

Review of “Competing multiple oxidation pathways shape atmospheric limonene-derived organonitrates simulated with updated explicit chemical mechanisms” by Guo et al.

General Comments

This manuscript addresses a critical gap in atmospheric chemistry modeling by developing and implementing an explicit chemical mechanism for limonene-derived organonitrates (ON) in both box and global models. The incorporation of 90 gas-phase reactions and 39 intermediates represents a substantial advance over simplified schemes, and the sensitivity experiments vividly illustrate nonlinear interactions among OH, O₃, and NO₃ oxidation pathways. The explicit chemical mechanisms developed here significantly advance the field and offer a robust framework for future studies on secondary organic aerosols. The work is timely, given the increasing recognition of ON’s role in secondary organic aerosol formation. I support publication after minor revisions to improve clarity in following comments.

Specific Comments

1. The introduction effectively contextualizes the importance of ON in SOA and the gaps in current understanding. However, the transition from general SOA/ON to limonene-specific mechanisms could be smoother. Consider briefly mentioning the structural uniqueness of limonene earlier (e.g., around Line 59) to better justify its selection as the focus of this study.
2. Lines 73-80: The discussion of model limitations is useful, but it would be helpful to explicitly state how this study addresses these limitations (e.g., by incorporating explicit mechanisms). This could be clarified further.
3. Lines 118: The vapor pressure estimation methods are well-explained, but a brief discussion on the potential uncertainties or limitations of these methods (e.g., sensitivity to molecular structure) would strengthen this section.
4. Lines 147-149: The global model setup is clearly described, but it would be helpful to briefly justify the choice of CESM/IMPACT over other models, especially given the focus on explicit mechanisms.
5. The decrease in ON production at high NO₃ concentrations (Line 185) is attributed to the dominance of the LIMAL + NO₃ pathway (yield: 9.2%). The abrupt transition in Figure 2c (from increase to decrease) warrants a brief discussion of the timescales involved. Is this a kinetic effect (e.g., NO₃ outcompeting other pathways) or a thermodynamic limitation?
6. Figure 2: The trends in ON production under different oxidant concentrations are clearly presented. However, the discussion of the NO₃-initiated pathway (Lines 183-191) could benefit from a more explicit comparison to the OH- and O₃-initiated pathways to highlight the mechanistic differences.
7. Figure 2: The y-axis label should specify whether ON concentrations are gas-phase, particle-

phase, or total?

8. The explanation for low ON burdens in the Amazon (despite high limonene) due to oxidant competition with isoprene (Lines 298-305) is plausible but speculative without quantification. Consider adding a sentence referencing modeled oxidant budgets or prior studies showing isoprene's oxidant sink role

9. The 44.7% increase in ON burden from adding OH (Line 330) contrasts sharply with the box model's lower OH-initiated yield (2.1%, Line 195). This discrepancy should be explicitly addressed: Is it driven by regional OH abundance (e.g., tropical OH hotspots) or nonlinear interactions in the global model?

10. Lines 341-345: The nonlinear responses to multiple pathways are well-explained, but a brief mention of how these findings align with or diverge from prior laboratory or modeling studies would provide broader context.

11. Lines 364-365: A specific example of a missing mechanism or future experimental validation could make this more concrete. Are there missing pathways (e.g., heterogeneous NO_3 reactions) that could alter conclusions?

12. The implications for policy or air quality management could be expanded slightly, given the anthropogenic-biogenic interaction focus.

Technical Corrections

1. Line 47: "evaded" should likely be "avoided".
2. Line 104: "limonaldehyde" → "limononaldehyde" (consistency with MCM).
3. Line 132: " $1.0 \times 10^{11} \text{ molecules} \cdot \text{cm}^{-3}$ " seems high for limonene; consider clarifying if this is a typo or based on specific experimental conditions.
4. Line 224: "phenomena" should be "phenomenon".