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# Comment on acp-2021-228

Anonymous Referee #1

Referee comment on "Reactions of $NO_3$ 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-RC1, 2021

The authors report rate coefficients for reaction of NO3 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.

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?

Abstract, Line 36: It might be better to say NO2, rather than NOx, as NO would not lead to PAN formation.

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

Line 175: 'recommended by Burkholder et al…' might sound better.

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?

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

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)?