Geophysical Research Abstracts
Vol. 15, EGU2013-6076-5, 2013
EGU General Assembly 2013

A new look at the reactive uptake of HOBr onto acidic aerosols in the troposphere, with application to volcanic plumes and acidified marine aerosol

Tjarda Roberts, Line Jourdain, and Michel Pirre
LPC2E, CNRS-Universite d'Orleans, Orleans, France (tjarda.roberts@cnrs-orleans.fr)

The reactive uptake of HOBr onto halogen-rich aerosols to form Br_2 is a key process enabling the autocatalytic formation of tropospheric BrO with impacts on atmospheric oxidants and mercury deposition. However, experimental data quantifying HOBr reactive uptake on tropospheric aerosols is limited, and reported values vary in magnitude. Here, we combine the reported experimental data into a single framework. By considering the elementary reaction mechanism of HOBr(aq) with Cl^-(aq) and H^+(aq) as two consecutive bi-molecular reactions rather than a ter-molecular process, we re-evaluate the acid-dependency of the reaction rate. HOBr(g) uptake coefficients are then calculated, reproducing the high uptake coefficient (>0.2) measured on HCl-acidified sea-salt particles and – for the first time – also the lower uptake coefficient (0.01) reported on highly H_2SO_4-acidified sea-salt particles. Our new HOBr uptake calculations also provide a first explanation for the observed Br^-(aq) excess in highly acidified sub-micron sea-salt particles simultaneous to Br^-(aq) depletion in less acidic supra-micron particles. Finally, the parameterisation is used to predict HOBr uptake in volcanic plumes in the free troposphere, demonstrating the HOBr uptake coefficient is high (accommodation limited) in the upper troposphere but is reduced by low halogen-solubility (a function of temperature and humidity) in sulphate aerosol at lower altitudes. The study indicates HOBr uptake can readily act to promote multi-day BrO chemistry in volcanic plumes dispersing into the free troposphere, both due to continuous degassing from elevated volcano summits (e.g. Etna) or episodic eruptions (e.g. Eyjafjallajokull). However, numerical models that assume the HOBr(aq) reaction kinetics are ter-molecular in acidified sea-salt or volcanic aerosol may overestimate the aqueous-phase reaction rate and HOBr uptake coefficient.