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This is the author’s manuscript

Original Citation:

Availability:
This version is available http://hdl.handle.net/2318/1652434 since 2017-11-21T12:18:20Z

Published version:
DOI:10.1016/j.atmosenv.2017.08.011

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

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Abstract. Polycyclic aromatic hydrocarbons and their oxidized derivatives are ubiquitous environmental pollutants that are toxic to different degrees. The NO₃ 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 NO₃ π−radical adducts in the presence of O₂, NO and NO₂ are examined by Density Functional Theory to ascertain the mechanistic features of their NO₃-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 peroxy radical intermediate and addition and loss of small species as NO, NO₃, NO₂ and O₂. 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.

Keywords: 1) anthracene; 2) phenanthrene; 3) nitrate radical; 4) NO₃ 5) tropospheric oxidation; 6) gas-phase 7) mechanism; 8) DFT

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Proposed running title: PAH oxidation promoted by NO₃
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; Dang et al., 2015c; Qu et al., 2008; Sasaki et al., 1997; Zhang P., 2014; Chapleski et al., 2016). The reaction with the NO$_3$ radical, 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$_2$O$_5$ (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 9349-9353), 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 Figures 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 phenanthrene (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 peroxy 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 Q. et al., 2014).

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-$\zeta$ 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 ΔE_{ZPE} = ΔE_{cc-pVTZ} + ΔZPE_{6-31G(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 wave-
function 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 S²) 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. NO₃ 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, with 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 (O₂
is the reactive species present with the highest density, close to 5 x 10¹⁸ molecules cm⁻³). Also taken
into account are NO and NO₂ reactions with relevant intermediate radicals (Scheme 2). Section A in
the Supplementary Material displays a larger number of less likely pathways. NOₓ species (collective
for NO + NO₂) are present in the troposphere at concentrations ranging from 10⁸–10⁹ (unpolluted
situation) to $10^{12}$ (polluted) molecules cm$^{-3}$. The role of NO$_x$ species can be particularly interesting in the formation of the concerning PAH nitro derivatives, which have drawn

Scheme 1. Anthracene. Initial steps departing from the NO$_3$ adduct in position 1, A1 (left, a), and in position 2, A2 (right, b). They also involve positions 2 and 1, respectively. Gibbs free energy differences at $T = 298.15$ K, with respect to A1 and with respect to A2; A2 is 4.2 kcal mol$^{-1}$ above A1. In A1, A2, and A4 the brace indicates delocalization.

attention in the years (Fiedler and Mücke, 1991; Finlayson-Pitts and Pitts, 2000; Ghigo et al., 2006; Gibson, 1982; Jariyasopit et al., 2014a, 2014b; Keyte et al., 2013; Pitts et al., 1978; Zimmermann et al., 2013). It needs to be taken into account that NO$_2$ concentration can be high in some laboratory experiments (Arey et al., 1989).
3.1.1 Nitroxy in position 1: initial steps. Of the initial steps possibly involving A1 (Scheme 1, left),
two are unimolecular with formation of one extra ring (A1-A4 and A1-A5). Other two (A1-A6 and
A1-A7) imply either H abstraction by O₂, or its addition to the π-system. Still another step similarly
sees NO₂ addition; also other free radicals would similarly add, as NO, HO, or NO₃ itself. In more
detail, (a) A1 could undergo a 5-membered ring formation (c-CCONO) to its radical isomer A4 with a
barrier ΔG°‡ = 27.5 kcal mol⁻¹. This cyclic intermediate is less stable than A1 by 4.5 kcal mol⁻¹. (b) As
an alternative, A1 could lose NO₂, and concertedly close an epoxide ring to give A5, with ΔG°‡ = 25.7
kcal mol⁻¹. This step is exoergic by ΔG = -14.4 kcal mol⁻¹. Regarding the bimolecular reactions, (c) O₂
could abstract the hydrogen geminal to the nitroxy group in A1 with consequent formation of 1-
nitroxy-anthracene A6 (an arylnitrate) and the hydroperoxyl radical with ΔG°‡ = 22.8 kcal mol⁻¹ and a
G gain of 14.7 kcal mol⁻¹ for the step. (d) in A1, O₂ could also add to the π-system, namely to the
allylic positions 2 or 4. The related spin densities (Δρ = α electron density - β electron density) are
0.55 on C₂, and 0.64 on C₄. This addition could proceed through four attacks differing in regio- and
diastereochemistry with respect to the nitroxy group (2 or 4, and syn or anti with respect to the
approximate molecular plane). Only one attack will be fully examined as far as the subsequent steps
are considered: it is the addition to position 2/syn, which presents a barrier ΔG°‡ = 12.7 kcal mol⁻¹ to
give the peroxyl radical A7 2/syn at -0.2 kcal mol⁻¹. By considering that the peroxyl radical
intermediates are located at approximately the same energy as the initial NO₃ adduct A1, the
dioxygen addition step (if considered alone) can be regarded as quite reversible.
(e) Also a variety of radicals X can similarly add with the same regio- and diastereochemistry, via a
very easy step as regards energy. For simple radical couplings, fairly high rate constants of the order
of 10⁻¹¹ – 10⁻¹² molec⁻¹ cm³ s⁻¹ have been assessed, depending on the reaction type.¹ For instance
NO₂ adds in position 2 without any E barrier, and a nitroxy nitro closed shell adduct forms, located
at -22.6 kcal mol⁻¹ (nitro in 4/syn) and -24.6 (4/anti), or -27.0 kcal mol⁻¹ (nitro in 2, syn and anti both).
A possible HNO₃ loss from the anti nitroxy nitro A8 intermediate (compare Ghigo et al. 2006) could
produce 2-nitro nitroanthracene, but this step results too demanding as a gas phase process (see Scheme
S1 in the Supplementary Material), though in conditions different from the gas phase we cannot
exclude such a step. This is consistent with the available experimental results (Kwok et al., 1994; see,
in particular, p 791).

¹ For the radical coupling phenyl + phenyl → biphenyl, for instance, k = 1.9 x 10⁻¹¹ molec⁻¹ cm³ s⁻¹ has
been assessed at T = 300 K (Park and Lin, 1997). For methyl + phenyl → toluene, k = 2.1 x 10⁻¹¹
molec⁻¹ cm³ s⁻¹ at T = 300 K (Tokmakov et al., 1999). But lower values are found in other cases, as
in the presence of delocalized π radicals. For cyclohexadienyl + NO at 296 K the values are: k = 6–12
(P-dependent, in the range 20–80 Torr of He) x 10⁻¹³ molec⁻¹ cm³ s⁻¹ (Nakashima et al., 2008).
Values for the hydroperoxyl radical are also reported. Similar considerations apply to A2 (see below). The extent to which bifunctional derivatives formation can compete, depends on the relative concentrations of O$_2$ and X, and on the accuracy of the relevant rate constants, hence it is rather hard to assess. Regarding A6 formation, an alternative pathway (O$_2$ addition to give A7, H abstraction from the position geminal to the nitroxy group operated by –O’; hydroperoxyl radical loss) would give the same aromatic nitrate (Scheme 1, pathway d). The barrier for intramolecular H abstraction is, for the syn isomer, much higher than for the step A1-A6 (see Supplementary Material, section A).

If the peroxy group is anti to the nitroxy, i.e. close to the hydrogen to be abstracted, it comes out by contrast to be lower: 19.6 kcal mol$^{-1}$ with respect to the preceding minimum (compare 22.8 kcal mol$^{-1}$ for the intermolecular process). In this case, hydroperoxyl loss is concerted with the H abstraction.

### 3.1.2 Nitroxy in position 2: initial steps.

Similarly to A1, the two intermediates A4 and A5 can be obtained from A2, through ring closure steps (Scheme 1b). In A2 the largest spin density is on C1, $\Delta \rho = 0.64$. It is somewhat higher than that associated to C2 in A1, 0.55: an allyl-like system similar to that found in A1 is present, but with larger spin density on one carbon, C1. Accordingly, the ring closures entail comparable, but slightly smaller, barrier heights than for A1: 24.0 kcal mol$^{-1}$ to get A4, and 24.7 kcal mol$^{-1}$ to get A5 from A2 (which is 4.2 kcal mol$^{-1}$ above A1).$^2$ Steps c, d, and e follow again, and present barriers not too dissimilar from those of Scheme 1a, somewhat lower in the case of dioxygen addition. Also the peroxy radicals A10 are more stable by ca. 5 kcal mol$^{-1}$ than those labeled A7, with the two substituents in ortho. Dioxygen addition is in this case significantly less reversible (in itself) than for A7. The step free energy differences are generally lower by ca. 4 kcal mol$^{-1}$, which can be traced back to the 4.2 kcal mol$^{-1}$ energy difference of A2 vs A1 (while the step products are quite alike).

### 3.1.3 Further steps from the peroxy radicals.

By considering further different radical additions to the peroxy intermediate A7, as those by NO, NO$_2$, NO$_3$, or HO, one can assess if its terminal oxygen can be successively abstracted in a viable way. Starting from the peroxy radical intermediate A7 located at -0.2 kcal mol$^{-1}$, some steps could be initiated by NO (Scheme 2a). NO could in principle abstract the terminal oxygen by an effective collision, to form the oxyl radical intermediate A13 + NO$_2$, at -11.0 kcal mol$^{-1}$, but we could not find such a transition structure.

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$^2$ In A2, the spin density $\Delta \rho$ is somewhat more localized with respect to A1. However, some delocalization occurs also in A2, involving a system C1(0.64)-C$_{tert}$-C9(0.33) ($\Delta \rho$ values here in parentheses). This situation bears some resemblance to an allylic system, but is less symmetric than in A1. All other $|\Delta \rho|$ values are lower than 0.09.
1. **Scheme 2.** Anthracene. Reaction steps of the peroxyl radicals \( A7 \) and \( A10 \) with NO (black arrows) and \( \text{NO}_3 \) (red arrows; red-underlined figures pertain to this pathway when double values appear). See text and Scheme 1. Value in parentheses do not include the Yamaguchi treatment.\(^3\) Gibbs free energy differences at \( T = 298.15 \) K, with respect to the initial adduct \( A1 \).

\(^3\) For both anthracene and phenanthrene, in the fragmentations of the trioxyl intermediates, \( A17, A23, A31 \) (Scheme 4), and \( P12 \) (Scheme 6), respectively, the earliness of the transition structures (in a geometrical sense: \( R_{O_{3}O} = 1.72-1.74 \) Å), causes the quartet, which is the next spin contaminant involved in the process of finding a stable wavefunction, to be quite high in energy. The ensuing Yamaguchi correction (Yamaguchi et al., 1988) comes out to be large enough to produce "negative barriers". If we can cast some doubts on the real existence of a trioxyl intermediate, we can deem (in any case) this fragmentation a very easy step.
Alternatively, NO could first add to A7 (radical coupling) to form the peroxynitrite A12. The addition step presents a low free energy barrier, 5.3 kcal mol\(^{-1}\), and A12 is located 10.6 kcal mol\(^{-1}\) lower than A7. If (Scheme 2a, first column) a subsequent NO\(_2\) loss from A12 were feasible, it would then give A13, and by \(\beta\)--fragmentation A14, bearing an aldehydic group. A14 is a radical stabilized by delocalization and \(\alpha\)--effect. Loss of NO\(_2\) would finally produce the closed shell dialdehyde A15.

The pathway A7-A13 shown in Scheme 2a (second column) resulted to be energetically the easiest. It leads to the dialdehyde A15, as well as to the closed shell nitroxyketone A18 (red arrows): these can be considered as end products for the reacting system considered here. Other less fortunate attempts are documented in the Supplementary Material, section A. The nitrate-mediated pathway A10-A20 opens the way to the formation of the same dialdehyde A15 and a nitroxyketone A25 (Scheme 2b).

**Scheme 3.** Anthracene. Initial steps involving positions 9 and 10. Gibbs free energy differences at \(T = 298.15\) K, with respect to the initial adduct A3.

### 3.1.4 Nitroxy in position 9.

In the case of the nitrate adduct having the –ONO\(_2\) group in position 9, A3, which is 7.5 kcal mol\(^{-1}\) below A1, three of the five cases of Scheme 1 can be considered (Scheme 3) because (a) an \(\cdots\text{O}--\text{N}--\text{O}\cdots\) bridge between two carbons forms only through a high barrier (Supplementary Material, Section A), and (b) an epoxide ring formation would cancel the aromaticity of one benzo group. Step A3-A25 corresponds to pathway c in Scheme 1 and leads to a structural isomer of A6. Step A3-A26 corresponds to pathway d. Step A3-A27 is, as for pathway e, a coupling of two radicals (here exemplified by the formation of 10-nitro-9,10-dihydroanthr-9-yl nitrate. Further viable pathways from A3 were not found. Steps relying on a \(\beta\)--fragmentation in an oxyl intermediate...
similar to A13 are to be ruled out because it would originate a phenyl radical, which proved to be too high in energy. From A26, further steps could lead to a very stable nitroxyketone. They are similar to those discussed in connection with Scheme 2 and are displayed in Scheme 4.

Scheme 4. Anthracene. Steps following initial O₂ addition to C10 in 9-nitroxyanthracene. Additions of NO (black arrows) and NO₃ (red arrows; red-underlined figures pertain to this pathway when double values appear). Value in parentheses do not include the Yamaguchi treatment. Gibbs free energy differences at T = 298.15 K, with respect to the initial adduct A3.

By comparing the two reaction channels, we see that NO addition to A26 is less demanding than NO₃ addition, while the adducts A28 and A30 have similar stability. The oxyl radical A29 that forms through further NO₂ or O₂ losses can undergo H abstraction by O₂ to give 9-nitroxy-anthr-10-one. This time a β-fragmentation similar to that seen in Scheme 2 cannot take place, because it implies formation of a rather unstable phenyl radical.
3.2 Phenanthrene. This PAH presents its equivalent positions 9 and 10 as the most reactive. NO$_3$ adds to these positions again without any energy barrier, to form the 9-phenanthrenylnitrate radical P1 (boxed structure, taken as our ΔG reference in Scheme 5 and Scheme 6). P1 could undergo a 5-membered ring formation (c-CCONO) to its radical isomer P2, step (a), with a barrier ΔG$^\ddagger$ = 22.8 kcal mol$^{-1}$. This substantial barrier should be overcome, to take a pathway that, through a ring opening, leads to a dialdehyde (biphenyl-2,2’-dicarbaldehyde). Details are provided in the Supplementary Material, section A. (b) As an alternative, P1 could lose NO$_2$, and concertedely close an epoxide ring to give P3, with ΔG$^\ddagger$ = 21.8 kcal mol$^{-1}$. Both these pathways do not appear to be very likely, since they correspond to quite slow reaction steps, though less difficult than the analogous steps seen for anthracene. (c) Coming to bimolecular processes, O$_2$ could abstract the hydrogen geminal to the nitroxy group “on the fly”, with ΔG$^\ddagger$ = 18.6 kcal mol$^{-1}$ and formation of 9-nitroxyphenanthrene, P4, an arylnitrate. (d) Otherwise, O$_2$ could first add to the adjacent position 10. This step cannot be seen as reversible, in itself, as A1-A7, and is more similar in this respect to A2-A10, even with a higher barrier for the backwards step.

O$_2$ addition, as already discussed, can occur with syn or anti diastereochemistry. In the case of anti addition, the terminal peroxyl –O• can abstract the hydrogen geminal to the nitroxy group and then a hydroperoxyl radical can leave. If H abstraction were impossible because of a syn arrangement, it could also occur as NO-mediated process (details in the Supplementary Material, section A). The barrier to the peroxyl intermediate P5 is 3.0 kcal mol$^{-1}$ high (2.2 if O$_2$ adds anti), and P5 lies at -8.7 (syn) or -8.6 (anti) kcal mol$^{-1}$. Formation of 9-nitroxy-phenanthrene P4 would ensue from both c and d pathways but with a second sizable barrier of ca. 22 kcal mol$^{-1}$ with respect to P5 along pathway d. Other possible reaction steps from P5 are discussed below (Scheme 6). (e) Any radical tropospheric species (as NO$_3$, NO$_2$, NO,...) could also add with the same diastereochemistry, and closed shell products would form. Here this termination step is exemplified in Scheme 5 by NO$_2$ addition, which takes place via a barrierless step as regards energy.
Scheme 5. Phenanthrene. Initial steps involving positions 9 and 10. Gibbs free energy differences at $T = 298.15$ K, with respect to the initial adduct $P_1$. In $P_2$, the brace indicates delocalization. Pathway e: NO$_2$ taken as an example of any termination step occurring via radical coupling.

Similarly to what described for anthracene, starting from the peroxy radical intermediate $P_5$, at -8.7 kcal mol$^{-1}$, further steps, initiated by NO, can in principle form an oxyl radical intermediate $P_8$ + NO$_2$ at -19.1 kcal mol$^{-1}$. However, we found no trace of a TS for O abstraction by NO “on the fly”. Instead, the 9-nitroxy-10-peroxynitrite $P_7$ first forms upon radical coupling (Scheme 6, left), with a barrier of 6.0 kcal mol$^{-1}$; $P_7$ is located at -19.7 kcal mol$^{-1}$. Upon NO$_2$ loss, it would give the oxyl intermediate $P_8$. If $P_8$ forms this way, further steps through a stabilized radical $P_{11}$ can finally give the closed shell dialdehyde, $P_{10}$. $P_8$ could also form through the NO$_3$-addition pathway shown on the right. The dialdehyde $P_{12}$, and to a slightly lesser extent the nitroxy ketone $P_{13}$, appear to be good candidates for being major products of the NO$_3$-mediated oxidation.
Scheme 6. Phenanthrene. Additions of NO (left, black arrows) and NO$_3$ (right, red arrows; red-underlined figures pertain to this pathway when double values appear). Value in parentheses do not include the Yamaguchi treatment. Gibbs free energy differences at T = 298.15 K, with respect to the initial adduct P$_1$.

The reaction of phenanthrene with HO and NO$_3$ radicals was studied experimentally (Kwok et al., 1994). In that study a kinetic constant of $1.2 \times 10^{-13}$ molecules$^{-1}$ cm$^3$ s$^{-1}$ for NO$_3$ ($1.3 \times 10^{-11}$ for HO) was determined, concluding that these reactions should dominate phenanthrene atmospheric loss processes. Their experiments were carried out in the presence of a varying initial concentration of...
NO$_2$, namely $0$, $4.4 \times 10^{13}$ and $2.4 \times 10^{14}$ molecules cm$^{-3}$. A non-zero intercept in a rate plot vs NO$_2$, concentration suggested that the phenanthrene-nitrate radical reaction must also involve a pathway independent of NO$_2$ concentration. This pathway could actually be a set of pathways of different importance, as shown in Schemes 1, 3, 5.

The results of our present study can be compared with those from the recent theoretical study on phenanthrene plus HO, O$_2$, and NO$_x$ (Zhao et al., 2016). In those studies, the principal products were indicated to be oxidized ring retaining products, as well as products from ring opening, namely, phenanthrones, phenanthrols, quinones and dialdehydes. The same research group had previously investigated the reaction of the nitrate radical with 9-chloro-anthracene in the presence of O$_2$ and NO$_x$ (Dang et al., 2015c), and the same kind of reactions involving naphthalene too (Qu et al., 2006c). They found that, following barrierless nitrate addition to the PAH $\pi$–system, the main products should be: 9-chloroanthryl nitrates, diones, epoxides, and dialdehydes.

4. Conclusions

In this study, we have investigated the NO$_3$-initiated gas phase oxidative degradation of anthracene and phenanthrene. A variety of reaction steps have been considered that contemplate the intervention of O$_2$, NO, NO$_2$, and also NO$_3$ (for a second time), and also unimolecular steps. Some reaction steps, considered less likely, are collected in the Supplementary Material. These results indicate that one NO$_3$-initiated pathway, which is also O$_2$ and NO$_3$-mediated, leads to the formation of a dialdehyde and a nitroxy-ketone. The same kind of pathway is effective for both anthracene (Schemes 2 and 4) and phenanthrene (Scheme 6). The key species is an early intermediate, a nitroxy peroxyl radical that forms after the initial NO$_3$ attack to the PAH upon dioxygen addition. It further evolves to carbonyl products, through free energy barriers that are significantly lower than those related to other possible intermediates or closed shell products. Some bifunctional PAH derivatives can also form through couplings of the initial nitroxy radical adducts with free radicals X present in the troposphere. The example of the formation of a nitroxy nitro product is shown (pathway e in Schemes 1, 3, 5). HNO$_3$ loss from the closed shell anti nitroxy nitro intermediate could allow the formation of a nitroaromatic. However, it but results very difficult in the gas phase.
Acknowledgments. This work was supported by the Università di Torino (Local Funding 2016). It was conducted in the frame of EC FP6 NoE ACCENT and ACCENT–PLUS projects (Atmospheric Composition Change, the European NeTwork of Excellence).

Supplementary Material for this article is available: it includes the geometries and energetics of all optimized structures, plus the illustration of other reaction channels explored but not reported in the main text because of their more demanding energetics.

References


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PAH oxidation by nitrate radical


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