



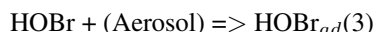
## Is the 'Bromine Explosion' generated from the reaction BrO HO<sub>2</sub> alone?

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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<sub>2</sub> as their photolytic precursors. The number and size of aerosols are measured as well as their chemical composition (Br<sup>-</sup>, Cl<sup>-</sup> and oxalic acid). Full records of raw data from the smog chamber runs are available at [www.eurochamp.org](http://www.eurochamp.org) for potential users.

Chemical box model calculations deliver concentrations of various intermediates, such as aldehydes, HO<sub>2</sub> and RO<sub>2</sub> radicals and the inorganic halogen compounds ClO, BrO, HOCl and HOBr, where HOBr from O<sub>3</sub> + Br<sup>-</sup> => BrO<sup>-</sup> + O<sub>2</sub> in the aqueous/adsorbed phase induces the following gas-phase/ heterogeneous chain reaction



Surface-adsorbed HOBr reacts with Br<sup>-</sup> or Cl<sup>-</sup> to produce Br<sub>2</sub> or BrCl, both of which are released and photolysed. Formation of Br<sub>2</sub> should prevail up to Cl<sup>-</sup>/Br<sup>-</sup> -ratios of about 10<sup>4</sup> (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<sub>2</sub> 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:  $k_{Cl}[O_3]/k_{Cl}[HC] \sim 0.1$ ;  $k_{Br}[O_3]/k_{Br}[\text{toluene}] \sim 100$ ). Formation of aldehydes (R-CHO) interferes with the chain reaction (1) - (3) markedly, since  $k_{Br}[O_3] \approx k_{Br}[R-CHO]$ .

The chain reaction is limited by availability of ozone (degradation of HCs by atomic Cl stops completely with vanishing ozone), of HO<sub>2</sub> (HCs are required to form HO<sub>2</sub>) and of aerosol. The central question is: will sufficient HO<sub>2</sub> be formed from degradation of HCs to explain the magnitude of the formed Br<sub>2</sub> and BrCl in our experiments? We found that the formation of HO<sub>2</sub> should be by a factor of 2-4 larger to explain the formation of Br<sub>2</sub> and BrCl. Which other sources for the formation of HOBr besides reaction (2a) are then available? The rate of CH<sub>3</sub>O<sub>2</sub> with BrO is 25% of that with HO<sub>2</sub> (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<sub>2</sub> radicals must contribute. In our model calculations we use this rate constant for all RO<sub>2</sub> radicals to obtain reasonable agreement between the produced HOBr and the formed BrCl and Br<sub>2</sub> necessary for our experimental degradation results. So reaction scheme (1) - (3) should be completed by:



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