

Identification of a BrOOO^- intermediate species in the ozonolysis of bromide at the liquid/vapor interface from liquid jet XPS

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Oxidation of bromide by gas phase ozone (O_3) in the absence of photochemistry is believed to be one of the important dark reactions to produce HOBr as the starting point of the multiphase cycling reaction mechanisms that release bromide out of sea water, sea spray or marine aerosols from aqueous solution that later drive O_3 depleting chemistry in the troposphere [1]. The reaction of bromide with O_3 occurs through an acid catalyzed mechanism involving a BrOOO^- complex as an intermediate [2]. Slow oxidation of bromide by O_3 in the bulk aqueous phase is of limited relevance; previous kinetic experiments have suspected the reaction to be enhanced at the surface of aqueous solutions. Thus, identifying BrOOO^- at the interface would be a major step to understanding the multiphase oxidation of bromide with O_3 .

Here, we provide a direct experimental evidence for the formation of a BrOOO^- reaction intermediate at the surface by investigating the reaction of aqueous solutions NaBr with gas phase O_3 after millisecond time scale exposure using the surface sensitive in situ liquid jet X-ray photoelectron spectroscopy (XPS) at the Swiss Light Source (SLS). We acquired Br 3d core level spectra of 0.125 M NaBr solution in presence and absence of ozone in the gas phase. We found a new feature with a peak position shifted towards higher binding energy (by ~ 0.7 eV) compared to Br^- , which was clearly different from the Br 3d core levels spectra of hypobromite and bromate measured with reference solutions. Our results suggest the appearance of the formation of the BrOOO^- reaction intermediate as a new component, in agreement with theoretical calculations of the Br^- ozonolysis mechanism [3]. Additionally, by varying the photoelectron kinetic energy and thus probe depth via variation of the probing photon energy, the new feature appears to be present near the liquid/vapor interface. Besides, kinetic experiments for the reaction of O_3 with bromide are ongoing to investigate the dependence on the temperature, ozone concentration, which may give further information such as the relative oxidation rate at the liquid/vapor interface versus that in the bulk phase.

[1] S. Wang, et al., Proceedings of the National Academy of Sciences, 2015, 112, 9281-9286.

[2] Q. Liu, et al., Inorganic Chemistry, 2001, 40, 4436-4442.

[3] I. Gladich, et al., The Journal of Physical Chemistry A, 2015, 119, 4482-4488.