NOx Effects on Secondary Organic Aerosol Formation of Biogenic and Anthropogenic Organic Gases


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Organic aerosol consists of a large fraction of atmospheric fine aerosol and shows important roles in climate change, visibility degradation, adverse public health (Pöschl, 2005). NOx is strongly associated with secondary organic aerosol (SOA) formation in atmospheric photochemical reactions (Kroll and Seinfeld, 2008). NOx effects are crucial in clear understanding of SOA formation and reliable SOA prediction. In this study, NOx effects were investigated for biogenic and anthropogenic reactive organic gases (ROGs) as a function of ROG/NOx and NO2/NOx ratios. α-pinene and d-limonene were examined as a representative of biogenic ROGs. Toluene and m-xylene were selected as a representative of anthropogenic ROGs.

An indoor smog chamber with 7.5 m3 Teflon bag was used in the photochemical SOA formation. SOA formations were conducted by photochemical reaction in the absence of seed particles at dry condition (<5% RH) of room temperature (~25°C). Hydrogen peroxide was used as OH radical source in the OH radical initiated SOA formation reactions. The photochemical reaction was began by irradiating the reaction mixture of ROG, NOx, and H2O2.

d-Limonene with 2 double bond showed much higher SOA yields of 12.0%-88.4% relative to 4.3%-43.2% of α-pinene with a double bond. SOA yields were ranged from 2.8%-9.4% and 1.1%-13.3% for toluene and m-xylene, respectively. The wide span of SOA yield was influenced by ROG/NOx ratio and NO2/NOx ratio. At both low and high NO2/NOx ratios, SOA yield peaked at ROG/NOx ratio around 0.77 and 1.10 for α-pinene and d-limonene, respectively. It decreased at lower and higher ROG/NOx ratios with abrupt decrease below the critical ROG/NOx ratio. For d-limonene, decreasing NO2/NOx ratio significantly suppressed SOA formation at both low and mid ROG/NOx ratios. In case of α-pinene, the effect of NO2/NOx ratio was negligible at mid ROG/NOx ratio, whereas it elevated SOA yield at high NO2/NOx ratio of low ROG/NOx ratio. It was more substantial for d-limonene at low ROG/NOx ratio. Discrepancies in the NOx effects are largely affected by the number and position of double bond of α-pinene and d-limonene. SOA yield peaked at ROG/NOx ratio of 9.5% and 13.3% for toluene and m-xylene, respectively. Toluene exhibited significantly enhanced SOA formation at higher NO2/NOx ratio, whereas m-xylene showed minimal influence of NO2/NOx ratio.

NOx effects might be caused by the contribution of reaction route of alkyl peroxy radicals and the resultant volatility distribution of products. Reaction of unsaturated intermediates from ring cleavage reaction with O3 could also affect the NOx effect. Time-dependent growth and yield curves were effectively used in the mechanistic understanding of SOA formation. Figure 1 and 2 show time-dependent growth curves of toluene and m-xylene at different ROG/NOx and NO2/NOx ratios.

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