Simulation of Aerosol formation in α-pinene Oxidation Experiments with a quasi-explicit Model

http://www.oma.be/TROPO/boream/

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1. Introduction

Biogenic volatile organic compounds (BVOC) are known to contribute to atmospheric aerosol. The precise mechanisms and aerosol yields for the different biogenic VOC are still not well known though. We have developed a box model named BOREAM for the oxidation and subsequent aerosol formation from the monoterpene α-pinene. It contains a quasi-explicit reaction mechanism for the oxidation of α-pinene to primary products. It is based as much as possible on objective grounds, using advanced quantum theoretical methods or structure activity relationships (SARs) derived from experimental data on reaction rates or thermodynamic properties. In total the model contains 5000 reactions and 1200 species. The goal of this model is to better characterize aerosol yields under varying conditions and to improve understanding of the processes involved. A detailed box model can then be reduced for introduction into a global model. Here we present a comparison of the modeled SOA yields with chamber experiments for photooxidation and dark ozonolysis of α-pinene.

2. Model Description

Chemical Mechanism

The oxidation of α-pinene by OH and O_3 down to primary products is described by a detailed mechanism which is based on quantum chemical calculations and SARs (Peeters et al. 2001, Capouet et al. 2004, Capouet et al. 2008).

As discussed in Capouet et al. (2008), credible pathways leading to key carboxylic acids (e.g. pinic acid) are still missing. Based on experiments (Yu et al. 1999) we have included a production of these compounds.

For primary products simplified chemistry based on SARs and experimental rates is included for reaction with OH, O_3 or NO_3 and for photolysis. Products of this simplified chemistry are lumped into generic species. For these generic species, information on important functional groups and the vapor pressure is retained, but the precise structure unspecified.

Figure 1: reaction mechanism for alpha-pinene ozonolysis (Capouet et al. 2008)

Aerosol formation

In our model the aerosol is assumed to be liquid, well mixed and composed of organic species. Products from α-pinene oxidation are allowed to partition between the gas phase and the aerosol phase. The fraction of the gas phase and aerosol phase concentration $C_{g,i}$ and $C_{p,i}$ of a product i depends on the total mass concentration of the aerosol M_O and on a partitioning equilibrium constant $K_{p,i}$ (Pankow 1994):

$$C_{p,i}/C_{g,i} = K_{p,i} \cdot M_O$$

The partitioning constant depends on temperature, mean molecular weight of the aerosol (MW_{aer}), the liquid vapour pressure of the product $p_{L,i}^0$ and the activity coefficient γ_i of the product in the aerosol mixture.

$$K_{p,i} = \frac{760 \cdot RT}{MW_{aer} \cdot 10^6 \cdot \gamma_i \cdot p_{L,i}^0}$$

The vapour pressure is calculated as a funtion of T with a group contribution method based on Marrero and Gani 2001 and Capouet and Müller 2006. The activity coefficients are calculated with the UNIFAC method (see **Compernolle et al, poster session EGU2008-A-03755**).

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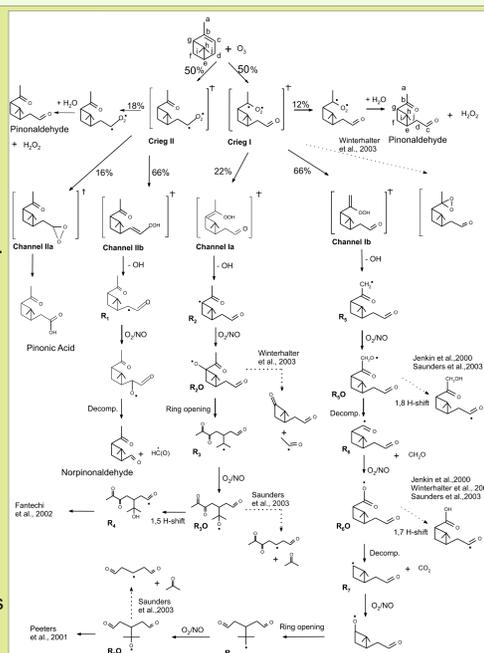Kamens et al., Environ. Sci. Technol., 33, 1430–1438,1999

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Oligomerization reactions

Recent work indicates that some products of α-pinene undergo oligomerization, resulting in large molecules with low vapor pressures. We investigate the possible impact of two such processes.

I. Peroxyhemiacetals from aldehydes and hydroperoxides in the liquid phase

This reversible reaction has been considered by Tobias and Ziemann 2001 to explain formation of peroxides in the aerosol and was investigated by Antonovskii and Terent'ev 1967:

ROOH + R'CHO ⇌ ROOC(OH)R'H
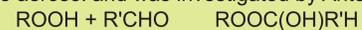
Forward and backward rates are based on these experiments, although the nature of the solvent and the precise structure of the reactants could influence these rates significantly.

$$k_{fwd} = 42500.\exp(-4000/T)\ M^{-1}s^{-1}$$
$$k_{back} = 2600.\exp(-5000/T)\ s^{-1}$$

II. Gas phase reactions of stabilized Criegee radicals and acids, aldehydes

Criegee biradicals can partly stabilize and undergo further reactions. Usually only the reaction with water vapor is considered, since it is present at high concentrations compared to most other reactants. Tobias and Ziemann (2001) measured the reaction rates of stabilized Criegee biradicals (SC) and a series of products relative to the reaction rate with H_2O. For low RH the SC could start reacting with acids in significant amounts yielding large molecules which are very condensable.
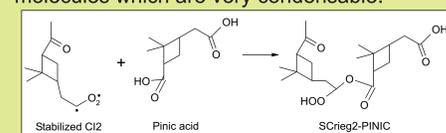

Figure 2: A reaction of a stabilized Criegee with pinic acid which has been included in the model

competing reactant	Reaction rate relative to water
heptanoic acid	17000
formic acid	6700
formaldehyde	2700
2-propanol	50
methanol	22
water	1

Table 1: Relative rates of reactions with stabilized Criegee radicals, Tobias and Ziemann 2001

3. Results of simulations

Photooxidation experiments

In Capouet et al. 2008 we compared experimental aerosol yields of 28 photooxidation experiments with modeled yields (**Figure 3**).
In most cases model and experiment agree within a factor 2. In some experiments at high temperatures, a stronger underestimation is found (Hoffmann et al., about 45 °C).
When ozonolysis is dominant, such as for the experiments of Presto et al., the agreement with experiment improves when pinic acid is included. Peroxyhemiacetal formation is found not to have a large influence on SOA yields, except when aerosol fractions are already high, such as for several experiments of Presto et al.
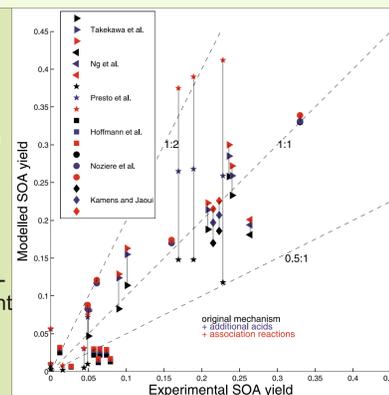

Figure 3: Photooxidation: Comparison of SOA yields for 28 experiments with modeled yields
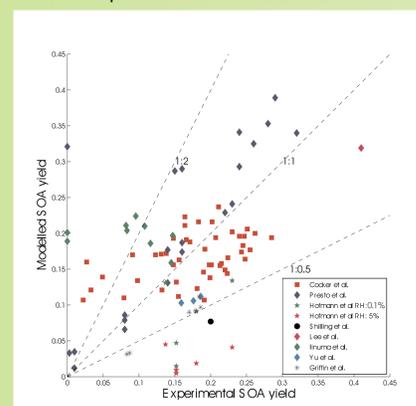
Dark ozonolysis experiments

In **Figure 4** model predictions are again compared with experimental yields from a large number of dark ozonolysis experiments.

Generally the model is again capable of predicting the SOA yield within a factor 2, although there are some overestimations (for Presto et al. and Iinuma et al) and serious underestimations in the case of Hoffmann et al.

Decreasing relative humidity from 5 to 0.1% improves the agreement in the case of Hoffmann et al. This is due to the increased formation of oligomers from stabilized Criegee radicals and acids, showing the possible importance of these reactions at low RH.

Figure 4 : Dark ozonolysis of α-pinene, modeled versus experimental SOA yields

Temperature dependence of SOA yields

For the experiments of Pathak et al. 2007 in **Figure 5** the majority of yields are predicted within a factor 2. Nonetheless there are overestimations at lower temperatures (0°C-20°C) and serious underestimations at higher temperatures (30°C-40°C).

For one of the runs at 40°C an experimental yield of 9% was measured by Pathak et al. Our standard model predicts hardly any aerosol formation (0.007% or an underestimation of more than a factor 1000). The model in which stabilized Criegee radicals can react with carboxylic acids increases this yield to 0.4% at RH 1%, still more than a factor 20 too low.
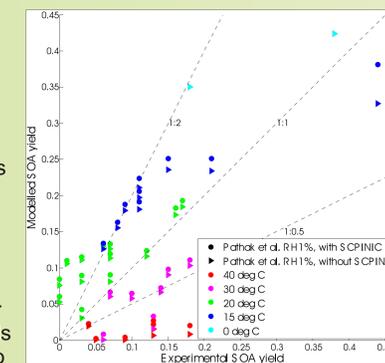

Figure 5: SOA yields for Pathak et al. 2001, with a test with and without stabilized Criegee oligomers

The same pattern is found for other experiments at high temperature. **Figure 6** compares modeled and experimental yields at different temperatures for both seeded and non-seeded experiments. Clearly experimental yields are not very temperature sensitive, while modeled yields decrease strongly with temperature. As proposed by Pathak et al., the production of very condensable species, which are always predominantly in the aerosol phase in the temperature interval 0°C-40°C, could explain the observations.
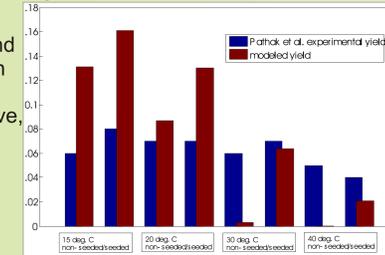

Figure 6: Temperature dependence of SOA yields for Pathak et al. 2001, experimental versus model
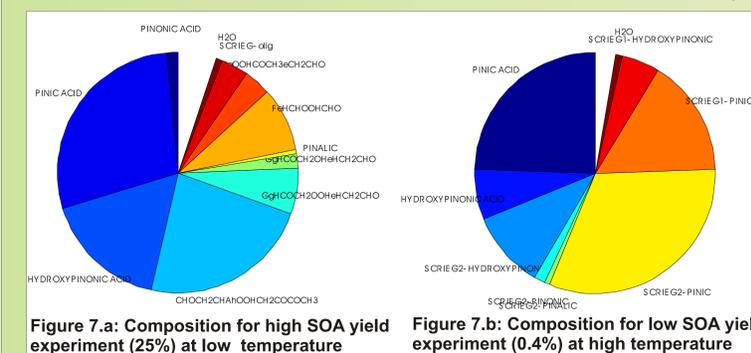

Figure 7.a: Composition for high SOA yield experiment (25%) at low temperature
Figure 7.b: Composition for low SOA yield experiment (0.4%) at high temperature

Figure 7 shows the modeled composition for one low-yield (0.4%) and one high-yield (25%) experiment. The low yield experiment is dominated by the oligomers from stabilized Criegees (containing 19 or 20 carbons), while the high yield aerosol is composed of more usual products with 9 or 10 carbons. The currently modeled production of these compounds is still too low to fully explain the serious discrepancies at high temperatures.

4. Conclusions

We have developed a box model for the oxidation and aerosol formation from α-pinene, which is based as much as possible on current knowledge about reaction rates and thermodynamic properties.

Comparison with experimental smog chamber studies shows that the model is capable of predicting the aerosol yield with a factor two for most experiments, although for some experiments more important deviations between model and experiment exist.

Overestimations usually occur at low temperatures, and could be due to uncertainties in the chemical reaction mechanism (yield of carboxylic acids, ...) or vapor pressure predictions.

Serious underestimations tend to occur at temperatures above 30°C. We propose that at low RH certain reactions of Criegee biradicals forming oligomers can partly solve this problem, but further improvements are still needed to obtain fully satisfactory model results at high temperature.