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Atmospheric Chemistry and Physics Discussions

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

Anonymous Referee #2

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General comments

The paper presents a detailed, carefully elaborated mechanism of the OH-initiated oxidation of alpha-pinene, to a large extent based on theoretical studies presented in previous papers, and a test of the model by comparison with the results of laboratory experiments performed in the presence as well as in absence of NOx. I find that it gives a comprehensive and clear description of the mechanism (apart from minor points mentioned in the following) and the considerations it is based on. The comparison to experimental results show that the mechanism gives a good description of the formation of several primary products, although with the important exception of acetone, where a discrepancy between model and experiment is found in the absence of NOx.

I have no important objections against the paper, which I find is generally well written and based on much careful thinking. The testing of the mechanism by comparison with laboratory experiments obviously has the weakness that the photochemical conditions of these experiments are rather far from the conditions that may be found in ambient air, both for what concerns chemical composition, concentrations and, in some experiments, the light source that is used; however I realise that it may not be possible to find more ‘realistic’ experimental data. I find that the paper can be published without major changes, but I would ask the authors to clarify a few points mentioned under ‘specific comments’ and consider a few suggestions I have made for amendments to the paper.

The main final scope of this kind of mechanism development for atmospheric reactions is obviously to describe the chemistry of the real atmosphere, so a main interest of many readers will be to know what the model tells about the chemistry of alpha-pinene under atmospheric conditions. In Chapter 3.6 this has been discussed for the cases of pinonaldehyde and acetone, but I think it could be interesting to know also what primary yields the mechanism predicts for other products (nitrates, hydroperoxides,Ě) under typical atmospheric conditions.

I agree with the final remarks in the conclusions of the paper about the need of further improvements of the understanding of the chemistry of alpha-pinene oxidation products and, certainly also, the of mechanisms of the reactions of alpha-pinene with ozone and with the nitrate radical. However, I also think that the authors are right when they write, that this will mean that “thousands of reactions will probably have to be carefully examined”, and, of course, there are several other terpenes with a probably equally complex chemistry that also are of importance in atmospheric chemistry. It would be interesting to have a comment from the authors regarding how far they believe that we can get in our understanding of these processes, particularly how they see the potential for application of theoretical calculations in these studies.

Specific comments

p. 4046, first paragraph: I think it should be mentioned, although it will be obvious to most readers, that the parameters mentioned here refer to the Troe expression.

p. 4051, l. 5: Why is the upper limit of the rate constant used in the mechanism, rather than a value in the middle of the range?

p. 4052, paragraph above R11: I do not see why the product formed by decomposition of the tertiary peroxy radical has to be acetic acid. I guess it would be better to write “RCOOH”.

Chapter 2.4: As far as I understand, the discussion here (e.g. the assumption that typically 4 peroxy radical reactions are needed to reach a stable product) refers to a high NOx situation. How was the chemistry of primary products treated in the NOx-free situation?

p. 4055, eq. R13a: I guess there should be a coefficient in front of the summation sign?

p. 4062, first paragraph of Chapter 3.2: I think that the procedure used in the paper for comparing experimental and calculated concentrations is OK. However, the sentence “Ěthis simplistic approach ignores the dependence of the yields on photochemical conditionsĚ” is not correct, because also the photochemical conditions are represented in the box model.

p. 4067, Chapter 3.3.3: It is really unfortunate that there is such a discrepancy between model and experiment regarding acetone in absence of NOx, as acetone is one of the terpene oxidation products of major interest in atmospheric chemistry, as mentioned in the paper. The authors suggest that this discrepancy between model and experimental results are due to secondary chemistry not represented in the mechanism and that may well be true. I believe that an analysis of the time concentration profiles of alpha-pinene, acetone and pinonaldehyde (precursor of acetone) in Fig. 8 would be useful for understanding the most likely origin of acetone.

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Interactive Discussion

Discussion Paper

It may be quite difficult to obtain really “NOx-free” conditions if a chamber previously has been exposed to NOx. Is it possible, that the explanation for the unexpectedly high acetone yields is that small concentrations of NOx were present also in the experiments were NOx was not added?

p. 4076, end of first paragraph: Here it is stated that the most likely reason for the underestimation of the acetone yield by the mechanism is “the chemistry following the ring closure reaction of R7O2 is not treated explicitly in the model". This idea appears only under "Conclusions"; it should be motivated in the previous discussion.

Technical corrections:

p. 4055, l. 8: “RxO” is not defined in Table 2. p. 4062, l. 10: photolysis->photolyse p. 4070, l. 8: Benzoyl peroxy nitrate cannot be called an “alkyled PAN analogue” (it does not even contain an alkyl group). Fig. 1: The sum of the contributions of the initial reaction pathways is not 100%.

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