Geophysical Research Abstracts, Vol. 7, 10814, 2005
SRef-ID: 1607-7962/gra/EGU05-A-10814

The effect of NO_2 on particle formation during ozonolysis of d-limonene and α-pinene

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Oxidation of monoterpenes by ozone (O_3) may to be a source of submicron particles in indoor air (Long et al., 2000; Wainmann et al., 2000; Weschler and Shields, 2003). Abundant monoterpenes indoors are d-limonene and α-pinene (Wolkoff et al., 2000). Several parameters influence these processes, e.g. nitrogen oxides have previously shown an effect on particle formation from ozonolysis of β-pinene in the presence of sunlight (Pandis et al., 1991). In the present study, the particle formation during ozonolysis of α-pinene and d-limonene was studied at low relative humidity (RH$<$1%) in 1000 liters Tedlar bags at 294$\pm$2 K and ambient pressure. Particle number concentrations, total particle volumes and size distributions were measured using a Differential Mobility Particle Sizer - Condensation Particle Counter (DMPS-CPC).

At 50 parts per billion (ppb) monoterpene and variable O_3, the particle number and -volume increased non-linearly with the O_3 concentration and leveled off at ca. 100 ppb O_3 after 60 min of reaction. The particle number concentration was ca. 6 times larger for d-limonene than α-pinene at 50 ppb O_3, and also with a faster onset. As little as 6 ppb O_3 produced more than 10^4 particles cm^{-3} during limonene ozonolysis, whereas 18 ppb O_3 produced only 10% during α-pinene ozonolysis.

A new series of experiments were conducted using 50 ppb of monoterpene and O_3,

and variable concentrations of nitrogen dioxide (NO_2). A small reduction in particle volume and -number was observed in the d-limonene experiments as NO_2 was added to the mixtures. The presence of NO_2 introduced an additional loss term for O_3, resulting in formation of the nitrate radical; $O_3 + NO_2 \rightarrow NO_3 + O_2$. This affected the particle formation, since the nucleation potential of NO_3 is much lower than O_3 with respect to α-pinene and d-limonene (Bonn and Moortgat, 2002). Modeling showed that the observed decrease in particle number could be ascribed to the O_3/NO_2 reaction. In the α-pinene experiments, particle volume and -number were substantially reduced, resulting in a complete suppression of particle formation at 450 ppb NO_2. Moreover, the onset of particle formation was further delayed as the NO_2 concentration was increased. The particle size distribution appeared to be unchanged. The observed effect could not be explained by the additional loss of O_3 from the O_3/NO_2 reaction, but may be due to reaction of NO_2 with precursors of the particle formation, e.g. Criegee intermediates (Bonn et al., 2002).

The results indicate that in concentrations of monoterpenes and O_3 typical of indoor environments, d-limonene may form new particles as supported by other studies (Weschler and Shields, 2003; Wainmann et al., 2000). α-Pinene ozonolysis is not likely to produce new particles indoors (this study, Berndt et al., 2003). Furthermore, NO_2 appears to inhibit particle formation from α-pinene, even in lower ppb concentrations, whereas d-limonene is less affected.

The effect of relative humidity and identification of reaction products are subject to further studies.

LITERATURE

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