Atmos. Chem. Phys. Discuss., 12, C4177–C4182, 2012
www.atmos-chem-phys-discuss.net/12/C4177/2012/

Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #1

Received and published: 29 June 2012

General comments:

This manuscript reports the reaction of cyclobutyl methyl ketone, CMK, as a surrogate compound for early generation oxidation products of α-pinene such as pinonaldehyde and pinonic acid. The study focuses on the elucidation of the gas phase mechanisms leading to the formation of CMK oxidation products that have an analogous structure to some of monoterpene oxidation products. The formation of succinic acid from the CMK was suggested to be analogous to the mechanisms leading to 3-methyl-1,2,3-tricarboxylic acid (MBTCA) that is a known α-pinene oxidation product. The oxidation of simpler cycloalkenes such as cyclohexene and methylenecyclohexane has been studied in the past as surrogates of α-pinene and β-pinene. Despite the simpler structures of these surrogate molecules, the resulting SOA contains a complex mixture of

compounds, and in my opinion, these experiments have not shed light on mechanisms leading to α-pinene and β-pinene SOA compounds. A major concern I have for this manuscript is that it suffers from poor handling of PTR-MS data for the quantification and identification of VOC species. In view of my comments/questions that is outlined below, it is recommended that this manuscript be reconsidered after major revision.

Major comments:

The PTR-MS data shown in the manuscript raise some questions about the data handling and analytical procedures. The detected signals appear to be uncorrected for background measurement (especially Fig. 7 right). Therefore, the calculated molar yields for the gaseous compounds are likely inaccurate. Furthermore, it is not clear from the manuscript how the authors calibrated the PTR-MS data, and how the PTR-MS data were interpreted to suggest the structures of the detected compounds. The m/z values measured by the PTR-MS do not provide information about the structures of the detected compounds nor about isobaric isomers detected at the same m/z values It is unfortunate that the authors did not have additional gas-phase off-line measurements to validate the PTR-MS data. This would provide important information about overlapping m/z from the precursor and formed products and better estimation of the consumption of the precursor and the formation of the products. In addition the authors should clearly spell out which kinds of peroxides are discussed in the manuscript. Peroxides mean a class of compounds that includes hydroperoxides, organic peroxides, peroxy carboxylic acids and more. It is not clear from the manuscript if the authors refer to the total peroxides or specific types of peroxides.

10652, Line 8: Pinonic acid is only one possible precursor for MBTCA.

10652, Line 13: Is succinic acid an analogous compound for the tricarboxylic acid (i.e. MBTCA)? The authors show much higher formation of succinic acid in the absence of NOx in Figure 8; however, it is unlikely that the formation of MBTCA proceeds without NOx under ambient conditions.

10652, Line 14: Do the authors mean 4-hydroxybutanic acid instead of butanoic acid? The hydrolysis results in the corresponding hydroxy carboxylic acid (4-Hydroxybutanic acid) instead of butanoic acid. In the line 2 of the page 10654, the hydrolysis product is described as 4-hydroxybutanoic acid.

10653, Line 28: Terpenylic acid and diaterpenylic acid acetate (DTAA) are known as early stage oxidation products. (Claeys et al., 2009)

10654, Line 1: How important is the hydrolysis of lactone containing compounds? High amounts of terpenylic acid are often detected in both ambient and laboratory samples, and it is suggested to react further to form higher molecular weight compounds. In comparison, diaterpenylic acid is detected at minor levels.

10655, Line 12: Is it correct that the TME ozonolysis started 4h before the CMK was injected? How much TME have the authors used, and how have the authors injected? This information appears to be missing. If the TME was injected at once before the CMK injection, it is likely that it reacted rapidly with 500 ppbv of O3, and the resulting OH radicals react mostly with TME oxidation products (i.e. acetone) rather than CMK. In addition, the formation of higher molecular weight compounds cannot be ignored for TME ozonolysis. This can result in the formation of a wide range of products (Sadetzky et al., 2010). It is recommended that the background measurement to be performed separately as an additional experiment. In Figures 4, 6, 7 and 8, the product signals start to go up before the OH exposure starts at 0h. Do the authors have explanation for this? How have the authors corrected the wall loss?

10655, Line 20: Have the authors considered the other fragments of CMK to estimate the consumption?

10656, Line 1: Why are the experiments performed under very different conditions and CMK consumptions? Especially the CMK consumptions in the NOx experiment and the dark OH experiment are much lower that other two. Can the authors comment on this?

10658, Line 12: If m/z 87 is a fragment of CMK the increase at 0h (injection) should be the same for “Dark OH”, “O3 + lights” and “NOx + lights” because the injected amount is the same. However, this is not the case. Especially the intensity of m/z 87 for “O3 + lights” is twice as much compared to “NOx + lights”. Can the authors comment on this?

10658, Line 16: The background of m/z 73 is high. This can be seen also in Figure 7 because the signal of m/z 73 does not start at 0 ppbv. The intensity of the m/z 73 signal can be normalized to the experiments without TME at the injection. This can reveal the real amount of produced m/z 73. In addition, the signal increases before reaction started, especially for “O3+lights”? How can it be?

10658, Line 23: The observation of a significant increase of m/z 87 can be caused by an enhanced formation of the succinaldehyde due to the change in the NO2/RO2 ratio (Kroll and Seinfeld, 2008). The authors should not exclude a possibility that the formation of other volatile compounds that are detected at m/z 87.

10659, Line 5: Do the authors suggest gas-phase carboxylic acid formation here? If this is so, the authors are requested to present more conclusive evidence to support the suggested mechanisms. The formation of terpenylic acid and DTAA from pinonic acid is possible but can this be concluded from the experiments conducted in this study?

10659, Line 8: Does this mean that the carboxylic acid forms in a single step? It is more likely that succindialdehyde and succinaldehyde serve as precursors.

10660, Line 7: Can the authors name a stable intermediate compound? Instead of MBTCA, succinic acid is formed from CMK. Why is it possible to exclude other intermediates? 4-Oxobutanoic acid can also be a succinic acid precursor, and this fits better with the formation of pinonic aldehyde (C10H16O2) in Müller et al., 2011.

10675, Figure 8: Unlike succinic acid and 4-oxobutanoic acid, there are no data for 4-hydroxybutanoic acid and the Mw 146 compound (monocarboxylic acid) prior to the

OH exposure. Can the author clarify this?

Minor comments:

10653, Line 19: The abbreviation for cyclobutyl methyl ketone is given before it is introduced. Abbreviations should be clearly spelled out not only in the abstract but also in the main text.

10654, Line 12: The legends used in the figures should be added to the experimental description here and to Table 1 (“Dark OH”, “O3 + lights”, “O3 + lights (high CMK)“ and “NOx + lights”).

10655, Line 3: Redundant words in the sentence: “alternated/alternatingly”

10655, Lines 4-5: Please provide more details about IC-MS systems (e.g. manufacturers, coupling techniques (electrospray isonization, atmospheric pressure chemical ionization, negative mode/positive mode, the presence of a suppressor etc.).

10655, Line 7: The sequence of figures is out of order. Figure 8 appears before Figures 3 to 7 are introduced.

10655, Line 9: Change “particulate phase” to “particle phase”.

10655, Line 19: Change “In the NOx case” to “In the experiment with NOx”.

10658, Line 6: Change “carbonyl compound” to “carbonyl group”.

10660, Line 8: Change “MBTCA” to the “succinic acid”. MBTCA does not form from CMK.

10660, Line 14/15: Change “report” to “reported” and “on the order of” to “in the order of”.

10661, Line 1: Change “similarly” to “similar”.

10663, Line 5: Change “many branching possibilities” to “various branching possibilities”.

10666, Table 1: Additional information will be helpful, e.g. seed particle concentration and $\triangle$CMK.

10669, Figure 2: There appears to be negative offsets, especially the “NOx + light” and “Dark OH” experiments do not go through the origin. Can the author clarify this?

References Claeys, M., Iinuma, Y., Szmigielski, R., Surratt, J. D., Blockhuys, F., Van Alsenoy,C., Böge, O., Sierau, B., Gómez-González, Y., Vermeylen, R., Van der Veken, P.,Shahgholi, M., Chan, A. W. H., Herrmann, H., Seinfeld, J. H., and Maenhaut, W.: Terpenylic acid and related compounds from the oxidation of alpha-pinene: Implications for new particle formation and growth above forest. Environ. Sci. Technol., 43, 6976–6982, 2009

Kroll, J.H and Seinfeld, J.H. Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere. Atmos. Environ., 42, 3593–3624, 2008

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Sadetzky, A., Winterhalter R., Kanawati B., Römpp A., Spengler B., Mellouki A., Le Bras, G., Chaimbault, P. and Moortgat G.K. Oligomer formation during gas-phase ozonolysis of small alkenes and enol ethers: new evidence for the central role of the Criegee Intermediate as oligomer chain unit, Atmos. Chem. Phys., 7, 14041-14102, 2007

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