

RE: A point-to-point response to the reviewer's comments

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Title: "Formation of Chlorinated Organic Compounds from Cl Atom-Initiated Reactions of Aromatics and Their Detection in Suburban Shanghai"

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Dear editor,

We appreciate reviewers' thorough evaluation and valuable comments, which have been taken into account when improving our manuscript. In the following response, we have addressed Reviewer #2's comments in detail. Key updates include the addition of time series plots for a broader range of Cl-OOMs, as well as modifications to specific reaction mechanisms as suggested by Reviewer #2.

The reviewers' comments are repeated in *italics* while the responses are in normal fonts.

We are looking forward to your decision at your earliest convenience.

Sincerely,

Lei Yao

Lin Wang

Reviewer #2:

Q0. I believe the authors have responded adequately to the initial comments from the first two reviewers. I also appreciate the authors' decision to conduct additional flow tube experiments using CO as an OH radical scavenger, which I believe is an effective way to isolate Cl and OH initiated chemistry within the system. However, looking through the authors' new Figure R1 and Scheme R2, I have some lingering questions about the underlying chemistry that I would like to have answered before recommending publication.

Response: We appreciate Reviewer #2's positive feedback.

Comments:

Q1: Can the authors show an alternate version of Figure R1 (either just for review or for the SI) that contains a larger number of the Cl-OOMs? I'm curious whether a larger subset of the Cl-OOMs identified in the paper have behavior similar to that of C₈H₁₁ClO₂ and don't show dependence towards OH reaction or more similar to that of C₈H₁₁ClO₄, which did show dependence towards OH reaction.

Response: We appreciate the reviewer's helpful suggestion. In response, we have added an updated Figure R1 to incorporate a broader range of Cl-OOMs (i.e., C₈H₁₁ClO₂₋₇ and C₈H₁₃ClO₅₋₈).

As shown in the updated Figure R1, most Cl-OOMs (specifically C₈H₁₁ClO₃₋₇ and C₈H₁₃ClO₅₋₈) exhibit a significant decrease in signal intensity upon the addition of CO, indicating that their formation is influenced by the OH reaction. In contrast, C₈H₁₁ClO₂—a first-generation product derived directly from Cl-initiated oxidation—remains largely unaffected by OH suppression. This distinction highlights the differential roles of Cl and OH radicals in the formation of these species, with the majority of the expanded Cl-OOMs showing behavior more similar to that of C₈H₁₁ClO₄, which did exhibit dependence towards OH reaction.

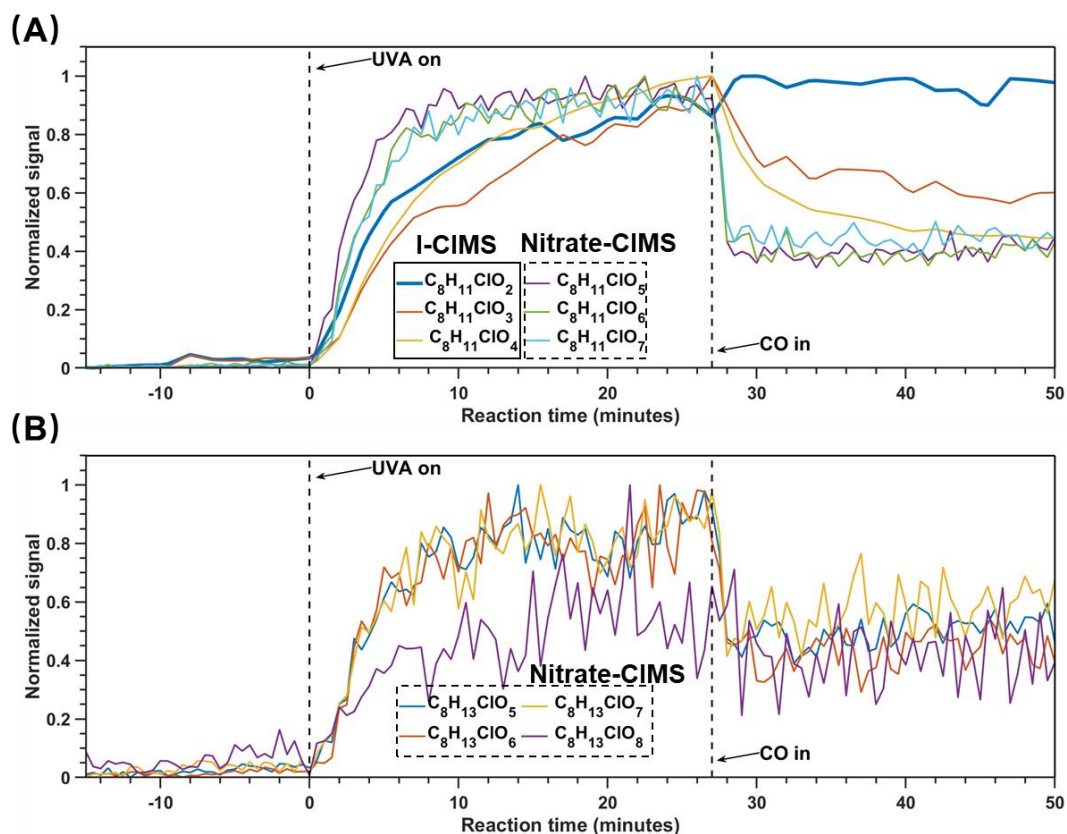


Figure R1. Time-resolved signal intensities of Cl-OOMs products (panel A: $C_8H_{11}ClO_{2-7}$; panel B: $C_8H_{13}ClO_{5-8}$) from the Cl + m-xylene reaction in the absence of NO_x . In the legend, the Cl-OOMs enclosed by solid lines are measured by I-CIMS, while those by dashed lines are measured by nitrate-CIMS.

Q2: The Cl-OOM shown in Figure R1 that does not decrease in intensity following CO introduction to the flow tube, $C_8H_{11}ClO_2$, is shown in Scheme R2 as forming from an alkyl radical undergoing reaction with HO_2 radical. Given the presence of O_2 in the system, I don't believe this reaction should be likely. Can the authors posit another formation mechanism or provide rate estimations showing the feasibility of this reaction?

Response: Thank you for raising this important point. We agree that the direct reaction between an alkyl radical and HO_2 is unlikely to be a dominant pathway. To resolve this, we propose another potential formation pathway for $C_8H_{11}ClO_2$, as illustrated in the revised Scheme R2. This updated mechanism draws inspiration from Bhattacharyya et al.'s work on the OH-initiated oxidation of m-xylene and suggests that $C_8H_{11}ClO_2$ may

with RO₂ would be less likely, but the opposite effect is observed. Can the authors provide an explanation or alternate formation mechanism to rationalize the observed decrease in C₈H₁₁ClO₄ concentration following CO introduction?

Response: We appreciate the reviewer's insightful observation, which highlights a key nuance in the system's chemistry. Indeed, the addition of CO is expected to convert OH radicals to HO₂, potentially enhancing the Cl-RO₂ + HO₂ pathway and thereby increasing Cl-OOM formation in principle. However, the observed decrease in the C₈H₁₁ClO₄ signal upon CO introduction (as shown in Figure R2) indicates that its production is influenced by OH-dependent pathways, overriding any potential benefits from elevated HO₂ levels.

To rationalize this, we propose that C₈H₁₁ClO₄ can form via multiple mechanisms. One pathway involves the reaction of the C₈H₁₀ClO₄ radical with HO₂, directly yielding C₈H₁₁ClO₄. An alternative and likely route is a secondary Cl-addition process: C₈H₁₀O₄ undergoes Cl addition to produce C₈H₁₁ClO₄. The introduction of CO suppresses OH availability, thereby reducing the formation of C₈H₁₀O₄ and limiting subsequent chlorination steps. This results in an overall decrease in C₈H₁₁ClO₄ concentration, despite the HO₂ increase.

This interpretation is supported by the experimental data in Figure R2, where both the C₈H₁₀O₄ (blue line) and C₈H₁₁ClO₄ (red line) signals rise sharply after UVA activation (indicating photolysis initiation) but decline following CO introduction. However, it should be noted that the decline in the C₈H₁₁ClO₄ signal is less pronounced than that of C₈H₁₀O₄; although we are currently unable to quantitatively describe these two species, their relative reduction extents suggest that C₈H₁₁ClO₄ has additional sources (namely, the reaction of the C₈H₁₀ClO₄ radical with HO₂).

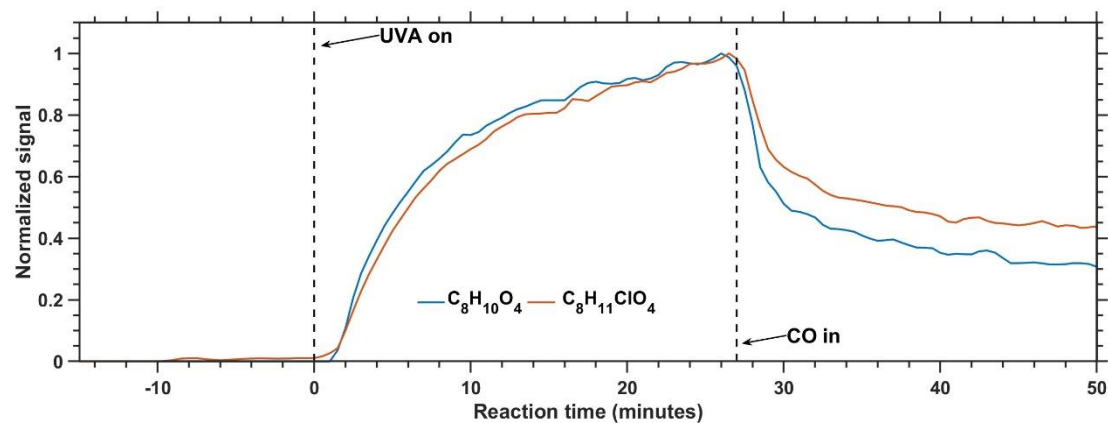


Figure R2. Normalized signal intensities of $C_8H_{10}O_4$ (blue line) and $C_8H_{11}ClO_4$ (red line) as a function of reaction time in the flow tube experiment.

Reference

Bhattacharyya, N., Modi, M., Jahn, L. G., and Ruiz, L. H.: Different chlorine and hydroxyl radical environments impact m -xylene oxidation products, *Environ. Sci.: Atmos.*, <https://doi.org/10.1039/d3ea00024a>, 2023.