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A group contribution method for estimating the vapour pressures of α-pinene oxidation products

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Abstract. A prediction method based on group contribution principles is proposed for estimating the vapour pressure of α-pinene oxidation products. Temperature dependent contributions are provided for the following chemical groups: carbonyl, nitrate, hydroxy, hydroperoxy, acyl peroxy nitrate and carboxy. On the basis of observed vapour pressure differences between isomers of diols and dinitrates, a simple refinement is introduced in the method to account for the influence of substitutions on the vapour pressure for alcohols and nitrates. The vapour pressures predicted with this new method have been compared with the predictions from UNIFAC (Asher et al., 2002). Given the large uncertainties of the vapour pressure data for the least volatile compounds, further experimental studies of subcooled vapour pressures of multifunctional compounds at ambient temperatures are required for better parameterizations. Among the α-pinene products identified to date, pinic acid and hydroxy pinonic acid are predicted to be the least volatile compounds, with estimated vapour pressures of 3×10^{-6} torr and 6×10^{-7} torr, respectively. The vapour pressure of the other primary products range from 10^{-5} to 10^{-3} torr, with hydroxy hydroperoxides presenting the lowest values. Noting that multifunctional carboxylic acids, in particular pinic acid, are believed to be mostly present as dimers in laboratory conditions, we suggest that the partial vapour pressure of the pinic acid dimer should be close to the experimental subcooled vapour pressure for pinic acid (estimated at $\sim10^{-6}$ torr) due to its large contribution to the total concentration (dimer+monomer) in experimental conditions.

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