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Atmos. Chem. Phys. Discuss., referee comment RC2
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Comment on acp-2021-1011

Anonymous Referee #2

Referee comment on "An experimental study of the reactivity of terpinolene and β -caryophyllene with the nitrate radical" by Axel Fouqueau et al., Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2021-1011-RC2, 2022

General Comments

This manuscript describes an experimental study of the reactions of a monoterpene and sesquiterpene with NO3 radicals. Rate constants were measured in a glass chamber using absolute and relative rate methods. Product and mechanism studies were conducted in a stainless-steel chamber and gas-phase products were analyzed online using a proton transfer reaction-mass spectrometer with a H2O+ and NO+ ion source. Gas and aerosol products were analyzed by infrared spectroscopy to quantify nitrate compounds. Particle size and volume concentrations were monitored with a scanning mobility particle sizer.

The study is relevant to understanding the nighttime formation of organic nitrates from VOC oxidation, which can impact SOA and ozone formation. The measured rate constants generally agree with those measured previously, thereby giving confidence to the reported values. The study also provides new yields of acetone, organic nitrates, and SOA; and the reaction mechanisms proposed for each compound seem to explain the observed products quite well. Overall, I think the measurements were well done, the interpretation of the date is accurate, and the paper is clearly and concisely written. I think the manuscript is publishable in ACP, and I have only a few minor comments.

Specific Comments

- Line 95: Please define IBBCEAS.
- Line 215: Can't you use ion-molecule reaction rate theory to estimate rate constants for ionization and then quantify products?
- Line 220: What products do you mean? Acetone? On line 215 you state that you can't quantify products because of the lack of standards.
- Line 355: Stating that the SOA yields are below 90% is not very useful, since that means they could be anywhere from 0 to 89%. I suggest giving the actual range of

yields.

- Line 376: Since you know the VOC-NO3 rate constant and approximate NO3 radical concentration, it seems that you can calculate the reaction lifetime and compare that to the mixing timescale. That would be useful support for the explanation given here.
- Figure 8. I think NO3 addition occurs preferentially to form the tertiary alkyl radical, so wouldn't it be better to show that reaction pathway?
- Neither Figure 8 nor Figure 9 consider possible isomerization of alkoxy radicals, and assume instead only reaction with O2 or decomposition. This assumption might be supported using SAR calculations of Vereecken & Peeters, PCCP, 2009 & 2010, although results from Aschmann et al. JPCA 2011 for cycloalkoxy radicals indicate that for b-caryophyllene some isomerization should occur.
- Line 588: Similar to Comment 3, it is not very useful to state that SOA yields are <100%.

Technical Comments

None