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Atmospheric Chemistry and Physics Discussions

Interactive comment on "DMS and MSA measurements in the Antarctic boundary layer: impact ofBrO on MSA production" *by* K. A. Read et al.

K. A. Read et al.

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Minor comments:

Introduction: The authors send many apologies to Preunkert et al. for neglecting to include their research within the discussion of previous dimethyl sulphide measurements within this paper. The authors were not aware of this recently published paper and so thank M. Legrand for highlighting its existence. The introduction will be altered to reflect these highly relevant measurements and the reasons for their variability.

Experimental: The paper has no further discussion of fluoride anions following the experimental introduction and so the reference to them has been removed from the experimental section.

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Section 4.1: Reiterating our comments regarding the reference to Preunkert et al, the authors were previously unaware of this publication, hence its omission. Section 4.1 has now been rewritten to include some discussion of these measurements.

In fact, a lower value of 1 x 105 molecules cm-3 (not 3 x 105 molecules cm-3) was used in the DMS lifetime calculation to reflect the lower values throughout winter (June-August) however the authors appreciate that the DMS lifetime detailed in the last sentence of Section 4.1 is in error nonetheless and also that it conflicts with the value in Table 2 and so this has been recalculated using recent kinetics for the addition pathway (See major comments below for discussion of Table 2). The bracketed section now reads: DMS has a lifetime of 6 days based on a 24hr [OH] of 1 x 105 molecules cm-3 at 260K.

Major comments:

The authors accept the comment of M. Legrand which states the incorrect use of kinetics to calculate the DMS lifetime in the table. Although the k2 addition value was used to calculate the lifetime of DMS in this table, a 298K rate constant was used rather than that at 260K (Column 2, 1.7 x 10-12 cm3 molecule-1 s-1, should be 2 x 10-11 cm3 molecule-1 s-1 giving a DMS lifetime of 2 days under these conditions). Table 2 will be altered accordingly.

Incorrect kinetics were not used for Figure 9, however the rate constant for BrO + DMS is incorrect in column 2 of Table 2. The rate constant should read 3.94 x 10-13 cm3 molecule-1 s-1 not 3.94 x 10-14 cm3 molecule-1 s-1. The lifetime of DMS with respect to BrO should therefore be 0.397 days in column 3 of table 2.

For the comment regarding k4, the heterogeneous reaction of DMSO the authors agree that it is more valid to use kinetic study data rather than empirically deduced values for this parameter. The temperature dependent value of 3.9 x 109 M-1 s-1, (which equates to 7.04 x 10-4 s-1 at 265K, assuming a diurnally averaged concentration [OH]aq = 1.8 x 10-13 molecules cm-3 scaled by gas-phase [OH]g for the Antarctic conditions, Zhu

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et al, 2003), has now been used in all relevant calculations rather than 2.4 x 10-4 s-1. The conclusions of the paper weren't affected by this recalculation but Figures 7 and 8 have been updated to reflect the faster heterogeneous loss rate of DMSO.

Zhu, L., Nicovich, J.M., and Wine, P.H., Temperature-dependent kinetics studies of aqueous phase reactions of hydroxyl radicals with dimethylsulfoxide, dimethylsulfone, and methanesulfonate, Aquatic Sciences, 65, 425-435 (2003).

In conclusion, M. Legrand has identified three main areas of error in his interactive comment. 1. The exclusion of the work of Preunkert et al. 2. The kinetic errors in Table 2 and subsequent consequences for the main impact of the paper. 3. The use of k4-the heterogeneous loss of DMSO.

The authors thank M. Legrand for his interactive comments. They hope that all three issues are now resolved and with particular regard to the second of these points that the role of BrO is in fact highly significant with respect to OH and that BrO does totally control the DMSO production in this region.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 2657, 2008.