

Kinetic study of a bromine monoxide radical (BrO) with a ethylperoxy radical (C₂H₅O₂) using cavity ring-down spectroscopy

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Halogen cycle in the marine boundary layer (MBL) is one of the attractive topics in tropospheric chemistry. Halogen monoxide radicals, XO (X = Cl, Br, and I), are the key species of ozone depleting cycles in MBL. XO radicals react with HO₂, NO₂ and themselves and finally result in the re-generation of X atoms, which destroy ozone effectively. Recent experimental studies suggested that the reaction of IO with RO₂ could be involved in the important ozone depleting cycles in MBL. However, the precise role of XO radicals in MBL is still uncertain, because of the shortage of the knowledge of the reaction rate constants, especially for radical-radical reactions.

We have measured the rate constants of BrO + C₂H₅O₂ at 233 - 333 K and 100 - 200 Torr total pressure of N₂ or O₂ diluents using cavity ring-down spectroscopy (CRDS) that has been widely used in spectroscopic and kinetic studies for radical reactions, which are applicable to the atmospheric modeling. CRDS is suitable for the experiments at wide ranges of pressure and temperature.

The BrO concentration profile was measured between 0.1 - 6.1 ms after the photolysis laser pulse. Numerical models were compiled in order to derive the rate constants of the reaction BrO + C₂H₅O₂ with the IBM Chemical Kinetics Simulator. The variable parameters were the initial concentrations of Br and rate constants in the simulations so that the simulation results reproduced the obtained decay time profiles of BrO. With numerical simulation results and best-fit procedures, rate constants was determined at 298 K and 100 - 200 Torr of N₂ or O₂ diluent. Temperature dependence of the rate constant was also investigated at 233 - 333 K.