

Interactive comment on “Investigation of the oxidation of methyl vinyl ketone (MVK) by OH radicals in the atmospheric simulation chamber SAPHIR” by Hendrik Fuchs et al.

Anonymous Referee #2

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General Comments

In this manuscript the authors present results of an experimental/modeling study of the oxidation of methyl vinyl ketone (MVK) under a range of atmospheric conditions. MVK is a major product of isoprene oxidation and its subsequent chemistry can affect radical cycling as well as aerosol formation. As an important but relatively simple organic molecule, its study provides an opportunity to evaluate current understanding of the fundamental reaction pathways involved in MVK (and other VOC) oxidation, which are here obtained using the Master Chemical Mechanism (MCM) with some modifications. Experiments were conducted in the large SAPHIR chamber, which was capable

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of providing NO levels over a wide range from “low NO” to “high NO” atmospheric conditions, and VOCs and radicals were monitored using a variety of state-of-the-art instruments/methods. The measured and modeled time profiles were compared and discrepancies used to suggest possible errors in the mechanism, some of which were addressed in part through the use of updated information on product yields, kinetics, or reaction pathways. The results agree well for the high NO regime but not so well for low NO. The authors have exhausted the most readily available modifications to the model and provided a reasonable list of possible causes for discrepancies that need to be addressed in the future. It is thus clear that more studies need to be conducted to improve the ability of the MCM to simulate the oxidation of MVK over the full range of possible atmospheric conditions. Given the much greater complexity of oxidation mechanisms for larger VOCs, studies such as this one are critical for the development and evaluation of accurate oxidation mechanisms needed for modeling atmospheric chemistry and aerosol formation. I think the manuscript is well written and the technical aspects and interpretations are reasonable. I recommend it be published in ACP after the following minor comments are addressed.

Specific Comments

1. Have the authors investigated the details of the RO₂ rate constants used in the MCM mechanism and the effect these might have on the results? For example, are rate constants appropriate for each RO₂ structure used or some kind of average? Furthermore, there are few rate constants available for multifunctional RO₂ radicals that capture the effects of neighboring functional groups.
2. What role might reactions of RO₂ radicals with particles or the walls play? These do not appear to be considered here (probably since its difficult to know what happens), even though they seem likely to compete with other RO₂ reaction pathways under low NO conditions when RO₂ lifetimes are long.

Technical Comments

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None.

Interactive comment on Atmos. Chem. Phys. Discuss., <https://doi.org/10.5194/acp-2018-265>, 2018.