

## ***Interactive comment on “A comparative and experimental study of the reactivity with nitrate radical of two terpenes: $\alpha$ -terpinene and $\gamma$ -terpinene” by Axel Fouqueau et al.***

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First, the authors would like to thank the anonymous referee for this discussion and its constructive comments, corrections and suggestions that ensued. We have carefully replied to all its comments and the paper has been improved following his recommendations. All technical corrections suggested by the referee have been carefully performed. Answers have also been provided for all comments and changes have been performed accordingly. Please find below the answers to the comments:

Specific comments

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1. Line 86: The purity of the  $\alpha$ -terpinene is not very high. Do the authors have any idea what else it contains? Are there any observed products that might not be explained by reaction of  $\alpha$ -terpinene?

The referee is right when saying that the low purity of  $\alpha$ -terpinene may affect the organic nitrates and SOA yields. At the time the experiments were carried out, no higher purity sample was commercially available. We have contacted the company in order to have information about impurities but it was not able to provide it. Nevertheless, prior to each  $\alpha$ -terpinene injection, a purification stage was performed by pumping the sample in the vacuum line. This stage may contribute to remove high volatility impurities. For low volatility impurities, it is expected that they will remain in the sample (condensed phase). For yield calculations, it was therefore considered that only terpinene was introduced into the chamber. However, because these impurities remain unknown, we cannot state with certainty that this purification stage is 100% efficient. Therefore, it should be considered that this may generate additional uncertainty on yields which may be slightly underestimated. This has been explained in the manuscript L.86, L.341 and L. 413.

2. Line 335 and beyond: SOA yields are explained strictly in terms of physical partitioning of monomers from the gas phase to the particles. ClaiřĆin and Ziemann, J. Phys. Chem. A, 2018, showed that the SOA formed from the  $\beta$ -pinene + NO<sub>3</sub> reaction consists almost entirely of acetal dimers formed in the particle phase. Could similar reactions occur in these systems, and how would the presence of oligomers alter the interpretation of SOA yields? & 4. Line 389: Could add SOA results from ClaiřĆin and Ziemann, J. Phys. Chem. A, 2018.

This was an omission but we agree that we have to discuss this point. The reason of this omission was that no analysis at the molecular scale was conducted in the particle phase during our experiments. Indeed, in this study we only measure the total organic nitrates in the aerosol phase from their IR absorption band. If polymers are formed in the particle phase, for example acetal dimers and trimers (as presented by ClaiřĆin

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and Ziemann, J. Phys. Chem. A, 2018), which have a nitrate group, they cannot be distinguished from the monomers in our analysis. The study of ClaiñCin and Ziemann showed that hydroxynitrates can react with carbonyl compounds, via an acid-catalyzed particle-phase reaction leading to the formation of acetal dimers and trimers. Our results are coherent with this statement: 1) For  $\gamma$ -terpinene, we identified hydroxynitrates and carbonyl nitrates in the gas phase, which have low enough volatility to transfer towards the particle phase. We are making the hypothesis that these molecules contribute the most to the SOA formation. Once in the particle phase, they can then react to form acetal dimers, but these last species can not be detected in our study. 2) For  $\alpha$ -terpinene, we did not observe the formation of hydroxynitrate, thus the formation of these dimers is expected to be negligible. This is also in good agreement with the low SOA yields for this compound. A discussion has been added L. 612 to discuss about these results: "The study of ClaiñCin and Ziemann, 2018 showed that the hydroxynitrates and the carbonyl compounds can react via an acid-catalyzed particle phase reaction leading to the formation of acetal dimers and trimers. No molecular analysis of the particle phase, except for the organic nitrates, was conducted. If polymers are formed in the particle phase, for example acetal dimers and trimers, which have a nitrate group, they cannot be distinguished from the monomers. For  $\gamma$ -terpinene, hydroxynitrates and carbonyl nitrates were detected in the gas phase, which have low enough volatility to go in particle phase and contribute the most to SOA formation. They can then react to form acetal dimers or trimers in the particle phase, but with no possible detection. For  $\alpha$ -terpinene, no hydroxynitrate formation was detected; the formation of these dimers is expected to be negligible. This is in good agreement with the low SOA yields for this compound. This study also showed the importance of RO<sub>2</sub> + RO<sub>2</sub> reaction and alkoxy decomposition, which are the key point in  $\alpha$ - and  $\gamma$ -terpinene chemistry. The importance of isomerization and acid-catalyzed particle phase reaction has not been proved but is coherent with the results."

The following citations were added to references: Clafin M. S. and Ziemann P. J.: Identification and Quantitation of Aerosol Products of the Reaction of  $\beta$ -Pinene with

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NO<sub>3</sub> Radicals and Implications for Gas- and Particle-Phase Reaction Mechanisms J. Phys. Chem. A, 122, 14, 3640–3652, 2018.

3. Line 335 and beyond: No mention is made as to the effects of loss of gas-phase products to the chamber walls. I would think this is quite high for stainless steel and possibly glass, and these sorts of products. This should be discussed.

The referee is right, organic nitrates are low volatile compounds, which can be lost on the walls. Mechanistic experiments were conducted in CESAM chamber, so with stainless steel walls, and it has been observed, from previous studies (Suarez-Bertoa et al., 2012; Picquet-Varrault et al., 2020), that organic nitrates adsorb on these walls. The loss rates of several multifunctional organic nitrates (in particular carbonyl-nitrates) have been studied and were found to range between  $0.5\text{-}2 \times 10^{-5} \text{ s}^{-1}$ . At the time scale of an experiment (3-4 hours), this may lead to a non-negligible loss of organic nitrates (up to 25%), and therefore to an underestimation of the yields, in particular of organic nitrates in the aerosol phase. However, yields of ONs in the gas-phase were calculated during the oxidation period, on a time scale of max. 1h and are therefore less affected by the wall losses (below 10%). The following text has been added: L. 379: "It is also expected that organic nitrates adsorb on the stainless steel walls. Indeed, the loss rates of several multifunctional organic nitrates (in particular carbonyl-nitrates) have been observed in previous studies (Suarez-Bertoa et al., 2012; Picquet-Varrault et al., 2020) and were found to range between 0.5 and  $2 \times 10^{-5} \text{ s}^{-1}$ . However, as yields of organic nitrates in the gas-phase were calculated during a relatively short period (less than 1 hour), these wall losses are expected to be low (less than 10%) and this is confirmed by the good linearity of the plots." And L. 408: "It should also be mentioned that these yields may be affected by wall losses of organic nitrates. Considering that these yields have been measured by collecting particles several hours after the beginning of the experiment, this may lead to a non-negligible loss of organic nitrates (up to 25%), and therefore to an underestimation of the yields. Because wall loss rates can vary from an experiment to another one, this can also explain the variability of YONp." The following

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citations were added to references: Suarez-Bertoa, R., Picquet-Varrault, B., Tamas, W., Pangui, E., and Doussin, J.-F.; Atmospheric Fate of a Series of Carbonyl Nitrates: Photolysis Frequencies and OH-Oxidation Rate Constants, *Environ. Sci. Technol.*, 46, 22, 12502–12509, 2012. Picquet-Varrault, B., Suarez, R., Duncianu, M., Cazaunau M., Pangui, E., David, M. and Doussin, J.-F.; Photolysis and oxidation by OH radicals of two carbonyl nitrates: 4 nitrooxy-2-butanone and 5-nitrooxy 2-pentanone, *Atmos. Chem. Phys.*, 20, 487–498, 2020.

5. Line 468: Peroxynitrates can decompose to a carbonyl + HNO<sub>3</sub> in the condensed phase. How might this affect the results?

We expect that these compounds are not formed. We indeed did not detect peroxynitrates both in the gas and particle phases, particularly using FTIR detection where these compounds have a very strong and distinctive signature. A precision has been added L.482: “It should also be noticed that peroxynitrates (RO<sub>2</sub>NO<sub>2</sub>), which have a characteristic absorption in the IR region, were not detected in our experiments, neither in the gaseous phase, nor in the aerosol one. This suggests that that RO<sub>2</sub> + NO<sub>2</sub> reactions are minor pathways.”

Technical comments

1. Line 208: I think “et” should be “and”. It has been corrected. 2. Line 476: “bound” should be “bond”. It has been corrected.

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