

Kinetic and Spectroscopic Investigations of the Br₂⁻-Radical in Aqueous Solution

A contribution to subproject CMD/APP

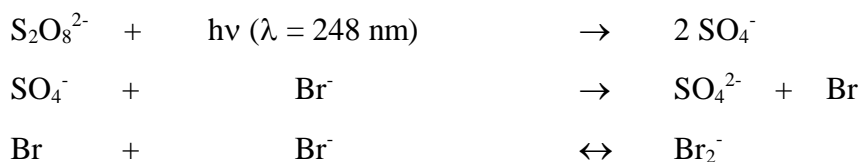
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Absolute decadic absorption coefficients of the dibromide radical anion Br₂⁻ in aqueous solution as a function of wavelength in intervals of 2 nm in the range of 250 to 750 nm have been recorded by means of a time-resolved UV/VIS- broadband diode array absorption spectroscopy experiment.

The kinetics of the Br₂⁻ radical have been investigated with another laser photolysis-long path laser absorption (LP/LPLA) apparatus. Br₂⁻ was generated by laser photolysis of peroxydisulfate according to:



Bromide is present in large excess (0.1 M) to shift the equilibrium between Br and Br₂⁻ towards the dibromide radical anion. The Br₂⁻ radical has been monitored by long path absorption applying the output of a high power halogene lamp at 360 nm recorded with a monochromator/photomultiplier combination. In this study the self-reaction and H-abstraction-reactions with several organic constituents of the tropospheric aqueous phase have been investigated. For H-abstraction reactions only one rate coefficient is available from literature up to now. A Correlation of the reaction rate constants with bond dissociation energies (BDE) will be presented. The presented data can be used in modelling studies to investigate the possible impact of the dibromide radical anion on the chemistry of free radicals in the tropospheric aqueous phase. The obtained data may be especially important for understanding the role of marine aerosol chemistry within the troposphere.