

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

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We would like to thank the referees for taking the time to read and comment on this manuscript and for their helpful and constructive comments. Reviewer comments are portrayed in regular font style, replies in *italic*.

### **Reply to Anonymous Referee #1**

Major comments:

The PTR-MS data shown in the manuscript raise some questions about the data han-

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dling 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.

*The PTR-MS was calibrated using gas standards, that however did not contain the compounds of interest. Thus higher uncertainties are attributed to the measurement of these compounds and some assumptions had to be done: the raw counts per second were transmission corrected and normalized to the primary ions. The unit (ppbv) is calculated assuming a proton transfer rate constant of  $2 \times 10^{-9} \text{ cm}^3 \text{ s}^{-1}$  as a default value.*

*No background correction was applied to the data. Usually, only few  $m/z$  in the presence of  $\text{O}_3$  and lights increase (e.g.  $m/z$  47 and 61, which are not discussed in our manuscript). For the dark  $\cdot\text{OH}$  experiment, the TME ozonolysis was started earlier than the CMK injection in order to control, which  $m/z$  results from TME ozonolysis and distinguish them from the ones resulting of CMK oxidation by  $\cdot\text{OH}$  (see later reply).*

*The interpretation of the PTR-MS data is based on the expected reactions from traditional gas phase chemistry. The expected  $m/z$  are attributed to the predicted products.*

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*While this approach is inaccurate due to possible other products that could be formed, unexpected  $m/z$  forces to update the interpretation of the formation mechanism of these species. The authors do not have off-line measurements to validate the PTR-MS data, but IC/MS provides online measurements of organic acids in the gas phase, which are also detected by PTR-MS.*

*In general, "peroxides" refer to organic hydroperoxides (ROOH). The general "peroxide" term was replaced in the text body by "hydroperoxide".*

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

*The sentence "MBTCA is formed from pinonic acid" was replaced by "MBTCA can be formed from pinonic acid".*

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 NO<sub>x</sub> in Figure 8; however, it is unlikely that the formation of MBTCA proceeds without NO<sub>x</sub> under ambient conditions.

*The authors do not understand why the referee states that the formation of MBTCA is unlikely to proceed without NO<sub>x</sub> under ambient conditions. It was indeed possible to observe MBTCA formation in the absence of NO<sub>x</sub> in our experiments (IC/MS measurements not shown in the manuscript). This is one of the main reason leading to this mechanism study. Because this was obviously not stated clearly enough, this important finding is now stressed at the beginning of the discussion.*

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.

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*Yes. "Butanoic acid" was incorrectly used and replaced by "4-hydroxybutanoic acid".*

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

*Claeys et al. (2009) proposed reaction mechanisms for terpenylic acid and DTAA based on the oxidation of stable (i. e. non-radical) carbonyl compounds. From Fig. 8, the authors show that the products formed in our experiments corresponding by analogy to terpenylic acid and DTAA (4-hydroxybutanoic acid and 4-oxobutanoic acid) are first generation products. Therefore, terpenylic acid and DTAA are expected to be formed directly from pinonic acid, without proceeding via oxidation of a stable non-radical intermediate.*

*The authors now emphasise this finding based on the results of Fig. 8 in the discussion to clarify the mechanism discussion.*

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.

*It is indeed not possible to distinguish between the lactone and the hydroxy carboxylic acid with the presented IC/MS method, due to hydrolysis of the former one. The authors assume that all the 4-hydroxybutanoic acid measured comes from the hydrolysis of butyrolactone. This is supported by the referee's comment, which states that diaterpenylic acid (hydroxy acid) is only detected at minor levels in ambient and laboratory samples. This is now explicitly mentioned in the introduction.*

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?

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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 O<sub>3</sub>, 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 (Sadezky et al. , 2008). 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?

*Yes, this is correct. The TME ozonolysis started 4h before the CMK injection, in order to identify, which masses are formed by the TME ozonolysis and distinguish them from the m/z increasing due to the formation of CMK products. If no change in the formation slope of a m/z is observed, then there is no product formation on top of the background.*

*No wall loss correction was applied.*

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

*The reacted CMK values from Fig. 2 are derived from the sum of the CMK fragments on m/z 99 of the PTR-MS and normalized to nominal input. No other fragment has been considered.*

10656, Line 1: Why are the experiments performed under very different conditions and CMK consumptions? Especially the CMK consumptions in the NO<sub>x</sub> experiment and the dark OH experiment are much lower than other two. Can the authors comment on this?

*The main purpose of the different conditions was to differentiate between high and*

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*low-NO<sub>x</sub> chemistry. No organic peroxides are expected to be formed under high-NO<sub>x</sub> conditions and as there is no offline complementary measurements, this approach was intended to help the interpretation of the data (distinction of isobaric organic peroxides and other oxidation products). This is now mentioned at the beginning of the discussion.*

10658, Line 12: If m/z 87 is a fragment of CMK the increase at 0h (injection) should be the same for "Dark OH", "O<sub>3</sub> + lights" and "NO<sub>x</sub> + lights" because the injected amount is the same. However, this is not the case. Especially the intensity of m/z 87 for "O<sub>3</sub> + lights" is twice as much compared to "NO<sub>x</sub> + lights". Can the authors comment on this?

*The increase is the same for the dark OH experiment and the one with NO<sub>x</sub>. For the O<sub>3</sub> with lights experiment, the increase is somewhat higher and this is due to the difference between the nominal amount injected (400 ppbv) and the real amount, which can deviate from this value. (The signal in this figure is not normalized to the nominal amount injected.) The increase for the injection of the higher CMK concentration (1600 ppbv) is roughly a factor 4 higher, which supports our interpretation of the data.*

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 "O<sub>3</sub>+lights"? How can it be?

*The signal of m/z 73 does not have to start at 0 ppbv. The background could be subtracted to get the real amount of m/z 73 produced, but because no quantitative statement is done, the data were not treated further. Moreover, the authors do not understand the suggestion of normalisation to the experiments without TME injection.*

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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  $\text{NO}_2/\text{RO}_2$  ratio ?. The authors should not exclude a possibility that the formation of other volatile compounds that are detected at  $m/z$  87.

*The authors agree that  $m/z$  87 could correspond to succinaldehyde. Also  $m/z$  71 ( $[\text{M} + \text{H} - \text{H}_2\text{O}]$ ) increases similarly, even though the signal is weaker. Fig. 5 present the formation mechanism of succinaldehyde from "alkoxy B". The influence of  $\text{NO}_x$  is not on the carbon-carbon bond dissociation leading to succinaldehyde, but on the formation of "alkoxy B" itself. This interpretation support the authors' hypothesis that the peroxy radical marked in orange can undergo "non-traditional" chemistry (e. g. in form of intramolecular reactions) to lead to the measured organic acids. This is now part of the discussion.*

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?

*Yes, this is what is suggested. Even though the suggested mechanism can still be subject to discussion, the authors believe that they can demonstrate from the obtained data that dicarboxylic acids can be formed in one reaction step from a compound without carboxylic acid functionality (CMK to succinic acid). By analogy, we found that terpenylic acid and DTAA can be formed from pinonic acid, even if other precursors may lead to the formation of these products too and even if this conclusion cannot be quantitative as discussed in the manuscript.*

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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.

*As previously mentionned, Fig. 8 demonstrates that all the products are formed simultaneously as first-generation products. Second generation products would be expected to take more time to be formed.*

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 ( $\text{C}_{10}\text{H}_{16}\text{O}_2$ ) in Müller et al. (2012).

*The sentence was clarified by adding "(i. e. non-radical compound)" to the sentence. "MBTCA" was uncorrectly used and therefore replaced by "succinic acid". It is unclear to the authors, to what refer the referee with "the formation of pinonic aldehyde in Müller et al. (2012)". However, even though 4-oxobutanoic could be a precursor for succinic acid, because both products are formed in parallel, they are expected to be oxidation products of the same precursor compound.*

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?

*This is simply because a small background peak in the chromatogram could be identified for succinic acid and 4-oxobutanoic acid, while no peak at all is present for the other compounds.*

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

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in the main text.

*The abbreviation is now defined here.*

10654, Line 12: The legends used in the figures should be added to the experimental description here and to Table 1 (“Dark OH”, “O<sub>3</sub> + lights”, “O<sub>3</sub> + lights (high CMK)” and “NO<sub>x</sub> + lights”).

*Table 1 and text was modified accordingly to the comment.*

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

*The sentence is now "The sampling time was 30 min and anions were concentrated on two anion trace concentrator columns (ATC, Dionex). Sampling and analysis of gas and aerosol phase are performed alternatingly on each ATC (one for each phase)".*

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

*The paragraph includes now more details about the IC/MS system: "The sampling time was 30 min and anions were concentrated on two anion trace concentrator columns (TAC-LP1, Dionex). Sampling and analysis of gas and aerosol phase are performed alternatingly on each ATC (one for each phase). The separation of the analytes was performed by ion chromatography (Dionex DX600 with guard column NG1 and analytical column AS11-HC) with an gradient eluent (0-60 mM OH<sup>-</sup>). Detection was performed after background suppression (Anion Self-Regenerating Suppressor, ASRS 300 2 mm, Dionex) by conductivity detection and by a quadrupole mass spectrometer (Thermo-Scientific MSQ) with electrospray ionisation in negative mode (Fisseha et al., 2004).*

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

*This was corrected.*

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

*This was modified.*

10655, Line 19: Change “In the NO<sub>x</sub> case” to “In the experiment with NO<sub>x</sub>”.

*This was modified.*

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

*This was modified.*

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

*This was modified.*

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

*This was modified.*

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

*This was modified.*

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

*This was modified.*

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

*Table 1 contains now amounts of CMK reacted (after 3 hours of oxidation) and seed particle concentrations at the beginning of the oxidation.*

10669, Figure 2: There appears to be negative offsets, especially the “NO<sub>x</sub> + light” and “Dark OH” experiments do not go through the origin. Can the author clarify this?

*This is only due to the variation of the signal around 0 ppbv and because some dots were hidden by data from other experiments. However, this figure was removed from the manuscript following comment of Anonymous Referee #3.*

## References

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

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