A Simple Kinetic Model to describe the Nucleation of Aerosol Formed in the Ozonolysis of Terpenes

A contribution to subproject CMD

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Introduction

Dicarboxylic acids are suggested to play a key role in the formation of secondary organic aerosol formed in the gas phase ozonolysis of terpenes (Winterhalter et al., 1998). For example, the ozonolysis of β-pinene leads to the formation of pinic acid which has been detected in filter samples of the aerosol with a yield of 3 %.

\[ \text{β-pinene} \xrightarrow{\text{O}_3} \text{pinic acid} \]

Due to the lack of thermodynamic data a simple kinetic homogeneous homomolecular nucleation model was chosen to describe the aerosol formation observed experimentally.

Experimental

Ozonolysis ([O_3]_0 = 6 \times 10^{12} \text{ molecules cm}^{-3} \approx 300 \text{ ppb}_v) of β-pinene ([β-pinene]_0 = 7 \times 10^{10} \text{ molecules cm}^{-3} \approx 3 \text{ ppb}_v) was performed in a 570 L spherical glass reactor (T = 294 K, P = 730 Torr) and particle formation was observed using a 3 nm and a 10 nm condensation nuclei counter (TSI 3025 A, TSI 3010).
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Model

The kinetic model assumes that pinic acid formed with a yield (Y) of 0.03 acts as monomer <1> in homogeneous homo-molecular nucleation of spherical particles <i>, where i denotes the number of monomers the particle consists of. Nucleation is described by collisions of particles of any size with a sticking probability of one while the size of particles is reduced by evaporation of monomers.

Reaction: \[ \beta\text{-pinene} + O_3 \xrightarrow{} Y\text{ pinic acid} + \text{products} \]

Nucleation: \[ <1> + <1> \rightarrow <2> \]
\[ <1> + <2> \rightarrow <3> \]
\[ <i> + <j> \rightarrow <i+j> \]

Evaporation: \[ <i> \rightarrow <i-1> + <1> \]

The discrete dynamic equations (Seinfeld, 1986) are numerically solved for a maximum particle size of \( i_{\text{max}} = 128 \) monomers.

\[
\frac{dN_i}{dt} = \frac{1}{2} \sum_{j=1}^{i-1} k_{i,j} N_j N_{i-j} - N_i \sum_{j=1}^{i_{\text{max}}} k_{i,j} N_j - k_i N_i + k_{i-1} N_{i-1} N_1 ,
\]

where \( k_{ij} \) are the gas kinetic collision coefficients and \( k_i \) the evaporation frequencies as functions of the equilibrium number density of monomers \( (N_i^{eq}) \), the surface area \( (4 \pi r_i^2 i^{2/3}) \) and the surface tension \( (\sigma) \).

\[
k_{i,j} = \sqrt{\frac{6kT}{\rho}} (r_i + r_j)^2 \sqrt{\frac{1}{r_i^3} + \frac{1}{r_j^3}} = \sqrt{\frac{6kT}{\rho}} r_i^{(3/2)} (3^{1/2} + 3^{1/2})^2 \sqrt{\frac{1}{i} + \frac{1}{j}}
\]

with

\[
r_i = r_1 \sqrt[3]{i} \quad r_1 = \frac{3M}{4\pi \rho N_A}
\]

\[
k_i = k_{i-1} N_i^{eq} \exp \left[ \frac{4\pi r_1^2 \sigma}{kT} \left( i^{2/3} - (i-1)^{2/3} \right) \right]
\]

The molecular mass \( (M) \) is 0.186 kg mole\(^{-1}\), the density \( (\rho) \) was assumed to be 1500 kg m\(^{-3}\) resulting in a monomer radius \((r_1)\) of \(3.7 \times 10^{-10}\) m.
Results and discussion

The number density of particles larger than 3 nm and 10 nm, respectively determined in an ozonolysis experiment together with the modelled signal for the 3 nm counter are displayed in Fig. 1.

Fig. 1: Number density of particles.

Fig. 2: Computed number density of i-mers
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In this model calculation evaporation was neglected ($N_1^{eq} = k_i = 0$); Fig. 2 shows the computed number density of particles containing $i$ monomers ($[i]$) as function of time. The effect of employing a vapour pressure ($N_1^{eq} = 3 \times 10^7$ molecules cm$^{-3} \approx 10^{-9}$ Torr) and a surface tension ($\sigma = 0.02$ kg s$^{-2}$) is demonstrated in Fig. 3; increasing the evaporation frequency leads to an increasing nucleation time.

![Diagram](attachment:image.png)

**Fig. 3:** Effect of vapour pressure.

The results of these calculations show that the simple model employed here represents only qualitatively the experimental data.

However, the filter samples of the aerosol represent a sticky, noncrystalline mixture of various carboxylic acids and carbonyl compounds, therefore, it may be suggested that the nucleation process taking place is of heteromolecular nature.

**References**
