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). NO_x is strongly associated with secondary organic aerosol (SOA) formation in atmospheric photochemical reactions (Kroll and Seinfeld, 2008). NO_x effects are crucial in clear understanding of SOA formation and reliable SOA prediction. In this study, NO_x effects were investigated for biogenic and anthropogenic reactive organic gases (ROGs) as a function of ROG/NO_x and NO_2/NO_x 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 m^3 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℃). 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, NO_x, and H_2O_2.

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/NO_x ratio and NO_2/NO_x ratio. At both low and high NO_2/NO_x ratios, SOA yield peaked at ROG/NO_x ratio around 0.77 and 1.10 for α-pinene and d-limonene, respectively. It decreased at lower and higher ROG/NO_x ratios with abrupt decrease below the critical ROG/NO_x ratio. For d-limonene, decreasing NO_2/NO_x ratio significantly suppressed SOA formation at both low and mid ROG/NO_x ratios. In case of α-pinene, the effect of NO_2/NO_x ratio was negligible at mid ROG/NO_x ratio, whereas it elevated SOA yield at high NO_2/NO_x ratio of low ROG/NO_x ratio. It was more substantial for d-limonene at low ROG/NO_x ratio. Discrepancies in the NO_x effects are largely affected by the number and position of double bond of α -pinene and d-limonene. SOA yield peaked at ROG/NO_x ratio of 9.5% and 13.3% for toluene and m-xylene, respectively. Toluene exhibited significantly enhanced SOA formation at higher NO_2/NO_x ratio, whereas m-xylene showed minimal influence of NO_2/NO_x ratio.

NO_x 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 O_3 could also affect the NO_x 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/NO_x and NO_2/NO_x ratios..

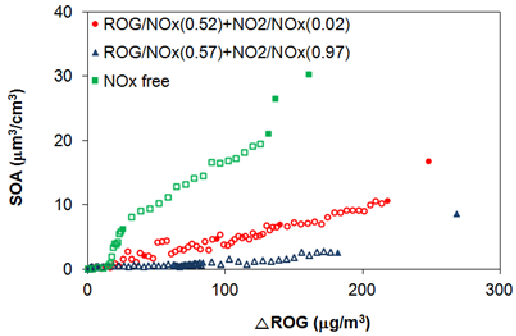

Figure 1. Time-dependent growth curves of toluene as a function of ROG/NO_x and NO_2/NO_x ratios.

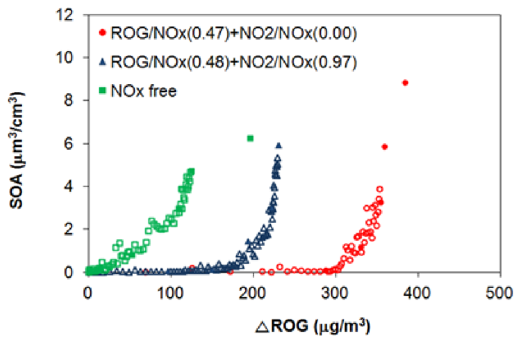

Figure 2. Time-dependent growth curves of m-xylene as a function of ROG/NO_x and NO_2/NO_x ratios.

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Pöschl, U. (2005) Atmospheric Aerosols: composition, transformation, climate and health effects, *Angew. Chem. Int. Ed.*, 44, 7520 – 7540.

Kroll, J.H. and Seinfeld, J.H. (2008) Chemistry of secondary organic aerosol: Formation and evolution of low-volatility organics in the atmosphere, *Atmos. Environ.*, 42, 3593–3624.