



Simulation of organic aerosol production from alpha-pinene oxidation in laboratory experiments.

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Atmospheric monoterpenes are important due to their high reactivity and large emissions into the atmosphere. The emissions and chemistry of α -pinene (as representative for the monoterpenes) are included in several tropospheric CTMs, but in a very simplified and unsubstantiated way. While the mechanisms involving simpler alkenes are fairly well understood, those involving monoterpenes oxidation present a different and more complex picture and are still not well characterised. In order to reduce these uncertainties, Peeters and co-workers have developed a detailed mechanism for the gas-phase oxidation of α -pinene by OH and O₃ based on quantitative structure-activity relationships and theoretical quantum chemistry methods, combined with transition state theory calculations or RRKM master equation analyses (Peeters et al., 2001; Fantechi et al, 2002). Recently, the gas-phase mechanism by OH has been validated successfully by model simulations of laboratory experiments (Capouet et al., 2004).

Here we present a model study of the secondary organic aerosol production from the gas-phase oxidation of α -pinene, based on these detailed mechanisms. A module describing the gas/particle partitioning of the semi-volatile products has been developed and coupled to the gas-phase box model. This module relies on a vapour pressure prediction method based on group contribution principles. It provides estimations for a large range of oxygen-containing species produced from the gas-phase oxidation including nitrates, peroxy acyl nitrates and hydroperoxides. The large number of species involved in the mechanism requires the method to be simple while still of the same accuracy as other methods dedicated to the prediction of the vapour pressures of poly-functional compounds. The method developed in this work is outlined in this poster and compared with the UNIFAC method (Asher et al, 2002).

In order to validate the gas-phase mechanism and the partitioning model, we present comparisons of simulation results with product concentrations measured in a series of laboratories experiments performed by Nozière et al. (1999) for the oxidation by OH, and by Hoffman et al (1997) and Yu et al (1999) for the ozonolysis. Note that the low humidities in these experiments reduces the possible importance of solubilisation and aqueous-phase reactions, which are not represented in the box model. The sensitivity of the results to uncertainties in the determination of the vapour pressures as well as to the possible formation of acid dimers is also discussed.

References

- Asher, W.E., Pankow, J.F., Erdakos, G.B., and Seinfeld, J.H., *Atmos. Environ.*, 36, 1483-1498, 2002.
- Capouet, M., Peeters, J., Nozière, B., and Müller, J-F., *Atmos. Chem. Phys.*, 4, 1-27, 2004.
- Fantechi G., Vereecken L. and Peeters J., *Phys. Chem. Chem.Phys.*, 4, 5795-5805, 2002.
- Hoffmann, T., Odum, J., R., Bowman, F., Collins, D., Klockow, D., Flagan, R., C., and Seinfeld, J., H., *J. Atmos. Chem.*, 189-222, 1997.
- Nozière, B., Barnes, I., and Becker, K.H., *J. Geophys. Res.*, 104, 23645-23656, 1999.
- Peeters, J., Vereecken, L., and Fantechi, G., *Phys. Chem. Chem. Phys.*, 3, 5489-5504, 2001.
- Yu, J., Cocker III, D.R., Griffin, R.J., Flagan, R.C., and Seinfeld, J.H., *J. Atmos. Chem.*, 34, 207-258, 1999.