

Interactive comment on “Alpha-pinene oxidation by OH: simulations of laboratory experiments” by M. Capouet et al.

Anonymous Referee #1

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This paper presents a detailed appraisal of the chemistry of the OH-initiated oxidation of alpha-pinene. A chemical mechanism has been assembled (drawing on the results of theoretical calculations of Peeters and coworkers), which is tested by its ability to simulate the time evolution of a series of oxidation products formed during the photo-oxidation of alpha pinene itself, and of the major oxidation product pinonaldehyde. A previous dataset of experiments performed in the presence and absence of NO_x is used for this purpose.

This is a very thorough piece of work, which provides a comprehensive account of the early stages of the OH-initiated oxidation of alpha-pinene, including a description of the probable participation of a number of novel processes predicted by theory. The paper makes a valuable contribution to the literature in this area, and it should certainly proceed to full publication in ACP. There are, however, a number of points which authors

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should consider in producing a revised manuscript.

General comments

Mainly as a result of the level of detail in the presented material, the manuscript is rather long and difficult to read in one sitting. Although much of the detail is necessary, I did find that there were some sections which seemed disproportionately long. One example is the description of the conventional set of RO₂ radical reactions (sub-sections 2.2.1-2.2.5), and the rate and mechanistic parameters adopted in the mechanism. These subsections, which actually bear a striking resemblance to the corresponding sections in the MCM protocol papers (e.g., Saunders et al., ACP, 3, 161, 2003), mainly describe rate coefficients for small peroxy radicals, whereas the thrust of the paper is the early stages of degradation of alpha pinene. In particular, half the subsection on reactions with HO₂ is a description of details of the methyl peroxy reaction, which is presumably not generated in the alpha-pinene system until the further breakdown of acetone, and therefore not really relevant (although see query below). The section on photolysis reactions (section 2.5) also seems unnecessarily long, and could be more focused on the actual information required for the present paper. In my opinion, it is not necessary to include a figure of the spectra of H₂O₂ and CH₃ONO.

Specific comments

Figure 1: The branching ratios indicate that the addition of OH was assumed to occur equally (44%) at the two possible positions. This appears inconsistent with the conclusions of structure-reactivity correlations (e.g. Peeters et al., 1994) which would predict more favourable production of the tertiary radical. The equal probability assumption does not appear to be justified in the present paper.

Page 4052, fourth line from top of page: I presume that '10⁻¹⁰ s⁻¹' should be '10⁺¹⁰ s⁻¹'.

Page 4052: It is stated that a tertiary alpha-hydroxyalkoxy radical in R10 yields

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CH₃COOH upon decomposition. Generically, this should be RCOOH. In the specific case of R3O, the coproduct organic radical is a strained four-membered ring. In view of this, could an alternative elimination of the methyl radical be competitive?

Page 4053, line 14: It is stated that R10 only plays a role at NO concentrations above 100 ppb. Given that R10 is being discussed for both R3O₂ and R13O₂ (for which the rates of R9 differ by an order of magnitude) a single NO concentration cannot be a 'significance threshold' for both radicals.

Page 4067, section 3.3.3: The only major failure of the mechanism appears to be its inability to describe the formation of acetone in the absence of NO_x. The authors suggest that it may actually be generated as a secondary product of the oxidation pinonaldehyde or hydroperoxides, with the implication that the degradation of these compounds is not well-described by the mechanism. In fact, the shape of the concentration-time profile is more consistent with acetone formation as a primary product. The crux of the matter therefore appears to be the ring closure reaction of R7O₂, which inhibits acetone formation at low NO_x. This reaction bears some resemblance to reactions postulated to occur during the degradation of aromatic hydrocarbons, but with the important distinction that the product radical is not resonance-stabilised. Is it therefore possible that the ring closure reaction of R7O₂ is not as dominant as the authors are assuming? It would seem sensible to me to raise this possibility, and to present the results of simulations performed with a lower ring-closure rate.

The alternative suggestion of the authors (raised a little belatedly in the conclusions, page 4076) is that the chemistry subsequent to the ring closure of R7O₂ generates acetone, but that this is not explicitly represented in the mechanism. I think that if this explanation is to be given, a description of the fate of the ring-closed radical needs to be provided, and at least an outline of how acetone might be formed should be suggested. I suspect it is unlikely that acetone would be formed, and that another explanation is required. This discussion should appear in section 3.3.3.

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Page 4076: the final statement concerning the amount of work required before the impact of the OH-initiated oxidation of alpha-pinene can be assessed is rather daunting. I believe there is definitely a need for continued elucidation of organic oxidation mechanisms: however it is also necessary to apply mechanistic representations in the interim if progress on environmental issues is to be made.

Minor points

Page 4042, line16: 'can not' should be 'cannot'.

Page 4043, line 21: should 'hydroxy' be in brackets?

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