

Review of 'The Production and Hydrolysis of Organic Nitrates from OH Radical Oxidation of  $\beta$ -Ocimene', by A. C. Morales and T. Jayarathne et al.

### Overview:

This paper presents a detailed and well described laboratory study of the OH radical-initiated oxidation of  $\beta$ -ocimene, an atmospherically significant species, in the presence of NO. This study investigates the formation of organic nitrates, the impact of  $\beta$ -ocimene on secondary organic aerosol (SOA) yields, and the subsequent hydrolysis rate constants for the organic nitrate products in solutions of differing pH. The experimental methodology is well thought through and clearly presented.

The authors build upon a previous study of  $\alpha$ -pinene (Rindelaub et al., 2015), experimental work presented by the same research group as here and compare the results of this study to their previous study on the  $\alpha$ -pinene system.

Overall the manuscript is very well written, with experimental work described to a good level of detail. The script can be slightly repetitive at times, but the scientific message is clearly conveyed to the reader. The significance of this detailed work could be further highlighted by the authors, by emphasising the implications of the described chemistry in terms of human health.

### General Comments:

The authors should take care in maintaining consistency in the text, for example always using "OH" over " $\bullet$ OH", and " $\alpha$ -pinene" over "alpha-pinene", " $\beta$ -ocimene" rather than just "ocimene". More detailed comments on text inconsistencies are given in the detailed comments section below.

The methods section would benefit from a little more discussion on how product loss to the chamber walls was accounted for. Would you expect any chemical reactions to occur at the wall? How do you account for losses to the chamber wall / dilution? Do you use an inert tracer species to examine loss effects?

Though their previous study on nitrate formation from  $\alpha$ -pinene + OH (Rindelaub et al., 2015) provides a useful comparison, sometimes the authors rely too heavily on referencing this study, and could expand more on their findings within this paper, without asking the reader to refer to their previous work.

The figure captions could provide more detail.

### Detailed Comments:

Abstract, lines 30-31: Inconsistent spacing after 'pH', "pH=4, and 24( $\pm$ 3) min at pH = 2.5"

Introduction, line 48: What is a 'criteria air pollutant'?

Introduction, line 48: This is a little unclear as BVOCs don't actually react with NO<sub>x</sub>. Maybe something like, "BVOCs participate in chemical reactions with the atmospheric oxidants OH, NO<sub>3</sub> and O<sub>3</sub>, which leads..."

Introduction, line 54: affects

Introduction, line 54: delete full-stop after 'quality'

Introduction, line 71: change "ozone" to " $O_3$ " for consistency with previous text

Methods, line 99: What is the uncertainty on the approximate experimental temperature quoted?

Methods, line 110: Replace "5 Imp" with " $5\text{ Lmin}^{-1}$ "

Methods, line 146: How did you account for the product loss to the chamber walls? And how did you account for species dilution from the chamber? Did you use an inert tracer?

Results and Discussion, 3.1, several lines: Replace "Fig" with "Figure" for consistency

Results and Discussion, 3.1, line 220: Can this sentence be re-written as... In this study we did this... (Rindelaub et al., 2015).

Results and Discussion, 3.1, line 226: '...summary of a range of previous observations...'

Results and Discussion, 3.1, line 249: "...yield, likely..."

Results and Discussion, 3.1, line 258: Replace "compound A" with "Compound A" for consistency

Results and Discussion, 3.2, lines 271: Is there a reference for this value from a 'moderately polluted forested environment'?

Results and Discussion, 3.2, lines 274 and 277: Replace " $\alpha$ -carbon-carbon" with " $\alpha$ -C-C" to maintain consistency with line 244

Results and Discussion, 3.2, lines 276: No need for 'e.g.' here

Results and Discussion, 3.2, lines 280/281: '...less but similar...', this doesn't convey useful information, can this be quantified?

Results and Discussion, 3.2, lines 289: No need for comma after 'humidities'

Results and Discussion, 3.3, lines 327 and 332: Replace " $pH=4$ " with " $pH = 4$ " for consistency

Results and Discussion, 3.3, line 328: Replace " $pH=1$ " with " $pH = 1$ " for consistency

Results and Discussion, 3.3, line 336: What does 'forest-impact environments' mean?

Atmospheric Implications and Conclusions, line 360: Remove "from"

Atmospheric Implications and Conclusions, line 361: Replace "as the nitrate ion" with "as a nitrate ion"

Atmospheric Implications and Conclusions, line 369: Define "UMBS"

Atmospheric Implications and Conclusions, line 386: "These results suggest that ocimene hydroxy organic nitrates may be an important sink for gas phase NO<sub>x</sub> in forest environments." seems out of place in the 'future work' paragraph of the conclusions. Perhaps start the paragraph with this before going into further detail on how future work could expand on your findings.

Acknowledgement, line 393: "We acknowledge Dr. Hartmut Hedderich of the (Jonathan Amy Facility for Chemical Instrumentation, Purdue University)" missing abbreviation, or remove brackets.

## **Figures and Tables:**

Figure 2: The alkoxy radical in row 2 comes from reaction of the peroxy radical in row 1 with NO (not reaction of the alkyl radical with NO as currently shown)

Figure 2: It is not clear what reaction pathways the two arrows pointing from **(A)** are supposed to represent. Is the top pathway supposed to be:

- I) OH addition at C1 (as for the bottom pathway), followed by NO reaction with the peroxy radical formed forming the alkoxy radical which then forms a carbonyl?

or

- II) OH addition at C2, followed by NO reaction with the peroxy radical formed and scission of the C1-C2 bond?

Either way I think that the product formed should have one less carbon (i.e. the C1 carbon is lost and the carbonyl is on the C2 carbon).

Figure 4: Rename x axis from “#C” to “Carbon number”, for clarity

Figure 6: As for Figure 2, the alkoxy radical should come from  $\text{RO}_2 + \text{NO}$ , not  $\text{R} + \text{NO}$

Figure 9: In figure caption, replace “ocimene” with “ $\beta$ -ocimene” and “alpha-pinene” with “ $\alpha$ -pinene” for consistency