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Atmospheric
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Discussions

Interactive comment on “Study of the heterogeneous reaction of O_3 with CH_3SCH_3 using the wetted-wall flowtube technique” *by* M. Barcellos da Rosa et al.

M. Barcellos da Rosa et al.

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We acknowledge the clear summary of the motivation of our work by referee #2 with thanks.

He raised the point that the dependence of the reactivity on ionic strength has been poorly described in our paper. In fact, we did not claim any significant dependence of ionic strength on reactivity. Any influence of ionic strength on the heterogeneous loss of ozone on DMS solution observed in our study can be explained by considering the influence on solubility and diffusion coefficient alone. The desirable investigation of such a dependence on DMS reactivity would require a homogeneous-phase (i.e., aqueous) measurement of the rate constant as a function of ionic strength (e.g., by using the stopped-flow technique) and not a determination by a heterogeneous technique, where solubility and diffusive transport are involved in the evaluation of the rate constant (not touching the question of a surface reactivity, that might be different from the bulk). At the beginning of our study we had some hope to investigate the homogeneous aqueous-phase reaction by employing the stopped flow technique - but failed as described in our manuscript (l. 24, p. 1958).

The following amendments of our manuscript have been made:

-We edited the manuscript according to the careful suggestions of the referee (improving the phrasing of the text and the style and appearance of chemical equations and shifting the second paragraph of the introduction to the third paragraph), considering the minor remarks listed at the end of his report and explaining the simplified equation (3) as requested.

- We missed to state that the statistical errors reported for H refer to one standard deviation and the those of k have been estimated on the basis of the variability at various levels of DMS and include this very important information.

-Page 1953, line 18: The DMS time profile in figure 1 does in fact not demonstrate a clear, limiting value, as would be expected for an equilibration (this holds even more so for the model curve). After completion of the measurements we became aware that the water flow did not remain constant for the whole run but was restricted by the Teflon tubing to decrease at smaller interaction lengths (by up to15% at 274.4 K). This effect was smaller at the higher temperatures of our study, but we chose this experiment for comparison with fig. 2. The additional loss was considered in the model calculation of HenryŠs law constant by arbitrarily adjusting the aqueous-phase diffusion coefficient to lower values. This explanation will be inserted in the revised manuscript.

Page 1954, line 6: The very slow exponential decrease of DMS, mentioned in line 6, does not refer to the time profile of fig. 1 with a time constant of a few seconds but to the much slower decrease of the DMS level in our reservoir of 400 ml stock solution in the bubbler. The stripping of gaseeous DMS by the gas flow of 70 ml/min from the reservoir into the wetted-wall flowtube (where the film of pure water is becoming saturated according to contact time) leads to a time constant of about 1 h for the DMS level in the reservoir (that is considererd by interpolation at each position of the movable inlet to obtain [DMS]0/[DMS]t).

Page 1954, line 13: As pointed out by the referee, there is a rapid exchange of DMS between the gas phase and the aqueous phase during the reactive uptake of ozone into the film. The corresponding surface depletion of DMS has been considered by the numerical model calculation, that takes this equilibration into account.

Page 1956, line 6: We added the references and Arrhenius expressions for the diffusion coefficients (taken from the paper by Gershenzon et al. but assigning the proper expressions for DMS to Saltzman et al. and for ozone to Johnson and Davis) and explain the expected influence of viscosity on diffusion coefficients according to the Stokes-Einstein equation.

Page 1957: The HenryŠs law coefficients are now summarised in a table and the units of the HenryŠs law coefficients included in equation (7), numbered incorrectly and mentioned as Eq. (6) in our text. We recognised that all signs of equations (4) and (7), including the equation given for ln H in the abstract, have to be changed to be consistent with the units M atm-1.

Page 1958: The experimental conditions of the measurements on pure water (excess of DMS) were in fact largely different from those on salt solutions (excess of ozone in some cases), and the values presented are those obtained after considering the influence of salt on solubility and diffusion coefficients. The deviations are not statistically significant and do not deserve a deeper discussion to our opinion.

All minor remarks are considered in the corrected manuscript, and the wording of equation (3) required improvement: Equation (3) describes the fraction of molecules reacted in the liquid layer per molecules colliding with the liquid layer.

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The valuable suggestions of referee #1 including the references are considered as follows:

Page 1953: We shifted the introduction to the WWFT technique to section 2.1 and thank the referee for this very good proposal. Furthermore, we provide some ideas about our measurement technique with the apparent additional loss after 5 s interaction time (see reply to referee #2).

Page 1954: The initial mixing ratio of ozone in the measurements displayed in figure 2 was 80 ppb at 274.4 K.

Page 1955: We added the references to the work of Utter et al. and to the book on Atmospheric Chemistry by B.J. Finlayson-Pitts and J.N. Pitts, Jr., where the solubility constraint is explained.

Page 1956: The lifetimes of gaseous DMS and ozone can be estimated to exceed half an hour under the conditions of figure 3. This is about two orders of magnitude longer than the maximum contact time in our experiments.

Page 1960: We have in fact overlooked the impressive model calculation by Boucher et al., where the heterogeneous transformation of DMS by ozone and the gas-phase reaction with BrO are treated in detail.

Interactive comment on Atmos. Chem. Phys. Discuss., 3, 1949, 2003.