Atmos. Chem. Phys. Discuss., 5, S5929–S5931, 2005
www.atmos-chem-phys.org/acpd/5/S5929/
European Geosciences Union

Atmospheric Chemistry and Physics Discussions

Interactive comment on "Estimating the contribution of bromoform to stratospheric bromine and its relation to dehydration in the tropical tropopause layer" *by* B.-M. Sinnhuber and I. Folkins

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Received and published: 18 April 2006

We thank referee #3 (Ross Salawitch) for his detailed review and helpful suggestions.

In our point-by-point response below we show the original comments of referee #3 in italics and our reply in plain text.

I especially liked discussion in the paper regarding how the 0.5 ppt "Source Gas" injection of bromine from bromoform could be checked by measurements of bromoform in the TTL (lines 170-174) and how "this situation constitutes only an upper limit ... if it

is assumed detrained air does not contain Bry (lines 178-180)". For the first of these, the paper would be stronger if the nomenclature of Source Gas Injection and Product Gas Injection were adopted throughout (e.g., use the nomenclature defined in Chapter 2 of WMO 2003). For the second of these key points, I am afraid this point (which is alluded to earlier in the paper) is buried in the middle of a long paragraph. I suggest devoting a single paragraph to this point (e.g., break up the long PP from lines 174 to 188 into several shorted PPs).

In the revised version of our paper we have now introduced the nomenclature of source gas injection and product gas injection.

We have followed the suggestion and have broken the paragraph into three.

In my opinion, two important aspects of CHBr3 and Bry chemistry are missingfrom the paper, and should be mentioned upon revision. First, it is assumed that once CHBr3 is lost by either photolysis or reaction with OH, Bry is immediately formed. Of course, in reality, OH+CHBr3 probably leads to C(O)Br2+Br, and hv+CHBr3 probably leads to C(O)HBr+Br+Br (see Fig 2-6 of WMO, 2003). There are little or no kinetics studies of C(O)Br2 and C(O)HBr: while they are probably shorter lived than CHBr3, I don t know if this is certain. Nonetheless, some comment about the intermediates is warranted. For a discussion of CHBr3 photochemistry, see R. Weller et al., Berichte der Bunsen-Gesellschaft-Physical Chemistry Chemical Physics, 96, 409, 1992. This study probably should be cited (a resourceful postdoc found this paper and pointed it out to me several months ago!).

Following this suggestion we have included the following paragraph:

Here we assume that the loss of CHBr3 either due to photolysis or reaction with OH immediately produces three Bry molecules. In reality CHBr3 + OH probably leads to Br2CO + Br and photolysis of CHBr3 leads to HBrCO + 2Br or Br2CO + Br as well (Weller et al., 1992). Little is known on the photochemical lifetimes of Br2CO or HBrCO.

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Interactive Comment

The second item that, if mentioned, would strengthen the paper, is the possibility that heterogeneous recycling of Bry species could lead to higher values of tau_washout. This is discussed in general terms by Platt and Hoenninger, Chemosphere, 52, 325, 2003 and in specific terms by the laboratory study of Iraci et al. (ACP, 5, 1577, 2005). I think both of these studies should be cited, and discussion should be added to state how tau_washout might be modified by the heterogeneous recycling of Bry species that are produced following decomposition of CHBr3.

We have now included the following paragraph:

Current models predict a large HBr/BrO-ratio in the free troposphere, so that most of the tropospheric inorganic bromine resides in the form of HBr which is highly soluble. However, heterogeneous recycling of Bry as discussed in general terms by Platt and Hönninger (2003) and more specifically by the recent laboratory study of Iraci et al. (2005) could lead to a higher BrO/Bry-ratio in the troposphere. This would then effectively increase the washout lifetime τ_w and could thus increase the product gas injection pathway for bromofrom.

Interactive comment on Atmos. Chem. Phys. Discuss., 5, 12939, 2005.