



Bromine explosion in smog chamber experiments above a model salt pan

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The importance of reactive halogen species (RHS), such as BrO, in the troposphere includes the destruction of ozone, change in the chemical balance, increased deposition of toxic compounds (like mercury) and potential indirect effects on global climate. Previous studies have shown that salt lakes can provide a significant source for gaseous RHS. For example up to 200 ppt BrO were detected at the Dead Sea and about 20 ppt at the Salar de Uyuni, Bolivia. On the other hand, measurements from field campaigns in Namibia/Botswana, Southern Russia and Mauritania showed 1 to 2 orders of magnitude lower BrO levels than expected based on previous observations at salt flats. Environmental conditions such as salt composition, relative humidity, pH and temperature might have a strong influence on reactive bromine levels. One of the main questions is: Under which conditions does halogen activation take place? In our laboratory experiments artificial salt samples of NaCl/NaBr of different composition were exposed to simulated sunlight in a Teflon smog-chamber experiment at the University of Bayreuth under different conditions (e.g. relative humidity, temperature) and a defined input of trace gases such as ozone. RHS levels were observed by a DOAS instrument in combination with a multi-reflection cell (White-cell). The setup of the 2-m base-path White-cell with a total optical path length of 320m, was specially designed for this smog chamber. The concentration of OH- and Cl- radicals were quantified by the radical clock method. For that purpose five hydrocarbon species (n-butane, 2,2-dimethylbutane, 2,2,3,3-tetramethylbutane, toluene including perfluorohexane as inert standard) were added, and their decay was measured by a GC - flame ionisation detector (FID). We present the first direct observation of “Bromine Explosion” (auto catalytic release of reactive bromine from salt surfaces – key to ozone destruction) in the laboratory. Detected BrO mixing ratios were found to be proportional to the initial O₃ mixing ratio. We also observed a strong dependence on relative humidity (RH). At high RH (60%), the Br release (converted to and detected as BrO) was much faster than for low RH. The maximum BrO mixing ratio of 6500 ppt at 60% RH was one order of magnitude higher than at 30% RH. But the total amounts of BrO released at both humidities (according to their integrated BrO curves) were very similar. At a RH of 2% a peak BrO mixing ratio up to 450 ppt within the first minutes was followed by a strong decrease, indicating that the halogen source is depleted. This dependency is possibly controlled by the thickness of liquid micro layer, as the humid layer thickness strongly depends on RH. We conclude that the exchange reactions on the air-water interface (with dissolved halogen ions) probably play a key role in halogen release.

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