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

U. Neuenschwander

uneuen@mit.edu

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The results presented by Praplan et al. are an interesting addition to current knowledge about radical oxidation chemistry of terpenoid substrates. The approach of using CMK as a model compound for an "indirect" study of pinonic acid oxidation is elegant.

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 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 et al., 2010; Zhu et al., 2007). The estimated rate constant for that 1,6-H shift at 298 K is about 100 sˆ-1, using a TST approximation based on a literature prefactor (A = 10ˆ10 sˆ-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.

References:

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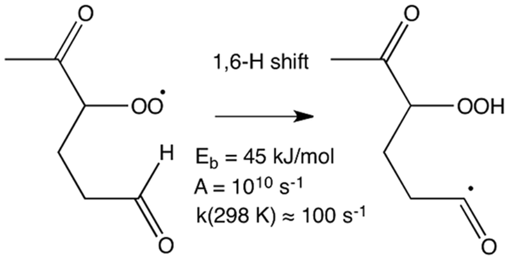

Fig. 1.

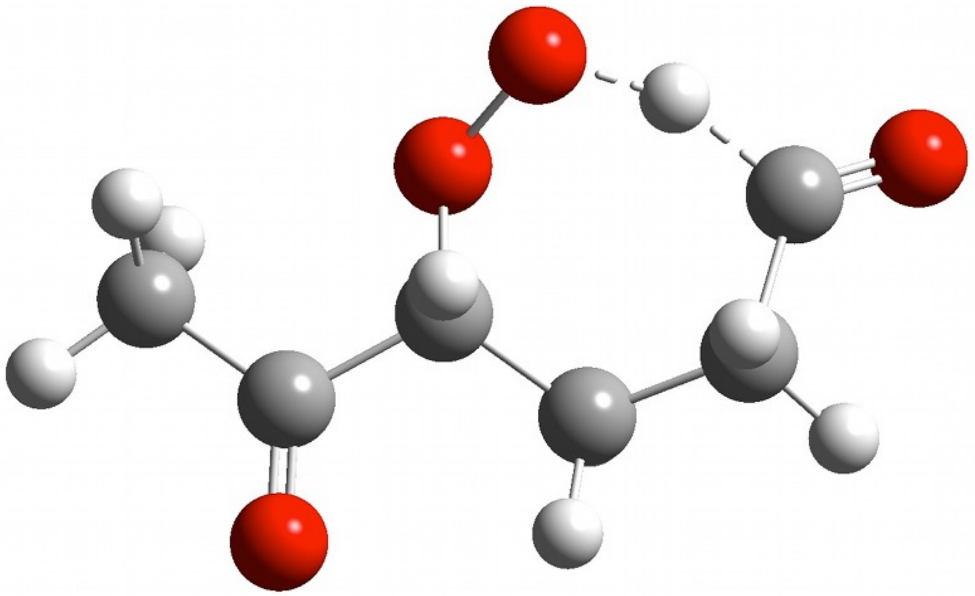

Fig. 2.