Atmospheric Chemistry and Physics Discussions

Atmos. Chem. Phys. Discuss., referee comment RC2
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# Comment on acp-2021-745

Anonymous Referee #2

Referee comment on "$NO_3$ chemistry of wildfire emissions: a kinetic study of the gas-phase reactions of furans with the $NO_3$ radical" by Mike J. Newland et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-745-RC2, 2021

## General comments

The manuscript presents a relative kinetic study in chamber simulation of a series of furans and relative compounds with $NO_3$ radical, major oxidant in the atmosphere by night. The studied compounds are furan, 2-methyl furan, 2,5-dimethylfuran, furan-2-aldehyde, 5-methyl-2(3H)-furanone, 2(5H)-furanone and pyrrole which are known to be emitted in the atmosphere during biomass burning.

This study reports for the first time rate coefficients for two furanones (α-angelicalactone and γ-crotonolactone) and investigate rate coefficients for the others compounds witch present few rate constant determinations in the literature. Although new kinetic studies are mandatory to complete and improve kinetic data bases the manuscript needs significant improvements before being published in ACP. The recommendations listed here after must absolutely be taken into consideration.

## Major comments

1) As the paper includes a relative kinetic study I would expect a detailed presentation of the experimental conditions, analysis of data, results and discussion. However, there is a certain number of information missing from the manuscript (and/or SI) to allow a proper evaluation of the quality of the data. My main comment is that relative rate plots and time series of concentrations are missing for the majority of the compounds. The plots are needed for example to investigate the presence of an eventual secondary chemistry or products interference. This is of particular interest for the compounds for which the rate constants obtained are not in agreement with the literature.

- please present relative rate plots and time series of concentrations for compounds of

interest (VOC, reference compound and $NO_2$) for 2,5-dimethyl furan, pyrrole, furfural, γ-crotonolactone, α-terpinene;

- please present relative rate plots and time series of concentrations for reference compound and $NO_2$ for α-angelicalactone;

Although there is no need to include all the time series and plots in the manuscript I suggest to complete the manuscript by including time series of concentration and relative rate plots for compounds for which this is the first rate constant determination (α-angelicalactone) or/and those experiencing fast reactivity (e.g 2,5-dimethylfuran or pyrrole). Representative plots that are not shown in the manuscript must be included in SI for all compounds.

2) The technique used for monitor VOCs is an in situ IRTF.

- The absorption bands used for reference compounds are missing. Please add a table with the missing information.

- The technique is not selective and reactants as well as the products of reaction are expected to absorb IR light and be presented on the absorption spectra at the level of concentration used here. Some of the products have absorption bands that may interfere with the reactant bands and thus perturb the data analysis. Is this the case? Can you comment on that?

- Generation of $NO_3$ via the thermal dissociation of $N_2O_5$ implies the presence of $N_2O_5$, $NO_2$ and $HNO_3$ (depending of the purity of the $N_2O_5$ synthesis) in the chamber. IRTF allows also to monitor these species. Please add information about the levels of these species in the experiments.

3) Although α-terpinene is a compound of interest in this work, there is very few information regarding this compound in the manuscript:

- The title and introduction of the paper are focused mainly on furans

- No information regarding the data analysis is presented (absorption bands in Table 1, absorption spectra in SI). Please complete

- The compound is used as reference compound in two experiments (2,5-dimethylfuran, pyrrole) but the recommended rate and uncertainties are not present in Table 2. Please complete.

- No concentration profiles, no relative rate plots are presented. Please complete.

- Not included in Figure 3 neither in table S1. Please complete.

- No discussion or explanation is given on the faster rate constant regarding the previous rate constant determinations. I would expect further discussion as previous values are in good agreement within the uncertainties.

-α-terpinene was used with 90% of purity without further purification. Can you specify the nature of the impurity and discuss impact on the rate constant?

In my opinion the data regarding this compound should be further presented and discuss or the authors should take in consideration to remove it from the manuscript.

4) While authors have investigated a possible OH generation and thus reactions of VOC of interest with OH no other sinks in the experiments were considered or discuss. The generation of $NO_3$ radicals by thermal dissociation of $N_2O_5$ has indeed the advantage to work in a $O_3$ free environment but implies large amounts of $NO_2$. I agree with the first referee, $NO_2$ may be possible sink for the studied compounds in the experimental conditions presented here (large concentrations of VOC, and $N_2O_5$). Authors should investigate this possible path for all compounds but especially for rate constants found higher that the already published ones (pyrrole, 2,5-dimethylfuran and α-terpinene).

**Minor comments**

Furan -2-aldehyde, 5 methyl-2(3H)-furanone and 2(H)-furanone are used either by their scientific names (eg. abstract, table 1) or by their common names (furfural, α-angelicalactone, γ-crotonolactone) ( eg. Materiels, Table 3) which is difficult to follow. For clarity, please homogenize.

Line 43: The sentence "Furan type compounds are removed from the atmosphere by reaction with the major oxidants OH, $NO_3$ and $O_3$" should be introduce earlier (line 34) for clarity.

**Experimental**

More information about the experiments is needed in my opinion.

Line 62: The authors mention that the experiments were conducted with the chamber operated at a slight overpressure to compensate from" removal of air sampling and to prevent ingress of outside air to the chamber". The reason for "air sampling" is unclear as the only instrument mentioned for these experiments is an in situ IRTF. Please clarify.

Line 67: Specify the order of introduction of VOCs (VOC of interest followed by Reference VOC?), continuous injection of $N_2O_5$, …

Line 74: Please specify the time and spectral resolution for the IR spectra

**Materials**

For clarity, please differentiate interest VOC from reference VOC.

**Results and discussion**

Table 3: A number of experiments are missing. Please complete.

Table 4: For α-terpinene: information are missing regarding previous studies: i) for Atkinson et al., et Berndt et al. please specify the type of study. For Fouqueau et al., 2020 please specify the study and method used.

**SI**

Table S1: for clarity: replace "NA" by "-"; reorganize the table (e.g. by Compound 1 or Reference)