International Journal of Mass Spectrometry 397–398 (2016) 6–17

Contents lists available at ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

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

Richard E. Cochran[1], Irina P. Smoliakova, Alena Kubátová*

University of North Dakota, Department of Chemistry, 151 Cornell St., Stop 9024, Grand Forks, ND 58202, USA

ARTICLE INFO

Article history:
Received 13 August 2015
Received in revised form
29 December 2015
Accepted 14 January 2016
Available online 22 January 2016

Keywords:
Polycyclic aromatic hydrocarbon derivatives
High resolution mass spectrometry
Ionization/fragmentation patterns
Identification of unknowns

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 using atmospheric pressure chemical ionization with high resolution mass spectrometry (APCI–HRMS) of 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 were 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.

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

* Corresponding author. Tel.: +1 701 777 0348; fax: +1 701 777 2331.
E-mail address: alena.kubatova@UND.edu (A. Kubátová).
[1] Current address: University of California San Diego, Department of Chemistry and Biochemistry, 9500 Gilman Dr., La Jolla, CA 92093-0314, USA.

http://dx.doi.org/10.1016/j.ijms.2016.01.001
1387-3806/

[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 $[M]^{\bullet-}$ and the deprotonated molecule $[M-H]^-$ [29]. In positive mode, protonation and the subsequent 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 molecule were reported [20]. In negative mode, C_2O_2 loss from the deprotonated molecule (giving the $[M-H-CO-CO]^-$ ion) and 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 and Slegel 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 analyses

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 C_{18} 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 (N_2) 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 μA.

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 × 9 cm I.D.) through ¼″ stainless