

Interactive comment on “Investigation of the α -pinene photooxidation by OH in the atmospheric simulation chamber SAPHIR” by Michael Rolletter et al.

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Comment on Rolletter et al. Submitted by Lu Xu, John Crounse, and Paul Wennberg

Rolletter et al. performed extensive measurements to investigate the α -pinene photooxidation by OH under atmospherically relevant conditions. One important and interesting finding is that the measured pinonaldehyde yield is only 0.05, the lowest yield ever reported (previous measurements range from 0.06 to 0.87). Further, by comparing measurements and 0-D box model results based on different mechanisms, the authors pointed out that both Master Chemical Mechanism and theoretical study by Vereecken et al. (2007) lead to significantly higher pinonaldehyde yields.

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Two critical parameters in determining the pinonaldehyde yield and HO_x concentrations are the fraction of OH adding onto the less-substituted olefinic carbon (denoted as BROH_less_sub) and the ring-opening fraction of activated hydroxy alkyl radicals (denoted as BRring-open). In current manuscript, these two parameters are described solely on the bases of previous theoretical calculations. Undiscussed are the experimentally constrained BROH_less_sub and BRring-open for α -pinene+OH photooxidation recently reported¹. We suggest that BROH_less_sub is ~70%, based on the OH addition branching ratio for 2-methyl 2-butene, a compound sharing similar substitutions around the C-C double bond with α -pinene². Using this constraint, we recommend BRring-open is very high (suggested to be 97%) based on the isomer distribution of α -pinene hydroxy nitrates. We recommend that Rolletter et al. implement these experimentally-constrained values into their box model simulations and evaluate the model performance in terms of both α -pinene oxidation products and HO_x budget. We further suggest the authors rephrase their discussions on the mechanism for acetone formation. In current manuscript (Figure 1, Page 3 Line 17, etc), it is implied that acetone is directly formed from the decomposition of ring-opened alkoxy radical. Both theoretical and experimental studies^{1, 3} have shown, however, that decomposition is negligible for the ring-opened alkoxy radical. The non-linear relationship between acetone and consumed α -pinene as observed in this study provides further evidence that secondary formation of acetone is an important (perhaps the dominant) source of acetone from α -pinene oxidation.

Reference

1. Xu, L.; Møller, K. H.; Crounse, J. D.; Otkjær, R. V.; Kjaergaard, H. G.; Wennberg, P. O. Unimolecular Reactions of Peroxy Radicals Formed in the Oxidation of a-Pinene and b-Pinene by Hydroxyl Radicals. *The Journal of Physical Chemistry A* 2019, 123, 1661-1674.
2. Teng, A. P.; Crounse, J. D.; Lee, L.; St. Clair, J. M.; Cohen, R. C.; Wennberg, P. O. Hydroxy Nitrate Production in the OH-Initiated Oxidation of Alkenes. *Atmos. Chem.*

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Phys. 2015, 15, 4297-4316.

3. Vereecken, L.; Muller, J. F.; Peeters, J. Low-Volatility Poly-Oxygenates in the OH-Initiated Atmospheric Oxidation of β -Pinene: Impact of Non-Traditional Peroxyl Radical Chemistry. *Phys. Chem. Chem. Phys.* 2007, 9, 5241-5248.

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