

Investigation of gaseous and heterogeneous reactions of RO₂ radicals using FAGE-LIF method

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Peroxy (RO₂) radicals are produced by oxidation of various volatile organic compounds (VOCs) in the atmosphere and play an important role. They are mainly removed by self-reactions under clean air conditions. On the other hand, they oxidize NO and produce NO₂. Since NO₂ produces O₃ via photochemical reactions, RO₂ radicals act as a part of the cyclic reaction producing tropospheric O₃. RO₂ radicals also react with NO₂ and generate a RO₂NO₂ complex, which can reproduce NO₂ via thermal decomposition and act as an atmospheric NO_x reservoir. Furthermore, in recent years, it has been suggested that the loss processes of RO_x radicals via heterogeneous reactions on the aerosol surface may be important. Despite these importance, there are limited kinetics data about RO₂. In particular, there were few reports of detection under atmospheric conditions, and it was limited to some RO₂ radicals. In this study, we improved a combination technique of Fluorescence Assay by Gas Expansion and Laser Induced Fluorescence (FAGE-LIF) system for detection of various RO₂ radicals and investigated their reactions including not only gaseous reactions but aerosol uptake processes.

All experiments were performed at 1 bar, 298 K. O₃/H₂O/sample VOC/N₂ carrier mixture were added into the reaction cell. By irradiation of pump laser pulses, OH radicals were generated by the photolysis of O₃ and subsequent reaction with H₂O. OH radicals reacted with VOC rapidly and generated RO₂ radicals. A part of main flow was added into the detection cell. In order to convert RO₂ radicals to OH radicals again, NO and O₂ were added into the detection cell. Then, OH radicals were detected by LIF method. The relative concentration of RO₂ radicals were measured from the LIF intensity of OH radicals.

Figure 1 shows time profiles of CH₃O₂ radicals, which were produced by the reaction of OH with CH₄, measured at various NO₂ concentrations. CH₃O₂ radicals decay single exponentially in the absence of NO₂. With the existence of NO₂, however, profiles include two decay components due to the reverse reaction. In order to determine the rate constants, double exponential fitting including the reverse reaction was performed. The fitting results are shown in figure as red lines. All lines reproduce the experimental results very well. The reaction rate constants including also reverse reaction have been determined from the NO₂ concentration dependence. Those rate constants agree with previous reported values. This indicates that the improved FAGE-LIF system allows us to measure the kinetics of RO₂ radicals appropriately. We also performed same experiments using C₂H₅O₂ radicals. We will discuss at the presentation.

Additionally, we investigated uptake processes of RO₂ radicals onto aerosols. Sample aerosols were deliquesced NaCl particles generated from 0.1 – 0.3 g L⁻¹ aqueous NaCl solutions via a collision-type atomizer. Those particles were added into the reaction cell with zero air carrier and another sample gases. The decay rates of RO₂ radicals due to aerosols were determined by the difference between the fitting results with and without aerosols. By using the decay rates due to the aerosols and aerosol size distributions, uptake coefficients have been determined for some RO₂ radicals (as shown in Fig.2). The aerosol size distributions were employed from the separate experiments under the almost same conditions. As a result, the increase of the uptake coefficients with the size of RO₂ radicals was observed for the first time. In addition, even small RO₂ radicals were uptaken into aerosols, although their values were small. This indicates that the heterogeneous reactions of RO₂ radicals can affect the O₃ production

mechanisms. Consequently, there is possibility that the considering the interaction between RO₂ radicals and aerosols should improve the accuracy of the atmospheric model.

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Keywords: RO₂ radical, reaction rate coefficient, NO₂, aerosol, uptake coefficient

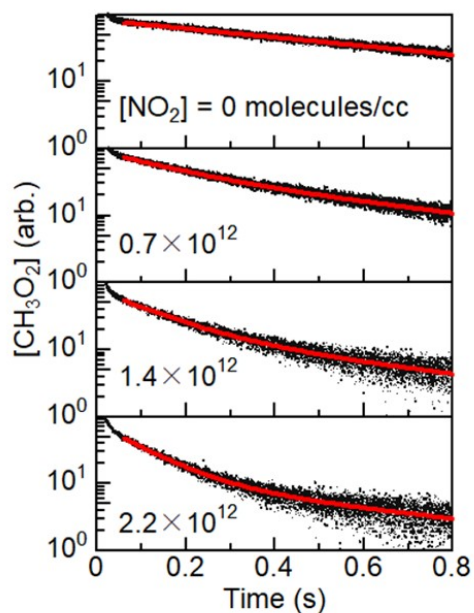


Figure 1. Time profiles of CH₃O₂ radicals.
Red lines show the fitting analysis results.

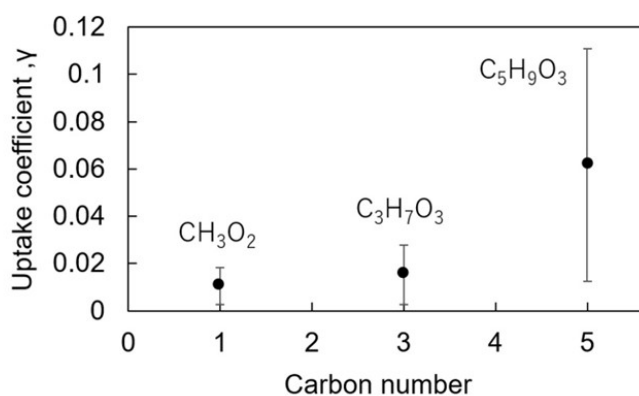


Figure 2. Radical size dependence of uptake coefficient.