

Atmos. Chem. Phys. Discuss., author comment AC2
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Reply on RC2

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-AC2>, 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 #2

This manuscript presents the results of experimentally determined rate constants for the reaction of NO₃ with a series of aromatic aldehydes. The authors employ two methods of determining the rate constants. Results from the absolute and relative methods are in good agreement, lending weight to the authors' overall findings. The authors first compare results for systems with published rate constant values, and then extend the study to three new systems. Support for the suggested reaction mechanisms using isotope effects and BDEs are convincing. Overall, this study is well-conducted and well-presented. The manuscript is publishable after considering the minor revisions listed below.

We thank you reviewer for the positive comments.

Specific Comments

The absolute method of determining the rate constants was repeated four times for each system. The relative method was only duplicated. Another experiment repeating the relative method (n=3) would be preferred.

Responses: Thank you. We repeated the relative rate coefficient measurements. The reported rate coefficients did not change noticeably but our uncertainties decreased. Now, the average of three measurements are reported in Table S2.

Line 130: For step one determining the dilution coefficient, were the SF₆ and air continually added to mimic the continual addition of air with N₂O₅ during the experiment? As written, the initial 30 minute observation would seem to determine diffusion. Some rewording could be useful here.

Responses: Yes, we continually added air to make up for the withdrawal of air for

analyses. We corrected the sentence to read "SF₆ was added at the beginning of the experiment and monitored to measure the dilution rate coefficient. During this time, air was continually added to make up for the loss due to the withdrawal for analysis using CIMS and CRDS".

Line 168: Do the authors mean the residuals were minimized?

Responses: Thank you. Yes. To be clear, we have rewritten the sentence to read: "In the algorithm, the sum of squares of the difference between calculated and measured values of both the NO₃ and N₂O₅ were minimized while varying the input parameters"

Figure 2: Panel b does not significantly add to understanding the system and might be removed.

Responses: Panel B is: Temporal profiles in linear scale and the fits to the data as discussed in the text to determine the wall loss of N₂O₅ and NO₃ during the experiment. We prefer to retain this panel because it shows the goodness of fit of the data. (That difference would not be visible on a log scale and so we prefer to show it on a linear scale. We have also changes the axes on panel (a) to be consistent with other panels.

Line 298-299: The overlap of combined error bars is not a valid statistical test or comparison. I recommend removing this statement.

Responses: Thank you. We just want to note that the overlap statement was based on the errors based on including estimated systematic errors. That was not a statistical test. In any case, we agree with the reviewer's sense that the sentence was redundant because the previous sentences give the sense of the agreement.

Section 3.1.4: Table S5, which compares this work with previously published experimental values, contains key findings that are discussed in detail in this section. This data is also presented in graphical form in Figure 5 later in the manuscript. The reader would be assisted if immediate access to these data were presented in this section. Solutions could include the following options: the text could referred to both the figure and the table to eliminate continual flipping between the manuscript and the SI, or Table S5 could be relocated to the main text of the manuscript, or combine Table 1 with Table S5. It is also unclear why the authors have selected a different exponent for Figure 5 than what is used in the rest of the manuscript.

Responses: Thanks the reviewer for the suggestion, We referred Table S5 (Now as the Table 2 in the main text) in the caption of Figure 5 as "values are presented in Table 2". We also mention it in section on the results and discussion.

Figure 3: The caption is missing a description of the different colors/markers used in the figure. Could the authors please clarify.

Responses: We added the following note in the caption of Figure 3:

"Note: the different colors/markers presented the repeated experiments with different initial NO₂ concentration as: red filled circles: initial [NO₂]= 1.4-2.9 ×10¹² molecule cm⁻³, blue triangle: initial [NO₂]= ~2.7 ×10¹³ molecule cm⁻³, green square : [NO₂]₀=~1.4×10¹⁴ molecule cm⁻³ and red open diamond: [NO₂]₀=~3.3 ×10¹⁴ molecule cm⁻³."

Figure S1 (and Table S1): Please include the offset values in the caption as you have done with previous figures. Would it make sense to also list the R² values in Table S1? I am assuming the detection sensitivity listed in this table is the slope. It would also be useful

to have the uncertainty listed here defined.

Responses: For Figure S1, we added the following sentence in the figure caption: "For the sake of clarity, the plots of 2,4-DMBA, 2,5-DMBA, 3,5-DMBA, M-TA and P-TA are displaced vertically by 0.05, 0.1, 0.15, 0.2 and 0.2, respectively."

We also added the R^2 (0.95-0.99) and defined the uncertainty (2 times of standard deviation of the linear fitting in Figure S1) in the Table S1 which was asked by the reviewer.

Technical Comments

Line 51: "their" is ambiguous in this sentence structure. I would recommend switching the placement of "their" and "aromatic aldehydes" to increase clarity.

Responses: Thank you. This sentence has been rewritten.