Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2020-684-RC1, 2020

Atmospheric Chemistry and Physics
Discussions
Open Access

Interactive comment on “On the importance of atmospheric loss of organic nitrates by aqueous-phase ·OH-oxidation” *by* Juan Miguel González-Sánchez et al.

Anonymous Referee #1

Received and published: 23 November 2020

This manuscript prepared by Gonzalez-Sanchez represents a full-bodied investigation into the aqueous-phase reactivities of organic nitrates of atmospheric relevance. The manuscript contains a few parts: 1) experimental determination of the OH rate coefficients of eight organic nitrates 2) extension to an existing structure-activity relationship (SAR) to incorporate ethers and nitrate, and 3) estimation of the OH reactivity of 49 organic nitrates based on their new SAR and discussions on their atmospheric fate. Multiple valuable results were obtained from this study, with a major one being that the -ONO2 group exhibits a significant suppression effect on OH reactivities in the aqueous phase, to a more extent than in the gas-phase. Thus, aqueous-phase OH oxidation can lead to a longer OH oxidation lifetime for some of the organic nitrates. With emissions

Printer-friendly version

Discussion paper

of NOx (e.g., from cars) constantly reduced in many parts of the world, the formation of organic nitrates is becoming more important in the atmosphere. Organic nitrates may represent a reservoir of NOx, and their atmospheric lifetimes need a careful assessment. A reliable SAR is highly valuable for the atmospheric chemistry community, given that experimental investigation for all the species is infeasible. The topic of this work is highly important, timely, and within the scope of ACP. I strongly recommend publication in ACP after the following points are addressed:

Major comment

My only major comment is regarding the ability of the SAR to be extrapolated to a wider spectrum of compounds. The linear relationship shown in Fig 6 is between the SAR-simulated values and the experimental values from which the SAR was derived; correct? For other empirically-derived relationships, such as free energy linear relationships (LFERs), it is important to derive the relationship with a training set, followed by validation using an experimental set. With the limited number of organic nitrates, this may be challenging. What about ethers? Either way, the authors should comment on the reliability of the SAR when used for other compounds.

Minor comments

- Can any of the secondary organic nitrates used in the experiment undergo hydrolysis within the time scale of the experiment? Maybe this is confirmed with the H2O2 control experiment?

- My understanding is that Figure 7 represents the phase partitioning of these species in equilibrium. Two minor questions:

Is partitioning equilibrium achieved in the atmosphere? Maybe yes for cloudwater, how about aerosol liquid water (e.g., viscosity)

Can some of the organic nitrate be surface active and partition to the air-water interface?

- Line 466, how did the authors consider the reactivities of carboxylic acid and carboxylate? Is this parameterized in the previous version of SAR?

Technical Comments

- Line 283, the sentence, “indicating a likely solvent kinetic effect which lowers more effectively the reaction.” is awkward. Maybe consider rephrasing to “implying a solvent kinetic effect that can more effectively suppress the reactivity”?

- In a few places “prior” should be “prior to” E.g., “Prior to each experiment.” Check lines 114, 154, 161, 193

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2020-684, 2020.

Printer-friendly version

Discussion paper