



## Uptake of ozone to mixed sodium bromide/ citric acid solutions

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Sea-salt solution – air interfaces play an important role in the chemistry of the marine boundary layer. The reaction of ozone ( $O_3$ ) with bromide is of interest in the context of formation of photolabile halogens ( $Br_2$ ,  $BrCl$ ) in the marine boundary layer. Recent experiments have suggested that the bromide oxidation rate is related to the surface concentration of bromide [1] and inversely related to the gas phase concentration of  $O_3$ , an indication for a precursor mediated reaction at the surface [2]. So far, the effect of organics (such as those occurring at the ocean surface or in marine aerosols) on the reaction of  $O_3$  with bromide aerosols has not been studied yet. In our study we investigate the uptake kinetics of  $O_3$  to a mixed solution of sodium bromide (NaBr) and citric acid (CA), which represents highly oxidized organic compounds present in the environment, with a well-established coated wall flow tube technique, which leads to exposure of the film to  $O_3$  allowing the heterogeneous reactions to take place and the loss of  $O_3$  being measured. The results indicate that the uptake of  $O_3$  to the films with the higher bromide concentrations (0.34M and 4M) is independent of the gas phase concentration and roughly consistent with uptake limited by reaction in the bulk. For the lower bromide concentration (84mM), however, we observe a trend of the uptake coefficient to decrease with increasing  $O_3$  concentration, indicating an increasing importance of a surface reaction.

In an attempt to constrain the kinetic data, we employed X-ray photoelectron spectroscopy (XPS) to get insight into the surface composition of the aqueous solution – air interface. Previous XPS studies have shown that halide ion concentrations are enhanced at the aqueous solution air interface [3-4], which likely promotes the surface reactions of bromide or iodide with  $O_3$ . A first XPS study of ternary solutions of KI with butanol indicated the importance of specific interactions of the cation with the alcohol headgroup [5]. In this study we would like to go one step further and look into the effect of a more complex organic compound, CA. We used ambient pressure XPS on a vacuum liquid microjet. The continuously refreshed free-flowing aqueous filament under vacuum permits photoelectron spectroscopy measurements from volatile aqueous interfaces in absence of beam damage [6]. Measurements were made at the SIM beam line of the Swiss Light Source (SLS) at the Paul Scherrer Institute. The ability to tune the photon energy (150-2000 eV) is crucial to get precise component ratios as a function of photoelectron kinetic energy and thus probe depth, thus allowing to determine relative concentrations of citric acid and bromide at the surface and in the bulk, respectively.

### REFERENCES

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