

Atmos. Chem. Phys. Discuss., author comment AC3
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Reply on RC3

Yangang Ren et al.

Author comment on "Reactions of NO₃ with aromatic aldehydes: gas-phase kinetics and insights into the mechanism of the reaction" by Yangang Ren et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-228-AC3>, 2021

The authors thank the Reviewers for the comments and suggestions. We have revised our manuscript in response to the reviewers' suggestions and comments. All the changes and responses to the reviewers' comments are listed below, point-by-point, according to the new line numbers in the revised manuscript. The major changes are highlighted in red in the revised manuscript.

Referee #3

This manuscript describes a detailed investigation of the reactions of seven aromatic aldehydes with the nitrate radical. Rate coefficients have been determined using two experimental methods and the results are in very good agreement. Theoretical calculations have also been carried out to understand the reactivity patterns and mechanisms. The data obtained in this work is of high quality and interpreted well. Overall, the manuscript is well written and presented. I recommend publication after the authors satisfactorily address my minor comments below.

We thank the reviewer for these positive comments.

- My main comment is that the authors have neglected direct photolysis as a potential degradation pathway for the aromatic aldehydes. As demonstrated by Clifford et al. (2011), this pathway is certainly important for o-tolualdehyde, where the lifetime due to photolysis can be as short as 1-2 hours. The authors should incorporate this into the relevant parts of their manuscript (lines 51-55, lines 543-560, Table 2).

Responses: We agree and are grateful to the reviewer for pointing out this obvious oversight. We apologize for leaving photolysis out. We were so focused on comparing NO₃ reactive loss with other free radical reactions that we neglected to note the importance (dominance) of photolysis during daytime. We have modified the introduction to note:

"It is known that the tropospheric removal of aromatic aldehydes occurs through photolysis (Clifford et al., 2011; Thiault et al.2004) and their reactions with the OH radical. During daytime, photolysis and reaction with OH dominates their atmospheric loss"

In addition, we added a column to Table 2 to show the rough photolysis rate, which, of

course, vary with time, location and season. We did not find good UV spectra of the three DMBA, which surely would absorb as well as or more than the mono-substituted aldehydes. Therefore we note their photolytic lifetime to be less than 2 hours.

We have re-written the atmospheric introduction section to take these changes into account.

In addition, we have included the lifetime due to photolysis in the Table 2. The footnote now notes the variability of these loss pathways.

- Line 103: please add detection limit for nitrate radical in units of molecule/cm³.

Responses: we added the detection limit for NO₃ radical as 1.23×10⁷ molecule cm⁻³ in line 106.

- Line 126: replace "watching" with "monitoring".

Responses: Done in line 130.

- Line 143: should be [ref]

Responses: we changed the [reference] to [ref] in line 146.

- Lines 174, 177 and maybe elsewhere: use a big K for the equilibrium constant.

Responses: We correct "k_{eq}" to "K_{eq}".

- Table 1, Table 2 and tables in SI: use "rate coefficients" instead of "rate constants" to be consistent with other parts of the manuscript.

Responses: Done

Reference for Clifford et al:

G.M. Clifford, A. Hadj-Aïssa, R.M. Healy, A. Mellouki, A. Muñoz, K. Wirtz, M. Martín Reviejo, E. Borrás, J.C. Wenger

The atmospheric photolysis of o-tolualdehyde

Environ. Sci. Technol., 40 (2011), pp. 9649-9657