



Alpha-pinene oxidation: from simulations of laboratory experiments to global modeling

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The importance of monoterpenes in the atmosphere stems from their large emissions from plants, their high reactivity, and their role as precursors for Secondary Organic Aerosol (SOA) production. Although the emissions and chemistry of α -pinene (as representative for the monoterpenes) are now included in many tropospheric CTMs, the representation of its oxidation mechanism is still speculative and oversimplified. For this reason, the formation of biogenic SOA remains highly parameterized in models, and its dependence to photochemical and meteorological conditions cannot be assessed with a good degree of confidence. Recent advances suggest that such representations can be improved, however. Based on objective theoretical methods, Peeters and co-workers (Peeters et al., 2001; Fantechi et al., 2002) have developed a detailed mechanism for the oxidation of α -pinene and pinonaldehyde by OH. This mechanism has been validated successfully by model simulations of laboratory experiments (Capouet et al., 2005). Recently, an ozonolysis mechanism has been also developed by this group.

We present here a module describing the gas/particle partitioning of the semi-volatile products. It relies on a vapour pressure prediction method which parameterizes the contributions of the carbonyl, hydroxy, acid, hydroperoxide, nitrate, and peroxy acyl nitrate functionalities to the vapour pressure of the degradation products. The impact of the degree of substitution of the carbon bearing the functionality is also parameterized. The comparison of both our method and the UNIFAC method (Asher et al., 2002) with the measurements suggests that our method compares favourably to UNIFAC. A good performance is obtained for (di-) carbonyls, alcohols, diols, (di-)nitrates, monocarboxylic acid and monohydroperoxides with vapour pressures predicted within a

factor 2. Uncertainties for dicarboxylic acids, hydroxy ketones and tri-O-acids are larger (up to a factor of 3), suggesting that more vapour pressure data are required for heterofunctional compounds, i.e. for compounds bearing different functionalities.

Next, the detailed α -pinene/OH/O₃ mechanism and the gas/particle partitioning model are used to simulate the formation of SOA in α -pinene oxidation experiments. A reduced version of the detailed α -pinene mechanism is also implemented in the global CTM IMAGES (Müller and Brasseur, 1995). Sensitivity studies are performed to seize the influence of vapour pressure uncertainties and the dimerization of carboxylic acids on the formation of aerosol in laboratory as well as in atmospheric conditions. Our results indicate a very low potential for aerosol formation of α -pinene in atmospheric conditions, which questions the validity of usual assumptions about biogenic SOA formation and budget.

References

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