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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Cyclobutyl methyl ketone as a model compound for pinonic acid to elucidate oxidation mechanisms" *by* A. P. Praplan et al.

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We thank U. Neuenschwander for taking the time to read and comment on this manuscript and for his helpful and constructive comments. Comments are portrayed in regular font style, reply in italic.

1 Reply to U. Neuenschwander

In terms of presented mechanisms (i.e. elementary reaction steps), I feel that an important reaction could be added to Figs. 5 and 10 in the manuscript: Whereas the authors correctly ignore the direct reaction between ozone and peroxyl radicals under

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the current experimental conditions, and invoke radical cross-reactions being the origin of alkoxyl radicals, the intermediate radical prior to "alkoxy B", being a 1,5-dicarbonyl 4-peroxyl species, can alternatively undergo intramolecular oxidation of the aldehyde moiety. Similar 1,6-H shifts have been published elsewhere (see e. g. Neuenschwander and Hermans (2010); Zhu et al. (2007)). The estimated rate constant for that 1,6-H shift at 298 K is about 100 s^{-1}, using a TST approximation based on a literature prefactor (A = 10^{10} s^{-1}; Zhu et al. (2007)) and an ab initio activation energy, as specifically calculated for this reaction, on an extensive gaussian basis set within the unrestricted B3LYP level of theory (45 kJ/mol; Neuenschwander (2012)). Note that this unimolecular rearrangement is favored both entropically (viz. molecular preorganisation) and enthalpically (viz. oxidation of weak aldehyde C-H bond). Thus, I think that it should be added to the presented framework of elementary reaction steps.

The authors are very grateful for this comment and calculations supporting the discussion about "non-traditional" reactivity. This 1,6-H shift for the 1,5-dicarbonyl 4-peroxyl marked in orange in Fig. 5 is now included in the section 3.5 as an example supporting our assumption that this compound may play a key role due to possible intramolecular reactions.

References

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