

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.

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We thank the reviewer for the helpful comments.

Comment: 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.

Response: The RO₂ reaction rate constants are used as suggested in the MCM. Be-

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cause there are no specific measurements of reaction rate constants of MVK derived RO₂, we tested the effect of faster reaction rate constants to increase product concentrations that are smaller in the model than measured values. An increase of the reaction rate constant with HO₂ would further deplete the modelled HO₂, which is not consistent with measurements. In addition, the effect on the glycolaldehyde yield is small, because glycolaldehyde is only formed in the subsequent photolysis of the product of the HO₂+RO₂ reaction, if the additional reaction channels suggested by Praske et al are not taken into account. Because of the low NO concentration in the “low-NO”-experiment, the sensitivity of the model results to an increased reaction rate constant of the RO₂+NO reaction is rather small. We add on p7 l22: “No measurements for the reaction rate constants of RO₂ species from MVK exist. The sensitivity of model results to a change of the RO₂ reaction rate constants, however, is rather small so that their uncertainties could not explain observed model-measurements discrepancies.”

Comment: 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.

Response: The experiments were performed without seed particles and particle formation in the chamber during these experiments were not sufficient to build-up substantial aerosol surface area. Therefore, effects from heterogeneous reaction on aerosol can be neglected. The SAPHIR chamber has a large volume to surface ratio to minimize wall loss effects. Experiments from the past do not hint that RO₂ loss reaction significantly impact the results. In addition, we observe the formation of product species (glycolaldehyde) in the experiments here, which would not be expected, if RO₂ was lost. We add on p4 l30: “No significant particle formation was observed in the experiments so that only gas-phase chemistry needs to be considered in the evaluation.”

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