

Interactive comment on “Are sesquiterpenes a good source of secondary organic cloud condensation nuclei (CCN)? Revisiting β -caryophyllene CCN” by X. Tang et al.

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As outlined in the introduction of this article, one of the main motivations of this work comes from the apparently extremely rapid rate ($1.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) with which β -caryophyllene reacts with ozone, which is reportedly so fast that it is the dominant oxidation pathway in the atmosphere (Shu and Atkinson, 1995). If true, the resulting oxidation products of the ozonolysis reaction would likely have a dominant effect on the aerosol-forming processes associated with this sesquiterpene. However, there are several lines of evidence which would suggest that the rate coefficient reported by Shu and Atkinson (1995) may be overestimated by several orders of magni-

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tude:

1.) A recent study by Ghalaieny et al. (2012) measured the rate of ozonolysis of β -caryophyllene at an elevated temperature of 366 K, where the effects of aerosol formation can be minimized. Experimental difficulties precluded the measurement of Arrhenius parameters for this reaction, however, when a structural analogue was used to estimate the activation energy of this reaction, extrapolation to room temperature yielded a rate coefficient of $3.62 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, a factor of 320 smaller than the determination of Shu and Atkinson (1995). Furthermore, the rate coefficient for the formation of first-generational products of Winterhalter et al. (2009) appears to be more consistent with a smaller rate coefficient of ozonolysis for β -caryophyllene.

2.) β -caryophyllene possesses a low saturation vapour pressure at room temperature and its oxidation products are likely to possess much lower vapour pressures. The hypothesis is that heterogeneous reactions may therefore influence the results of experiments conducted at room temperature for certain species. This has been tested in an analogous system at high temperature with large terminal alkenes (McGillen et al., 2011a) and the results suggested that the previous literature data possesses an artifact which leads to an overestimate in the gas-phase rate coefficient.

3.) It has been demonstrated by SAR analysis of the aliphatic alkenes and dialkenes that the rate of ozonolysis is largely dictated by the counteractive effects of induction and steric hindrance (McGillen et al., 2008, Leather et al., 2010, McGillen et al., 2011). The results of these studies suggest that gas-phase ozonolysis rate coefficients of alkenes ought not to exceed the rate with which 2-butene, 2,3-dimethyl reacts with ozone ($1.24 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) With these points considered, if the rate of ozonolysis of β -caryophyllene is taken to be $3.62 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ instead of $1.16 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, the atmospheric lifetime with respect to ozone increases from 1 minute to 7 hours, implying that reactions with NO_3 and OH are likely to play a far more important role in determining the atmospheric processing of this compound. Given this reduced role of ozonolysis in the atmosphere how does this

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impact on the paper's conclusion that β -caryophyllene ozonolysis SOA is a potentially important contributor to biogenic CCN?

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