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

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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 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 $\pi-$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 $\beta-$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; 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_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 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

1   reaction mechanisms of NO_3-triggered oxidative degradation of anthracene and phenanthrene.

2   Therefore, we will consider how ground electronic state O_2, NO, and NO_2 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 phenantrene (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 NO_2 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 peroxyl radical (from benzene) plus NO, (Yan et al., 2013) those on benzene

21 (Qu et al., 2006a) or naphthalene (Qu et al., 2006b) plus NO_3, one on 9-chloroanthracene plus NO_3

22 (Dang et al., 2015c), and one on the role of water in the formation of nitro-PAHs (Zhang Q. et al.,

23 2014).

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-pV*TZ* (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-pV*TZ* 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

3

4   thermochemistry was assessed in all cases at T = 298.15 K and ΔG values at this temperature are

5   reported in Scheme 1 (in kcal mol^{-1}). Geometry optimization and thermochemistry calculations were

6   carried out by using the GAUSSIAN 09 system of programs (Frisch et al., 2009).
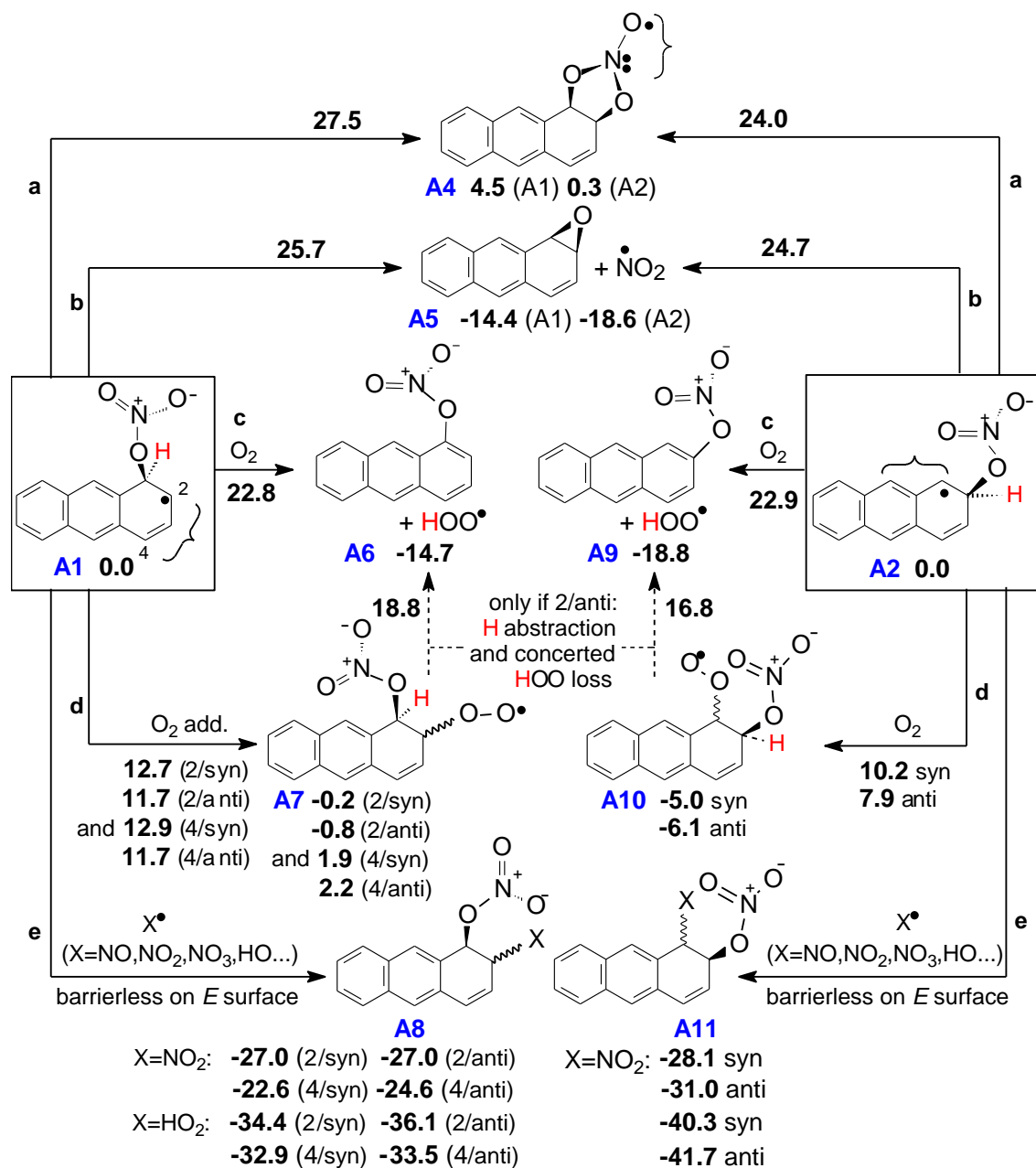
7   For singlet diradicaloid structures (such as those corresponding to homolytic dissociations), the

8   "automatic" restricted closed shell singlet solution yields zero spin densities. Therefore, the wave-

9   function stability was checked and obtained by relaxing the wavefunction in the orbital rotations

10   space. The desired spin densities, as expected for diradicaloid structures, were obtained in

11   correspondence of the attained ('singlet' unrestricted) wavefunction stability. Because the resultant

12   spin-mixing (the unrestricted wavefunction is not an eigenfunction of $\hat{S}^2$) gives a better description

13   of the electron distribution but alters the energy, the energy values were refined by Yamaguchi's

14   formula to get rid of the contribution of the closest spin contaminant of the same parity (Baker et

15   al., 1993; Goldstein et al., 1996; Wittbrodt and Schlegel, 1996; Yamaguchi et al., 1988; Yamanaka et

16   al., 1994).

3. Results and Discussion.

18   **3.1 Anthracene.** NO_3 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 peroxyl 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 (O_2

30   is the reactive species present with the highest density, close to 5 x 10^{18} molecules cm^{-3}). Also taken

31   into account are NO and NO_3 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 + NO_2) are present in the troposphere at concentrations ranging from 10^8–10^9 (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

27.5

24.0

a

A4 **4.5** (A1) **0.3** (A2)

a

25.7

24.7

b

A5 **-14.4** (A1) **-18.6** (A2)

b

A1 0.0

c
O$_2$

22.8

c
O$_2$

22.9

A2 0.0

A6 **-14.7**

A9 **-18.8**

18.8

only if 2/anti:
H abstraction
and concerted
HOO loss

16.8

d

O$_2$ add.

12.7 (2/syn)
11.7 (2/anti)
and **12.9** (4/syn)
11.7 (4/anti)

A7 **-0.2** (2/syn)
-0.8 (2/anti)
and **1.9** (4/syn)
2.2 (4/anti)

A10 **-5.0** syn
-6.1 anti

d

O$_2$

10.2 syn
7.9 anti

e

X$^\bullet$
(X=NO,NO$_2$,NO$_3$,HO...)

barrierless on E surface

A8

X=NO$_2$: **-27.0** (2/syn) **-27.0** (2/anti)
-22.6 (4/syn) **-24.6** (4/anti)

X=HO$_2$: **-34.4** (2/syn) **-36.1** (2/anti)
-32.9 (4/syn) **-33.5** (4/anti)

A11

X=NO$_2$: **-28.1** syn
-31.0 anti

-40.3 syn
-41.7 anti

e

X$^\bullet$
(X=NO,NO$_2$,NO$_3$,HO...)

barrierless on E surface

a

b

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 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).

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 O_2, or its addition to the π–system. Still another step similarly sees NO_2 addition; also other free radicals would similarly add, as NO, HO, or NO_3 itself. In more detail, (a) **A1** could undergo a 5-membered ring formation (c-CCONO) to its radical isomer **A4** with a barrier $\Delta G^\ddagger$ = 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 NO_2, and concertedly close an epoxide ring to give **A5**, with $\Delta G^\ddagger$ = 25.7 kcal mol^{-1}. This step is exoergic by ΔG = -14.4 kcal mol^{-1}. Regarding the bimolecular reactions, (c) O_2 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 $\Delta G^\ddagger$ = 22.8 kcal mol^{-1} and a G gain of 14.7 kcal mol^{-1} for the step. (d) in **A1**, O_2 could also add to the π–system, namely to the allylic positions 2 or 4. The related spin densities ($\Delta \rho$ = 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 $\Delta G^\ddagger$ = 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 NO_3 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} $molec^{-1}$ cm^3 s^{-1} have been assessed, depending on the reaction type.[1] For instance NO_2 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 HNO_3 loss from the anti nitroxy nitro **A8** intermediate (compare Ghigo et al. 2006) could produce 2-nitro anthracene, 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).

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[1] For the radical coupling *phenyl + phenyl → biphenyl*, for instance, k = 1.9 x 10^{-11} $molec^{-1}$ cm^3 s^{-1} has been assessed at T = 300 K (Park and Lin, 1997). For *methyl + phenyl → toluene*, k = 2.1 x 10^{-11} $molec^{-1}$ cm^3 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} $molec^{-1}$ cm^3 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 O_2 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 (O_2 addition to give **A7**, H abstraction

5   from the position geminal to the nitroxy group operated by $-O^{\bullet}$, 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 peroxyl 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^{-}

10   ^{1} 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 peroxyl 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 peroxyl radicals.*** By considering further different radical additions

24   to the peroxyl intermediate **A7**, as those by NO, NO_2, NO_3, or HO, one can assess if its terminal oxygen

25   can be successively abstracted in a viable way. Starting from the peroxyl 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   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.
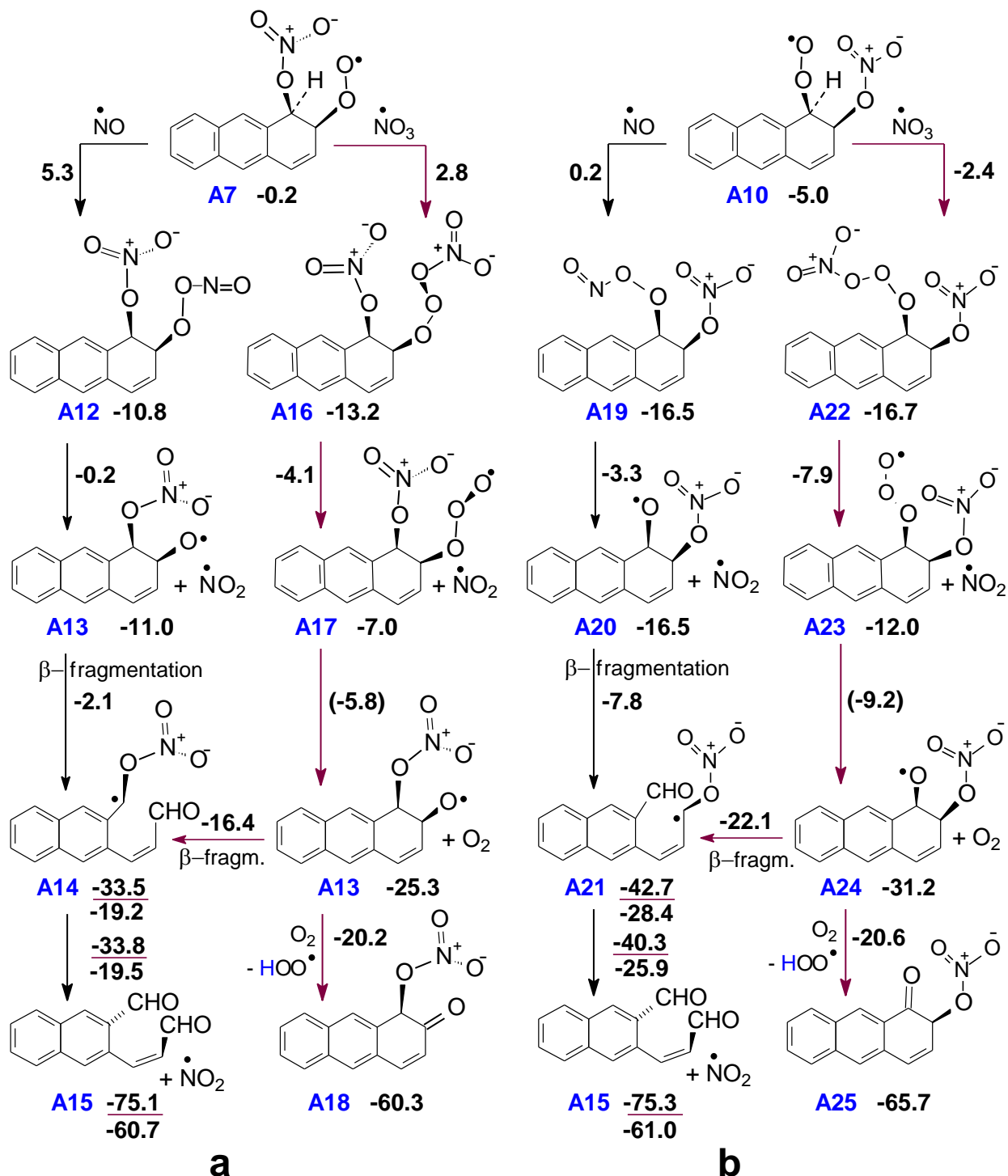
Scheme 2. Anthracene. Reaction steps of the peroxyl radicals **A7** and **A10** with NO (black arrows) and NO₃ (red arrows; red-underlined figures pertain to this pathway when double values appear). See text and Scheme 1. Value in parentheses do not include the Yamaguchi treatment.[3] Gibbs free energy differences at T =298.15 K, with respect to the initial adduct **A1**.

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[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.

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 β–fragmentation **A14**, bearing an aldehydic group. **A14** is a radical stabilized by delocalization and α–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).
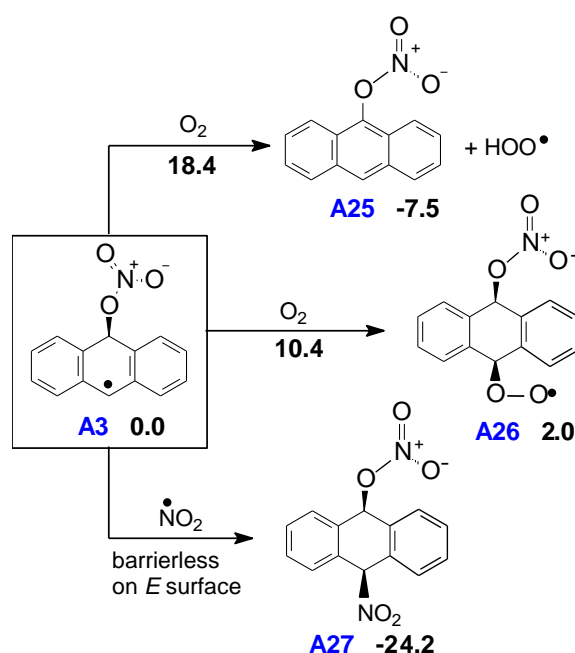
Scheme 3. Anthracene. Initial steps involving positions 9 and 10. Gibbs free energy differences at T =298.15 K, with respect to the initial adduct **A3**.

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 –O–N–O– 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 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.
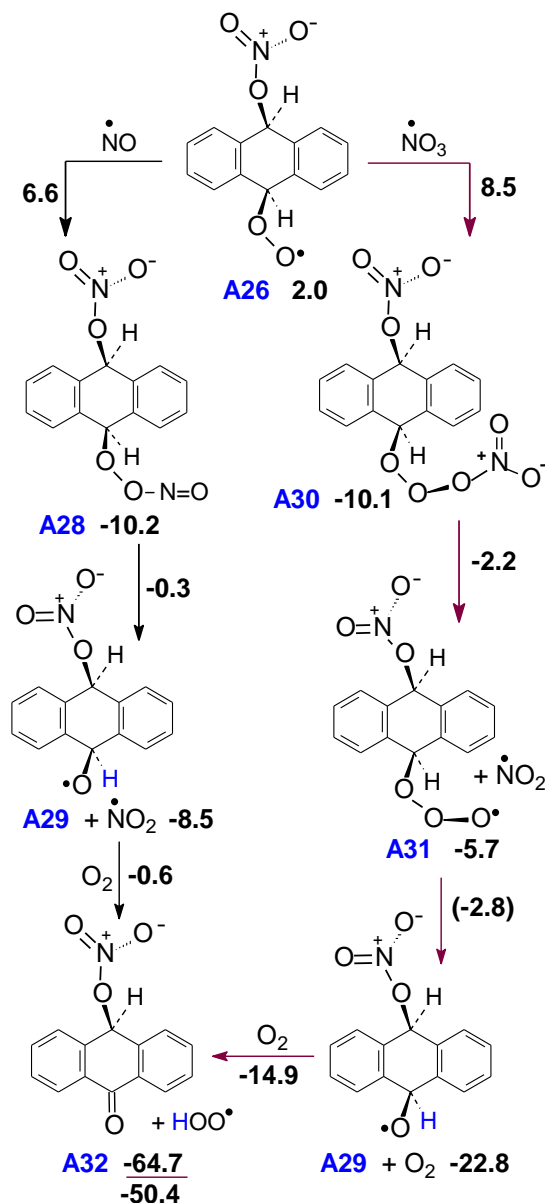

4
5
6 **Scheme 4.** Anthracene. Steps following initial O_2 addition to C10 in 9-nitroxyanthracene.
7 Additions of NO (black arrows) and NO_3 (red arrows; red-underlined figures pertain to this
8 pathway when double values appear). Value in parentheses do not include the Yamaguchi
9 treatment.[3] Gibbs 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 NO_3 addition, while the adducts **A28** and **A30** have similar stability The oxyl radical **A29** that forms

13 through further NO_2 or O_2 losses can undergo H abstraction by O_2 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.

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,[1] 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 $\Delta G^{\ddagger} = 22.8$ 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 concertedly close an epoxide ring to give **P3**, with $\Delta G^{\ddagger} = 21.8$ 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 $\Delta G^{\ddagger} = 18.6$ 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 $-O^{\bullet}$ 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.
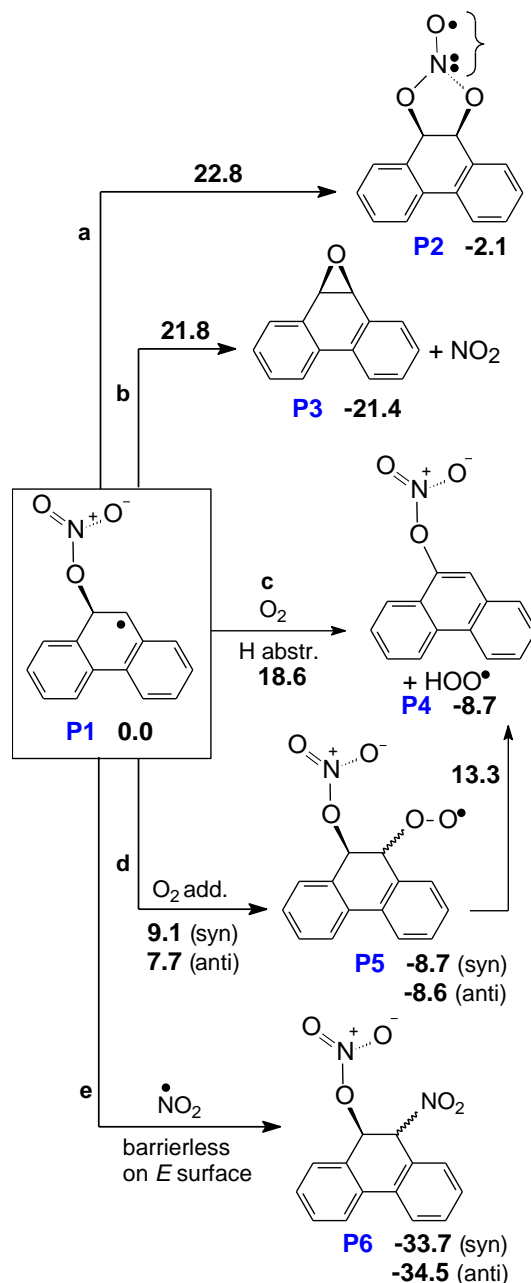
Scheme 5. Phenanthrene. Initial steps involving positions 9 and 10. Gibbs free energy differences at T = 298.15 K, with respect to the initial adduct P1. In P2, the brace indicates delocalization. Pathway e: NO$_2$ taken as an example of any termination step occurring via radical coupling.

Similarly to what described for anthracene, starting from the peroxyl radical intermediate P5, at -8.7 kcal mol^{-1}, further steps, initiated by NO, can in principle form an oxyl radical intermediate P8 + 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 P7 first forms upon radical coupling (Scheme 6, left), with a 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 intermediate P8. If P8 forms this way, further steps through a stabilized radical P11 can finally give the closed shell dialdehyde, P10. P8 could also form through the NO$_3$-addition pathway shown on the right. The dialdehyde P12, and to a slightly lesser extent the nitroxy ketone P13, appear to be good candidates for being major products of the NO$_3$-mediated oxidation.

1
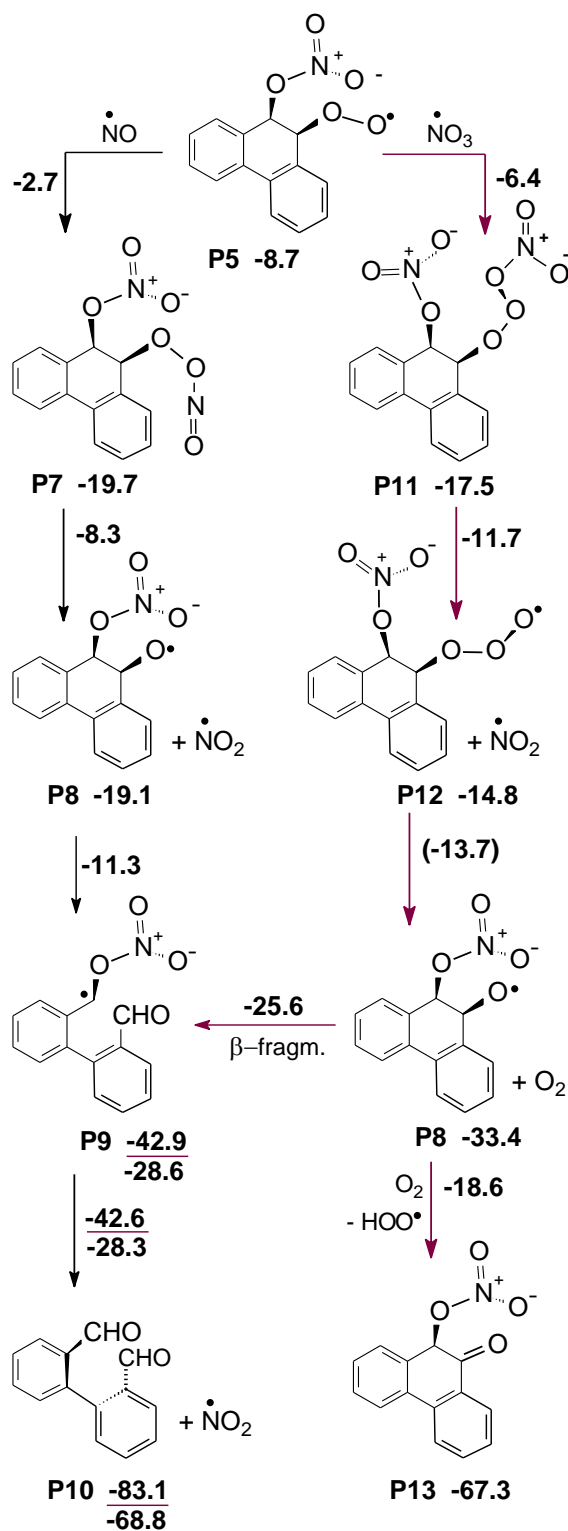
Scheme 6. Phenanthrene. Additions of NO (left, black arrows) and NO₃ (right, red arrows; red-
underlined figures pertain to this pathway when double values appear). Value in parentheses do not
include the Yamaguchi treatment.[3] Gibbs free energy differences at T =298.15 K, with respect to the
initial adduct **P1**.

The reaction of phenanthrene with HO and NO₃ radicals was studied experimentally (Kwok et

al., 1994). In that study a kinetic constant of 1.2×10^{-13} molecules^{-1} cm^3 s^{-1} for NO₃ (1.3×10^{-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

1   NO$_2$, namely 0, 4.4 x 10^{13} and 2.4 x 10^{14} molecules cm^{-3}. A non-zero intercept in a rate plot vs NO$_2$,

2   concentration suggested that the phenanthrene-nitrate radical reaction must also involve a pathway

3   independent of NO$_2$ 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, O$_2$, 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   phenanthrones, 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 O$_2$ 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 $\pi-$system, the main products

12   should be: 9-chloroanthryl nitrates, diones, epoxides, and dialdehydes.

4. Conclusions

14   In this study, we have investigated the NO$_3$-initiated gas phase oxidative degradation of

15   anthracene and phenanthrene. A variety of reaction steps have been considered that contemplate

16   the intervention of O$_2$, NO, NO$_2$, and also NO$_3$ (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 NO$_3$-initiated pathway, which is also O$_2$ and NO$_3$-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   peroxyl radical that forms after the initial NO$_3$ 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). HNO$_3$ 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

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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.

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