

4.023 Improved analyzer for biogenic volatile organic compounds as total ozone reactivity and its application to kinetics of gas-phase reactions.

Presenting Author:

Jun Matsumoto, Faculty of Human Sciences, Waseda University, Japan,
jmatsumoto@waseda.jp

Abstract:

Biogenic volatile organic compounds (BVOCs) have been focused on as precursors of tropospheric ozone (O_3) and secondary organic aerosols. Various species of BVOCs have C=C double bonds and can react with O_3 . To capture BVOCs comprehensively, a total ozone reactivity (R_{O_3} , the sum of $k_i[VOC_i]$) analyzer has been developed [1-3]. R_{O_3} of sample BVOCs can be determined when decrease of O_3 due to BVOCs+ O_3 is precisely monitored. Initial O_3 concentration was set to be 30 ppbv. Cyclohexane was added as an OH scavenger. Detection limit of the prototype analyzer was $1.4 \times 10^{-4} s^{-1}$ ($S/N=3$, 60-s average, 60-s reaction). To apply the analyzer to field observations and/or laboratory studies where precise measurements of O_3 and R_{O_3} are essential, further improvement of the analyzer is necessary. In this study, the analyzer was successfully improved through optimization of (1) O_3 detector, (2) O_3 supply, and (3) reaction chamber. The acquired detection limit of R_{O_3} was $0.2 \times 10^{-4} s^{-1}$. As an application, temperature dependence of rate constant, $k(T)$, for gas-phase reaction of a BVOC with ozone was explored. In this study, linalool, $(CH_3)_2C=CHCH_2CH_2C(CH_3)(OH)CH=CH_2$, was examined. For linalool, $k(296K)$ can be referred as $4.3 \times 10^{-16} cm^3 molecule^{-1} s^{-1}$ [4]. The detection limit of improved R_{O_3} analyzer corresponded to 5 ppbv as linalool equivalent. R_{O_3} of linalool at 310 K was quantified as 5 % smaller than that at 296 K. $k(310K)$ was estimated as $4.1 \times 10^{-16} cm^3 molecule^{-1} s^{-1}$. Consequently, it was indicated that the rate constant of linalool+ O_3 reaction decreased by 5 % when the temperature changed from 296 K to 310 K.

[1] Matsumoto, J., AGU Fall Meeting 2011, USA, A51A-0232 (2011).

[2] Matsumoto, J., Aerosol Air Qual. Res., 14, 197-206 (2014).

[3] Matsumoto, J., 1st OH Reactivity Specialists Uniting Meeting, Germany (2014).

[4] Atkinson, R., et al., Int. J. Chem. Kinet., 27, 941-955 (1995).