1. Introduction
Biogenic volatile organic compounds (BVOC) are known to contribute to atmospheric aerosol. The precise mechanisms and aerosol yields for the different biogenic VOCs are still not well known, though. We have developed a box model named BOREAM for the oxidation and subsequent aerosol formation from the monoterpenes 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 (30% activity relationships (SARs)), and from experimental data on reaction rates and 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 O3 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. 2006).

As discussed in Capouet et al. (2008), credible pathways leading to key carbonylic 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 CH3, O3 or NO3 and for photoysis.

Product distributions of photolyzed species are still missing. We also consider the possible impact of pinic acid which has been included in the model.

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 and the aerosol phase. The fraction of the gas phase and aerosol phase concentration Cg and Ca of a product i depends on the total mass concentration of the aerosol M, and on a partitioning equilibrium constant K<sub>P</sub>

\[ C_i = \frac{K_P M_i}{K_P + M_i} \]

The partitioning constant depends on temperature, molecular weight of the aerosol (MW), the liquid vapour pressure of the product P<sub>L</sub>, and the activity coefficient \( \gamma^* \) of the product in the aerosol mixture.

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

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 overestimation is found (Hoffmann et al., about 45 °C).

When ozone is dominant such as for the experiments of Presto et al., the agreement with experimental results is improved when pinic acid is included. Overestimations usually occur at low temperatures, and could be due to uncertainties in the reaction rates and thermodynamic properties.

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 in which stabilized Criegee radicals are used predicts an aerosol yield of 22% (0.007% or an underestimation of more than a factor 1000). The model in which stabilized Criegee radicals can react with carbonylic acids increases this yield to 67% at 0.4% at RH 1%, still more than a factor 2 too low.

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.

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 experimental result.

Overestimations usually occur at low temperatures, and could be due to uncertainties in the chemical reaction mechanism (yield of carbonylic 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 temperatures.

Figure 3: dark ozonolysis of α-pinene, modeled versus experimental SOA yields

Figure 4: Photooxidation: Comparison of SOA yields for 28 experiments with modeled yields

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

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