Response to Reviewers

15/12/21

Response to Reviewers of:

NO_3 chemistry of wildfire emissions: a kinetic study of the gas-phase reactions of furans with the NO_3 radical
by Newland et al., 2021, submitted to ACP

General Response

We thank the reviewers for giving up more of their time to make further insightful comments, helping to clarify and improve our manuscript. Responses to each reviewer are given below. Responses to specific points raised by each reviewer are given separately beneath that point. Reviewers' comments are bold and italic, the authors' comments are inset in plain type.

Reviewer 1

This revised manuscript reports a relative rate study of the reactions of NO3 with a series of furans and related compounds, which are known to be important components of biomass burning emissions. The authors have taken account of the reviewers' comments on the original version, leading to improvements in the analysis and manuscript.

Importantly, the authors have considered the potential reaction of NO2 with the target and reference compounds, which was found to be significant for the reference compound a-terpinene. The experiments using a-terpinene as a reference have therefore logically been excluded from the revised analysis. As a result of this and other improvements, the paper is now acceptable for publication in ACP. I have a few minor/technical corrections and suggestions, which are listed below.

Following removal of the a-terpinene experiments, a few rogue pieces of information appear not to have been deleted:

Line 82: "a-terpinene" is still listed in the Materials section.

Done

Line 181: The sentence "A recommendation of an updated rate coefficient for a-terpinene+NO3 is also given in Table 3." needs to be deleted.

Done

The Berndt et al. (1996) and Fouqueau et al. (2020) references no longer appear to be required.

Done

Other comments:

Line 60: The Zhou et al. (2017) reference is missing. I could not check experimental details

elsewhere (e.g. if the chamber is fixed volume or collapsible) - hence my query about dilution below.

This reference has been added to the reference list

Line 69: Presumably the SF6 is added to monitor dilution when the N2O5/air mixture is continuously added during the experiment. It is therefore not clear why there should be any dilution during the 30 minute standing time, unless a dummy air flow is included. Does the specified dilution rate (line 70) refer to the experiment or the 30 minutes standing time?

A flow of 5 L/min of purified air was continuously added through the experiment (this is the same flow that is used to add the samples and N_2O_5). Air is then also removed to maintain a constant pressure (at a slight overpressure to prevent possible ingress of air from outside the chamber). Hence the dilution rate should remain the same throughout the whole experiment period (i.e. both prior to and after addition of N2O5). The following sentence has been added to the experimental approach to clarify this:

> "A flow of 5 L/min of purified air was continuously added throughout the experiment, and air is then removed from the chamber to maintain a constant pressure (this is a slight overpressure to prevent possible ingress of air from outside the chamber)."

Line 171: The authors' discussion comment could be referred to here for further details on the NO2 experiments.

We have added the following line from the discussion comment to provide more detail on the NO_2 experiments:

> "The experiments were performed with initial VOC mixing ratios of 3 ppmv, and initial NO_2 mixing ratios of roughly 5 ppmv, similar to the maximum amount of NO_2 observed during the NO_3 experiments."

Line 199: "....the values for furan and 2,5-dimethylfuran are ~ 50 % and 100 % greater respectively." To make the statement a bit clearer, I suggest inserting "reported here" after "2,5-dimethylfuran".

Done

Line 217: This sentence appears to say that cyclohexane was selectively diluted by 10 %, which is clearly impossible. Does this mean that a 10% loss of g-crotonolactone could not be measured reliably?

The sentence is supposed to suggest that 10 % of the cyclohexane was removed by reaction with NO_3. I.e. both compounds will have had a certain loss to dilution, but cyclohexane has an additional chemical loss to NO_3 on top of that, whereas g-crotonolactone does not. The sentence has been changed to the following to hopefully make it slightly more clear:

"In this experiment, roughly 10 % of the cyclohexane was removed by reaction with NO_3 (accounting for loss by dilution), whereas there was no appreciable chemical loss of γ-crotonolactone."

Line 230 (Table 3): Should the 2,5-dimethylfuran entries with pyrrole and 2-methylfuran as references have E-11 exponents?

Yes, thank you! This has been changed.

Line 246: The comparison in Table 5 is a very good way of summarizing the comparative reactivity of the compounds to the different oxidants, and should be included. However, I am always a little nervous of presenting such information as "black and white" conclusions. The oxidant concentrations are very variable and, particularly for NO3, are very conditions dependent. If there is any residual NO in a plume, NO3 is removed very quickly and its concentration is suppressed; and if NO is completely removed, there must be enough O3 remaining to allow NO3 to be formed from O3 + NO2. Also, it is noted in the second sentence of the abstract, that the (presumably elevated) concentrations of the target compounds results in a likely elevated NO3 reactivity under biomass plume conditions, which might mean that [NO3] can easily be suppressed relative to "typical" night-time or daytime levels when the NO3 reactivity is lower. Perhaps a little more qualification in the discussion is required.

The following sentence has been added in the Atmospheric Implications section, at line 268:

"It is noted that oxidant concentrations have a high spatial and temporal variability due to variability in their sources and sinks, and that oxidant levels within biomass burning plumes in particular are poorly understood. Hence the relative importance of the oxidants shown in Table 5 is likely to vary dependent on conditions."

Reviewer 2

The authors have properly addressed my comments as well as those of the other review. I find the new manuscript harmonized, clear and complete.
I still have some minor comments that need to be addressed by the authors before publication. The comments are listed below.

Line 82 : Please remove "α-terpinene (90%, Sigma-Aldrich)"

Done

Line 171: Please add text to justify why the rate coefficients for reaction of NO2 with 2-methylfuran, furfural, and α-angelicalactone have not been investigated.

We have added the following sentence after line 171:

> "Based on these experiments, it was assumed that the $k(NO_2)$ rate coefficients for 2-methylfuran, furfural, and a-angelicalactone are likely to be of a similar magnitude, and hence provide negligible interference under the experimental conditions employed."

Line 182: please remove: "A recommendation of an updated rate coefficient for a-terpinene+NO3 is also given in Table 3".

Done

Table 3: A number of experiment repeats are still missing for:
- α-angelicalactone with α-pinene and cyclohenxane as reference compounds. Please complete.
- Furan with cyclohexane, α-pinene and camphene as reference compounds. Please complete.
- γ-crotonolactone with cyclohexane as reference compound. Please complete.

Done

- For furfural, it seems like the value of the rate constant kNO3 with furan as reference compound is missing from the table while the experiment is plotted in Figure 2. Please complete.

Done