A kinetic investigation on the gas-phase reaction of ozone with four sesquiterpenes

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Sesquiterpenes ($C_{15}H_{24}$, SQT) are emitted by plants with a global emission rate of about 15 Tg per year (Seinfeld and Pankow, 2003). They are possibly an important source of secondary organic aerosol (SOA) but their oxidation processes are scarcely examined.

This study focusses on the kinetics of the reaction of ozone with four atmospherically relevant SQT: β-caryophyllene, α-humulene, α-cedrene and isolongifolene.

Up to now there are only two studies available in the literature describing kinetic measurements of the ozonolysis of a series of SQT, (Shu and Atkinson, 1994; Ghalaieny et al., 2012). As a result of these studies the rate coefficients of the ozone reaction with β-caryophyllene and α-humulene differ by three orders of magnitude making a reinvestigation necessary.

Both literature studies were carried out in a reaction chamber with long reaction times. Shu and Atkinson (1994) used high concentrations of [SQT] = 2.4 • 1013 molecules cm-3 and [O_3] = 2.5 • 1012 molecules cm-3 making particle formation and consecutive reactions relevant. The latter study of Ghalaieny et al. (2012) investigated the reaction at even higher concentrations ([SQT] = (2.1 - 3.5) • 1014 molecules cm-3, [O_3] > 2.1 • 1015 molecules cm-3) at elevated temperatures (366 K) to avoid particle formation.

Our study was carried out with very low SQT concentrations ((1 - 2) • 1010 molecules cm-3), [O_3] = (1 - 15) • 1011 molecules cm-3, in a flow tube at atmospheric pressure and room temperature. The relative rate coefficients were investigated by means of an online GC-MS technique allowing measuring SQT concentrations down to 109 molecules cm-3. Particle formation was detected using an ultrafine condensed particle counter (TSI-3025 with a 50% cut-off size of 2.5 - 3 nm) and was found to be negligible under the chosen reaction conditions.

Our study supports the rate coefficients as given by Shu and Atkinson (1994).

References:

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