m/z 179 was observed for both compounds (Fig. S3). The latter ion was likely formed after the loss of CO. Signals of the fragments corresponding to the loss of O were also discernable for both monocarboxaldehydes, with a higher abundance observed for 9-phenanthrenecarboxaldehyde (Table 2, Fig. S3). The latter compound provided the abundant $[M+15]^+$ ion, the signal of which was not detected in the spectra of other oxo-PAHs except 9,10-phenanthrenedione. This ion was attributed to the formation of the $[M+CH_3]^+$ adduct. Scheme 4 shows the proposed pathway for its formation through the addition of methanol to the carbonyl group followed by the loss of water.

The ionization of oxo-PAHs with APCI in negative mode resulted in a very limited, if any, fragmentation compared to that in positive mode, with observed fragments having lower relative abundances (Table 2, Fig. 3S). Similar to previous investigations [18,30], spectra of all studied oxo-PAHs with the exception of anthrone and 9-phenanthrenealdehyde featured the major peak assigned to the $[M+e]^-$ anion. For anthrone, the main ionization pathway was deprotonation forming the $[M-H]^-$ anion while 9-phenanthrenealdehyde was not ionized at all.

Additional fragmentation/ionization processes in APCI negative mode were observed for 1,4-phenanthrene-1,4-dione and 9-anthracenecarboxaldehyde (Fig. S4). We identified an oxygen adduct of the deprotonated molecule, $[M-H+O]^-$, and confirmed its composition with by high mass accuracy (-2 ± 5 ppm; Table 2). This species was previously proposed to be the $[M+CH_3]^-$ ion.[31] The occurrence of the $[M+CH_3]^-$ adduct was ruled out based on a high mass error of -166 ± 5 ppm from the measured value. The proposed pathway for the formation of the oxygen adduct using 1,4-phenanthrene-1,4-dione as a model compound is shown in Scheme 5. A deprotonated methanol molecule $[CH_3O]^-$ may undergo a nucleophilic addition to the carbonyl group to create the $[M+OCH_3]^-$ fragment that loses CH_4 to give the $[M-H+O]^-$ ion.

3.3. Nitro-PAHs

The APCI ionization/fragmentation of three- and four-ring PAH derivatives with either one or two nitro groups were investigated to evaluate the ionization processes and confirm the identities of fragments with HRMS data. To our knowledge, the ionization/fragmentation processes for dinitro-PAHs in APCI have not been previously reported. The studied species were chosen to represent differences in the location of the nitro groups and the ring fusion pattern of the aromatic backbone, allowing the identification of structure-specific processes.

In positive APCI mode, all nitro compounds underwent similar ionizations and fragmentations with varied relative abundances of major ions (see Table 3, Fig. S5). All species consistently yielded the $[M+H-16]^+$ ion, which was likely formed due to the loss of oxygen from the protonated ion ($[M+H-O]^+$) as shown in Scheme 6. This ionization process was highly specific for 9-nitroanthracene and 9-nitrophenanthrene as the signal of the $[M+H-16]^+$ ion was the most prevalent for both compounds. However, this species was not observed for 3-nitrophenanthrene (Fig. S5). Spectra of mononitro-PAHs exhibited the $[M+H-30]^+$ fragment. Our ~~high-resolution~~ HRMS data (< 10 ppm) support the previously proposed elemental composition of this ion as $[M+3H-2O]^+$ [33]. This fragment is formed upon reduction of the NO_2 group to NH_3^+ . The relative abundance of the $[M+H]^+$ ion was low for all mononitro-PAHs studied (ranging from 5 to 50% of the base peak response). This may be due to a competition between protonation of the neutral molecule and gas-phase reduction.

Dinitro-PAHs, 9,10-dinitroanthracene and 1,6-dinitropyrene, provided rather complex spectra in APCI positive mode (Table 3, Fig. S5). The spectra appear to have two competitive fragmentation pathways involving each of the two nitro groups. As expected, the nitro group reduction to the protonated amino moiety was the major ionization pathway for both compounds. However, the most abundant ion registered in the mass spectra of 1,6-dinitropyrene corresponded to the $[M+H-30]^+$ species with only one nitro group reduced, while the base peak for 9,10-dinitroanthracene belonged to the $[M+H-62]^+$ ion formed upon reduction of both nitro groups. Spectra of both compounds showed peaks for $[M+H-O]^+$ fragments with different relative abundances.

APCI-MS spectra of both mono- and dinitro-PAHs in negative mode displayed a significantly smaller number of fragments compared to that in positive mode (Fig. S5; see also Table 3). For

all species studied, the most abundant ion was produced via associative electron capture by the neutral molecule, giving $[M+e]^-$. This corroborates the observation reported in previous studies performed using low resolution MS detection.[11,32] The associative addition of oxygen following deprotonation to give the $[M-H+O]^-$ ion was common for mononitro-PAHs. The oxygen adduct has been reported previously [11,35]. To evaluate the eluent solvents as possible oxygen contributors to the $[M-H+O]^-$ ions, direct infusion of 1-nitropyrene at 1 ppm was performed in various solvents; the results are shown in Fig. 2. When 1-nitropyrene was dissolved in acetonitrile, the response ratio of $[M-H+O]^-$ to $[M+e]^-$ (m/z 262: m/z 247) was minimal; this was in contrast to the spectra produced when oxygen-containing solvents were used. It should be noted that dinitro-PAHs did not undergo this oxygen addition. Thus, the presence of the second nitro group might play a key role in deactivating the deprotonated molecule towards oxygen addition. As with positive APCI mode, abundance of the $[M-H+O]^-$ ion varied for each constitutional isomer. 9-Nitrophenanthrene exhibited a low relative abundance (~ 8% of $[M+e]^-$ base peak) of the $[M-H+O]^+$ ion, while 3-nitrophenanthrene and 9-nitroanthracene yielded abundances of 30% and 50% of the analogous ion relative to the base peak.

3.4. Products from the Heterogeneous Ozonation of PAHs

The interpretation of APCI ionization/fragmentation pathways using HRMS data demonstrated above enabled the identification of unknown products formed upon exposure of pyrene embedded on a quartz filter to ozone (see Fig. 3) [36,37]. We were able to confirm the identity of two compounds using standards and tentatively identify five additional compounds based on the EICs (obtained with high resolution of ± 0.03 m/z) for the major fragment ions observed with the standards (Table 4; mass spectra shown in Figs. S6 & S7).

336 Hydroxy-PAHs, carboxy-PAHs and oxo-PAHs identified were the compounds formed through
337 the ring-opening pathway as opposed to a direct oxidation [7,36,37]. Although most of these
338 products have been previously observed both in aqueous media and on model particles [7,36,38],
339 the present study is the first to report HRMS data to confirm their elemental composition.

340 From the mass spectra of each chromatographic peak, specific trends in common ions were
341 observed (Fig. 3). Several compounds showed a significant fragment of 205 m/z , tentatively
342 assigned to an ionized phenanthrene carbonyl ion. The common ions of 205, 235 and 191 m/z
343 enabled the tentative identification of three compounds: 4-carboxy-5-
344 phenanthrenecarboxaldehyde, phenanthrene-4,5-dicarboxaldehyde and hydroxymethyl-
345 phenanthrenecarboxylic acid, assuming that their formation occurred via the ring-opening
346 oxidation of pyrene (Figs. 3 and S6. The first compound confirmed by a standard seemed to
347 coelute with 4-phenanthrenecarboxylic acid (also confirmed by using the corresponding
348 standard). 4-Carboxy-5-phenanthrenecarboxaldehyde was previously detected upon the
349 ozonation of pyrene coated on azelaic acid particles [7]. The dicarboxaldehyde was identified
350 based on the concurrent ions of 205 m/z (from the neutral loss of CH_2O) and 191 m/z (loss of
351 CO_2), both formed from the protonated molecule $[\text{M}+\text{H}]^+$ of 235 m/z . This product was
352 previously observed during the homogeneous and heterogeneous ozonation of pyrene [5,7,38].

353 One of the possible constitutional isomers of phenanthrenecarboxylic acid was identified through
354 the observed $[\text{M}+\text{H}]^+$, $[\text{M}+\text{H}-\text{H}_2\text{O}]^+$ and $[\text{M}+\text{H}-\text{CH}_2\text{O}_2]^+$ ions. While this compound was
355 previously identified as a product of pyrene ozonation in aqueous solution [5,38], to our
356 knowledge, it has never been reported in heterogeneous ozonation reactions. We were not able
357 to unequivocally identify the last of the m/z 205 peaks; however, this compound is likely to be
358 another isomer of phenanthrenecarboxylic acid.

Two additional products proposed to result from a ring-opening attack by ozone were tentatively identified as (1,1'-biphenyl)-2,2',6,6'-tetracarboxaldehyde (peak 6 in Fig. 3) and 4-oxapyrene-5-one (peak 3 in Fig. 3). The former was identified based on the $[M+H-O]^+$ and $[M+H-CO]^+$ ion fragments observed with the aldehyde standards. For 4-oxapyrene-5-one, similar to the studied diketone standards, the $[M+H-CO]^+$ ion was observed. In addition, the spectrum of this compound displayed the peak assigned to the $[M+H-CO_2]^+$ ion, which was not detected in the spectra of other ketone standards. This could be explained by the absence of the ester moiety on the pyrene scaffold in the available standards.

4. Conclusions

Derivatives of PAHs containing either one or combination of two functional groups (i.e., hydroxyl, carboxyl, carbonyl, and nitro groups) were analyzed using HPLC-APCI-HRMS. High resolution data for common fragmentation patterns provided by three and four-ring PAH derivatives with similar functional groups were reported for the first time. The data described in this study are expected to be useful for identification of unknown species when standards are not available. The fragments observed for different types of PAH derivatives with various functional groups reported in this study may facilitate future investigations aimed at determining the mechanisms behind their formation. Using APCI-HRMS data, a number of products of pyrene ozonation were tentatively identified based on common ions of 205, 235 and 191 m/z as well as relative intensities of common fragments exhibited by standard compounds. For the first time, HRMS data were obtained to support the identities of these products. Formation of some of the pyrene ozonation products under the heterogeneous conditions is reported for the first time.

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387

6. Figure Captions

Figure 1.

Structures of PAH derivatives studied in this work.

Figure 2.

The contribution of various solvents to formation of $[M-H+O]^-$ ions for 1-nitropyrene in APCI with negative polarity. Spectra were recorded and averaged during the direct infusion of 1-nitropyrene (at 1 ppm with 5 mM formic acid) in three different solvents at a flow rate of 0.2 mL min^{-1} . The height of each mass peak was used as the response (intensity, counts per second).

Figure 3.

HPLC-APCI-HRMS smoothed TIC and EIC chromatograms obtained in positive mode of products formed during the heterogeneous ozonation of pyrene in a small-scale flow reactor. Numbers shown correspond to those listed in Table 4 and Fig. S6 & S7.

7. Scheme Captions

Scheme 1.

Proposed fragmentation pathway for 9-phenanthrenecarboxylic acid with APCI in negative mode. Steps shown with losses or additions only reflect changes in the empirical formula between the parent and product ions, and do not necessarily show the exact mechanisms of fragmentation.

Scheme 2.

Proposed fragmentation pathway for 4-carboxy-5-phenanthrenecarboxaldehyde with APCI in positive mode. Steps shown with losses or additions only reflect changes in the empirical formula between the parent and product ions, and do not necessarily show the exact mechanisms of fragmentation.

Scheme 3a.

Proposed fragmentation pathway for 9,10-phenanthrenedione with APCI in positive mode. Steps shown with losses or additions only reflect changes in the empirical formula between the parent and product ions, and do not necessarily show the exact mechanisms of fragmentation.

Scheme 3b.

Proposed fragmentation pathway for pyrene-4,5-dione with APCI in positive mode. Steps shown with losses or additions only reflect changes in the empirical formula between the parent and product ions, and do not necessarily show the exact mechanisms of fragmentation.

Scheme 4.

Proposed fragmentation pathway for 9-phenanthrenecarboxaldehyde with APCI in positive mode. Steps shown with losses or additions only reflect changes in the empirical formula between the parent and product ions, and do not necessarily show the exact mechanisms of fragmentation.

Scheme 5.

432 Proposed fragmentation pathway for 1,4-phenanthrenedione with APCI in negative mode. Steps
433 shown with losses or additions only reflect changes in the empirical formula between the parent
434 and product ions, and do not necessarily show the exact mechanisms of fragmentation.

435

436 **Scheme 6.**

437 Proposed fragmentation pathway for 3-nitrophenanthrene with APCI in positive mode. Steps
438 shown with losses or additions only reflect changes in the empirical formula between the parent
439 and product ions, and do not necessarily show the exact mechanisms of fragmentation.

440

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Tables

Table 1

Pseudomolecular ions and fragments observed for hydroxy- and carboxy-PAHs with HPLC-APCI-HRMS in both positive and negative modes.

Compound	t _R ^a (min)	Positive Polarity							Negative Polarity						
		Measured Mass ^b (Da)		Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error ^e (ppm)	Measured Mass ^b (Da)		Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error ^e (ppm)
4-carboxy-5-phenanthrenecarboxaldehyde	18.55	235.07633	± 0.00075	100	[M+H-O] ⁺	C ₁₆ H ₁₁ O ₂	235.07536	4.1 ± 3.2	177.07074	± 0.00014	100	[M-H-C ₂ O ₃] ⁻	C ₁₄ H ₉	177.07097	-1.3 ± 0.8
		205.06540	± 0.00084	95	[M+H-CH ₂ O ₂] ⁺	C ₁₅ H ₉ O	205.06479	3.0 ± 4.1	249.05509	± 0.00023	90	[M-H] ⁻	C ₁₆ H ₉ O ₃	249.05572	-2.5 ± 0.9
		251.07032	± 0.00087	92	[M+H] ⁺	C ₁₆ H ₁₁ O ₃	251.07027	0.2 ± 3.4	205.06497	± 0.00047	40	[M-H-CO ₂] ⁻	C ₁₅ H ₉ O	205.06589	-4.5 ± 2.3
		265.08714	± 0.00123	85	[M+H+CH ₂] ⁺	C ₁₇ H ₁₃ O ₃	265.08590	4.7 ± 4.6							
		191.08524	± 0.00065	75	[M+H-CO ₃] ⁺	C ₁₅ H ₁₁	191.08550	-1.4 ± 3.4							
		233.05973	± 0.00091	65	[M+H-H ₂ O] ⁺	C ₁₆ H ₉ O ₂	233.05971	0.1 ± 3.9							
		177.06931	± 0.00067	50	[M+H-C ₂ H ₂ O ₃] ⁺	C ₁₄ H ₉	177.06988	-3.2 ± 3.8							
1-hydroxypyrene	19.21	219.08350	± 0.00158	100	[M+H] ⁺	C ₁₆ H ₁₁ O	219.08044	13.9 ± 7.2	217.06663	± 0.00098	100	[M-H] ⁻	C ₁₆ H ₉ O	217.06589	3.4 ± 4.5
		218.07520	± 0.00122	85	[M-e] ⁺	C ₁₆ H ₁₀ O	218.07262	11.8 ± 5.6	232.05210	± 0.00103	20	[M-2H+O] ⁻	C ₁₆ H ₈ O ₂	232.05188	0.9 ± 4.4
		233.06141	± 0.00055	75	[M+O-H] ⁺	C ₁₆ H ₉ O ₂	233.05971	7.3 ± 2.4							
		202.07679	± 0.00046	2	[M-e-O] ⁺	C ₁₆ H ₁₀	202.07770	-4.5 ± 2.3							
9-phenanthrenecarboxylic acid	18.34	209.05907	± 0.00182	100	[M+H-CH ₂] ⁺	C ₁₄ H ₉ O ₂	209.05971	-3.0 ± 8.7	221.06048	± 0.00054	100	[M-H] ⁻	C ₁₅ H ₉ O ₂	221.05971	3.5 ± 2.4
		237.08894	± 0.00057	25	[M+H+CH ₂] ⁺	C ₁₆ H ₁₃ O ₂	237.09101	-8.7 ± 2.4	177.07080	± 0.00083	25	[M-H-CO ₂] ⁻	C ₁₄ H ₉	177.06988	5.2 ± 4.7
		223.07783	± 0.00054	20	[M+H] ⁺	C ₁₅ H ₁₁ O ₂	223.07536	11.1 ± 2.4	193.06566	± 0.00048	5	[M-H-CO] ⁻	C ₁₄ H ₉ O	193.06479	4.5 ± 2.5
		205.06627	± 0.00086	10	[M+H-H ₂ O] ⁺	C ₁₅ H ₉ O	205.06479	7.2 ± 4.2	208.05256	± 0.00044	4	[M-CH ₂] ⁻	C ₁₄ H ₉ O ₂	208.05188	3.3 ± 2.1
4-phenanthrenecarboxylic acid	18.56	221.05919	± 0.00011	100	[M-H-2e] ⁺	C ₁₅ H ₉ O ₂	221.05971	-2.3 ± 0.5	221.06036	± 0.00049	100	[M-H] ⁻	C ₁₅ H ₉ O ₂	221.05971	3.0 ± 2.2
		205.06477	± 0.00005	80	[M+H-H ₂ O] ⁺	C ₁₅ H ₉ O	205.06479	-0.1 ± 0.3	177.07064	± 0.00042	40	[M-H-CO ₂] ⁻	C ₁₄ H ₉	177.06988	4.3 ± 2.4
		237.09060	± 0.00060	50	[M+H+CH ₂] ⁺	C ₁₆ H ₁₃ O ₂	237.09101	-1.7 ± 2.5	235.03951	± 0.00045	5	[M-3H+O] ⁻	C ₁₅ H ₇ O ₃	235.03897	2.3 ± 1.9
		223.07500	± 0.00010	45	[M+H] ⁺	C ₁₅ H ₁₁ O ₂	223.07536	-1.6 ± 0.5	193.06484	± 0.00088	4	[M-H-CO] ⁻	C ₁₄ H ₉ O	193.06479	0.3 ± 4.6
9-anthracenecarboxylic acid	18.94	209.09353	± 0.00091	100	[M+3H-O] ⁺	C ₁₅ H ₁₃ O	209.09609	-8.3 ± 4.4	221.05990	± 0.00042	100	[M-H] ⁻	C ₁₅ H ₉ O ₂	221.05971	0.9 ± 1.9
		195.07990	± 0.00047	85	[M+H-CO] ⁺	C ₁₄ H ₁₁ O	195.08044	-2.8 ± 2.4	177.07022	± 0.00009	40	[M-H-CO ₂] ⁻	C ₁₄ H ₉	177.06988	2.0 ± 0.5
		205.06547	± 0.00059	60	[M+H-H ₂ O] ⁺	C ₁₅ H ₉ O	205.06479	3.3 ± 2.9	208.05184	± 0.00100	10	[M-CH ₂] ⁻	C ₁₄ H ₉ O ₂	208.05188	-0.2 ± 4.8
		237.09103	± 0.00093	30	[M+H+CH ₂] ⁺	C ₁₆ H ₁₃ O ₂	237.09101	0.1 ± 3.9	193.06603	± 0.00012	5	[M-H-CO] ⁻	C ₁₄ H ₉ O	193.06479	6.4 ± 0.6

^a Using a C₁₈ 200 mm x 3.2 mm column (Restek) with 5 µm particle size. A gradient program of A:H₂O and B:MeOH was used with a 0.20 mL min⁻¹ flow rate: 20% B for 5 min, linear increase to 90% B at 20 min and held to 27 min, linear decrease to 20% B at 30 min and held to 35 min.

^b Measure masses are reported as averages and standard deviations of the masses observed at three different points along the chromatographic peak.

^c Fragments are shown to reflect changes in the empirical formula from the neutral molecule and do not necessarily reflect the ionization or fragmentation pathway.

^d Possible empirical formula matches for the observed mass were calculated with elemental ranges of C:8-18, H:6-16, O:0-4, and Na:0-1 for monomers and C:16-32, H:12-32, O:0-4, and Na:0-1 for suspected dimers.

^e The standard deviation calculated from the observed masses was converted to ppm error to show its influence on empirical formula estimations.

Table 2

Pseudomolecular ions and fragments observed for oxo-PAHs with HPLC-APCI-HRMS in both positive and negative modes.

Compound	t _R ^a (min)	Positive Polarity							Negative Polarity						
		Measured Mass ^b (Da)		Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error (ppm) ^e	Measured Mass ^b (Da)		Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error (ppm) ^e
anthrone	21.45	195.07934	± 0.00043	100	[M+H] ⁺	C ₁₄ H ₁₁ O	195.08040	-5.5 ± 2.2	193.06546	± 0.00015	100	[M-H] ⁻	C ₁₄ H ₉ O	193.06589	-2.2 ± 0.8
		165.06976	± 0.00070	10	[M+H-CH ₂ O] ⁺	C ₁₃ H ₉	165.06990	-0.8 ± 4.3	208.05230	± 0.00057	30	[M-2H+O] ⁻	C ₁₄ H ₈ O ₂	208.05290	-2.9 ± 2.7
		385.12075	± 0.00125	8	[M+M-3H] ⁺	C ₂₈ H ₁₇ O ₂	385.12231	-4.0 ± 3.2	385.11995	± 0.00827	10	[M+M-3H] ⁻	C ₂₈ H ₁₇ O ₂	385.12340	-8.9 ± 2.1
		223.07483	± 0.00047	4	[M+H+CO] ⁺	C ₁₅ H ₁₁ O ₂	223.07530	-2.1 ± 2.1							
9,10-anthracenedione	23.37	209.06013	± 0.00040	100	[M+H] ⁺	C ₁₄ H ₈ O ₂	209.05971	2.0 ± 1.9	208.05187	± 0.00031	100	[M+e] ⁻	C ₁₄ H ₈ O ₂	208.05298	-5.3 ± 1.5
		193.06482	± 0.00033	30	[M+H-O] ⁺	C ₁₄ H ₈ O	193.06479	0.1 ± 1.7							
		385.12241	± 0.00151	10	[M+M+H-2O] ⁺	C ₂₈ H ₁₇ O ₂	385.12230	0.3 ± 3.9							
9,10-phenanthrenedione	18.92	181.06486	± 0.00021	100	[M+H-CO] ⁺	C ₁₃ H ₈ O	181.06479	0.4 ± 1.1	208.05205	± 0.00073	100	[M+e] ⁻	C ₁₄ H ₈ O ₂	208.05298	-4.5 ± 3.5
		209.06165	± 0.00033	90	[M+H] ⁺	C ₁₄ H ₈ O ₂	209.05971	9.3 ± 1.6							
		153.06918	± 0.00009	60	[M+H-C ₂ O ₂] ⁺	C ₁₂ H ₈	153.06988	-4.6 ± 0.6							
		226.08584	± 0.00011	50	[M+NH ₄] ⁺	C ₁₄ H ₁₂ NO ₂	226.08620	-1.6 ± 0.5							
		223.07472	± 0.00030	50	[M+CH ₃] ⁺	C ₁₅ H ₁₁ O ₂	223.07530	-2.6 ± 1.4							
1,4-phenanthrenedione	21.65	209.05992	± 0.00043	100	[M+H] ⁺	C ₁₄ H ₈ O ₂	209.05971	1.0 ± 2.1	208.05282	± 0.00074	100	[M+e] ⁻	C ₁₄ H ₈ O ₂	208.05298	-0.8 ± 3.6
		239.07032	± 0.00018	50	[M+CH ₃ O] ⁺	C ₁₅ H ₁₁ O ₃	239.07020	0.5 ± 0.7	195.04460	± 0.00082	45	[M+e-CH] ⁻	C ₁₃ H ₇ O ₂	195.04510	-2.6 ± 4.2
		181.06548	± 0.00087	15	[M+H-CO] ⁺	C ₁₃ H ₈ O	181.06479	3.8 ± 4.8	223.03901	± 0.00075	20	[M-H+O] ⁻	C ₁₄ H ₇ O ₃	223.04007	-4.8 ± 3.4
pyrene-4,5-dione	21.06	233.05827	± 0.00029	100	[M+H] ⁺	C ₁₆ H ₈ O ₂	233.05970	-6.1 ± 1.2	232.05187	± 0.00110	100	[M+e] ⁻	C ₁₆ H ₈ O ₂	232.05298	-4.8 ± 4.7
		205.06545	± 0.00056	85	[M+H-CO] ⁺	C ₁₅ H ₈ O	205.06470	3.6 ± 2.7							
		177.06969	± 0.00025	70	[M+H-C ₂ O ₂] ⁺	C ₁₄ H ₈	177.06980	-0.6 ± 2.5							
		250.08569	± 0.00036	60	[M+NH ₄] ⁺	C ₁₆ H ₁₂ NO ₂	250.08620	-2.0 ± 1.5							
phenanthrene-9-carboxaldehyde	23.47	207.07998	± 0.00017	100	[M+H] ⁺	C ₁₅ H ₁₁ O	207.08040	-2.0 ± 0.8							
		221.09549	± 0.00019	90	[M+CH ₃] ⁺	C ₁₆ H ₁₃ O	221.09600	-2.3 ± 0.9							
		191.08501	± 0.00036	60	[M+H-O] ⁺	C ₁₅ H ₁₁	191.08550	-2.6 ± 1.9							
		179.08487	± 0.00024	40	[M+H-CO] ⁺	C ₁₄ H ₁₁	179.08553	-3.7 ± 1.4							
		233.06034	± 0.00051	10	[M+CO-H] ⁺	C ₁₆ H ₉ O ₂	233.05970	2.7 ± 2.2							
		165.06739	± 0.00007	5		C ₁₁ H ₁₀ Na	165.06747	-0.5 ± 0.4							
anthracene-9-carboxaldehyde	23.47	207.07961	± 0.00042	100	[M+H] ⁺	C ₁₅ H ₁₁ O	207.08040	-3.8 ± 2.0	206.07313	± 0.00042	100	[M+e] ⁻	C ₁₅ H ₁₀ O	206.07371	-2.8 ± 2.1
		179.08665	± 0.00064	50	[M+H-CO] ⁺	C ₁₄ H ₁₁	179.08553	6.3 ± 3.6	221.06031	± 0.00120	50	[M-H+O] ⁻	C ₁₅ H ₉ O ₂	221.06080	-2.2 ± 5.4
		178.07803	± 0.00036	20	[M+H-CHO] ⁺	C ₁₄ H ₁₀	178.07770	1.9 ± 2.0							
		191.08519	± 0.00022	8	[M+H-O] ⁺	C ₁₅ H ₁₁	191.08550	-1.6 ± 1.1							

^a Using a C₁₈ 200 mm x 3.2 mm column (Restek) with 5 µm particle size. A gradient program of A:H₂O and B:MeOH was used with a 0.20 mL min⁻¹ flow rate: 20% B for 5 min, linear increase to 90% B at 20 min and held to 27 min, linear decrease to 20% B at 30 min and held to 35 min.^b Measure masses are reported as averages of the masses observed at three different points along the chromatographic peak.^c Fragments are shown to reflect changes in the empirical formula from the neutral molecule and do not necessarily reflect the ionization or fragmentation pathway.^d Possible empirical formula matches for the observed mass were calculated with elemental ranges of C:8–18, H:6–16, O:0–4, and Na:0–1 for monomers and C:16–32, H:12–32, O:0–4, and Na:0–1 for suspected dimers.^e The standard deviation calculated from the observed masses was converted to ppm error to show its influence on empirical formula estimations.

Table 3

Pseudomolecular ions and fragments observed for nitro-PAHs with HPLC-APCI-HRMS in both positive and negative modes.

Compound	t_R^a (min)	Positive Polarity							Negative Polarity						
		Measured Mass ^b (Da)	Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error (ppm) ^e		Measured Mass ^b (Da)	Rel. Abund. (%)	Fragment ^c	Calculated Empirical Formula ^d	Calculated Mass (Da)	Mass Error (ppm) ^e	
9-nitroanthracene	23.74	208.07546	± 0.00024	100	[M+H-O] ⁺	C ₁₄ H ₁₀ NO	208.07569	-1.1 ± 1.2	223.06308	± 0.00062	100	[M+e] ⁻	C ₁₄ H ₉ NO ₂	223.06388	-3.6 ± 2.8
		194.09603	± 0.00082	17	[M+3H-2O] ⁺	C ₁₄ H ₁₂ N	194.09643	-2.0 ± 4.2	238.05027	± 0.00102	50	[M-H+O] ⁻	C ₁₄ H ₉ NO ₃	238.05097	-2.9 ± 4.3
		194.09603	± 0.00082	17	[M+H-NO] ⁺	C ₁₄ H ₁₀ O	194.07262	121 ± 4.2	193.06543	± 0.00030	20	[M+e ⁻ -NO] ⁻	C ₁₄ H ₉ O	193.06589	-2.4 ± 1.6
		224.07114	± 0.00060	10	[M+H] ⁺	C ₁₄ H ₁₀ NO ₂	224.07060	2.4 ± 2.7	208.05150	± 0.00095	3	[M-H+O-NO] ⁻	C ₁₄ H ₉ O ₂	208.05243	-4.5 ± 4.6
		178.07725	± 0.00003	3	[M+H-NO ₂] ⁺	C ₁₄ H ₁₀	178.07770	-2.6 ± 0.1	256.06066	± 0.00090	3	[M+e ⁻ +HO ₂] ⁻	C ₁₄ H ₁₀ NO ₄	256.06153	-3.4 ± 3.5
3-nitrophenanthrene	24.65	194.09626	± 0.00031	100	[M+3H-2O] ⁺	C ₁₄ H ₁₂ N	194.09643	-0.9 ± 1.6	223.06250	± 0.00049	100	[M+e] ⁻	C ₁₄ H ₉ NO ₂	223.06388	-6.2 ± 2.2
		208.07553	± 0.00012	80	[M+H-O] ⁺	C ₁₄ H ₁₀ NO	208.07569	-0.8 ± 0.6	238.04966	± 0.00107	30	[M-H+O] ⁻	C ₁₄ H ₉ NO ₃	238.05097	-5.5 ± 4.5
		178.07699	± 0.00015	15	[M+H-NO ₂] ⁺	C ₁₄ H ₁₀	178.07770	-4.0 ± 0.8	209.05960	± 0.00109	3	[M+e ⁻ +O-NO] ⁻	C ₁₄ H ₉ O ₂	209.06080	-5.7 ± 5.2
		224.07080	± 0.00048	6	[M+H] ⁺	C ₁₄ H ₁₀ NO ₂	224.07060	0.9 ± 2.1	193.06676	± 0.00043	2	[M+e ⁻ -NO] ⁻	C ₁₄ H ₉ O	193.06589	4.5 ± 2.2
9-nitrophenanthrene	24.12	208.07512	± 0.00031	100	[M+H-O] ⁺	C ₁₄ H ₁₀ NO	208.07569	-2.7 ± 1.5	223.06354	± 0.00086	100	[M+e] ⁻	C ₁₄ H ₉ NO ₂	223.06388	-1.5 ± 3.9
		194.09530	± 0.00012	70	[M+3H-2O] ⁺	C ₁₄ H ₁₂ N	194.09643	-5.8 ± 0.6	238.05060	± 0.00114	8	[M-H+O] ⁻	C ₁₄ H ₉ NO ₃	238.05097	-1.5 ± 4.8
		178.07645	± 0.00044	10	[M+H-NO ₂] ⁺	C ₁₄ H ₁₀	178.07770	-7.0 ± 2.5	209.05954	± 0.00054	4	[M+e ⁻ +O-NO] ⁻	C ₁₄ H ₉ O ₂	209.06080	-6.0 ± 2.6
		224.07182	± 0.00064	5	[M+H] ⁺	C ₁₄ H ₁₀ NO ₂	224.07060	5.4 ± 2.8	193.06529	± 0.00057	4	[M+e ⁻ -NO] ⁻	C ₁₄ H ₉ O	193.06589	-3.1 ± 3.0
1-nitropyrene	26.46	218.09619	± 0.00162	100	[M+3H-2O] ⁺	C ₁₆ H ₁₂ N	218.09643	-1.1 ± 7.5	247.06206	± 0.00079	100	[M+e] ⁻	C ₁₆ H ₉ NO ₂	247.06388	-7.4 ± 3.2
		248.06993	± 0.00109	50	[M+H] ⁺	C ₁₆ H ₁₀ NO ₂	248.07060	-2.7 ± 4.4	217.06424	± 0.00096	30	[M+e ⁻ -NO] ⁻	C ₁₆ H ₉ O	217.06589	-7.6 ± 4.4
		232.07624	± 0.00100	40	[M+H-O] ⁺	C ₁₆ H ₁₀ NO	232.07569	2.4 ± 4.3	262.05055	± 0.00105	27	[M-H+O] ⁻	C ₁₆ H ₉ NO ₃	262.05097	-1.6 ± 4.0
		202.07816	± 0.00035	20	[M+H-NO ₂] ⁺	C ₁₆ H ₁₀	202.07770	2.3 ± 1.7	233.05968	± 0.00149	5	[M+e ⁻ +O-NO] ⁻	C ₁₆ H ₉ O ₂	233.06080	-4.8 ± 6.4
9,10-dinitroanthracene	24.16	207.09072	± 0.00041	100	[M+3H-4O] ⁺	C ₁₄ H ₁₁ N ₂	207.09160	-4.2 ± 2.0	268.04708	± 0.00089	100	[M+e] ⁻	C ₁₄ H ₈ N ₂ O ₄	268.04896	-7.0 ± 3.3
		208.07501	± 0.00045	90	[M+2H-NO ₃] ⁺	C ₁₄ H ₁₀ NO	208.07570	-3.3 ± 2.2	238.04936	± 0.00070	60	[M+e ⁻ -NO] ⁻	C ₁₄ H ₉ NO ₃	238.05097	-6.7 ± 3.0
		194.07443	± 0.00050	60	[M+2H-N ₂ O ₃] ⁺	C ₁₄ H ₁₀ O	194.07260	9.4 ± 2.6	254.04414	± 0.00035	10	[M+e ⁻ +O-NO] ⁻	C ₁₄ H ₉ NO ₄	254.04588	-6.9 ± 1.4
		224.07017	± 0.00069	25	[M+H-NO ₂] ⁺	C ₁₄ H ₁₀ NO ₂	224.07060	-1.9 ± 3.1	223.06213	± 0.00069	4	[M+e ⁻ +H-NO ₂] ⁻	C ₁₄ H ₉ NO ₂	223.06388	-7.8 ± 3.1
		223.08860	± 0.00070	22	[M+3H-3O] ⁺	C ₁₄ H ₁₁ N ₂ O	223.08650	9.4 ± 3.1	208.05118	± 0.00074	4	[M+e ⁻ -N ₂ O ₂] ⁻	C ₁₄ H ₉ O ₂	208.05298	-8.6 ± 3.5
		239.08356	± 0.00144	8	[M+3H-2O] ⁺	C ₁₄ H ₁₁ N ₂ O ₂	239.08150	8.6 ± 6.0	193.06499	± 0.00042	2	[M+e ⁻ +H-N ₂ O ₃] ⁻	C ₁₄ H ₉ O	193.06589	-4.7 ± 2.2
		180.08218	± 0.00074	8	[M+2H-CNO ₄] ⁺	C ₁₃ H ₁₀ N	180.08078	7.8 ± 4.1							
		178.07527	± 0.00096	4	[M+2H-2NO ₂] ⁺	C ₁₄ H ₁₀	178.07770	-8.0 ± 5.4							
		253.06031	± 0.00062	3	[M+H-O] ⁺	C ₁₄ H ₉ N ₂ O ₃	253.06077	-1.8 ± 2.4							
1,6-dinitropyrene	25.17	263.08100	± 0.00014	100	[M+3H-2O] ⁺	C ₁₆ H ₁₁ N ₂ O ₂	263.08151	-2.0 ± 0.5	292.04801	± 0.00131	100	[M+e] ⁻	C ₁₆ H ₈ N ₂ O ₄	292.04896	-3.2 ± 4.5
		277.06074	± 0.00014	60	[M+H-O] ⁺	C ₁₆ H ₉ N ₂ O ₃	277.06070	0.1 ± 0.5	262.05035	± 0.00115	20	[M+e ⁻ -NO] ⁻	C ₁₆ H ₉ NO ₃	262.05097	-2.4 ± 4.4
		247.08933	± 0.00050	30	[M+3H-3O] ⁺	C ₁₆ H ₁₁ N ₂ O	247.08660	-1.6 ± 2.7	276.05313	± 0.00148	10	[M+e ⁻ -O] ⁻	C ₁₆ H ₈ N ₂ O ₃	276.05404	-3.3 ± 5.4
		232.07572	± 0.00044	25	[M+2H-NO ₃] ⁺	C ₁₆ H ₁₀ NO	232.07570	0.1 ± 1.9							
		231.07159	± 0.00177	25	[M+H-NO ₃] ⁺	C ₁₆ H ₉ NO	231.06786	7.5 ± 4.9							
		246.07829	± 0.00021	25	[M+2H-3O] ⁺	C ₁₆ H ₁₀ N ₂ O	246.07870	-1.7 ± 0.8							
		261.06604	± 0.00015	20	[M+H-2O] ⁺	C ₁₆ H ₉ N ₂ O ₂	261.06590	0.5 ± 0.6							
		218.09593	± 0.00020	15	[M+4H-NO ₄] ⁺	C ₁₆ H ₁₂ N	218.09640	-2.1 ± 0.9							
		216.08061	± 0.00026	10	[M+2H-NO ₄] ⁺	C ₁₆ H ₁₀ N	216.08080	-0.9 ± 1.2							

^a Using a C₁₈ 200 mm x 3.2 mm column (Restek) with 5 µm particle size. A gradient program of A:H₂O and B:MeOH was used with a 0.20 mL min⁻¹ flow rate: 20% B for 5 min, linear increase to 90% B at 20 min and held to 27 min, linear decrease to 20% B at 30 min and held to 35 min.

^b Measure masses are reported as averages and standard deviations of the masses observed at three different points along the chromatographic peak.

^c Fragments are shown to reflect changes in the empirical formula from the neutral molecule and do not necessarily reflect the ionization or fragmentation pathway.

^d Possible empirical formula matches for the observed mass were calculated with elemental ranges of C:8–18, H:6–16, O:0–4, and Na:0–1 for monomers and C:16–32, H:12–32, O:0–4, and Na:0–1 for suspected dimers.

^e The standard deviation calculated from the observed masses was converted to ppm error to show its influence on empirical formula estimations.

Table 4

Pseudomolecular ions and fragments observed for products from the heterogeneous ozonation of pyrene in a small-scale flow reactor using HPLC-APCI-HRMS in positive mode.

Peak #	Proposed Compound	ID ^a	t _R ^b (min)	Positive						
				Measured Mass ^c (m/z Da)		Rel. Abund. (%)	Fragment ^d	Calculated Empirical Formula	Calculated Mass ^e (m/z Da)	Mass Error ^f (ppm)
1	4-carboxy-5-phenanthrenecarboxaldehyde	S	18.18	235.07392	± 0.00040	100	[M+H-O] ⁺	C ₁₆ H ₁₁ O ₂	235.07536	-8.0 ± 1.7
				251.06876	± 0.00045	65	[M+H] ⁺	C ₁₆ H ₁₁ O ₃	251.07027	-5.5 ± 1.8
				205.06395	± 0.00041	40	[M+H-CH ₂ O ₂] ⁺	C ₁₅ H ₉ O	205.06479	-3.4 ± 2.0
				191.08474	± 0.00052	25	[M+H-CO ₃] ⁺	C ₁₅ H ₁₁	191.08550	-3.7 ± 2.7
				233.05831	± 0.00063	20	[M+H-H ₂ O] ⁺	C ₁₆ H ₉ O ₂	233.05971	-5.2 ± 2.7
				265.08434	± 0.00052	20	[M+H+CH ₂] ⁺	C ₁₇ H ₁₃ O ₃	265.08590	-4.5 ± 2.0
2	phenanthrenecarboxylic acid	T	18.28	177.06856	± 0.00039	5	[M+H-C ₂ H ₂ O ₃] ⁺	C ₁₄ H ₉	177.06988	-4.9 ± 2.2
				205.06503	± 0.00034	100	[M+H-H ₂ O] ⁺	C ₁₅ H ₉ O	205.06479	-0.4 ± 1.7
				221.06055	± 0.00107	50	[M-H-2e] ⁺	C ₁₅ H ₉ O ₂	221.06036	-3.8 ± 4.9
				223.07667	± 0.00037	40	[M+H] ⁺	C ₁₅ H ₁₁ O ₂	223.07536	4.0 ± 1.6
3	4-oxapyrene-5-one	T	19.43	193.06518	± 0.00024	100	[M+H-CO] ⁺	C ₁₄ H ₉ O	193.06479	3.4 ± 1.2
				221.06031	± 0.00037	50	[M+H] _s ⁺	C ₁₅ H ₉ O ₂	221.05971	4.6 ± 1.7
				177.07143	± 0.00043	25	[M+H-CO ₂] ⁺	C ₁₄ H ₉	177.06988	8.6 ± 2.4
4	phenanthrenecarboxaldehyde	T	19.54	191.08438	± 0.00043	100	[M+H-O] ⁺	C ₁₅ H ₁₁	191.08553	-3.4 ± 2.3
				207.08104	± 0.00015	40	[M+H] ⁺	C ₁₅ H ₁₁ O	207.08044	3.7 ± 0.7
				179.08597	± 0.00010	5	[M+H-CO] ⁺	C ₁₄ H ₁₁	179.08553	1.9 ± 0.5
5	phenanthrene-4,5-dicarboxaldehyde	T	19.84	235.07533	± 0.00046	100	[M+H] ⁺	C ₁₆ H ₁₁ O ₂	235.07536	-0.2 ± 2.0
				205.06556	± 0.00062	50	[M+H-CH ₂ O] ⁺	C ₁₅ H ₉ O	205.06479	3.2 ± 3.0
				191.08508	± 0.00098	5	[M+H-CO ₂] ⁺	C ₁₅ H ₁₁	191.08553	-7.3 ± 5.1
6	(1,1'-biphenyl)-2,2',6,6'-tetracarboxaldehyde	T	19.93	239.06893	± 0.00054	100	[M+H-CO] ⁺	C ₁₅ H ₁₁ O ₃	239.07027	-5.9 ± 2.3
				251.07065	± 0.00050	10	[M+H-O] ⁺	C ₁₆ H ₁₁ O ₃	251.07027	3.7 ± 2.0
				267.06482	± 0.00052	10	[M+H] ⁺	C ₁₆ H ₁₁ O ₄	267.06518	-3.3 ± 1.9
7	hydroxymethyl)-phenanthrenecarboxylic acid	T	21.45	235.07457	± 0.00068	100	[M+H-H ₂ O] ⁺	C ₁₆ H ₁₁ O ₂	235.07536	-4.2 ± 2.9
				205.06375	± 0.00101	60	[M+H-CH ₂ O ₂] ⁺	C ₁₅ H ₉ O	205.06479	0.6 ± 4.9
				191.08645	± 0.00041	20	[M+H-CH ₂ O ₃] ⁺	C ₁₅ H ₁₁	191.08553	7.2 ± 2.2
				253.08556	± 0.00041	5	[M+H] ⁺	C ₁₆ H ₁₃ O ₃	253.08592	-1.9 ± 1.6

^a Identification was either confirmed by comparison of MS spectra to that of a standard (S) or tentatively confirmed through interpretation of measure MS spectra (T).

^b Using a C₁₈ 200 mm x 3.2 mm column (Restek) with 5 μm particle size. A gradient program of A:H₂O and B:MeOH was used with a 0.20 mL min⁻¹ flow rate: 20% B for 5 min, linear increase to 90% B at 20 min and held to 27 min, linear decrease to 20% B at 30 min and held to 35 min.

^c Measure masses are reported as averages of the masses observed at three different points along the

^d Fragments are shown to reflect changes in the empirical formula from the neutral molecule and do not necessarily reflect the ionization or fragmentation pathway.

^e Possible empirical formula matches for the observed mass were calculated with elemental ranges of C:8–18, H:6–16, O:0–4, and Na:0–1 for monomers and C:16–32, H:12–32, O:0–4, and Na:0–1 for suspected dimers.

^f The standard deviation calculated from the observed masses was converted to ppm error to show its influence on empirical formula estimations.

Figures

Figure 1 (2 column figure)

Figure 2 (single column figure)

Figure 3 (1.5 column figure)

Schemes

Scheme 1

Scheme 2

Scheme 4

Scheme 5

Scheme 6