

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

Anonymous Referee #2

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The manuscript describes a new relative rate approach to measure aqueous kinetics and its application to determine rate constants for hydroxyl radical (OH) with a series of organic nitrates. The new approach is clever and takes advantage of the fact that first-order kinetics do not require knowledge of absolute concentrations of analytes, only the relative concentrations. The method is also clever in that it can couple a gas-phase reference measurement in conjunction with an aqueous-phase target measurement for compounds that have low vapor pressures. The resulting rate constants for organic nitrates are useful, as is the new structure-activity relationship (SAR) that was constructed. Finally, the paper also examines the environmental relevance of the kinetic data, which is a helpful scaling-up of the results. While I have a number of issues that

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need to be addressed, overall, I am supportive of the manuscript.

»Major points«

The manuscript text is overall fine, but would be strengthened if unnecessary portions were removed (e.g., the discussion of the “direct method” to determine rate constants on lines 60 - 63), repetition was eliminated (e.g., lines 291-292 repeat lines 286-288), and the text was edited for issues such as noun-verb agreement (e.g., “Measurements were performed. . .” on line 178). In addition, using parentheses to try to put the opposite case inside of a sentence makes for difficult reading, e.g., line 516: “For molecules which partition to the aqueous-phase, a positive (respectively negative) value of $\ln(k_{aq}/k_{atm})$ indicates that the aqueous-phase reactivity increases (respectively decreases) the atmospheric loss of the molecule.” This should be revised.

There are some issues with pH. First, the solution is listed as “pH < 3” (line 109), but the value should be closer to pH 2 since solutions contained 5 mM H₂SO₄ (line 764). This should be clarified. Second, I appreciate that an acidic solution is needed to keep Fe dissolved, but pH 2 is not relevant for most atmospheric waters, which are much less acidic. The low pH values used in the experiments are a bit concerning since past work has shown that the OH rate constant is sometimes pH dependent for classes of compounds that do not have a change in acid-base speciation across the pH range (e.g., Kroflic et al., PCCP, DOI: 10.1039/c9cp05533a). Third, the SAR lumps the current rate constants with 32 literature values without any tabulation or discussion of the pH values for the literature results. It’s likely they were not done at pH 2, so it’s not clear they can be considered along with the organic nitrates studied in this work. This should be examined and discussed.

The 2-ethylhexyl nitrate kinetic data looks suspicious (Figure 4) and produce a rate constant that is lower than expected and not included in the SAR (line 345). The authors (line 278) suggest that the experiments might have suffered from solubility issues,

but they don't test this. As it currently stands, this compound is thus in publication purgatory: the data is reported in the manuscript, but is not trusted. The authors need to take a stand on the compound, either (1) eliminate it entirely from the manuscript or (2) do additional experiments (e.g., at a lower concentration) to try to get good data.

The calculation and discussion of the lifetimes of the organic nitrates should be improved. (a) Fates other than OH (gas and aqueous) need to be better described. There is little discussion of hydrolysis, mostly just three lines about the rapid hydrolysis of compounds with the nitrate group on a tertiary carbon (lines 506-510). But don't other nitrates also have significant hydrolysis rate constants? This should be described and quantified. In addition, isn't photolysis (in both phases) a significant sink for some of the nitrates with an aldehyde or ketone group? This should be discussed, especially in terms of how these other fates would alter the lifetimes that are presented. (b) The aqueous (and thus multiphase) lifetimes depend on the aqueous OH concentrations. The aqueous [OH] used in the manuscript ($1\text{E}-14\text{ M}$) is from a numerical model and is approximately 2 – 10 times higher than measurements. For example, Kaur et al. (2018) report aqueous [OH] of approximately $5\text{E}-15\text{ M}$ in cloud drops and an extrapolated $1\text{E}-15\text{ M}$ in particle water. These model-measured differences, and their impact on calculated multiphase lifetimes, should be discussed. (c) On first read, Figure 8 suggests that compounds with high W values (i.e., where most oxidation occurs in the aqueous phase) will have shorter lifetimes because of this aqueous sink. But this is not the case - for many of the compounds there is very little difference between gas-phase lifetime and multiphase (i.e., gas and PM) lifetime, as discussed only later with Figure 9. It would be helpful to incorporate the lifetimes into Figure 8, e.g., as symbol color or size, to more clearly show this. Showing the lifetimes in a figure would be very helpful, as this information is currently buried in Supplemental Table S5.

»Other points«

Line 39. Hydrolysis to form nitrate is also an important sink for some nitrates, especially some isoprene-derived organic nitrates. Photolysis should be mentioned also.

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I. 79. The absolute uncertainty on the $k(\text{OH}+\text{SCN}^-)$ rate constant might be larger than the target rate constant, but this doesn't matter: it is the relative – not absolute – uncertainty (i.e., 0.20/1.12) that is propagated in the relative rate calculation to determine the uncertainty on the target compound.

I. 125. To avoid any confusion that $k(\text{OH},\text{X})$ is a pseudo-first order rate constant for loss of X, the authors should explicitly state that this is the second-order rate constant and give the units ($\text{M}^{-1} \text{s}^{-1}$).

I. 135. The method works as long as the reference and target compounds are in Henry's law equilibrium in the reaction flask. For highly reactive compounds this condition might break down. Based on an estimated characteristic time for aqueous mixing in the flask, is there an upper limit to the rate constants that can be determined under their [OH] conditions?

I. 243. Where is the "...previous calculation of the quantity of OH radicals..." that is referenced here?

Section 3.2 Indicate how uncertainties were determined. Were they based on the standard deviation between replicates propagated with the uncertainty in the MeOH rate constant?

I. 429 (and throughout). Typically, the liquid water content abbreviation "LWC" has no subscripted portion.

I. 461. The gas-phase units are shown here but not described until later. Since they're not standard, clarify here that $[\text{OH}](\text{gas})$ is in $\text{mol-OH} / \text{L-air}$ and that the same volume unit is used for gas-phase rate constants.

I. 471. Both values of what?

Table 2. Include the number of experiments for each compound in the table. Also indicate in the table that uncertainties are 95% CI.

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Figure 5 is a helpful comparison of data across compounds and phases.

Figure 8. Put the symbol for the isoprene-derived nitrates in the figure legend (along with the rest of the classes) rather than as a sentence in the caption.

Figure 9. Include another panel that shows the analogous results for the cloud LWC condition.

The SI does not have a list of references.

Table S5 includes the multiphase lifetime for the particle LWC condition, but not for the cloud LWC condition. The latter should be included.

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