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Comment

Interactive comment on “Cyclobutyl methyl ketone as a model compound for pinonic acid to elucidate oxidation mechanisms” by A. P. Praplan et al.

A. P. Praplan et al.

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Received and published: 10 September 2012

We would like to thank the referee for taking the time to read and comment on this manuscript and for his helpful and constructive comments. Referee's comments are portrayed in regular font style and the replies in italic.

Reply to Anonymous Referee #3

1. The abstract should be completely rewritten, starting from scratch. Something more along the lines of the big-picture assessment I present above would work well. At present the abstract is a succinct summary of the work, but as such it is even more

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densely packed with detail than the body of the paper. No non- specialist could possibly read the abstract and have any idea why the work is important.

The abstract was rewritten from scratch, focusing on the big-picture assessment presented by the referee and is now: "Even if the oxidation of the atmospheric relevant compound α -pinene has been extensively studied, uncertainties remain on the chemical mechanisms of the reactions leading to later generation oxidation products. The present work uses a simple compound, cyclobutyl methyl ketone (CMK), to study the reaction mechanism of the oxidation of pinonic acid by hydroxyl radicals (\cdot OH). Results show that by analogy with the complex pinonic acid system, that organic acids identified in secondary organic aerosol from α -pinene (3-methyl-1,2,3-tricarboxylic acid (MBTCA), terpenylic acid and diaterpenylic acid acetate) can be formed in the gas phase and are second generation products (first generation products of pinonic acid by \cdot OH oxidation. Nevertheless, traditional atmospheric chemistry cannot explain mechanistically the formation of these compounds. New routes need to be explored, involving unimolecular reactions."

2. To me, the big-picture important point of this work is that "non-traditional" chemistry can quickly dominate over "traditional" chemistry even in situations where there is no doubt that the chemistry is occurring in the gas phase. This strongly supports the conclusions of Müller et al. (2012) that the triacid MBTCA is formed in a single generation of gas-phase oxidation from pinonic acid, but significantly refines the constraints on the mechanism. The authors should be aware that the mechanistic detail pervading the manuscript will be off putting to many readers, and so the writing should surface from those details from time to time to emphasize the big-picture implications of the work.

The authors are aware of the fact that it is a difficult task to discuss complex mechanism. The manuscript was slightly modified to simplify the discussion and taking more the big-picture into consideration.

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3. I don't think Fig. 2 serves much of a purpose – it shows that different OH sources produced different absolute amounts of OH. That is not a surprise.

Figure 2 and its corresponding section in the discussion was removed from the manuscript. The authors simply mention that the OH levels were different for the different experiments and that normalisation based on the amount of 1,3,5-trimethylbenzene (TMB) reacted is done.

4. There are a few points where it is obvious the authors are not native speakers of English. For example:

(a) “are increasing” on p 10659 (hereafter 59) line 4 should be “increase”.

(b) “mechanisms ... needs” on lines 21-23 of the abstract should be “mechanisms ... need”

etc.

The authors corrected both mentioned points and improved the overall quality of the language in the manuscript.

References

Müller, L., Reinnig, M.-C., Naumann, K. H., Saathoff, H., Mentel, T. F., Donahue, N. M., and Hoffmann, T.: Formation of 3-methyl-1,2,3-butanetricarboxylic acid via gas phase oxidation of pinonic acid – a mass spectrometric study of SOA aging, Atmos. Chem. Phys., 12, 1483–1496, doi:10.5194/acp-12-1483-2012, 2012.

Interactive comment on Atmos. Chem. Phys. Discuss., 12, 10651, 2012.

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