

Improvement of measurement system for organic nitrates produced in the mixture of VOC, NO_x and O₃

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Organic nitrates, ONs, are important as an intermediate of secondary organic aerosols (SOAs). Additionally, the branching ratio between ONs and NO₂ formation after the reactions of NO with peroxy radicals (RO₂) are critical for tropospheric ozone formation. In this study, laboratory experiments were conducted for the reaction of VOCs/O₃/NO mixture. After the reactor, total ONs were monitored by the thermal-desorption laser-induced fluorescence (TD-LIF) technique. At this time, an improved glass double-tube flow reactor was constructed. The inner tube (Pyrex, O.D. 10 mm, I.D. 8 mm) was for the O₃ flow, and the outer (Pyrex, O.D. 150 mm, I.D. 143 mm, length 500 mm) was for the additional flow (VOC sample and NO) to reduce the wall loss of ozone at the edges of reactor. As a result, after the improvement of the reactor and its conditions, the sensitivity of formed ONs was three times as large as the previous system. The sensitivity was defined as the slope of the regression line between VOC concentration and ONs increment. Observed sensitivities for isoprene and limonene were 0.00085 and 0.013 ppbv/ppbv, respectively. Sensitivity for limonene was 15 times as large as that for isoprene. Meanwhile, the reaction rate constant of limonene with ozone is 16 times larger than that of isoprene with ozone. It was experimentally indicated that the initial reaction of VOCs with ozone be critical for production of organic nitrates. It was also confirmed that measurements of ONs produced in the mixture of VOC, NO_x and O₃ was promising. As a next step, RO₂ productivity of initial reactions (VOC+O₃) and branching ratio between ONs and NO₂ formation will be explored to clarify characteristics of ONs production in detail.

Acknowledgements: This work has been supported financially by a Grant-in-Aid for Scientific Research (No. 24651014), from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government.

Keywords: Nitrogen oxides, Volatile organic compounds, Tropospheric ozone, Organic nitrates, Laboratory experiments, Gas phase reactions