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Atmospheric
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Discussions

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

M. Capouet et al.

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We are grateful to both referees for their comments on this work. Each discussion point is addressed in the same order as in their reports. A revised manuscript taking the referees' suggestions into account is submitted.

Referee 1

General comments

The referee found the sub-sections 2.2.1–2.2.5 unnecessarily long and showing resemblance with Saunders et al. (2003). Redundant formula and statements have been removed, and references to Saunders et al. are now mentioned when needed in the revised paper. However, the detailed description of the treatment of RO_2 reactions remains necessary for the following reasons:

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- There are differences between our adopted kinetic rates and those of Saunders et al. (2003) and Jenkin et al. (1997), e.g., the higher acyl peroxy radicals + NO reactions, the organic nitrates yields, the CH_3O_2 + HO_2 or CH_3COO_2 + HO_2 reactions.

- Small peroxy radicals are produced in small, but not negligible amounts in the photooxidation of alpha-pinene. Furthermore, the interaction between small peroxy radicals (like CH_3O_2) and the large alpha-pinene radicals play an important role in atmospheric conditions (that are simulated in Sect. 3.6). Therefore, we think that the description of the chemistry of small peroxy radicals is relevant to this study.

- The treatment of the permutation reactions (Sect. 2.2.5) differs significantly from Saunders et al. (2003). Our study focuses on the reactions between large peroxy radicals ($C \geq 7$) while Saunders et al. based their work on the reactions of peroxy radicals with CH_3O_2. This results in different classifications of the peroxy radicals as well as different self-reaction rates and branching ratios (e.g. for the cyclic radicals).

As suggested by the referee, the figure showing the spectra of H_2O_2 and CH_3ONO is now removed. However, the sections describing the photolysis reactions remain unchanged due to the importance of photolysis for products like pinonaldehyde and the organic nitrates, in particular in the UV experiments.

Specific comments

Figure 1:
This question is answered in Peeters et al. (2001): For reasons detailed in that paper, with respect to hyperconjugation the R_6 radical does not behave as a tertiary, but rather as a secondary radical, and thus R_6 is not significantly more stable than the secondary adduct radical.

P. 4052:
The referee asks if elimination of the methyl radical can compete with the CH_3COOH elimination reaction upon decomposition of R_3O. Answer to this question can be found in Peeters et al. (2001): They calculated that the dissociation into CH_3COOH and a secondary cyclobutyl radical faces a sizeably lower barrier than the alternative decomposition yielding a CH_3 radical.

P. 4053:
We agree that a single NO concentration cannot be a valid threshold for both radicals R_3O_2 and $R_{13}O_2$. The reaction (R10) involving $R_{13}O_2$ competes with (R9) for NO concentrations $\gg 100$ ppb. Because of the faster decomposition rate of R_3O_2, its reaction with NO becomes effective for concentration $\gg 5$ ppm.

P. 4067, section 3.3.3.:
The referee questions the origin of the acetone production measured in NO_x free conditions (~11%). We believe that the production of acetone could have primary as well as secondary origins. In a sensitivity test, turning off the ring closure reactions (thus freeing the path to R_7) results in only 3.5% acetone. This low production is due to the tertiary structure of the peroxy radical R_7O_2. Its low self reaction rate favors the reaction with HO_2 against the permutation reactions. If the ring closure is the dominant process in the NO_x-free conditions, hypothesizing an acetone production upon complete decomposition of R_8O (generated from reactions of R_8 with O_2 and then with other peroxy radicals) gives a maximum yield of 6%. This yield remains below the experimental value, indicating that secondary production should be significant. Secondary production is also suggested by the concentration-time profiles in Fig. 8, since acetone is seen to increase even after complete oxidation of alpha-pinene. Note that numerous products could be precursor of acetone. For example, the fast photolysis of the peroxide functionality of the species produced from the reactions of the peroxy radicals R_8O_2 (R_8OOH, R_8OH, R_8-HO) forms a $C(CH_3)_2O$ group that could dissociate and form acetone.

P.4076:
We acknowledge that, given the complexity of the chemistry of biogenic compounds, the rigorous evaluation of every possible oxidation step is not possible in a realistic time frame, since thousands of reactions should be investigated. As in past studies, focus should therefore be given to the main oxidation pathways and to the formation of critical compounds, e.g., acetone or SOA precursors. Methodologies, of the type of the MCM mechanism, which allow to construct VOC degradation mechanisms on the basis of known reactions of similar (and more simple) compounds remain therefore complementary to theoretical studies if progress on environmental issues is to be made.

Minor points:

Technical corrections were made according to the referee's suggestions.

Referee 2

General comments

The referee suggested that the primary yields of products other than pinonaldehyde and acetone should be discussed. A brief description of the influence of NO on the yields of hydroperoxides and nitrates in atmospheric conditions has been added to the revised paper.

The referee asks about the potential for application of theoretical calculations in the elucidation of organic oxidation mechanism. Oxidation processes of terpenoid compounds present a different and more complex chemistry compared to the oxidation of simple organic alkenes. In this context, theoretical analysis proved to be an adequate tool to elucidate oxidation mechanism in parallel with the laboratory investigations. However, as stated in a specific comment to referee 1, the rigorous evaluation of every possible oxidation step is not possible in a realistic time frame due to the large number of reactions. Focus should therefore be given to the main oxidation pathways and to the

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formation of critical compounds, e.g., acetone or SOA precursors.

Specific comments

P. 4046:
The reference to the Troe expression is now included in the revised paper.

P. 4051:
The referee asks why the upper limit of as 1.5$\times 10-11$ cm^{3}molec^{-1}s^{-1} for the self-reaction rate constant of R1M radicals is used in the mechanism. There is at least a difference of one order of magnitude between the rate constants of C_3 and C_6 radicals in the R1R and R2R classes (see Table 3). Therefore, a value as high as 1.5$\times 10-11$ cm^{3}molec^{-1}s^{-1}, (extrapolated from the self-reaction rate of a C_3 R1M) is therefore plausible for C$\geq$7 R1M radicals. In absence of experimental data, we adopt this value for radicals bearing more than one chemical functionality. It is also the highest observed self-reaction rate for all peroxy radical classes.

P. 4052:
The decomposition of a tertiary peroxy radical produces indeed a RCOOH. This is corrected in the revised paper.

Chapter 2.4:
The referee questions the treatment of the chemistry of the primary products in the NO_x-free situation. As stated in this section, the implementation of the generic peroxy radicals is mainly designed in order to represent the NO to NO_2 conversions due to the oxidation of primary products and to the peroxy radicals for which the chemistry is still unknown. It is therefore essentially designed for high NO_x conditions. The production of (per)oxy radicals generated by the oxidation of a specific peroxy radical depends on the $[HO_2]/[RO_2]$ ratio and on the permutation reaction rates for this peroxy radical. The oxy radical yield in peroxy radical reactions is lower in NO_x free conditions compared to the high NO_x situation. Therefore the value of the parameter λ (Eq. 12) that would be required to represent peroxy radical production in NO_x free conditions is much closer

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to 1. Replacing λ=2 by λ=1.2 in the model is found to have little effect on the modeled pinonaldehyde yield in NO_x-free conditions, however.

P. 4055:
There is no coefficient in front of the summation term. The reaction R13a represents the traditional reaction RO_2+NO⇒RO+NO_2. We assumed that LXO (produced from the reactions of the peroxy radical LXO_2) dissociates into a lower carbon number radical SX and a (unknown) stable product. SX reacts with O_2 to give SXO_2. R13a represents the net reaction while the nitrate production is given by the reaction R13b. The possibility that LXO dissociates into two small radicals was neglected. The isomerisation to another radical of the same carbon number is represented through the coefficient λ being larger than unity.

P. 4062:
We agree with the remark. The yields deduced from the box model are indeed dependent on the photochemical conditions simulated by the model. The text is amended accordingly.

P. 4067, Chapter 3.3.3:
The referee questions the origin of the acetone production in NO_x-free conditions. We believe that the production of acetone may have both primary and secondary origins. An analysis of the concentration-time profiles in Fig. 8 suggests that secondary production could be significant since acetone concentration increases even after complete oxidation of alpha-pinene. Numerous products could be precursor of acetone. For example, the fast photolysis of the peroxide functionality of the species produced from the reactions of the peroxy radicals R_8O_2 (R_8OOH, R_8OH, R_8-HO) forms a $C(CH_3)_2O$ group that could dissociate and form acetone. Further theoretical studies are required to investigate the possibility of acetone production subsequent to the ring closure.

We believe that the NO_x-free experiments were clear from any trace of NO for two reasons: 1) Prior to each series of experiments described in Nozière et al., the cham-

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ber was depressurized down to low pressures (2–10 Torr). It was then exposed to UV and visible light. Wall desorption was measured by FTIR. This procedure (depressurization and irradiation) was continued until all compounds that could interfere with the experiments were removed. 2) In presence of NO, we would have observed a higher pinonaldehyde yield.

P. 4076. End of the first paragraph:
As suggested by the referee, the absence of explicit chemistry following the ring closure of R_7O_2 as a cause of underestimation of the acetone yield is now rediscussed earlier in Sect. 3.3.3. Moreover, the absence of explicit chemistry subsequent to the ring closure is mentioned in Sect. 2.3.

Technical corrections:
Corrections will be incorporated in the revised version.

Interactive comment on Atmos. Chem. Phys. Discuss., 4, 4039, 2004.