

Chapter 2

PAHs and NPAHs in Airborne Particulate Matter: Initial Formation and Atmospheric Transformations

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Abstract In this chapter, the formation of early benzene and naphthalene rings is first discussed in the context of soot formation. While the hydrogen abstraction-acetylene addition (HACA) pathway is the most commonly accepted pathway, studies have shown that it is insufficient to account for the rapid formation of larger PAHs and soot, and so other mechanisms for PAH formation are discussed. Once the initial PAHs are formed, they can undergo further transformation, for example, forming nitrated (NPAHs) or oxygenated analogues. The formation of NPAHs can occur through three routes: formation through combustion processes (primary production), through the transformation of PAHs in the atmosphere (secondary processes) or through gas-particle heterogeneous transformations. Through these processes various isomers of nitrated PAH analogues, such as nitropyrene and nitrofluoranthene, can be formed. The specific isomers that are formed are characteristic of certain types of formation processes and therefore are useful in determining the source origins of NPAHs.

Keywords Polycyclic aromatic hydrocarbon formation · Soot · Nitrated polycyclic aromatic hydrocarbons · Heterogeneous transformations · Particulate matter

2.1 Polycyclic Aromatic Hydrocarbon Formation: From Small Aliphatic Chains to Nascent Soot

Polycyclic aromatic hydrocarbons (PAHs) are molecules that contain two or more fused aromatic rings and are formed primarily through the incomplete combustion of organic materials (Ravindra et al. 2008). They are present in the environment through both natural and anthropogenic sources, though the latter constitutes the

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majority (Krauss et al. 2005). The mutagenic potential of PAHs is well known (Jung et al. 1991; Pashkin and Bakhitova 1979). Because PAHs are major constituents of soot, their formation from small aliphatic chains to soot aggregates is an active area of study.

PAH formation is dictated by a number of factors such as combustion temperature and pressure (Comandini et al. 2012; Yoon et al. 2008; Zhou et al. 2014) as well as fuel types, both aliphatic and aromatic fuels (Tregrossi et al. 1999; Hansen et al. 2016). While the experimental conditions may vary, in composite, a wide body of research has provided insight into the general mechanisms of soot formation. Broadly, this formation occurs through the initial decomposition of fuels, the subsequent production of initial aromatics from small aliphatic molecules, the nucleation to form larger PAHs and further growth and coagulation into larger soot particles (Richter and Howard 2000). For the purposes of this chapter, PAH formation is briefly discussed as a preface to discussion on the further transformation of PAHs into their nitrogenated analogues.

Pyrolytic processes above 500°C produce a number of reactive intermediates and radicals such as ethylene and acetylene which become the building blocks for constructing the initial aromatic rings (Llamas et al. 2017; Ravindra et al. 2008; Shukla and Koshi 2012). In general, the formation of the initial benzene ring is thought to occur through either the self-reaction between 3-carbon C_3H_3 species, the reaction between a 4-carbon species ($n-C_4H_5$, $n-C_4H_3$) and 2-carbon species or the reaction of a cyclopentadienyl (C_5H_5) with CH_3 (Frenklach 2002; Marinov et al. 1997, 1998; McEnally et al. 2006; Richter and Howard 2002; Shukla and Koshi 2012). While a number of precursor molecules can be involved, the type of fuel source decomposed will dictate which pathway is dominant (McEnally et al. 2006). For example, the reaction between two 3-carbon molecules in benzene formation is a dominant reaction in acetylene and ethylene flames (Richter and Howard 2002) and premixed propane (Marinov et al. 1997). Benzene, however, is not necessarily the first PAH formed. Naphthalene formation, through the self-reaction between C_5H_5 radicals, has been demonstrated and does not require the initial formation of benzene (Cavallotti and Polino 2013; Frenklach 2002; Marinov et al. 1997; Richter and Howard 2000).

After the formation of the initial ring(s), a number of mechanisms have been proposed for the further growth of PAHs, the most notable being the hydrogen abstraction-acetylene addition (HACA) pathway, which was generally thought to be the predominant route in PAH synthesis (Appel et al. 2000; Comandini et al. 2012; Frenklach 2002). HACA is a process where initial benzene rings and aliphatic hydrocarbon building blocks are converted to larger PAHs through an iterative process of hydrogen abstraction and acetylene (C_2H_2) additions (Frenklach 2002; Richter and Howard 2000). More specifically, the hydrogen abstraction of a hydrocarbon results in a radical that can react with C_2H_2 to form phenylacetylene which in turn forms the substrate for subsequent HACA steps to create the next ring (Comandini et al. 2012). Through this iterative process, PAHs can be built from benzene to naphthalene into larger PAH molecules (Frenklach 2002). Ultimately it is this procedure in the soot formation process that is the rate-controlling step in the further growth of soot (Frenklach 2002).

Though widely accepted as a mechanism for PAH growth, there is evidence that HACA is too slow and cannot be the sole factor involved (D'Anna and Violi 1998; Böhm et al. 1998; Richter and Howard 2002). Growth through methyl radical additions in a process similar to HACA has also been investigated (Hansen et al. 2016; Shukla et al. 2008; Yoon et al. 2008) as well as propargyl addition reactions (Raj et al. 2014; Slavinskaya and Frank 2009). An efficient method for the growth of PAHs is also seen through phenyl and benzene additions and can account for the rapid development of PAHs (Benish et al. 1996; Comandini et al. 2012; Constantinitis et al. 2015; Ono et al. 2015; Shukla et al. 2008) and is likely more efficient than HACA mechanisms. In aggregate, numerous studies are showing that there are a multitude of ways in which PAHs can grow from the initial aromatic ring(s) beyond HACA mechanisms and account for the rapid formation of soot particles.

From the creation of the first PAHs, reactions between PAHs and PAH radicals into larger PAHs (e.g. through dimerization and trimerization) form the basis for incipient soot which marks the transition into particulate matter (McKinnon and Howard 1992; Ono et al. 2015). The formation of initial soot particles is followed by their agglomeration to form larger soot particles and is followed by fractal spherical growth (Frenklach 2002). While much investigation has been performed on the formation of these initial rings, the transition from gas to particulate matter remains a poorly understood process (Frenklach 2002).

2.2 NPAHs and Their Formation from PAHs

While efforts to understand the mechanisms of PAH and soot formation are ongoing, there is also a concerted effort to understand the formation processes and environmental distributions of PAH derivatives such as the nitrated PAHs (NPAHs) and oxygenated PAHs (OPAHs). Research on NPAHs began when it was found that the mutagenicity of air pollution and diesel emissions could not be solely accounted for by PAHs (Pitts et al. 1978). This would ultimately lead to the discovery of the outsized contribution of NPAHs to air contaminant mutagenicity and has since been more closely investigated (Fu et al. 1985; Ishii et al. 2000; Pitts et al. 1978; Tokiwa et al. 1985), despite existing at levels between one and three orders less than their parent PAHs (Albinet et al. 2007; Bamford and Baker 2003; Wang et al. 2011). The increasing polarity of these NPAHs makes them more reactive with biological tissue and accounts for their disproportionate mutagenicity (De Guidi et al. 2012). For example, the dinitropyrenes (DNPs) possess a mutagenicity among the highest known (Arce and Morel 2013; Nakagawa et al. 1983) and therefore constitute a major toxicological threat. This outsized toxicity has created the imperative to include NPAHs in analyses that go beyond the EPA 16 PAHs that are routinely studied (Andersson and Achten 2015). Beyond toxicity however, their environmental fate differs from their parent PAHs, as they differ in parameters such as melting point, various partitioning coefficients (i.e. k_{ow}), vapour pressure and solubility.

The formation of NPAHs can be generalized as occurring through one of three routes: through direct emissions, through secondary atmospheric transformations and through gas-particle heterogeneous transformations. These different processes can produce distinct NPAH isomers that are characteristic of their sources, though as will be discussed, these distinctions are not always clear.

2.3 NPAH Formation Through Primary Combustion Processes

The primary production of NPAHs occurs through incomplete combustion processes and has been studied specifically within the context of diesel engine combustion (Bamford et al. 2003; Kameda et al. 2006; Karavalakis et al. 2012), though they can also form through gasoline engine combustion (Gibson 1983), coal combustion (Harris et al. 1984), biodiesel combustion (Llamas et al. 2017) as well as through cooking processes (Kinouchi et al. 1986). Primary transformation occurs as a result of the high temperatures and the electrophilic nucleation with NO_2^+ (Fu et al. 2012) as seen in the case of 1-nitropyrene (1-NP) formation from the PAH pyrene (Fig. 2.1).

Nitration occurs at the position of the molecule with the highest electron density to form 1-NP, and further nitration can produce the dinitropyrenes (DNPs) such as 1,3-DNP, 1,6-DNP and 1,8-DNP. As the NO_x species involved in the creation of these NPAHs is a function of temperature, the NPAH yield and composition are highly temperature dependent (Hayakawa 2016).

While a particular focus of NPAH studies has been on 1-NP (Bezebeh et al. 2003; Kojima et al. 2010), there is indication that 2-nitrofluorene (2-NF) may also appear in greater abundance (Beije and Möller 1988) as seen in heavy-duty diesel engines (Draper 1986). Beyond 1-NP and 2-NF, 3-nitrofluoranthene (3-NFr), 9-nitroanthracene (9-NA) and 6-nitrobenz[*a*]pyrene (6-NBaP) are also found in abundance in diesel exhaust and contribute to the exhaust mutagenicity (Bamford

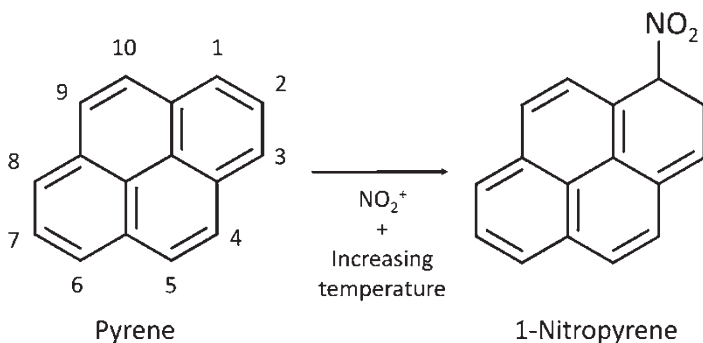
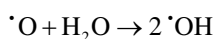
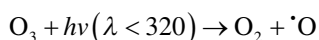


Fig. 2.1 The nitration of pyrene occurs at the site of the greatest electron density, producing a nitrated analogue at the first position

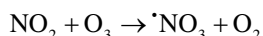
et al. 2003; Dimashki et al. 2000; Feilburg et al. 2001; Paputa-Peck et al. 1983; Salmeen et al. 1984; Schuetzle 1983). Furthermore, while certain NPAHs are used to characterize diesel emissions, the composition of diesel exhaust can change according to factors such as diesel particulate filters (Heeb et al. 2008) and biodiesel types (Karavalakis et al. 2010, 2011).

2.4 NPAH Formation Through Secondary Atmospheric Processes

While NPAHs formed through combustion processes comprise a significant component of atmospheric toxins, NPAHs can also be formed in the atmosphere, through gas-phase reactions. The atmospheric transformation of PAHs to NPAHs can occur via homogenous gas-phase reactions or secondary heterogeneous transformations of PAHs contained on particulate matter. The former is thought to constitute the majority of the atmospheric NPAHs (De Guidi et al. 2012; Reisen and Arey 2005) and involves nitration through reaction with NO_2 but is initiated by either OH or NO_3 radicals which form adducts that subsequently react with NO_2 . The OH radicals are found in the troposphere (Vione et al. 2004) and form through reactions involving ozone:



Because this is a photochemical reaction and the $\cdot\text{OH}$ radical rapidly degrades, this reaction occurs during the day (Arey 1998). One reported value for their abundance was modelled at 11.1×10^5 molecules/cm³ (Naik et al. 2013). By contrast, the $\cdot\text{NO}_3$ radical is formed primarily through a tropospheric reaction between O_3 and NO_2 (Geyer et al. 2001):



The $\cdot\text{NO}_3$ radical is prevalent during the night, as it otherwise undergoes rapid photolysis during the day and has undergone a significant increase since pre-industrial times (Khan et al. 2015). Ambient levels of the NO_3 radical have been difficult to quantify but, for example, have been observed to have a production rate between 4×10^5 cm³s⁻¹ and 8×10^6 cm³s⁻¹ at a site near Berlin, Germany (Geyer et al. 2001).

Whether via $\cdot\text{OH}$ or $\cdot\text{NO}_3$, both radicals attack the position of the molecule at the carbon position with the highest electron density (Zielinska and Samy 2006) to create an intermediate adduct that reacts with NO_2 to form a nitrated group at the *ortho* position, relative to the carbon initially attacked by the radical (Zielinska and Samy 2006; Atkinson and Arey 1994). This is followed by the removal of water or nitric

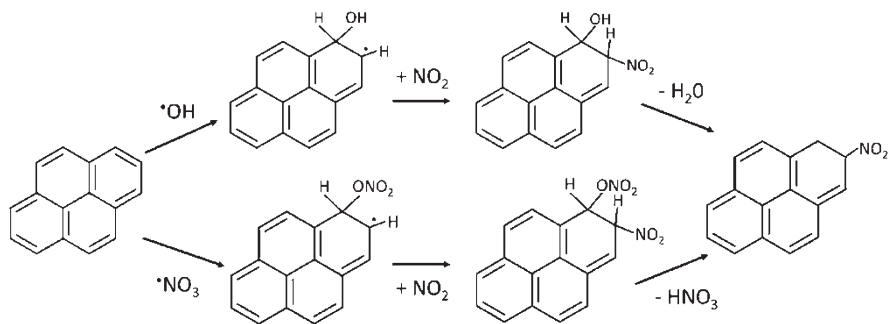


Fig. 2.2 The formation of 2-nitropyrene can occur through two mechanisms that differ in the radical that initially attacks the site of the greatest electron density. NO_2 will be added to the position *ortho* to this site

acid, depending on whether the initial radical is $\cdot\text{OH}$ or $\cdot\text{NO}_3$, respectively (Sasaki et al. 1997). The general formation in the case of pyrene transformation is summarized in Fig. 2.2.

Through these radical-assisted processes, the isomers of pyrene and fluoranthene (2-NP and 2-NFr) are the most commonly formed NPAHs and are not thought to form through combustion processes (Arey et al. 1986; Ciccioli et al. 1996; Kameda et al. 2006; Murahashi et al. 1999). However, the yields may differ from each other, with, for example, 2-NFr being produced in greater concentrations from $\cdot\text{NO}_3$ rather than $\cdot\text{OH}$ (Feilburg et al. 2001; Reisen and Arey 2005). While the formation of NP and NFr isomers in gas-phase reactions is studied extensively, other NPAHs such as nitrotriphenylenes (Kameda et al. 2006) and nitrobenzanthrones (Phousongphouang and Arey 2003) have also been examined and provide insight into the formation of otherwise lesser studied NPAHs.

2.5 NPAH Isomer Ratios as Source Indicators

Because of their differing formation mechanisms, NPAH isomers found in a sample are used as markers to identify the NPAH source. As mentioned above, 2-NP and 2-NFr are thought to form through the atmospheric transformations of parental PAHs and not through diesel combustion. By contrast 1-NP and 3-NFr are not thought to be formed through atmospheric reactions and are primarily combustion products, most notably found in diesel emissions (Kameda et al. 2006; Paputa-Peck et al. 1983). By using ratios of these specific isomers, it is possible to create values that can be used across different studies to identify the sources of NPAHs. For example, 2-NFr/1-NP ratios are commonly used in identifying whether atmospheric transformations or combustion products are the predominant source of NPAHs (Albinet et al. 2007; Bamford and Baker 2003; Lin et al. 2015; Marino et al. 2000; Wang et al. 2011). These ratios can be influenced by seasonality. For example, a

study the Beijing atmosphere found that the lower 2-NFr/1-NP ratios in the winter could be attributed to increased coal and biomass combustion for heating purposes (Lin et al. 2015). The increased combustion that occurs in winter months and the influence this has on the distribution of NPAHs has been reported by many (Bandowe et al. 2014; Barrado et al. 2012; Sarti et al. 2017; Wada et al. 2001).

Furthermore, since $\cdot\text{NO}_3$ radicals react with pyrene to form 2-NFr and negligible amounts of 2-NP, and $\cdot\text{OH}$ radicals will form both 2-NFr and NP (Wei et al. 2012), 2-NFr/2-NP ratios are commonly used to approximate whether daytime OH or night-time NO_3 radical initiation is the more dominant driver of atmospheric NPAH creation (Albinet et al. 2007; Bamford and Baker 2003; Huang et al. 2014; Kameda et al. 2006; Marino et al. 2000; Reisen and Arey 2005; Wang et al. 2011). Values greater than 5 suggest a greater atmospheric secondary transformation, while values less than 5 suggest that primary emissions are dominant (Ciccioli et al. 1996; Wang et al. 2011). One study examined 2-NFr/2-NP concentrations at locations in Antarctica, Asia, Europe and South America and confirmed that these NPAHs were globally ubiquitous and formed from gases in the troposphere (Ciccioli et al. 1996). The utility of ratios like the 2-NFR/1-NP and 2-NFr/2-NP highlights the importance of being able to distinguish NPAH isomers, despite the inherent analytical challenges this may pose.

2.6 NPAH Partitioning onto Particulate Matter

Atmospheric PACs are associated primarily with particulate matter (PM), and numerous studies have found that the majority of PACs are found on finer and smaller $\text{PM}_{2.5}$ (Bozek et al. 2016; Di Filippo et al. 2010; Kong et al. 2010; Hayakawa et al. 1995; Kawanaka et al. 2008; Ohura et al. 2004; Tang et al. 2009). This is particularly alarming as $\text{PM}_{2.5}$ accounts for the majority of PM in the atmosphere (Lonati and Giugliano 2006) and is known to penetrate deeper into the respiratory system, creating not just a mechanical hazard but a greater toxicological threat (Bozek et al. 2016; Kawanaka et al. 2008). As a result of this toxicity, the PAH/NPAH associations with PM have been researched globally (Albinet et al. 2007; Barrado et al. 2012; Bozek et al. 2016; Dimashki et al. 2000; Marino et al. 2000; Wang et al. 2011; Wei et al. 2012).

In general, PACs have low vapour pressures, especially as molecular weight increases (Yaffe et al. 2001; Barrado et al. 2012). NPAHs in particular are more polar and have vapour pressures in general about 2–3 orders of magnitude less than PAHs, thus making condensation onto particulate matter more likely (Ciccioli et al. 1996; Heeb et al. 2008; Shen et al. 2012). An NPAH of a molecular weight equivalent to phenanthrene or less is more likely to exist in the gas phase, with 3–4 ring congeners such as NFr and NP (nominal mass: 247 g/mol) more likely to partition onto PM (Cochran et al. 2016; Yaffe et al. 2001). The structure of the sorption surface may also play a role. For example, in a study of PAH sorption to soot, it was found that the strong affinity for PAHs to soot is likely the result of π - π bonding as well as

the planar structure of PAHs allowing them to penetrate deeper into the pores (Jonker and Koelmans 2002) and making them less available for reaction. Thus, being sorbed onto PM can protect the PAC from further gas-phase transformations, prolonging their atmospheric lifetimes and allowing for greater geographic dispersal. Sorption has also been shown to be dependant on weather, with colder weather causing greater partitioning onto aerosols such as PM, as a result of reduced vapour pressure and poor mixing of air (Bandowe et al. 2014; Ravindra et al. 2008). It should be noted, however, that the formation of PAH derivatives is driven by season, with winter having greater reactions with nitrogen oxides and summers having more photochemical reactions (Barrado et al. 2012). There is also the fact that winters have more fuel combustion occurring for heating purposes (Sarti et al. 2017). As a result, studies have shown that there is a greater concentration of PACs adsorbed onto PM in winter than in summer (Bandowe et al. 2014; Barrado et al. 2012; Ravindra et al. 2008; Sarti et al. 2017; Wada et al. 2001).

2.7 NPAHs and Particulate Matter: Heterogeneous Transformations

While it is believed that homogeneous gas-phase reactions, based on $\cdot\text{OH}$ and $\cdot\text{NO}_3$ radical intermediates, are the predominant routes for NPAH formation, there is a growing interest in understanding how PAHs sorbed onto atmospheric PM may be transformed by atmospheric oxidizing agents. This is especially salient, given the greater longevity and mobility of these PM-sorbed compounds.

The reactions of condensed PAHs with a number of gases such as O_3 , OH , HNO_3 and $\text{NO}_3/\text{N}_2\text{O}_5/\text{NO}_3$ have been performed by many (Carrara et al. 2010; Gross and Bertram 2008; Jariyasopit et al. 2014; Kamens et al. 1990; Kwamena and Abbatt 2008; Perraudin et al. 2007; Wang et al. 2015; Zhang et al. 2011, 2014a, b; Zhou et al. 2015; Zielinska et al. 1986; Zimmermann et al. 2013) using a variety of sorption substrates such as quartz fibre filters (Cochran et al. 2016), natural aerosols (Ringuet et al. 2012) and mineral surfaces (Kameda et al. 2016), and the products of these heterogeneous reactions can differ markedly from gas-phase homogeneous reactions. The multitude of different gases and reaction substrates has produced a range of products. For this reason, the uptake of gases onto the particle surfaces has been performed to help understand the efficiency and likelihood of these transformations. Studies of this have been performed for gases such as O_3 , OH , HNO_3 , N_2O_5 , NO_2 and NO_3 (Gross and Bertram 2008; Perraudin et al. 2007; Zhou et al. 2015).

For example, while it was initially thought that NO_3 had a minimal role in the heterogeneous transformations of PAHs and that N_2O_5 was the greater oxidizing agent (Pitts et al. 1985), more recently, there is evidence of a rapid uptake of NO_3 on soot surfaces (Mak et al. 2007). Furthermore, relative to NO_2 and O_3 , NO_3 has been observed to have the highest reaction rate constants with particle-sorbed PAHs and

that these reactions with NO_3 radicals are 4–5 orders faster than the gas-phase reactions (Liu et al. 2012). Similarly, the reaction of particle-associated PAHs with NO_3 was about four orders larger than with N_2O_5 or NO_2 despite existing in much lower concentrations (Gross and Bertram 2008).

In addition to the reacting gas, the actual substrate characteristics may also dictate the extent to which heterogeneous formation may occur. For example, Zhou et al. (2013) demonstrated that the secondary organic aerosols that comprise a significant part of $\text{PM}_{2.5}$ coatings can shield underlying contaminants such as PAHs from gas-phase oxidizing agents, thus shielding them from reaction over long transportation events. Another set of experiments showed that there was a difference in PAH reactivity with OH between graphite particles and combustion-derived surfaces, with the latter showing lower reactivity, possibly due to differences in site accessibility (Esteve et al. 2004, 2006).

Heterogeneous reactions can produce some of the NPAH isomers that characterize primary and secondary NPAH formation. For example, Zimmermann et al. (2013) found that reactions of ambient PM with $\text{N}_2\text{O}_5/\text{NO}_3/\text{NO}_2$ produced 1-NP, which they concluded was based on N_2O_5 reaction and not an NO_3 radical-assisted reaction. This would suggest an electrophilic nitration (Wang et al. 2015) and differs from the 2-NP isomer that would be expected from gas-phase reactions. Furthermore, 1-NP has also been formed through other heterogeneous processes, for example, through the reaction of NO_2 on mineral dust surfaces (Kameda et al. 2016) and silica particles (Miet et al. 2009) and OH reactions with aerosol particles (Ringuet et al. 2012). This contrasts with the belief that 1-NP is formed solely through combustion processes (viz. diesel engine combustion). Furthermore, Miet et al. (2009) also found that 1-NP sorbed onto silica particles could undergo transformation to form 1,3-DNP, 1,6-DNP and 1,8-DNP which correspond to the DNPs formed through electrophilic nitration. The formation of 2-NP and 2-NFr through heterogeneous interactions has been demonstrated as well (Ringuet et al. 2012; Zhang et al. 2014a, b; Zimmermann et al. 2013), showing that these isomers may not be specific to gas-phase transformations. For example, it was found that N_2O_5 , with increasing humidity, could promote the formation of NO_2^+ , which could produce the NP and NFr isomers characteristic of electrophilic nitration (Zhang et al., Zhang et al. 2014a, b). Studies of other NPAHs have also been performed, with, for example, studies on larger (five rings or greater) PAHs (Ishii et al. 2000; Jariyasopit et al. 2014). These studies of heterogeneous reactions suggest that the mechanisms of NPAH formation are more complicated than the primary/secondary source dichotomy presented earlier. However, although some of these reactions may call into question the use of marker isomers to identify primary and secondary NPAH formation, it should be noted that the heterogeneous transformations are likely to play a relatively minor role in PAH removal/transformation and so are unlikely to undermine the NPAH ratios discussed earlier.

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