Anthracene and phenanthrene tropospheric oxidation promoted by the nitrate radical in the gas-phase. Theoretical modelistic study

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HIGHLIGHTS

- Gas phase anthracene or phenanthrene NO_3 adducts give with O_2 peroxyl intermediates.
- NO_3, NO_x, O_2 addition/loss, β−fragmentation, give dialdehydes or nitroxyketones.
- With typical tropospheric concentrations, these PACs are the most likely products.

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ABSTRACT

Polycyclic aromatic hydrocarbons and their oxidized derivatives are ubiquitous environmental pollutants that are toxic to different degrees. The NO_3 radical is known to be an important actor in fostering nighttime atmospheric chemistry; hence it could elicit some nocturnal PAH-loss processes. In this study the gas phase pathways open to the initial anthracene and phenanthrene NO_3 π−radical adducts in the presence of O_2, NO and NO_2 are examined by Density Functional Theory to ascertain the mechanistic features of their NO_3-initiated oxidative degradation. Unimolecular steps involving the initial adducts (ring closures or fragmentation) present rather high free energy barriers and seem unlikely. Regarding bimolecular reactions, any radical present in the tropospheric environment can give an intrinsically fast radical coupling with the initial adducts, thus producing bifunctional closed shell species. The addition of ground state dioxygen is a relatively fast step that is reversible in some cases, less so in others. It entails subsequent reaction steps, which involve the peroxyl radical intermediate and addition and loss of small species as NO, NO_3, NO_2 and O_2. These steps can either trigger a β−fragmentation with formation of a closed shell dialdehyde or formation of a closed shell nitroxy ketone, bifunctional species that appear to be the most likely products when typical tropospheric concentrations are taken into account.

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1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) and their oxidized derivatives are ubiquitous environmental pollutants present in the troposphere, which are toxic to different extents (Finlayson-Pitts and Pitts, 2000; Keyte et al., 2013). They are emitted during incomplete combustion of fossil fuels (Lim et al., 1999) and biomass (Jenkins et al., 1996; Mandalakis et al., 2005; Samburova et al., 2016). PAHs can undergo oxidation and functionalization in general, both during combustion and their subsequent transport in the troposphere (Calvert et al., 2002; Kameda, 2011). In particular,

anthracene and phenanthrene belong to the list of the 16 priority PAHs indicated by the US Environmental Protection Agency. This list has played an important role in monitoring programs (Lammel, 2015), though reservations about its future use has been recently put forth (Andersson and Achten, 2015).

Homogeneous (gas phase) and heterogeneous (particle phase) experimental and theoretical studies have been published on the reactions of PAHs with ozone (Finlayson-Pitts, 1997; Perraudin et al., 2007, 2006; Zhang et al., 2013) or with the hydroxyl radical (Biermann et al., 1985; Brubaker and Hites, 1998; Dang et al., 2015a, 2015b, 2014; Giordana et al., 2008; Helmig and Harger, 1994; Sasaki et al., 1997; Zhao et al., 2016). Some publications have also dealt with the action of the nitrate radical (Atkinson et al., 1990, 1991; Dang et al., 2015c; Qu et al., 2008; Sasaki et al., 1997; Zhang et al., 2014a; Chapleski et al., 2016). The reaction with the NO_3 radical,

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known to play in general a significant role in nighttime tropospheric chemistry (Stone et al., 2014), may have some importance in contributing to nocturnal PAH loss pathways. Current knowledge of the NO_3-initiated gas phase atmospheric oxidation of different PAHs, based on experimental results, is mostly limited to cases in which a high concentration of NO_2 is also present. For example, in their studies on naphthalene and fluoranthene, Sasaki et al. found nitro-derivatives as important products (Arey et al., 1989; Sasaki et al., 1997). In their reacting system they had not only NO_3, but also substantial concentrations of NO_2, both coming from N_2O_5 (NO_2 was also added with concentration in the order of 10^{13} molecules cm^{-3}). Whereas a variety of experimental studies dealing with naphthalene and its derivatives $+ NO_3$ reacting system is available (see Keyte et al., 2013, pp 9 349–9 353), much less has been done for anthracene and phenanthrene, considering both the gas phase and the particle phase (Arey et al., 1989; Jariyasopit et al., 2014b; Kwok et al., 1994).

Some of the oxidized PAH derivatives are of concern for human health (Asare et al., 2009, 2008; Durant et al., 1996; Landvik et al., 2007; Talaska et al., 1996), and in addition a large share of oxidation products are not identified. Therefore it is worthwhile to further investigate the mechanistic details of these processes. Theoretical investigations as the present one can be complementary to experimental studies, and the comparison be informative. Within it, we explore the gas phase reaction mechanisms of NO_3-triggered oxidative degradation of anthracene and phenanthrene. Therefore, we will consider how ground electronic state O_2, NO, and NO_2 will react with PAH-derived intermediate radicals. We model these reactions in a semi-quantitative way to ascertain their mechanistic features (reaction pathways and related free energy barriers) and also with the purpose of suggesting, on that basis, likely closed shell products. Accordingly, we deliberately do not extend the investigation to all possible reaction pathways when differing for regio- and diastereochemistry, as is done with the goal of obtaining *quantitative* predictions.

Under typical atmospheric conditions, anthracene and phenanthrene are partitioned between gas and particle phases (see Fig. 10.2 and 10.3 in Finlayson-Pitts and Pitts, 2000) for which oxidative degradation might present mechanistic differences. In the present study we begin by focusing only on the gas phase reaction pathways, for which the syn additions are explored in a more complete and detailed way (syn additions are expected to be more pertinent to the adsorbed system, in which one face of the PAH system is engaged with the underlying surface).

To our knowledge experimental results are scarce for phenantrene (Kwok et al., 1994) and anthracene (Arey et al., 1989; Jariyasopit et al., 2014b; Ringuet et al., 2012), with more data available for naphthalene. Some publications deal with our title PAHs, but are either carried out in the presence of high NO_2 concentration, or deal with heterogeneous chemistry of these and other PAHs (Mak et al., 2007; Zhang et al., 2011; Liu et al., 2012; Cochran et al., 2016). Some theoretical papers published in the last few years also bear similarities to the present study. In particular, a study on hydroxycyclohexadienyl peroxyl radical (from benzene) plus NO (Yan et al., 2013), those on benzene (Qu et al., 2006a) or naphthalene (Qu et al., 2006b) plus NO_3, one on 9-chloroanthracene plus NO_3 (Dang et al., 2015c), and one on the role of water in the formation of nitro-PAHs (Zhang. et al., 2014b).

2. Theoretical method

All stationary points on the energy hypersurface, *i.e.* minima and first order saddle points, corresponding to transition structures

(TS), were determined by gradient procedures (Pople et al., 1992; Schlegel, 1982a, 1982b, 1981; Schlegel et al., 1984) within the Density Functional Theory (DFT) (Parr and Yang, 1989), and making use of the M06–2X (Zhao and Truhlar, 2008, 2007) functional. Reactants, transition structures, intermediates, and products have been optimized with the 6-31G(d,p) basis set. Single-point energies of various species were calculated with Dunning's correlation-consistent polarized valence triple-ζ basis set cc-pVTZ (Kendall et al., 1992). On the basis of previous studies (Trogolo et al., 2014), this computational approach is expected to perform acceptably. The nature of the critical points (and the thermochemistry) was assessed by vibrational analysis: the 6-31G(d,p) thermochemical corrections gave estimates of the zero point vibrational energy (ZPE), by which the cc-pVTZ relative energies were corrected [here $\Delta E_{ZPE} = \Delta E_{cc\text{-}pVTZ} + \Delta ZPE_{6\text{-}31G(d,p)}$], and similarly enthalpy (ΔH) and Gibbs free energy (ΔG) differences were obtained. The thermochemistry was assessed in all cases at T = 298.15 K and ΔG values at this temperature are reported in Scheme 1 (in kcal mol^{-1}). Geometry optimization and thermochemistry calculations were carried out by using the GAUSSIAN 09 system of programs (Frisch et al., 2009).

For singlet diradicaloid structures (such as those corresponding to homolytic dissociations), the "automatic" restricted closed shell singlet solution yields zero spin densities. Therefore, the wavefunction stability was checked and obtained by relaxing the wavefunction in the orbital rotations space. The desired spin densities, as expected for diradicaloid structures, were obtained in correspondence of the attained ('singlet' unrestricted) wavefunction stability. Because the resultant spin-mixing (the unrestricted wavefunction is not an eigenfunction of $\hat{S}^2$) gives a better description of the electron distribution but alters the energy, the energy values were refined by Yamaguchi's formula to get rid of the contribution of the closest spin contaminant of the same parity (Baker et al., 1993; Goldstein et al., 1996; Wittbrodt and Schlegel, 1996; Yamaguchi et al., 1988; Yamanaka et al., 1994).

3. Results and discussion

3.1. Anthracene

NO_3 adds to anthracene, without any barrier on the potential energy surface, to form three anthracenyl nitrate radicals. These are the boxed structures **A1** (addition to position 1) and **A2** (position 2) in Scheme 1, and **A3** (position 9) in Scheme 3. Adduct **A1,** at -12.7 kcal mol^{-1} below the two reactants, is more stable than **A2** by 4.2 kcal mol^{-1}; adduct **A3** is the stablest, being located at -20.2 kcal mol^{-1}, i.e. 7.5 below **A1**. The energetics (ΔG at 298.15 K) for each reaction pathway is reported relative to **A1** in Scheme 1, left, relative to **A2** in Scheme 1, right, and relative to **A3** in Scheme 3. The intermediates **A4** and **A5**, shared by both pathways, are associated with two free energy values, and the relevant zero is indicated in parentheses. Scheme 2 displays further steps departing from the peroxyl structures **A7** and **A10** in Scheme 1.

First we will describe the different reaction steps possibly undergone by the initial adducts **A1**, **A2**, and **A3**. Then, we will assess their relative importance. We have taken into account possible unimolecular reaction steps departing from the initial adducts, as well as dioxygen intervention (O_2 is the reactive species present with the highest density, close to 5×10^{18} molecules cm^{-3}). Also taken into account are NO and NO_3 reactions with relevant intermediate radicals (Scheme 2). Section A in the Supplementary Material displays a larger number of less likely pathways. NO_x species (collective for $NO + NO_2$) are present in the troposphere at