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Review of acp-2021-745

Anonymous Referee #1

Referee comment on "NO₃ chemistry of wildfire emissions: a kinetic study of the gas-phase reactions of furans with the NO₃ radical" by Mike J. Newland et al., Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2021-745-RC1>, 2021

A relative rate study is reported, which considers the reactions of NO₃ with a series of furans and related compounds, which are known to be important components of biomass burning emissions. The experiments were carried out in the large CNRS-ICARE chamber, using N₂O₅ decomposition as the source of NO₃, with the rate coefficients being mainly determined relative to those of a series of alkenes of comparable reactivities. The target compounds include furan, 2-methylfuran, 2,5-dimethylfuran, furan-2-aldehyde, 5-methyl-2(3H)-furanone, 2(5H)-furanone and pyrrole. In the case of 5-methyl-2(3H)-furanone, this is the first reported determination. A rate coefficient for the reaction of NO₃ with the reactive monoterpene, alpha-terpinene, is also reported which is higher than previous absolute and relative rate determinations.

This paper considers an important topic, where new and confirmatory kinetic data are required, and the paper is clearly presented and written. I have one major comment on the experimental set-up and its interpretation, and some minor comments, which are outlined below. The major comment relates to the possible impact of NO₂ chemistry in the system, particularly for the alpha-terpinene rate coefficient determination, but which should probably also be checked in other cases where the current and previous results differ. I have submitted this review promptly, and I hope this will give the authors time to consider this and make adjustments, if required.

Major comment

The NO₃ source employed (N₂O₅ decomposition) produces an equivalent amount of NO₂, and additional NO₂ is likely formed as a product of the NO₃-initiated organic chemistry (i.e., from decomposition of nitro-oxy oxy radicals). Given the timescale of the experiments (0.5 – 2 hours), and the lack of reaction partners for NO₂, the potential reaction of NO₂ with the unsaturated organics needs to be considered and assessed, to confirm that the assumption of NO₃ being the only reagent is valid (i.e., Eq. (E1)).

NO₂ has previously been shown to react only very slowly with monoalkenes, but systematically more rapidly with conjugated dienes – and with further increases in reactivity resulting from alkyl substitution and in cyclohexadiene rings (Atkinson et al., 1984; Niki et al., 1986; Ohta et al., 1986; Jenkin et al., 2005; Bernard et al., 2013). The rate coefficient reported for α-terpinene (1-isopropyl-4-methyl-cyclohexa-1,3-diene: $6.5 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) is therefore one of the highest measured to date (Atkinson et al., 1984). The lifetime of NO₂ with respect to reaction with 3 ppm alpha-terpinene is therefore about 0.5 hours, such that some supplementary removal of α-terpinene by this reaction is likely to have occurred under the conditions employed in the present work. In contrast, the alkene reference compound, 2,3-dimethyl-2-butene, reacts much more slowly with NO₂ ($1.5 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). As a result, this interference may contribute to the present k(NO₃) determination for α-terpinene being higher than all previous determinations. The previous relative rate studies either corrected for NO₂ reaction (Atkinson et al., 1985) or employed flowing systems with short residence times (Berndt et al., 1996). The authors therefore need to check for this potential interference (which presumably would be a very straightforward experiment) and make corrections if required.

For completeness, the possible reaction of NO₂ with the furans etc. also ideally needs to be checked, although these are likely slower reactions than for α-terpinene. Atkinson et al. (1985) verified that the NO₂ reaction was unimportant for furan under their NO₃ + furan experimental conditions.

The α-terpinene k(NO₃) determinations using 2,5-dimethylfuran and pyrrole as references yield results that are similar (but not identical) to that obtained using 2,3-dimethyl-2-butene as the reference, suggesting that they also probably do not react rapidly with NO₂. However, the observed differences between the systems could also result from the differences in NO₂ generation from the NO₃ + reference compound chemistry and the secondary effect on α-terpinene decay.

Minor comments

Abstract: The common names furfural, α-angelicalactone and γ-crotonolactone are generally used for furan-2-aldehyde, 5-methyl-2(3H)-furanone and 2(5H)-furanone throughout the manuscript. It might be useful to include the common names in the abstract summary (i.e., as done on line 54).

Line 70: Please further clarify whether the N₂O₅ sample was introduced “continually” (i.e., repeatedly in aliquots) or “continuously” (i.e., without interruption in a constant flow throughout the experiment).

Lines 79-83: Cyclohexane (used as the reference for γ-crotonolactone) needs to be included in the materials list. Its rate coefficient should also be included in Table 2.

Line 101: It would be helpful to have some explanation of why the rate of alkene and furan loss rates increase with time during the experiment (Fig. 1). It is not clear from the information given. At what point was the N_2O_5 flow added? It also would be good to have similar plots for other studied compounds in the Supplement.

Line 113: Terminology: The term "rate(s)" is used incorrectly in many places where "rate coefficient(s)" should be used. As the authors are of course aware, a reaction rate (dimension: concentration/time) is the product of the rate coefficient and reagent concentration(s) – i.e., "k" is a rate coefficient, not a rate.

Line 138: Note that there is also a direct source of HO_2 from the reaction of NO_3 with α -terpinene. Like other conjugated cyclohexadienes, a minor H abstraction channel occurs to form a substituted cyclohexadienyl radical, followed by its reaction with O_2 to form p-cymene and HO_2 (Berndt et al., 1996).

Lines 134-150. Because the $\text{NO}_3 + \text{HO}_2$ reaction also forms OH, it might be worth mentioning that this is (presumably) uncompetitive under the experimental conditions.

Line 206, Table 3: α -terpinene entries should be " α -terpinene".

Line 215: The derived values of $k(\text{NO}_3)$ for 2,5-dimethylfuran and pyrrole are highlighted as being significantly smaller using α -terpinene as the reference. But, inspection of Table 3 suggests that the values obtained using 2,3-dimethyl-2-butene are further from the average in each case, the highest and lowest of the sets respectively.

Line 224. Replace "TME" by "2,3-dimethyl-2-butene".

Line 227, Table 4: "Kind et al. (2006)" or "Kind et al. (1996)"?

Line 347: Berndt et al. (1996) reference is missing.

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