Atmospheric degradation of two short-lived brominated hydrocarbons ($CHBr_3$ and CH_2Br_2)

G. Krysztofiak[1], G. Poulet[1], V. Marécal[2], M. Pirre[1], F. Louis[3], S. Canneaux[3] and V. Catoire[1,*]

[1] Laboratoire de Physique et Chimie de l'Environnement et de l'Espace (LPC2E), CNRS - Université d'Orléans (UMR 6115), 45071 Orléans cedex 2, France
[2] Centre National de Recherches Météorologiques- Groupe d'études de l'Atmosphère Météorologique (CNRM-GAME), Météo-France - CNRS (URA 1357), 31057 Toulouse cedex 1, France
[3] Physico Chimie des Processus de Combustion et de l'Atmosphère (PC2A) CNRS - Université Lille 1 Sciences et Technologies (UMR 8522), 59655 Villeneuve d'Ascq Cedex, France
*Corresponding author: Valery.Catoire@cnrs-orleans.fr

Two brominated VSLS, bromoform ($CHBr_3$) and dibromomethane (CH_2Br_2), which have natural sources in coastal regions, have the potential to transport reactive bromine into the stratosphere and to contribute to the bromine budget. In order to better evaluate the impact of these two species, chemical schemes for their atmospheric degradation have been developed from a detailed kinetic and mechanistic analysis of all the gas phase reactions involved, specially of the peroxy radicals. The most likely pathways for the reactions of HO_2 with brominated peroxy radicals RO_2 (with R = CH_2Br, $CHBr_2$ and CBr_3) have been established using *ab initio* calculations. The Henry's law constants of the brominated organics products have been also estimated using empirical methods. Using these constants, the less soluble species formed from the brominated VSLS degradation are found to be CBr_2O, CHBrO, $CBr_3O_2NO_2$, $CHBr_2O_2NO_2$, BrO, $BrONO_2$ and HOBr. In the presence of deep convection, these species could be transported into the TTL (tropical tropopause layer).

Then, these data have been implemented in a meteorological/tracer transport model (CATT-BRAMS), including a simplified chemistry of other atmospheric species The full degradation schemes have been run under realistic conditions of "clean" and moderately NO_x-polluted atmospheres, which are representative of tropical coastal regions. The influence of the reactions of the RO_2 radicals with HO_2, CH_3O_2 and NO_2 on the nature and abundance of the stable intermediate and end-products has been tested. In the case of $CHBr_3$ degradation, it results that the reactions of RO_2 with NO_2 have no impact, and that the inclusion of the reactions of RO_2 with CH_3O_2 and with HO_2 (with "new" branching ratios) leads to a slight decrease of the bromine potentially able to reach the TTL. In contrast to $CHBr_3$, the CH_2Br_2 degradation leads to a negligible production of organic species. Finally, for both bromoform and dibromomethane degradation, the effect of a moderate NO_x pollution significantly increases the production of the less soluble species and thus approximately doubles the bromine potentially able to reach the TTL. By taking into account the results of these analysis, simplified degradation schemes for $CHBr_3$ and CH_2Br_2 are proposed.