Kinetics of the Gas-Phase Reaction of O$_3$ with Selected Terpenes and Products from the Reaction of O$_3$ with α-Pinene

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Terpenes are released into the atmosphere from vegetation with an estimated global emission rate in the order of 10^{14} g yr^{-1}. α-Pinene (35%), β-pinene (23%) and limonene (23%) are the most important compounds in this process accounting for *ca.* 80 % of the emitted terpenes (Günther et al., 1995). Especially in the last years interest focused on the contribution of terpene oxidation products on the formation and the growth of particles.

In the present work the gas-phase reaction of O$_3$ with a series of terpenes has been performed at 295 K in a new quartz flow-tube (called *IfT*-LFT: *Institute for Tropospheric Research* – **L**aminar **F**low **T**ube) with a length of 505 cm and an inner diameter of 8.0 cm using synthetic air as the carrier gas. The *IfT*-LFT is surrounded with a thermo-jacket controlling the temperature with a precision of ± 0.5 K. For analysis of gaseous products the *IfT*-LFT is equipped with a White cell for long-path (80 m) FT-IR detection (Bruker, IFS 66) and a sampling device for on-line GC-FID (HP 5890) and GC-MS analyses (HP 6890 with HP-MSD 5973). A dew point sensor (General Eastern, HygroM4) measured the humidity in the flow system. Particle size distributions (d_p > 3 nm) were determined using a Differential Mobility Particle Sizer (DMPS) consisting of a Vienna-type Differential Mobility Analyzer (DMA) and an Ultrafine Particle Counter (UCPC, TSI 3025). For integral measurements, an additional UCPC (TSI 3025) was attached directly to the outlet of the *IfT*-LFT.

In the presence of a large excess of *m*-xylene as an OH radical scavenger, rate constants k(O$_3$+terpene) were obtained with a relative rate technique for seven terpenes (unit: cm^3 molecule^{-1} s^{-1}, errors represent 2σ): α-pinene: (1.05 ± 0.09) x 10^{-16}, ^{3}Δ-carene: (5.6 ± 0.7) x 10^{-17}, d-limonene: (2.4 ± 0.1) x 10^{-16}, myrcene: (4.6 ± 0.3) x 10^{-16}, *trans*-ocimene: (5.3 ± 0.4) x 10^{-16}, terpinolene: (1.6 ± 0.1) x 10^{-15}, α-terpinene: (1.5 ± 0.2) x 10^{-14} as well as for 2,3-dimethyl-2-butene: (9.8 ± 0.5) x 10^{-16}.

Pinonaldehyde and α-pinene oxide were analysed as gaseous products of the reaction of O$_3$ with α-pinene. The yield of pinonaldehyde increased with decreasing amount of reacted α-pinene resulting in a maximum value of 0.62 ± 0.06. The α-pinene oxide yield of 0.09 ± 0.03 was found to be independent of experimental conditions. An OH radical yield < 0.41 results from a rough estimate using the observed product yields. The formation of new particles was investigated in dependence on the amount of reacted α-pinene, the relative humidity in the system and additions of further organic compounds to the gas mixture.

Reference

Günther, A., C.N. Hewitt, D. Erickson, A. Fall, C. Geron, T. Graedel, P. Harley, L. Klinger, M. Lerdau, W.A. McKay, T. Pierce, B. Scholes, R. Steinbrecher, R. Tallamraju, J. Taylor, P. Zimmermann, *J.Geophys.Res.* 100 (1995) 8873-8892.