Reply on RC1
Yangang Ren et al.

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 #1

The authors report rate coefficients for reaction of NO\(_3\) radicals with a series of aromatic aldehydes (benzaldehyde, and mono- and di-methyl substituted derivatives), some of which have not been previously studied. Overall, I think this is an excellent study. Multiple approaches (relative and absolute) are used to obtain the kinetic data – the overall good agreement between the methods lends confidence to the obtained values. The work is very nicely put into broader context through a product study (showing formation of a PAN species), a determination of the H/D KIE for benzaldehyde, as well as theoretical calculations, etc., all of which contribute to a deeper understanding of the mechanism involved in the reactions and some of the reasons for the variation in the rate coefficients for the different methyl substitutions. The work is, in my opinion, publishable subject to minor revisions. I have one concern of some potential significance (first point below), as well as a few questions and suggestions which the authors may wish to consider.

We thank the reviewer for the positive comments.

I am not sure what the connection is between panel (a) and the other panels in Figure 2. They have different timescales, and different concentrations. Is there something mislabeled here? Or am I missing something?

Responses: We have revised the time scale in panel (a) to be in seconds and the concentration scales to be in ppbv. Just to clarify: The panels b’)-(d) are in linear scale so that the fit can be compared with the data.

Abstract, Line 36: It might be better to say NO\(_2\), rather than NO\(_x\), as NO would not lead to PAN formation.
Responses: Agreed. NO is changed to “NO2”.

Introduction, Line 44: Maybe pyrogenic sources is a better description than biogenic? None of the sources listed are what I would consider ‘biogenic’.

Responses: Thank you. Indeed it is better terminology. We changed “biogenic” to “pyrogenic”.

Line 175: ‘recommended by Burkholder et al...’ might sound better.

Responses: Thank you. Done!

Line 205: There is at least one other measurement of NO3 + methyl methacrylate from Canosa-Mas et al. (1999). Is it best to include this (slightly higher) value in arriving at the best value for the reference rate?

Responses: We agree with the reviewer that the rate constant of NO3 reaction with methyl methacrylate has been determined by Canosa-Mas et al., (1999), Wang et al., (2010) and Sagario Salgado et al., (2011). The reported experiments were very similar to that of Zhou et al., (2017) where the rate coefficient of interest was measured by both absolute and Relative methods. To enable placing the measured relative rate coefficient comparable to our absolute method, we prefer to use Zhou et al. value. We have provided all the measured values so that one could recalculate the rate coefficient for any value for the reference reactions.

Line 369: Wouldn’t increasing (not decreasing) the NO2 concentration suppress pathway B (by favoring PAN formation in pathway A)?

Responses: Apologies. That is correct. It was an error. It is now fixed.

Around line 485: Regarding the bond strength calculations, the para-ta and meta-ta have similar bond strengths to benzaldehyde, yet faster rate coefficients. Are the authors stating that this is due to the electron-donating effect of the methyl group, while the even faster o-ta rate coefficient includes an additional effect due to the weaker bond strength? Maybe a summary statement or two would be helpful at the end of this section? Also, is there any connection that can be made between the results here and the observation that k(NO3/aliphatic aldehydes) increase (to a point) with size of the alkyl chain (e.g., Noda et al., 2003)?

Responses: Yes, we are saying that the combination of the pre-reaction complex formation and the changes in the C-H bond energies contribute to the observed trends. We have added a summing up statement: “To sum up, the combination of the changes in the C-H bond energies and the changes in the variations in the initial addition to form a pre-reaction complex contributed to the observed reactivity trend.”

Thank you for pointing us to the work of Noda et al. We hesitate to comment on the variation of the reactivity of NO3 with alkane chain length in aliphatic aldehydes without doing further calculations since strengths of some of the secondary C-H bond strengths and their number, as well as steric effects could influence the reactivity.