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# Tropospheric oxidative degradation of anthracene with $NO_3$. Theoretical Study.

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## 1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous and toxic[1] environmental pollutants present in atmosphere. They are emitted into the atmosphere during incomplete combustion of fossil fuels[2] and biomass. Under typical atmospheric conditions, anthracene is partitioned between gas and particle phases [Figures 10.2 and 10.3 in ref. 3] for which oxidative degradation can present mechanistic differences. The reaction with $NO_3$ might dominate the loss pathway during night-time. However, current knowledge of the $NO_3$-initiated atmospheric oxidation of naphthalene is still limited[4]. The reactivity of PAHs in the gas phase is significantly greater than when associated with carbonaceous particles [**Errore. Il segnalibro non è definito.**], suggesting that the particle surface may have an inhibiting effect on the heterogeneous reaction. However, the reaction of PAHs with ozone adsorbed on graphite particles is 2 orders of magnitude faster than the corresponding gas phase reactions [5].

With this theoretical study we explore the reaction mechanisms of anthracene with $NO_3$, in the gas and particle phases (in this study a soot platelet is modelled by a larger $C_{60}H_{20}$ PAH) in order to explain possible differences in terms of mechanism and kinetics.

## 2. Results

The geometries of the reactants, transition structures, intermediates, and products have been optimized at the M06-2X level with the 6-31G(d,p) basis set. Single-point energies of various species were calculated at the M06-2X/cc-pVTZ level.

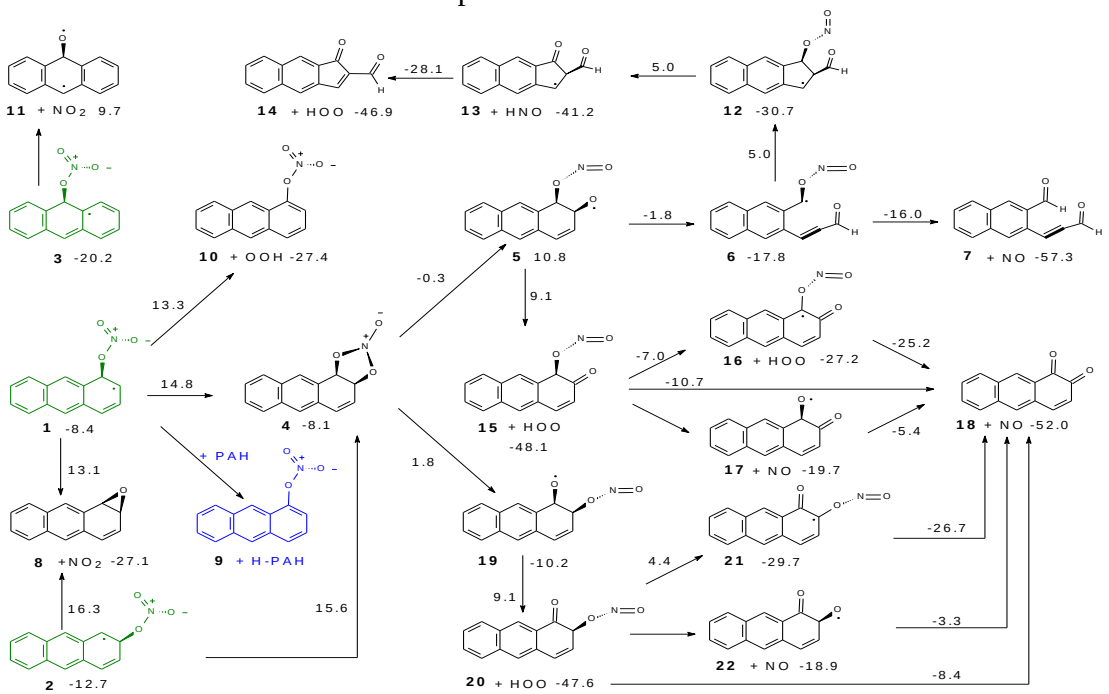


**Fig. 1** – *Reaction mechanism in the gas phase*

$NO_3$ adds to anthracene without any barrier on the potential energy surface to form three anthracenyl nitrate radicals (**1**, **2** and **3** in Figure 1). We focused our attention on the intermediate **1**. Several competitive reactions could occur from **1**: a) it could lose $NO_2$ and concertedly close the epoxide ring **8**. b) Hydrogen is abstracted by $O_2$ and form the anthracen-1-yl nitrate **10** (Figure 2a). c) 5-membered ring **4** formation, d) in the particle phase, also hydrogen abstraction operated by the $C_{60}H_{20}$ substrate can be conceivable (**1-9**), shown in Figure 2b. In the gas phase, the first three reactions have similar free energy barriers: $\Delta G^{\ddagger}$= 13.1, 13.3, and 14.8 kcal mol$^{-1}$, respectively.

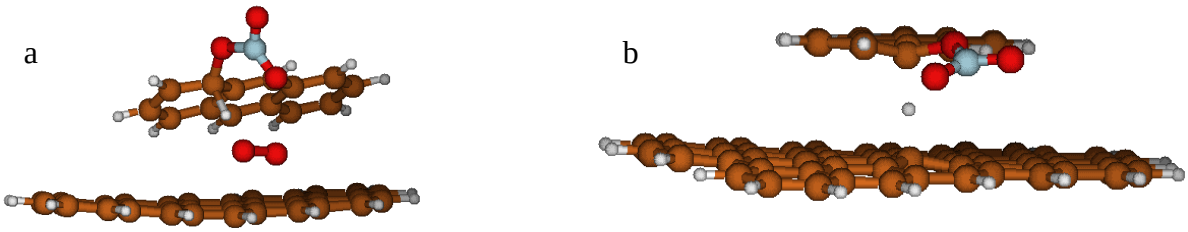


**Fig. 2** – a) *Hydrogen abstraction by $O_2$.* b) *H-transfer to the soot platelet.*

From the intermediate **4**, two N–O cleavages (**4-5** and **4-19**) open the way to other reactions. The pathway characterized by the lowest barriers implies a C–C bond cleavage (**5-6**) followed by NO loss to form the very stable dialdehyde **7** (-57.3 kcal mol$^{-1}$). Other reactions to form ketone **18** or aldehyde **14** present higher free energy barriers and they can hardly compete. They represent only minor pathways.
When anthracene is adsorbed on a soot platelet, reactivity seems to drop. This part of the study is still underway.

## 3. Conclusions.

In the gas phase the most probable products are the epoxide **8**, the aromatic nitrate **10** (or analogous isomers from **2** and **3**), and the dialdehyde **7**.
After completing this study we will be able to compare the reactivity of $NO_3$ in the gas phase and in the particle phase, and to rationalize the possible differences in the reaction mechanisms.
Future developments could include the study of different tropospheric temperatures, and the comparison of our results with similar reactions operated by $O_3$.

## References

[1] I. J. Keyte, R. M. Harrisonz, G. Lammel: "Chemical reactivity and long-range transport potential of polycyclic aromatic hydrocarbons – a review", Chem. Soc. Rev., 42, 9333-9391, 2013.
[2] L.H. Lim, R.M. Harrison, S. Harrad: "The Contribution of Traffic to Atmospheric Concentrations of Polycyclic Aromatic Hydrocarbons", Env. Sci. Tech. 33, 3538-3542, 1999.
[3] B. J. Finlayson-Pitts, J. N., Jr. Pitts: "Chemistry of the Upper and Lower Atmosphere: Theory, Experiments, and Applications", Academic Press, 1999.
[4] J. Sasaki, S.M. Aschann, E.S.C. Kwok, R. Atkinson, J. Arey: "Products of the gas-phase OH and 3 radical-initiated reactions of naphthalene.", Environ. Sci. Technol. 31, 3173-3179, 1997.
[5] E. Perraudin, H. Budzinski, E. Villenave: "Kinetic study of the reactions of ozone with polycyclic aromatic hydrocarbons adsorbed on atmospheric model particles", J. Atm. Chem., 56, 57-82, 2007.