Geophysical Research Abstracts
Vol. 12, EGU2010-3250, 2010
EGU General Assembly 2010

Is the 'Bromine Explosion' generated from the reaction BrO HO2 alone?

Wolfgang Behnke (1) and Cornelius Zetzsch (1,2)

(1) Fraunhofer-Institute for Toxicology and Experimental Medicine, Hannover, Germany (behnke@item.fraunhofer.de), (2) Atmospheric Chemistry Research Laboratory, Bayreuth Center of Ecology and Environmental Research, University of Bayreuth, Germany

We observed bromine explosions (a fast production of atomic Br and Cl under tropospheric conditions) in various smog chamber experiments in Teflon bags at room temperature at a relative humidity of about 80% in the presence of NaCl/NaBr-aerosol, simulated sunlight and ozone (200 - 400 ppb). Time profiles of ozone and hydrocarbons (HCs: n-butane, 2,2-dimethylbutane, tetramethylbutane and toluene, initially about 2 ppb each) were monitored to determine concentrations and source strengths of OH radicals, atomic Cl and Br and the corresponding time profiles of BrCl and Br_2 as their photolytic precursors. The number and size of aerosols are measured as well as their chemical composition (Br^-, Cl^- and oxalic acid). Full records of raw data from the smog chamber runs are available at www.eurochamp.org for potential users.

Chemical box model calculations deliver concentrations of various intermediates, such as aldehydes, HO_2 and RO_2 radicals and the inorganic halogen compounds ClO, BrO, HOCl and HOBr, where HOBr from O_3 + Br^- => BrO^- + O_2 in the aqueous/adsorbed phase induces the following gas-phase/ heterogeneous chain reaction

$Br + O_3 => BrO + O_2 (1)$

$BrO + HO_2 => HOBr + O_2 (2a)$

$HOBr + (Aerosol) => HOBr_{ad} (3)$

Surface-adsorbed HOBr reacts with Br^- or Cl^- to produce Br_2 or BrCl, both of which are released and photolysed. Formation of Br_2 should prevail up to Cl^-/Br^- -ratios of about 10^4 (Fickert, S., J.W. Adams, J.N. Crowley, J. Geophys. Res., D104, 23719-23727, 1999). A maximum of this ratio is reached about 30 minutes after the beginning and decreases during the next hours - probably by reaction of Br_2 with oxalate and absorption of HBr, formed from the reaction of Br with aldehydes.

Parallel to chain reaction (1)-(3) a chain reaction replacing Br by Cl seems possible but can not be realized, since the main sink of atomic Cl is its reaction with hydrocarbons - leading to chain termination - in contrast to atomic Br (ratio of rates: $k_{Cl}[O_3]/k_{Cl}[HC] \sim 0.1$; $k_{Br}[O_3]/k_{Br}[toluene] \sim 100$). Formation of aldehydes (R-CHO) interferes with the chain reaction (1) - (3) markedly, since $k_{Br}[O_3] \approx k_{Br}[R\text{-}CHO]$.

The chain reaction is limited by availability of ozone (degradation of HCs by atomic Cl stops completely with vanishing ozone), of HO_2 (HCs are required to form HO_2) and of aerosol. The central question is: will sufficient HO_2 be formed from degradation of HCs to explain the magnitude of the formed Br_2 and BrCl in our experiments? We found that the formation of HO_2 should be by a factor of 2-4 larger to explain the formation of Br_2 and BrCl. Which other sources for the formation of HOBr besides reaction (2a) are then available? The rate of $CH_3O_2$with BrO is 25% of that with HO_2 (Enami, S.; Yamanaka, T.; Nakayama, T.; Hashimoto, S.; Kawasaki, M.; Shallcross, D.E.; Nakano, Y.; Ishiwata, T., J. Phys. Chem. A, 11, 3342 - 3348, 2007), suggesting that other RO_2 radicals must contribute. In our model calculations we use this rate constant for all RO_2 radicals to obtain reasonable agreement between the produced HOBr and the formed BrCl and Br_2 necessary for our experimental degradation results. So reaction scheme (1) - (3) should be completed by:

$BrO + RO_2 => HOBr + products (2b)$

The German Science Foundation (DFG) supported this research in unit 783 (HALOPROC).