Gas-Phase Reaction of NO₃ Radicals with β -Pinene

A guest contribution to subproject CMD

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Monoterpenes, in particular β -pinene, are amongst the most abundant naturally emitted hydrocarbons in the troposphere, with a globally averaged annual emission of *ca.* 125 Tg C (Guenther *et al.*, 1995). Thus, biogenic hydrocarbons play an important role in the chemistry of the troposphere. Their degradation can be initiated by the reaction with OH radicals, O₃ and NO₃ radicals. Tropospheric lifetimes show that the night-time reaction of NO₃ radicals with terpenes is an important sink for such substances. In spite of the importance of terpenes in the troposphere, the knowledge of product distributions and mechanisms of the radical- or ozoneinitiated degradation is very limited. This fact is valid especially for NO₃ radical reactions.

In the present study, the gas-phase reaction of NO₃ radicals with β -pinene has been investigated in a flow-tube system at 298 K in the pressure range 10 < P(mbar) < 200 in N₂ as well as in N₂/O₂ mixtures using GC-MS/FID, long-path FT-IR and CPC / DMA-CPC as detection techniques.

Product distributions have been detected in dependence on total pressure in pure N_2 as well as in the presence of O_2 . In the absence of O_2 , organic nitrates and a to date unknown compound were found. In the presence of sufficient amounts of O_2 , peroxynitrates and nopinone were observed. Under all experimental conditions, β -pinene oxide, myrtanal and myrtenol as traces were identified additionally.

Independent on the O_2 concentration in the carrier gas, the occurrence of new formed particles with a diameter > 100 Å was observed. Their formation process was studied in dependence on time.

The application of our results to the troposphere is discussed.

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