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1 Anthracene and phenanthrene tropospheric oxidation promoted by 2 the nitrate radical in the gas-phase. Theoretical modelistic study.

3
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6
7 **Abstract.** Polycyclic aromatic hydrocarbons and their oxidized derivatives are ubiquitous
8 environmental pollutants that are toxic to different degrees. The NO₃ radical is known to be an
9 important actor in fostering nighttime atmospheric chemistry; hence it could elicit some nocturnal
10 PAH-loss processes. In this study the gas phase pathways open to the initial anthracene and
11 phenanthrene NO₃ π-radical adducts in the presence of O₂, NO and NO₂ are examined by Density
12 Functional Theory to ascertain the mechanistic features of their NO₃-initiated oxidative degradation.
13 Unimolecular steps involving the initial adducts (ring closures or fragmentation) present rather high
14 free energy barriers and seem unlikely. Regarding bimolecular reactions, any radical present in the
15 tropospheric environment can give an intrinsically fast radical coupling with the initial adducts, thus
16 producing bifunctional closed shell species. The addition of ground state dioxygen is a relatively fast
17 step that is reversible in some cases, less so in others. It entails subsequent reaction steps, which
18 involve the peroxy radical intermediate and addition and loss of small species as NO, NO₃, NO₂ and
19 O₂. These steps can either trigger a β-fragmentation with formation of a closed shell dialdehyde or
20 formation of a closed shell nitroxy ketone, bifunctional species that appear to be the most likely
21 products when typical tropospheric concentrations are taken into account.

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

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30 **Proposed running title:** PAH oxidation promoted by NO₃

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1 **1. Introduction.**

2 Polycyclic aromatic hydrocarbons (PAHs) and their oxidized derivatives are ubiquitous
3 environmental pollutants present in the troposphere, which are toxic to different extents (Finlayson-
4 Pitts and Pitts, 2000; Keyte et al., 2013). They are emitted during incomplete combustion of fossil
5 fuels (Lim et al., 1999) and biomass (Jenkins et al., 1996; Mandalakis et al., 2005; Samburova et al.,
6 2016). PAHs can undergo oxidation and functionalization in general, both during combustion and
7 their subsequent transport in the troposphere.(Calvert et al. 2002; Kameda 2011) In particular,
8 anthracene and phenanthrene belong to the list of the 16 priority PAHs indicated by the US
9 Environmental Protection Agency. This list has played an important role in monitoring programs
10 (Lammel, 2015), though reservations about its future use has been recently put forth (Andersson and
11 Achten, 2015).

12 Homogeneous (gas phase) and heterogeneous (particle phase) experimental and theoretical
13 studies have been published on the reactions of PAHs with ozone (Finlayson-Pitts, 1997; Perraudin
14 et al., 2007, 2006; Zhang et al., 2013) or with the hydroxyl radical (Biermann et al., 1985; Brubaker
15 and Hites, 1998; Dang et al., 2015a, 2015b, 2014; Giordana et al., 2008; Helmig and Harger, 1994;
16 Sasaki et al., 1997; Zhao et al., 2016). Some publications have also dealt with the action of the nitrate
17 radical (Atkinson et al., 1990; Dang et al., 2015c; Qu et al., 2008; Sasaki et al., 1997; Zhang P., 2014;
18 Chapleski et al., 2016). The reaction with the NO₃ radical, known to play in general a significant role
19 in nighttime tropospheric chemistry (Stone et al., 2014), may have some importance in contributing
20 to nocturnal PAH loss pathways. Current knowledge of the NO₃-initiated gas phase atmospheric
21 oxidation of different PAHs, based on experimental results, is mostly limited to cases in which a high
22 concentration of NO₂ is also present. For example, in their studies on naphthalene and fluoranthene,
23 Sasaki et al. found nitro-derivatives as important products (Arey et al., 1989; Sasaki et al., 1997). In
24 their reacting system they had not only NO₃, but also substantial concentrations of NO₂, both coming
25 from N₂O₅ (NO₂ was also added with concentration in the order of 10¹³ molecules cm⁻³). Whereas a
26 variety of experimental studies dealing with naphthalene and its derivatives + NO₃ reacting system
27 is available (see Keyte et al. 2013, pp 9349-9353), much less has been done for anthracene and
28 phenanthrene, considering both the gas phase and the particle phase (Arey et al., 1989; Jariyasopit
29 et al., 2014b; Kwok et al., 1994).

30 Some of the oxidized PAH derivatives are of concern for human health,(Asare et al., 2009, 2008;
31 Durant et al., 1996; Landvik et al., 2007; Talaska et al., 1996) and in addition a large share of oxidation
32 products are not identified. Therefore it is worthwhile to further investigate the mechanistic details
33 of these processes. Theoretical investigations as the present one can be complementary to
34 experimental studies, and the comparison be informative. Within it, we explore the gas phase

1 reaction mechanisms of NO₃-triggered oxidative degradation of anthracene and phenanthrene.
2 Therefore, we will consider how ground electronic state O₂, NO, and NO₂ will react with PAH-derived
3 intermediate radicals. We model these reactions in a semi-quantitative way to ascertain their
4 mechanistic features (reaction pathways and related free energy barriers) and also with the purpose
5 of suggesting, on that basis, likely closed shell products. Accordingly, we deliberately do not extend
6 the investigation to all possible reaction pathways when differing for regio- and diastereochemistry,
7 as is done with the goal of obtaining *quantitative* predictions.

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

14 To our knowledge experimental results are scarce for phenanthrene (Kwok et al., 1994) and
15 anthracene (Arey et al., 1989; Jariyasopit et al., 2014b; Ringuet et al. 2012), with more data available
16 for naphthalene. Some publications deal with our title PAHs, but are either carried out in the
17 presence of high NO₂ concentration, or deal with heterogeneous chemistry of these and other
18 PAHs. (Mak et al 2007; Zhang et al. 2011; Liu et al. 2012; Cochran et al. 2016) Some theoretical papers
19 published in the last few years also bear similarities to the present study. In particular, a study on
20 hydroxycyclohexadienyl peroxy radical (from benzene) plus NO, (Yan et al., 2013) those on benzene
21 (Qu et al., 2006a) or naphthalene (Qu et al., 2006b) plus NO₃, one on 9-chloroanthracene plus NO₃
22 (Dang et al., 2015c), and one on the role of water in the formation of nitro-PAHs (Zhang Q. et al.,
23 2014).

24 **2. Theoretical Method.**

25 All stationary points on the energy hypersurface, *i.e.* minima and first order saddle points,
26 corresponding to transition structures (TS), were determined by gradient procedures (Pople et al.,
27 1992; Schlegel, 1982a, 1982b, 1981; Schlegel et al., 1984) within the Density Functional Theory (DFT),
28 (Parr and Yang, 1989) and making use of the M06-2X (Zhao and Truhlar, 2008, 2007) functional.
29 Reactants, transition structures, intermediates, and products have been optimized with the 6-
30 31G(d,p) basis set. Single-point energies of various species were calculated with Dunning's
31 correlation-consistent polarized valence triple- ζ basis set cc-pVTZ (Kendall et al., 1992). On the basis
32 of previous studies, (Trogolo et al., 2014) this computational approach is expected to perform
33 acceptably. The nature of the critical points (and the thermochemistry) was assessed by vibrational

1 analysis: the 6-31G(d,p) thermochemical corrections gave estimates of the zero point vibrational
 2 energy (ZPE), by which the cc-pVTZ relative energies were corrected [here $\Delta E_{\text{ZPE}} = \Delta E_{\text{cc-pVTZ}} + \Delta \text{ZPE}_{6-31\text{G(d,p)}}$], and similarly enthalpy (ΔH) and Gibbs free energy (ΔG) differences were obtained. The
 3 thermochemistry was assessed in all cases at $T = 298.15$ K and ΔG values at this temperature are
 4 reported in [Scheme 1](#) (in kcal mol⁻¹). Geometry optimization and thermochemistry calculations were
 5 carried out by using the GAUSSIAN 09 system of programs (Frisch et al., 2009).

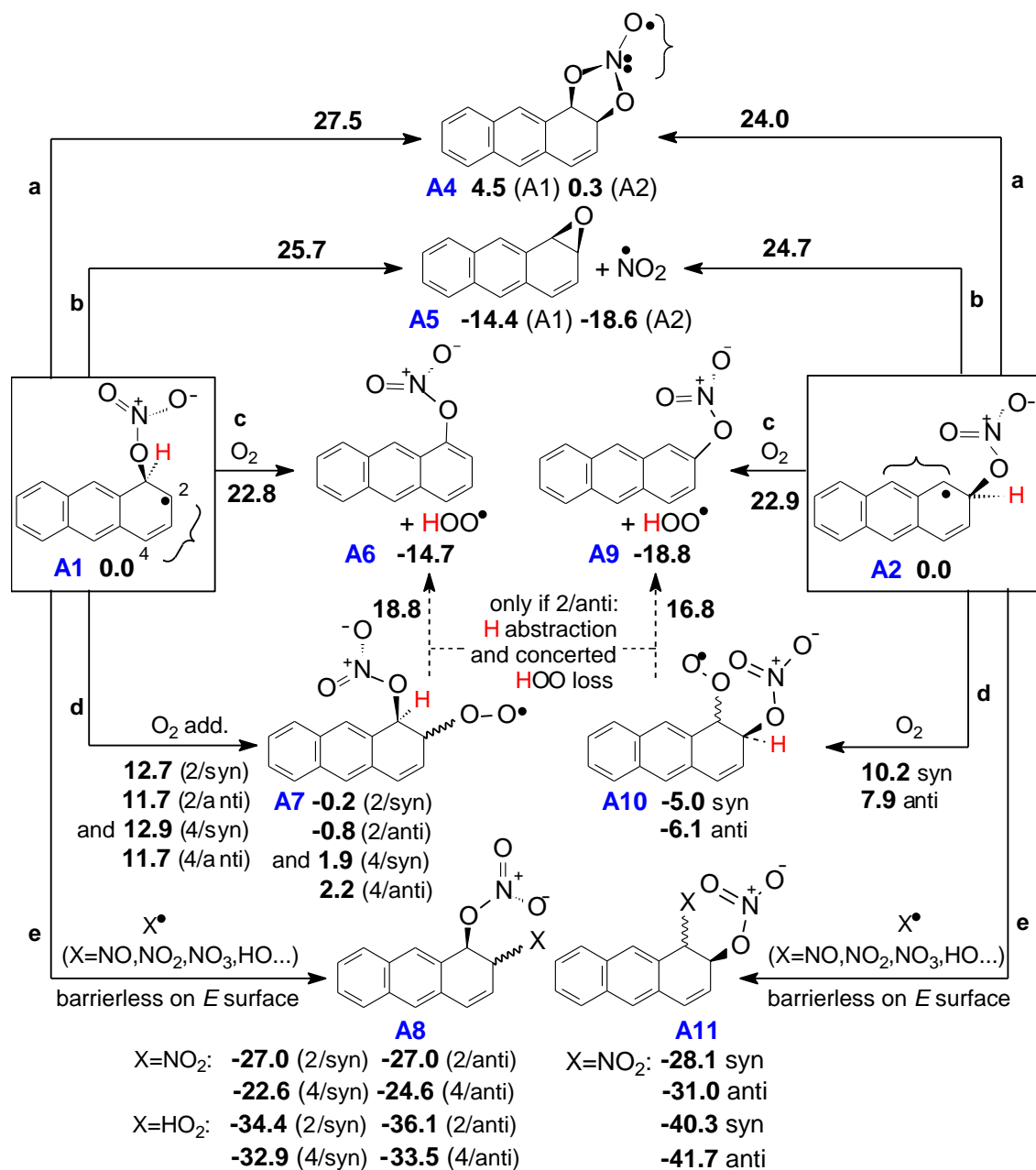
6 For singlet diradicaloid structures (such as those corresponding to homolytic dissociations), the
 7 “automatic” restricted closed shell singlet solution yields zero spin densities. Therefore, the wave-
 8 function stability was checked and obtained by relaxing the wavefunction in the orbital rotations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

17 3. Results and Discussion.

18 **3.1 Anthracene.** NO₃ adds to anthracene, without any barrier on the potential energy surface,
 19 to form three anthracenyl nitrate radicals. These are the boxed structures **A1** (addition to position
 20 1) and **A2** (position 2) in [Scheme 1](#), and **A3** (position 9) in [Scheme 3](#). Adduct **A1**, at -12.7 kcal mol⁻¹
 21 below the two reactants, is more stable than **A2** by 4.2 kcal mol⁻¹; adduct **A3** is the stablest, being
 22 located at -20.2 kcal mol⁻¹, i.e. 7.5 below **A1**. The energetics (ΔG at 298.15 K) for each reaction
 23 pathway is reported relative to **A1** in [Scheme 1](#), left, relative to **A2** in [Scheme 1](#), right, and relative to
 24 **A3** in [Scheme 3](#). The intermediates **A4** and **A5**, shared by both pathways, are associated with two
 25 free energy values, with the relevant zero is indicated in parentheses. [Scheme 2](#) displays further
 26 steps departing from the peroxy structures **A7** and **A10** in [Scheme 1](#).

27 First we will describe the different reaction steps possibly undergone by the initial adducts **A1**,
 28 **A2**, and **A3**. Then, we will assess their relative importance. We have taken into account possible
 29 unimolecular reaction steps departing from the initial adducts, as well as dioxygen intervention (O₂
 30 is the reactive species present with the highest density, close to 5×10^{18} molecules cm⁻³). Also taken
 31 into account are NO and NO₃ reactions with relevant intermediate radicals ([Scheme 2](#)). Section A in
 32 the [Supplementary Material](#) displays a larger number of less likely pathways. NO_x species (collective
 33 for NO + NO₂) are present in the troposphere at concentrations ranging from 10⁸–10⁹ (unpolluted

- 1 situation) to 10^{12} (polluted) molecules cm^{-3} . The role of NO_x species can be particularly interesting
 2 in the formation of the concerning PAH nitro derivatives, which have drawn



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4

5 **Scheme 1.** Anthracene. Initial steps departing from the NO_3 adduct in position 1, **A1** (left, **a**), and in
 6 position 2, **A2** (right, **b**). They also involve positions 2 and 1, respectively. Gibbs free energy
 7 differences at $T = 298.15$ K, with respect to **A1** and with respect to **A2**; **A2** is $4.2 \text{ kcal mol}^{-1}$ above **A1**.
 8 In **A1**, **A2**, and **A4** the brace indicates delocalization.

9 attention in the years (Fiedler and Mücke, 1991; Finlayson-Pitts and Pitts, 2000; Ghigo et al., 2006;
 10 Gibson, 1982; Jariyasopit et al., 2014a, 2014b; Keyte et al., 2013; Pitts et al., 1978; Zimmermann et
 11 al., 2013). It needs to be taken into account that NO_2 concentration can be high in some laboratory
 12 experiments (Arey et al., 1989).

1 **3.1.1 Nitroxy in position 1: initial steps.** Of the initial steps possibly involving **A1** (Scheme 1, left),
 2 two are unimolecular with formation of one extra ring (**A1-A4** and **A1-A5**). Other two (**A1-A6** and
 3 **A1-A7**) imply either H abstraction by O₂, or its addition to the π-system. Still another step similarly
 4 sees NO₂ addition; also other free radicals would similarly add, as NO, HO, or NO₃ itself. In more
 5 detail, (a) **A1** could undergo a 5-membered ring formation (c-CCONO) to its radical isomer **A4** with a
 6 barrier $\Delta G^\ddagger = 27.5 \text{ kcal mol}^{-1}$. This cyclic intermediate is less stable than **A1** by 4.5 kcal mol⁻¹. (b) As
 7 an alternative, **A1** could lose NO₂, and concertedly close an epoxide ring to give **A5**, with $\Delta G^\ddagger = 25.7$
 8 kcal mol⁻¹. This step is exoergic by $\Delta G = -14.4 \text{ kcal mol}^{-1}$. Regarding the bimolecular reactions, (c) O₂
 9 could abstract the hydrogen geminal to the nitroxy group in **A1** with consequent formation of 1-
 10 nitroxy-anthracene **A6** (an aryl nitrate) and the hydroperoxyl radical with $\Delta G^\ddagger = 22.8 \text{ kcal mol}^{-1}$ and a
 11 *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
 12 allylic positions 2 or 4. The related spin densities ($\Delta\rho = \alpha$ electron density - β electron density) are
 13 0.55 on C2, and 0.64 on C4. This addition could proceed through four attacks differing in regio- and
 14 diastereochemistry with respect to the nitroxy group (2 or 4, and syn or anti with respect to the
 15 approximate molecular plane). Only one attack will be fully examined as far as the subsequent steps
 16 are considered: it is the addition to position 2/syn, which presents a barrier $\Delta G^\ddagger = 12.7 \text{ kcal mol}^{-1}$
 17 to give the peroxy radical **A7** 2/syn at -0.2 kcal mol⁻¹. By considering that the peroxy radical
 18 intermediates are located at approximately the same energy as the initial NO₃ adduct **A1**, the
 19 dioxygen addition step (if considered alone) can be regarded as quite reversible.
 20 (e) Also a variety of radicals X can similarly add with the same regio- and diastereochemistry, via a
 21 very easy step as regards energy. For simple radical couplings, fairly high rate constants of the order
 22 of 10⁻¹¹ – 10⁻¹² molec⁻¹ cm³ s⁻¹ have been assessed, depending on the reaction type.¹ For instance
 23 NO₂ adds in position 2 without any *E* barrier, and a nitroxy nitro closed shell adduct forms, located
 24 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).
 25 A possible HNO₃ loss from the anti nitroxy nitro **A8** intermediate (compare Ghigo et al. 2006) could
 26 produce 2-nitro anthracene, but this step results too demanding as a gas phase process (see Scheme
 27 S1 in the [Supplementary Material](#)), though in conditions different from the gas phase we cannot
 28 exclude such a step. This is consistent with the available experimental results (Kwok et al., 1994; see,
 29 in particular, p 791).

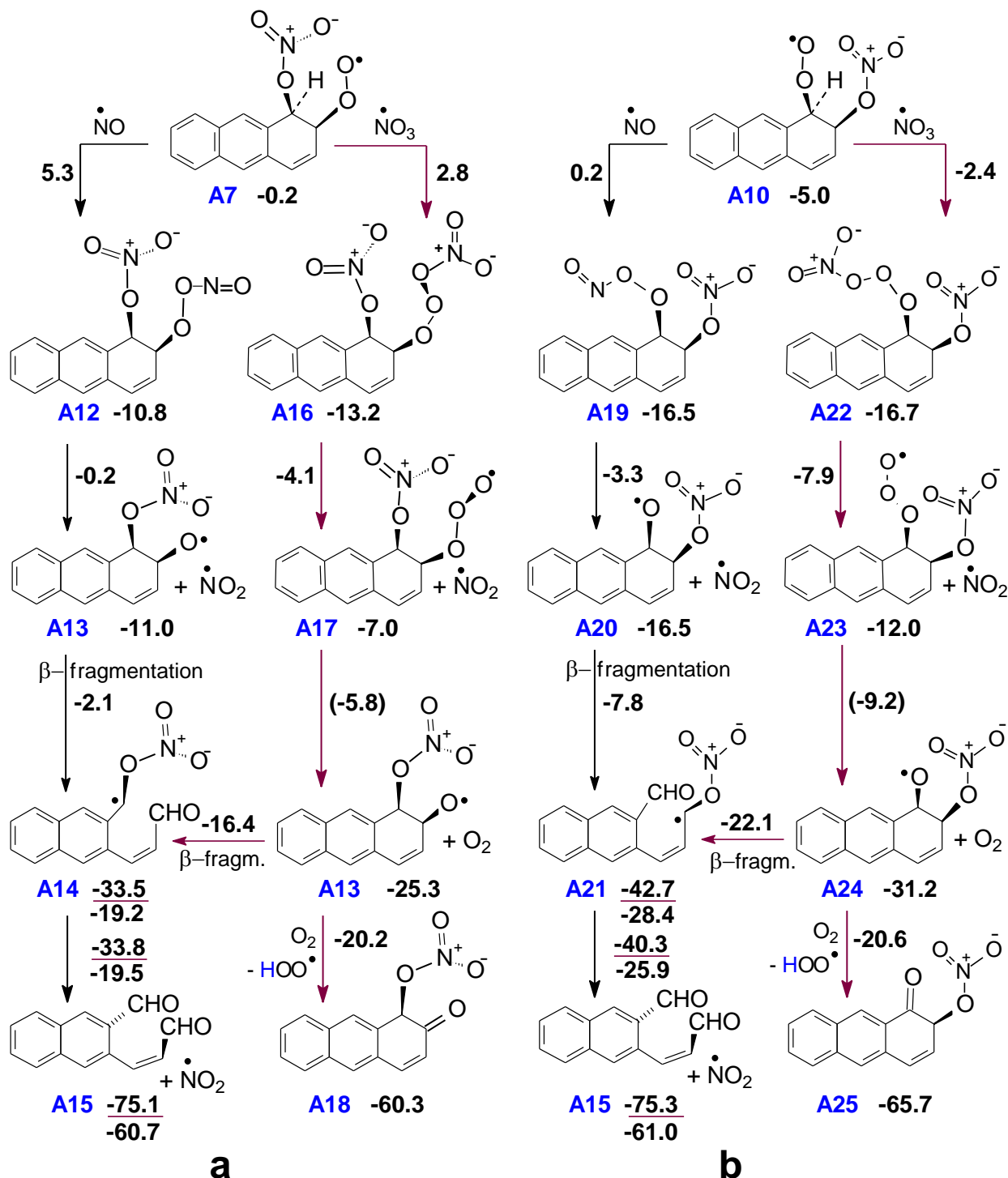
¹ For the radical coupling *phenyl + phenyl* → *biphenyl*, for instance, $k = 1.9 \times 10^{-11} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ has been assessed at T = 300 K (Park and Lin, 1997). For *methyl + phenyl* → *toluene*, $k = 2.1 \times 10^{-11} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ 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: $k = 6\text{--}12$ (P-dependent, in the range 20–80 Torr of He) $\times 10^{-13} \text{ molec}^{-1} \text{ cm}^3 \text{ s}^{-1}$ (Nakashima et al., 2008).

1 Values for the hydroperoxyl radical are also reported. Similar considerations apply to **A2** (see
 2 below). The extent to which bifunctional derivatives formation can compete, depends on the relative
 3 concentrations of O₂ and X, and on the accuracy of the relevant rate constants, hence it is rather
 4 hard to assess. Regarding **A6** formation, an alternative pathway (O₂ addition to give **A7**, H abstraction
 5 from the position geminal to the nitroxy group operated by -O[•], hydroperoxyl radical loss) would
 6 give the same aromatic nitrate (Scheme 1, pathway d). The barrier for intramolecular H abstraction
 7 is, for the syn isomer, much higher than for the step **A1-A6** (see Supplementary Material, section A).
 8 If the peroxy group is anti to the nitroxy, i.e. close to the hydrogen to be abstracted, it comes out by
 9 contrast to be lower: 19.6 kcal mol⁻¹ with respect to the preceding minimum (compare 22.8 kcal mol⁻¹
 10 for the intermolecular process). In this case, hydroperoxyl loss is concerted with the H abstraction.

11 **3.1.2 Nitroxy in position 2: initial steps.** Similarly to **A1**, the two intermediates **A4** and **A5** can
 12 be obtained from **A2**, through ring closure steps (Scheme 1b). In **A2** the largest spin density is on C1,
 13 $\Delta\rho = 0.64$. It is somewhat higher than that associated to C2 in **A1**, 0.55: an allyl-like system similar to
 14 that found in **A1** is present, but with larger spin density on one carbon, C1. Accordingly, the ring
 15 closures entail comparable, but slightly smaller, barrier heights than for **A1**: 24.0 kcal mol⁻¹ to get **A4**,
 16 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
 17 again, and present barriers not too dissimilar from those of Scheme 1a, somewhat lower in the case
 18 of dioxygen addition. Also the peroxy radicals **A10** are more stable by ca. 5 kcal mol⁻¹ than those
 19 labeled **A7**, with the two substituents in ortho. Dioxygen addition is in this case significantly less
 20 reversible (in itself) than for **A7**. The step free energy differences are generally lower by ca. 4 kcal
 21 mol⁻¹, which can be traced back to the 4.2 kcal mol⁻¹ energy difference of **A2** vs **A1** (while the step
 22 products are quite alike).

23 **3.1.3 Further steps from the peroxy radicals.** By considering further different radical additions
 24 to the peroxy intermediate **A7**, as those by NO, NO₂, NO₃, or HO, one can assess if its terminal oxygen
 25 can be successively abstracted in a viable way. Starting from the peroxy radical intermediate **A7**
 26 located at -0.2 kcal mol⁻¹, some steps could be initiated by NO (Scheme 2a). NO could in principle
 27 abstract the terminal oxygen by an effective collision, to form the oxyl radical intermediate **A13** +
 28 NO₂, at -11.0 kcal mol⁻¹, but we could not find such a transition structure.

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.



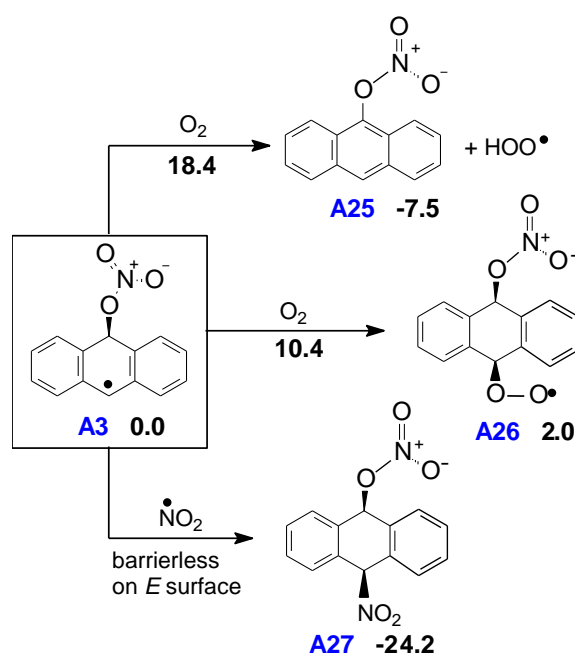
- 1
- 2 **Scheme 2.** Anthracene. Reaction steps of the peroxy radicals **A7** and **A10** with NO (black arrows)
- 3 and NO₃ (red arrows; red-underlined figures pertain to this pathway when double values appear).
- 4 See text and [Scheme 1](#). Value in parentheses do not include the Yamaguchi treatment.³ Gibbs free
- 5 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-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.

1

2 Alternatively, NO could first add to **A7** (radical coupling) to form the peroxyxynitrite **A12**. The
 3 addition step presents a low free energy barrier, 5.3 kcal mol⁻¹, and **A12** is located 10.6 kcal mol⁻¹
 4 lower than **A7**. If (Scheme 2a, first column) a subsequent NO₂ loss from **A12** were feasible, it would
 5 then give **A13**, and by β-fragmentation **A14**, bearing an aldehydic group. **A14** is a radical stabilized
 6 by delocalization and α-effect. Loss of NO₂ would finally produce the closed shell dialdehyde **A15**.

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



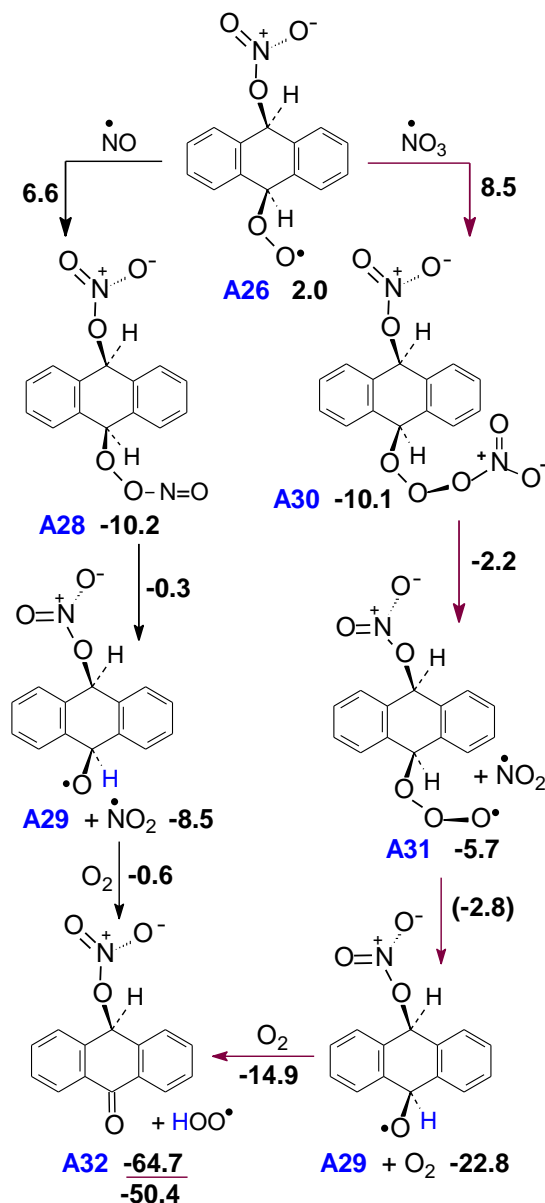
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15 **Scheme 3.** Anthracene. Initial steps involving positions 9 and 10. Gibbs free energy
 16 differences at T = 298.15 K, with respect to the initial adduct **A3**.

17 **3.1.4 Nitroxy in position 9.** In the case of the nitrate adduct having the -ONO₂ group in position
 18 9, **A3**, which is 7.5 kcal mol⁻¹ below **A1**, three of the five cases of Scheme 1 can be considered
 19 (Scheme 3) because (a) an -O-N-O- bridge between two carbons forms only through a high barrier
 20 (Supplementary Material, Section A), and (b) an epoxide ring formation would cancel the aromaticity
 21 of one benzo group. Step **A3-A25** corresponds to pathway c in Scheme 1 and leads to a structural
 22 isomer of **A6**. Step **A3-A26** corresponds to pathway d. Step **A3-A27** is, as for pathway e, a coupling
 23 of two radicals (here exemplified by the formation of 10-nitro-9,10-dihydroanthr-9-yl nitrate. Further
 24 viable pathways from **A3** were not found. Steps relying on a β-fragmentation in an oxyl intermediate

- 1 similar to **A13** are to be ruled out because it would originate a phenyl radical, which proved to be
 2 too high in energy. From **A26**, further steps could lead to a very stable nitroxyketone. They are
 3 similar to those discussed in connection with [Scheme 2](#) and are displayed in [Scheme 4](#).



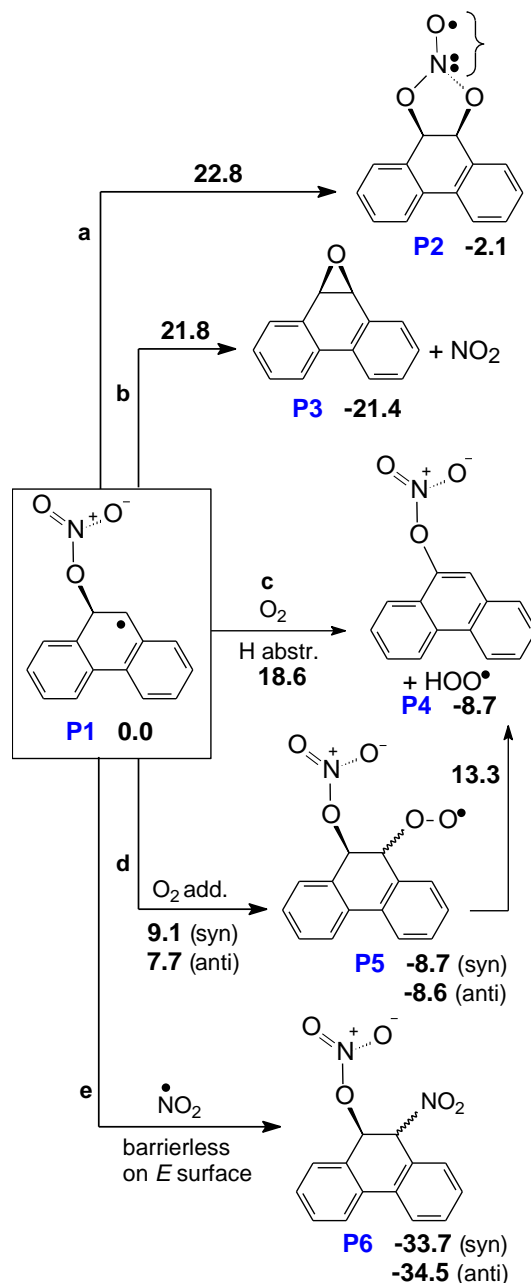
- 4
 5
 6 **Scheme 4.** Anthracene. Steps following initial O₂ addition to C10 in 9-nitroxyanthracene.
 7 Additions of NO (black arrows) and NO₃ (red arrows; red-underlined figures pertain to this
 8 pathway when double values appear). Value in parentheses do not include the Yamaguchi
 9 treatment.³ Gibbs free energy differences at T = 298.15 K, with respect to the initial adduct
 10 **A3**.

- 11 By comparing the two reaction channels, we see that NO addition to **A26** is less demanding than
 12 NO₃ addition, while the adducts **A28** and **A30** have similar stability. The oxyl radical **A29** that forms
 13 through further NO₂ or O₂ losses can undergo H abstraction by O₂ to give 9-nitroxy-anthr-10-one.
 14 This time a β-fragmentation similar to that seen in [Scheme 2](#) cannot take place, because it implies
 15 formation of a rather unstable phenyl radical.

1 **3.2 Phenanthrene.** This PAH presents its equivalent positions 9 and 10 as the most reactive. NO₃
2 adds to these positions again without any energy barrier,¹ to form the 9-phenanthrenyl nitrate radical
3 **P1** (boxed structure, taken as our ΔG reference in [Scheme 5](#) and [Scheme 6](#)). **P1** could undergo a 5-
4 membered ring formation (c-CCONO) to its radical isomer **P2**, step (a), with a barrier $\Delta G^\ddagger = 22.8$ kcal
5 mol⁻¹. This substantial barrier should be overcome, to take a pathway that, through a ring opening,
6 leads to a dialdehyde (biphenyl-2,2'-dicarbaldehyde). Details are provided in the [Supplementary](#)
7 [Material](#), section A. (b) As an alternative, **P1** could lose NO₂, and concertedly close an epoxide ring
8 to give **P3**, with $\Delta G^\ddagger = 21.8$ kcal mol⁻¹. Both these pathways do not appear to be very likely, since they
9 correspond to quite slow reaction steps, though less difficult than the analogous steps seen for
10 anthracene. (c) Coming to bimolecular processes, O₂ could abstract the hydrogen geminal to the
11 nitroso group “on the fly”, with $\Delta G^\ddagger = 18.6$ kcal mol⁻¹ and formation of 9-nitroso-phenanthrene, **P4**,
12 an aryl nitrate. (d) Otherwise, O₂ could first add to the adjacent position 10. This step cannot be seen
13 as reversible, in itself, as **A1-A7**, and is more similar in this respect to **A2-A10**, even with a higher
14 barrier for the backwards step.

15 O₂ addition, as already discussed, can occur with syn or anti diastereochemistry. In the case of
16 anti addition, the terminal peroxy radical -O· can abstract the hydrogen geminal to the nitroso group and
17 then a hydroperoxy radical can leave. If H abstraction were impossible because of a syn
18 arrangement, it could also occur as NO-mediated process (details in the [Supplementary Material](#),
19 section A). The barrier to the peroxy intermediate **P5** is 3.0 kcal mol⁻¹ high (2.2 if O₂ adds anti), and
20 **P5** lies at -8.7 (syn) or -8.6 (anti) kcal mol⁻¹. Formation of 9-nitroso-phenanthrene **P4** would ensue
21 from both c and d pathways but with a second sizable barrier of ca. 22 kcal mol⁻¹ with respect to **P5**
22 along pathway d. Other possible reaction steps from **P5** are discussed below ([Scheme 6](#)). (e) Any
23 radical tropospheric species (as NO₃, NO₂, NO,...) could also add with the same diastereochemistry,
24 and closed shell products would form. Here this termination step is exemplified in [Scheme 5](#) by NO₂
25 addition, which takes place via a barrierless step as regards energy.

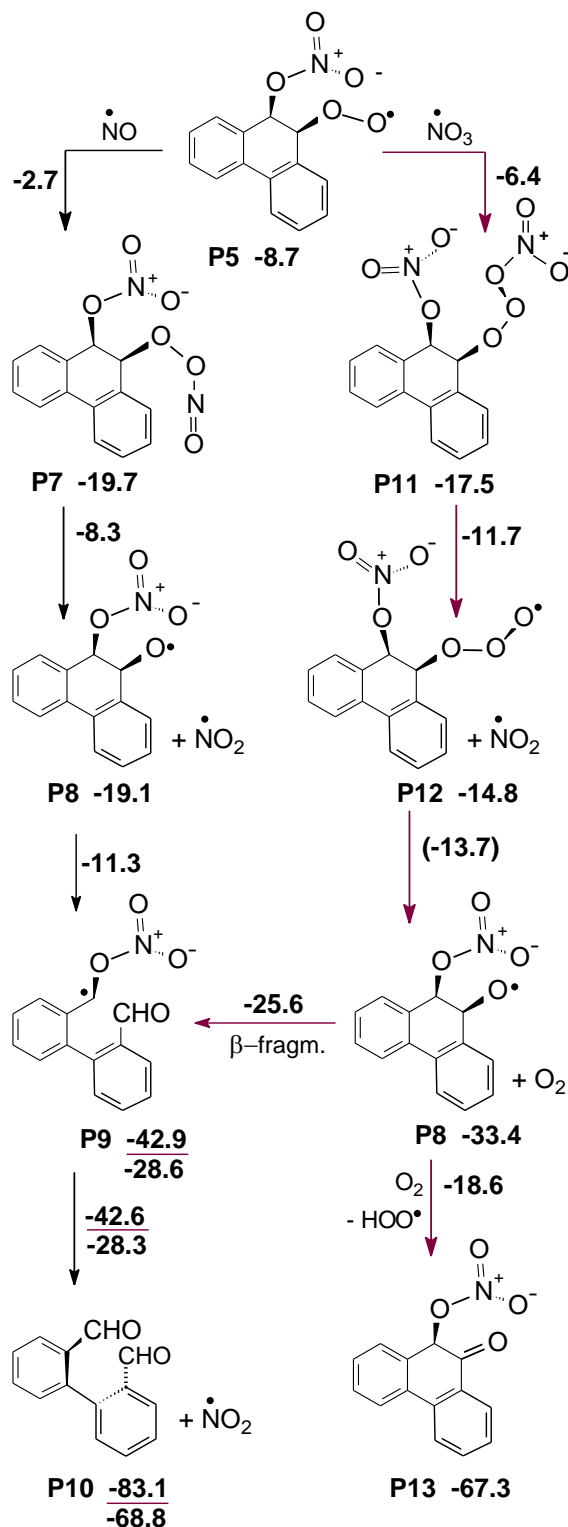
26



1

2 **Scheme 5.** Phenanthrene. Initial steps involving positions 9 and 10. Gibbs free energy differences at
 3 $T = 298.15$ K, with respect to the initial adduct **P1**. In **P2**, the brace indicates delocalization. Pathway e:
 4 NO_2 taken as an example of any termination step occurring via radical coupling.

5 Similarly to what described for anthracene, starting from the peroxy radical intermediate **P5**, at
 6 -8.7 kcal mol $^{-1}$, further steps, initiated by NO , can in principle form an oxyl radical intermediate **P8** +
 7 NO_2 at -19.1 kcal mol $^{-1}$. However, we found no trace of a TS for O abstraction by NO “on the fly”.
 8 Instead, the 9-nitroso-10-peroxynitrite **P7** first forms upon radical coupling (Scheme 6, left), with a
 9 barrier of 6.0 kcal mol $^{-1}$; **P7** is located at -19.7 kcal mol $^{-1}$. Upon NO_2 loss, it would give the oxyl
 10 radical intermediate **P8**. If **P8** forms this way, further steps through a stabilized radical **P11** can finally give
 11 the closed shell dialdehyde, **P10**. **P8** could also form through the NO_3 -addition pathway shown on
 12 the right. The dialdehyde **P12**, and to a slightly lesser extent the nitroso ketone **P13**, appear to be
 13 good candidates for being major products of the NO_3 -mediated oxidation.



1

2 **Scheme 6.** Phenanthrene. Additions of NO (left, black arrows) and NO₃ (right, red arrows; red-
 3 underlined figures pertain to this pathway when double values appear). Value in parentheses do not
 4 include the Yamaguchi treatment.³ Gibbs free energy differences at T = 298.15 K, with respect to the
 5 initial adduct P1.

6 The reaction of phenanthrene with HO and NO₃ radicals was studied experimentally (Kwok et
 7 al., 1994). In that study a kinetic constant of 1.2 × 10⁻¹³ molecules⁻¹ cm³ s⁻¹ for NO₃ (1.3 × 10⁻¹¹ for HO)
 8 was determined, concluding that these reactions should dominate phenanthrene atmospheric loss
 9 processes. Their experiments were carried out in the presence of a varying initial concentration of

1 NO₂, namely 0, 4.4 x 10¹³ and 2.4 x 10¹⁴ molecules cm⁻³. A non-zero intercept in a rate plot vs NO₂,
2 concentration suggested that the phenanthrene-nitrate radical reaction must also involve a pathway
3 independent of NO₂ concentration. This pathway could actually be a set of pathways of different
4 importance, as shown in [Schemes 1, 3, 5](#).

5 The results of our present study can be compared with those from the recent theoretical study
6 on phenanthrene plus HO, O₂, and NO_x (Zhao et al., 2016). In those studies, the principal products
7 were indicated to be oxidized ring retaining products, as well as products from ring opening, namely,
8 phenantrones, phenanthrols, quinones and dialdehydes. The same research group had previously
9 investigated the reaction of the nitrate radical with 9-chloro-anthracene in the presence of O₂ and
10 NO_x (Dang et al., 2015c), and the same kind of reactions involving naphthalene too (Qu et al., 2006c).
11 They found that, following barrierless nitrate addition to the PAH π-system, the main products
12 should be: 9-chloroanthryl nitrates, diones, epoxides, and dialdehydes.

13 **4. Conclusions**

14 In this study, we have investigated the NO₃-initiated gas phase oxidative degradation of
15 anthracene and phenanthrene. A variety of reaction steps have been considered that contemplate
16 the intervention of O₂, NO, NO₂, and also NO₃ (for a second time), and also unimolecular steps. Some
17 reaction steps, considered less likely, are collected in the [Supplementary Material](#). These results
18 indicate that one NO₃-initiated pathway, which is also O₂ and NO₃-mediated, leads to the formation
19 of a dialdehyde and a nitroxy-ketone. The same kind of pathway is effective for both anthracene
20 ([Schemes 2 and 4](#)) and phenanthrene ([Scheme 6](#)). The key species is an early intermediate, a nitroxy
21 peroxy radical that forms after the initial NO₃ attack to the PAH upon dioxygen addition. It further
22 evolves to carbonyl products, through free energy barriers that are significantly lower than those
23 related to other possible intermediates or closed shell products. Some bifunctional PAH derivatives
24 can also form through couplings of the initial nitroxy radical adducts with free radicals X present in
25 the troposphere. The example of the formation of a nitroxy nitro product is shown (pathway e in
26 [Schemes 1, 3, 5](#)). HNO₃ loss from the closed shell anti nitroxy nitro intermediate could allow the
27 formation of a nitroaromatic. However, it but results very difficult in the gas phase.

28

29

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3 Composition Change, the European NeTWork of Excellence).

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

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