

Interactive comment on “Photochemical Degradation of Isoprene-derived 4,1-Carbonyl Nitrate” by F. Xiong et al.

Anonymous Referee #2

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The manuscript, "Photochemical degradation of isoprene-derived 4,1-carbonyl nitrate" by Xiong et al. reports on the photolysis rate of the trans-4-1 carbonyl nitrate derived in the atmosphere from the NO₃ radical oxidation of isoprene. The manuscript is well written and describes a great deal of well-thought-out work. The main implication of this work is that this conformer of isoprene carbonyl nitrate will have a short lifetime in the atmosphere due mainly to photolysis, with non-negligible contribution from OH oxidation. The work also identifies some of the major byproducts of OH oxidation and photolysis of this compound, thereby improving our understanding of isoprene photochemistry. The work should be published in ACP with a few minor clarifications.

Minor questions/comments/suggestions: I disagree with the "double" and "single" exponential discussion (lines 175-178). That a double exponential will be observed if large amounts of cis is present is unconvincing without additional information and likely

C1

cannot be concluded without knowing the isomerization rate. What is the chamber residence time? A cis-trans equilibrium at some point will be reached. If the rate at which this occurs is instantaneous (or at least much faster than residence time), a single exponential will always be observed because the CIMS only ever sees a mixture of the two isomers. Would you expect a significant difference in the photolysis rate of cis versus trans? If not, does it matter which isomer you are measuring? All that matters for this part of the experiment is the decay rate. If photo lifetime of cis versus trans is very different, you would have to qualify that the 1.3e-5 sec⁻¹ rate is some average of the two isomers.

It would be helpful to know which compounds whose structures are drawn in figures 10 and 15, as well as those boxed in figures 11 and 12 are observed by both GC and CIMS. The CIMS captures signal at nominal masses, therefore, to infer not only molecular composition (C_xH_yO_z) but molecular structure (i.e. identifying functional groups) would impart a certain amount of uncertainty. If only the CIMS without GC is used to infer a compound identity (such as dinitrates which I imagine do not survive GC column), this is worth clarifying. Also, how well can you distinguish MVK nitrate from MACR nitrate with GC /CIMS?

Given CIMS observations of boxed compounds in figures 12 and 16, can you infer branching ratios of OH oxidation paths (a versus b in figure 12) and the two photolysis paths (figure 16).

How were the spectra in figure 3 obtained? Are they of three different samples, one containing pure carbonyl nitrate in solvent, the second pure MACR, and the third pure isopropyl nitrate? If the spectra are of one mixture containing all three compounds, how were the spectra distinguished or attributed to a particular compound? Is each a simulated or calculated spectrum from the observed (the sum of the three spectra shown in figure 3). This needs to be better explained, in particular, for the discussion on lines 142 to 165. This discussion tries to establish that the excitation features of carbonyl nitrate is well understood, that the one near 255 nm is from the nitrate group

C2

and the one near 330 nm is from the aldehyde group. However, there are some aspects of this discussion that are difficult to follow, hence, the argument is not as convincing as can be.

For instance, figure 3 shows isopropyl nitrate along with MACR and carbonyl nitrate, whereas figure 4 shows n-butyl nitrate. Explain why the combination of these 3 compounds was chosen for this part of the study...similarity in structure, overlapping functional groups, etc. Figure 4 and 5 involve calculations...why not include isopropyl nitrate as well? It would make comparison simpler and argument more convincing.

Figure 4 is described as an absorption spectrum. But it looks very different from figure 3. Figure 4 looks more like band strength or absorption lines. Is it possible to simulate actual absorption spectra (one for MACR, one for carbonyl nitrate, one for n-butyl nitrate) given data shown in figure 4 under conditions similar to those in figure 3 and compare that result to figure 3? Would provide stronger support to TDDFT calculation.

Lines 142-144, reads as if authors are saying there is a transition for n-butyl nitrate near 330 nm when there is not. Please re-word. Lines 148-149..."...Earth's surface..." what is the significance of this statement?

Figure 5 and lines 159-165. What is the relevance of including the excitation feature near 210 nm (figure 4) when there is no experimental data (figure 3) to compare against. This spectral region is also "beyond atmospheric relevance" as authors note.

Figure 1. Is the reaction between the NO₃ radical and nitroxy peroxy radical the only route to the alkoxy radical, hence carbonyl nitrate? Isn't reaction with RO₂ more likely than NO₃ to generate the alkoxy given abundance of RO₂ in most BVOC rich region? At the very least, RO₂ should be included. Rollins et al 2009 ACP (www.atmos-chem-phys.net/9/6685/2009/).

Application to field observation was demonstrated in figure 9. Out of curiosity, is there direct observation of isoprene carbonyl nitrate from the field using CIMS+GC? Spec-

C3

trum or chromatogram or time series or diel average? How abundant is isoprene carbonyl nitrate considering it is produced at night when loss rate is presumably slow? How well can the CIMS distinguish C₅H₇NO₄ from potential interference due to the isotope of the signal at m/z 271. Do you have carbonyl nitrate + NO₃ oxidation results, similar to those of OH and photolysis shown here? These would be nice additions to this work, but perhaps saving for separate manuscript.

Figure 4. Many have a difficult time distinguishing red from blue. May help to choose different color scheme. Also, are vertical lines necessary to show this data? The three lines at 210 nm are difficult to distinguish from one another. Perhaps use markers instead? Also, change "1 × 10^{exponent}" to just "10^{exponent}"

The wall loss rate constant is fairly high compared to the photolysis rate constant. What is the residence time in the 5.2 m long tubing? Is laminar flow maintained? Also, curious if heating the inlet to 50 degC can induce cis-trans isomerization.

Line 235. Why is there no gas phase spectrum? Is it technically challenging? If so, it would be helpful for community to know.

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C4