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"Chlorine explosion" from sea-salt aerosols in a polluted atmosphere

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Bromine and chlorine 'explosions' (BE and CE) refer to autocatalytic, heterogeneous releases of reactive halogen species (RHS). ClO and BrO play a key role as RHS, as they influence the tropospheric oxidation capacity through destruction of ozone and fast reactions with nitrogen oxides. Besides OH radicals, Cl atoms react at a fast rate with the greenhouse gas methane, but the global effect is not clear yet. From smog-chamber experiments under tropospheric light conditions, ClO, OClO (from CE) and BrO (from BE) released from artificial sea salt aerosols were detected using a White system in combination with Differential Optical Absorption Spectroscopy (DOAS). Up to 17 ppb of ClO, 6 ppb of OClO and 1.6 ppb of BrO were observed under the influence of high NO_2 and O_3 concentrations. The RHS activation is triggered by NO_2 reactions starting during the dark period. Formation of $ClNO_2$ and $ClONO_2$ and acidification of the aerosol by HNO_3 or HONO play key roles. The lifetime of Cl_2 of 645 s against photolysis in our smog chamber was estimated to be longer than the uptake onto the aerosol surface with a lifetime of 83s. The fact that Cl_2 photolysis is slower compared to uptake, indicates that Cl_2 might not be sufficient as a precursor for the observed ClO and OClO mixing rations during the chamber experiments at high NO_x. Furthermore, OClO (40ppt/s) is formed at a faster rate than ClO (15ppt/s) in our experiments. A simple model, including the known gas phase reactions of halogen oxides, O_3 and NO_x, predicts the maximum ClO concentration to occur before the maximum OClO concentration. The measurement indicates the opposite. This suggests heterogeneous OClO formation. The lifetime of OClO against photolysis is only 20s in our chamber. But an actual heterogeneous release mechanism to form OClO has not been confirmed yet. Nevertheless, these results suggest that OClO is important for the heterogeneous release process. While BE has been demonstrated to occur in nature, the question remains how important CE is in the troposphere. The chlorine mechanism might become important in highly polluted marine areas, where high NO_2 and O_3 levels are present.