



Investigation of bromine chemistry in volcanic plumes in smog chamber experiments

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Volcanic gas emissions are of importance for atmospheric chemistry on local and global scales. The discovery of reactive halogen chemistry in volcanic plumes brought new insights into the significance of volcanic halogen emissions. The investigation of reactive halogen species (RHS, e.g. BrO, OClO, IO, I₂) made great progress in recent years, but also revealed uncertainties concerning the formation mechanisms and the impact of environmental parameters (e.g. plume gas and aerosol composition, relative humidity). Understanding the influence of these parameters on the halogen activation (i.e. conversion from hydrogen halides to RHS) in volcanic plumes is essential for an interpretation of field observations e.g., relating them to magmatic processes and investigating the atmospheric impact of volcanic halogen emissions (e.g. ozone destruction, oxidation of mercury or reduced methane life time).

Atmospheric simulation chamber experiments were undertaken at Bayreuth to investigate a simplified volcanic plume (initial conditions: sulfuric acid aerosols with H₂O (RH 10-70 %), SO₂ (10 ppm) and HBr (5 and 25 ppb) as trace gas components) under controlled conditions in a 4 m³ Teflon chamber. Solar like radiation was provided by a solar simulator. A White multi-reflection cell as well as a multichannel cavity enhanced DOAS (Differential Optical Absorption Spectroscopy) instrument enabled online observation of BrO formation and other trace gases. Additional instruments and sampling techniques were employed such as alkaline trap sampling for total bromine and sulfur measurements and gas diffusion denuders for bulk reactive bromine species measurements. Particle size distributions were determined by SMPS (Scanning Mobility Particle Sizer Spectrometer) and SO₂, NO_x and O₃ were monitored by standard in-situ gas analyzers. The artificial plume was diluted with a constant admix of ozone and zero air to simulate the dilution of volcanic gases by the atmosphere after being emitted from a volcanic vent.

By varying the initial experiment conditions, the influence of following parameters on the extent and rate of BrO formation were investigated: (1) initial HBr/SO₂ ratio, (2) relative humidity, (3) O₃ admixing, (4) particle abundance and composition. Within the scope of the experiments, BrO formation with peak values between 100 and 900 ppt was observed with BrO/SO₂ ratios ranging from 0.3E-4 to 1.8E-4. The choice of the initial plume composition also had a significant impact on the delay of the BrO formation. Surprisingly, although not a strict prerequisite for Br-activation, SO₂ seems to have an accelerating effect on the formation of reactive bromine species.

The results of the atmospheric simulation chamber experiments are further investigated by atmospheric box model simulations employing the CAABA/MECCA model in order to identify key steps of the reaction mechanism.