



Formation of Ultrafine Particles by Chemical Reactions in Indoor Air

S. Langer (1), K. Pointet (1), J. Moldanová (2), E. Ljungström (3), L. Ekberg (4)

(1) SP Swedish National Testing and Research Institute, Department of Chemistry and Materials Technology, Brinellgatan 4, P.O. Box 857, SE-501 15 Borås, Sweden

(2) IVL Swedish Environmental Institute, Box 5302, SE-400 14 Göteborg, Sweden

(3) Chalmers University of Technology, Inorganic Environmental Chemistry, SE-412 96 Göteborg, Sweden

(4) CIT Energy Management, SE-412 96 Göteborg, Sweden

(Contact: e-mail: sarka.langer @ sp.se; fax +46-33-16 52 87)

Atmospheric chemistry of indoor air involves in principal the same reaction mechanisms and rates as that of natural atmosphere, however premises for the indoor chemical reactions are different due to the absence of UV light and due to the significantly different concentrations of indoor air pollutants. Concentrations of hydroxyl radicals are orders of magnitudes lower (Weschler and Shields, 1997), indoor/outdoor concentration ratios of ozone, transported indoors with the ventilation system, vary between 0.1 – 1.0 (Finlayson-Pitts and Pitts, 2000), and concentrations of volatile organic compounds are higher in the indoor environments due to degassing from building materials and furniture, not speaking about the influence of humans and their activities. Nitrogen dioxide is often found in the similar concentrations indoors as outdoors.

Wooden furniture and cleaning agents are known sources of terpenes; limonene is one example that often is present in higher concentrations. Since concentrations of hydroxyl radicals are low, ozone becomes more important for initialization of VOC oxidation in the indoor environments. The reactions of terpenes and ozone have been thoroughly studied over the past decades, and the reaction rate coefficients together with reaction mechanisms and products formed have been elucidated. One interesting moment of the terpene/ozone reactions is the potential of particle formation due to

gas-to-particle conversion of reaction products with sufficiently low vapor pressure to begin nucleation.

In this work, the reaction of ozone with limonene, as a source of ultrafine particles ($< 0.1 \mu\text{m}$), has been investigated at concentrations relevant to indoor environments. A stainless steel chamber with a volume of 17 m^3 supplied with limonene and ozone at different concentration scenarios has been used for the experiments. The chamber/reaction temperature was $23 \pm 2 \text{ }^\circ\text{C}$, and the ventilation was shut down in order to simulate static conditions. Limonene was introduced in the chamber by injecting microliter amounts of the pure liquid substance onto sheets of Cleenex paper in a washing bottle in a stream of cleaned and dried air. Ozone was generated using an ozone generator (UltraViolet Products, SOG-3; HydroAir Bath and Spa Ozonator 20-5133). The concentration of ozone was monitored using an O_3 42M (Environnement, France) instrument; the limonene concentration was determined by GC/MS/FID analysis of samples collected on Tenax TA adsorbent tubes. The concentrations of limonene ($17 - 190 \text{ ppbv}$) were in excess over the ozone concentrations during the experiments in order to limit secondary reactions of ozone with the limonene oxidation products. The range of ozone concentrations in the set of experiments was $6-19 \text{ ppbv}$. Particle number concentration and size distribution between $0.003 \mu\text{m}$ and $10 \mu\text{m}$, was monitored as a function of time using the following set of instruments: A scanning mobility particle sizer together with a condensation particle counter TSI 3936 SMPS-instrument, a “stand alone” condensation particle counter (TSI, model 8525, P-Trak) and an optical particle counter (MetOne, model 3313).

The experiments clearly showed formation and growth of ultrafine particles from the chemical reactions taking place in the test-chamber (by gas-to-particle conversion of the low vapor pressure reaction products). The initial concentrations of the reactants are well within the ranges normally present in real indoor environments. The aerosol mass in the reaction chamber increased by $1-49 \mu\text{g}/\text{m}^3$ in the set of experiments (initial aerosol mass in the chamber was typically $1-2 \mu\text{g}/\text{m}^3$). This corresponded to the aerosol yield of $10 - 75\%$ on reacted limonene mass bases. For example, at an initial ozone concentration of about 13 ppbv and a limonene concentration of 30 ppbv the number concentration of particles in the size range $4-106 \text{ nm}$ started to increase immediately after injection of the reactants. After about 50 minutes the concentration peaked at a concentration 25-times higher than the initial. Particles smaller than 20 nm constituted up to 95% of the total number concentration, and peaked after 25 minutes. The number concentration of particles larger than 20 nm began to increase after 22 minutes, which indicates particle growth, e.g. by condensation. A mathematical model was used to analyze the ongoing gas phase chemistry and to describe the formation of condensable oxidation products.

References:

Weschler CJ, Shields HC. "Measurements of the Hydroxyl Radical in a Manipulated but Realistic Indoor Environment", *Environ Sci Technol* **1997**, 31, 3719-3722.

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