

Interactive comment on “Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α -Al₂O₃ and MgO” by Y. Liu et al.

Anonymous Referee #2

Received and published: 27 July 2009

The manuscript titled “Comparative study of the effect of water on the heterogeneous reactions of carbonyl sulfide on the surface of α -Al₂O₃ and MgO” by Liu et al., reports on laboratory measurements of OCS on two relevant model mineral surfaces under dry and humid conditions using a Knudsen Cell at very low humidities and a DRIFTS reaction system to determine uptake at higher humidities, as well as Temperature programmed measurements. Given that Knudsen cell systems do not have capabilities to measure heterogeneous uptake at atmospherically relevant humidities, the use of additional DRIFTS methods is an excellent way to circumvent this limitation. Overall, I believe that the measurements and laboratory techniques used are sound and are within the scope of Atmospheric Chemistry and Physics Journal. However, there are

C3342

some important issues that need to be addressed prior to publication and potentially more experiments that need to be performed. Please see my specific comments below.

1) Abstract, 1st sentence: the authors indicate that they consider OCS uptake on minerals as a “new” sink to OCS in the troposphere. However, this theory is not new, because it has been shown by this group in the past to be a potential sink for OCS, even under dry conditions. This is misleading and I recommend leaving this first sentence in the abstract out.

2) I am not completely convinced that there are trends in the gamma values obtained using the KCMS with RH. There are only very small increases/decreases in gamma upon increasing RH and there is no indication of the uncertainty in these measurements to prove that the trends do indeed occur. For example, the gamma for OCS on Al₂O₃ decreases from 4.70×10^{-7} to 3.59×10^{-7} . These values differ only by 1.11×10^{-7} . Thus, a very careful evaluation of measurement uncertainty is warranted. In addition, there should be some mention regarding the detection limits of the two methods and how they were determined. 3) I agree with Reviewer 1, in that the discussion of results as well as the summary of results in the abstract is often vague as to which method was used. Please clarify in the abstract as well as throughout the manuscript precisely what method was used to determine the uptake coefficients discussed.

4) The authors indicate that they used the BET surface area of the minerals to account for adsorption on the underlying sample layers and microstructure in the KCMS studies. However, they did not perform a mass study. Considering that the sample masses used in the KCMS studies were rather large, I suggest performing a mass study that will allow for a more accurate determination of whether the OCS does indeed access all of the mineral surfaces within the time scale of the KCMS measurement, or if it only accesses the top most layers. In any case, the use of the BET surface area may over estimate the amount of accessible surfaces and thus the gamma determined this way should be considered a lower limit. Additionally, for the DRIFTS gamma measurements, the authors use the geometric surface area of the sample holder because they do not

C3343

know if the OCS accesses the entire surface area of the sample. However, there is no discussion about the implications of the use of this surface area on their results. For example, even if only the top layer of particles were available for reaction, the microstructure of the particles in the top layer may give a higher surface area than just assuming a flat layer (SA_{geom}). Thus, the gamma obtained using this SA should be considered an upper limit. Some discussion regarding the choice of surface area and implications of that choice should be included in the manuscript.

5) 67

6) I do not see any comments regarding a correction for wall loss of OCS on the KCMS and DRIFTS measurements. Was this accounted for, and if so, was it negligible? Please include a discussion of the detection limits based on blank measurements.

7) Please note on Page 12488, line 1 what m/z values were monitored for OCS. In addition, it should be noted the time scale in which the initial gamma was determined from the KCMS and DRIFTS measurements. It is mentioned that 100 scans were collected for each DRIFTS measurement, which would take a very long time compared to the KCMS measurements. Some discussion regarding the use of the DRIFTS measured gamma for an initial uptake coefficient should be included based on the widely different timescales of the two measurements.

8) It is also not mentioned within the manuscript about whether there was a calibration of OCS with the MS done. How did the authors perform this calibration?

9) Please include more detail as to how the OCS concentration was calibrated for the DRIFTS measurements (Page 12490, line 2).

10) When reporting the vapor pressure of water in the KCMS measurements, some idea of the resulting RH should be given as well. For example, what RH occurs at a water vapor pressure of 2.5×10^{-6} Torr?

11) A table of gamma values determined using both methods would be very helpful in

C3344

hashing out what values came from what method.

12) Page 12495, Line 1: The authors state that the concentration of the feed gas was held at 1000 ppm OCS. Is this the concentration of OCS in the DRIFTS measurements? There is no mention of the concentration of OCS, besides the partial pressure, in the KCMS measurements. Please add the corresponding concentration of OCS to Page 12491, line 6 for comparison. Also, 1000 ppmv is very high compared to the concentration of OCS in the troposphere. Some discussion regarding the relevance of the concentrations of OCS used in the KCMS and DRIFTS measurements should be included as well as the potential implications of measurements at these concentrations.

13) Page 12496, Line 5-6: The sentence stating "the hydrolysis pathway has not been elucidated due to the absence of reaction products such as H₂S" is confusing. Are you trying to say that previous measurements have not measured H₂S as a reaction product? Please clarify.

14) Page 12496, Lines 11-12: Did the authors scan the entire mass spectrum to see if any other reaction products occurred in the gas phase? That is, they mention that gaseous SO₂ could be a reaction product. Did you see SO₂ in the mass spectrum?

15) Page 12499: A clearer connection needs to be drawn between your work and the previously reported results.

16) Does heating the sample have any effect on the uptake of OCS? Did the authors investigate the effects of sample heating? This could be important considering that the samples were heated to rather high temperatures during "pretreatment". Was the sample completely dehydroxylated? If so, how does the reaction occur under dry conditions with no surface -OH groups? A closer investigation of the effects of pretreatment could help nail down the reaction pathway. On page 12501, the authors state that their ML coverages occurred at higher RH values than were previously reported. Could this also be due to pretreatment effects? Also, the authors indicate that significant uptake of OCS still occurred (higher than the background value) at RH values of 0.47 to 0.67

C3345

on Page 12501, Line 24. Some discussion regarding surface sites available for uptake should be discussed. For example, it could be that not all of the surface OH sites were consumed by adsorbed water. Instead, as some previous studies (Baltrusaitis et al., 2007) have found that there are adsorbed water islands. That is, water is not adsorbed according to their hypothetical ML, but rather in islands such that some surface adsorption sites are still available for reaction by OCS.

17) Page 12502, Line 7: What do you mean specifically by “At the typical relative humidity...”

18) Page 12503, Atmospheric implications: Can you give some idea of what the lifetime of OCS is in the troposphere with respect to heterogeneous loss on mineral surfaces at different RH values and compare this lifetime to other loss processes in the troposphere. Your results should be considered more carefully with respect to whether it truly is significant loss mechanism in the troposphere. See Frinak et al., 2004 for the calculation.

19) Figure 3: Please label each according to what species is being monitored.

20) Figures 4, 5, 6, 8, and 9: Please give some indication of the uncertainty in your measurements. Error determination is critical to interpretation of your results.

References: Baltrusaitis, J.; Schuttlefield, J.; Jensen, J. H. and Grassian, V. H. “FTIR Spectroscopy Combined with Quantum Chemical Calculations to Investigate Adsorbed Nitrate on Aluminum Oxide Surfaces in the Presence and Absence of Co-Adsorbed Water, *Physical Chemistry Chemical Physics* 2007, 9, 4970 – 4980.

Frinak, E.; Wermeille, S.; Mashburn, C.; Tolbert, M.; Pursell, C. “Heterogeneous reaction of nitric acid on γ -phase iron(III) oxide, *Journal of Physical Chemistry A*, 2004, 108, 1560-1566.

Interactive comment on *Atmos. Chem. Phys. Discuss.*, 9, 12483, 2009.