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Discussions

Interactive comment on "Different Pathways of the Formation of Highly Oxidized Multifunctional Organic Compounds (HOMs) from the Gas-Phase Ozonolysis of β-Caryophyllene" *by* S. Richters et al.

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Comment to RC2:

We thank the reviewer for the comments that we will carefully take into account for the revised version of our manuscript. In this short reply, we react to the main criticism that the reviewer "is not sure if the manuscript, as it currently stands, brings enough new insight to merit it's publication in ACP" in advance. We agree with the referee, that the "normal" autoxidation mechanism is not completely understood yet. Nevertheless, autoxidation mechanisms were proposed in order to explain the detected product formation from the ozonolysis of cyclohexene (Berndt et al., 2015; Rissanen et al., 2014) and limonene (Jokinen et al., 2014). These reaction schemes can be regarded as the "normal" autoxidation mechanisms in line with the well-known process in the liquid phase. Based on these publications, we believe that the two proposed, extended reaction pathways, "ext. AutOx." and "ext. AutOx. -CO2" in our manuscript, represent indeed real extensions of the "normal" autoxidation mechanism that were not yet shown in the literature. We are aware of the publication by Rissanen et al. (2015) in which it is stated, that additional reaction steps are needed to explain the product formation and the results of H/D exchange experiments from the ozonolysis of alpha-pinene. Indeed, Rissanen et al. (2015) proposed among others also endoperoxide formation based on the literature data from the OH-radical initiated oxidation of aromatic compounds and pinenes. However, alpha-pinene does not contain a second double bond needed for endoperoxide formation as shown for the aromatics. Therefore, an opening of the four-membered ring in the course of the alpha-pinene oxidation was discussed. However, Kurtén et al. (2015) calculated, that the ring opening pathways which include the formation of a double bond, are not likely to occur. We show in our manuscript that the second double bond is indeed crucial for endoperoxide formation allowing to explain the results of the H/D exchange experiments. The structurally similar sesquiterpenes beta-caryophyllene and alpha-cedrene differ mainly by their number of double bonds, two in alpha-caryophyllene and only one in alpha-cedrene. Product spectra and H/D exchange experiments from alpha-cedrene agree perfectly with the "normal" autoxidation mechanism, whereas experimental results for beta-caryophyllene differ and need further reaction pathways for explanation. We think that we can show in our manuscript, that new unimolecular reaction pathways of RO2 radicals in the gas phase are enabled by the presence of a double bond. Certainly, these reaction pathways need further investigations. Overall, we believe that these new reaction pathways for unsaturated RO2 radicals represent an extension of the "normal" autoxidation mechanism in the gas phase not clearly stated before in the literature.

References:

Berndt, T., et al.: (2015), J. Phys. Chem. A 119, 10336-10348. Jokinen, T., et al.: (2014), Angew. Chem., Int. Ed. 53, 14596-14600. Kurtén, T., et al.: (2015), J. Phys. Chem. A 119, 11366-11375. Rissanen, M. P., et al.: (2014), J. Am. Chem. Soc. 136, 15596-15606. Rissanen, M. P., et al.: (2015), J. Phys. Chem. A 119, 4633-4650.

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