

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 #1

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This paper reports the heterogeneous kinetics for OCS reacting with Al₂O₃ and MgO surfaces. The effect of water vapor on the kinetics and some information regarding the reaction products are presented. While the experimental methods and data are sound, the discussion of the results is often confusing so as to appear conflicting. This makes it difficult to follow the main conclusions derived from the results by the authors. Discussion of results obtained from the two principle experimental techniques used are also often muddled. The subject matter is within the scope of ACP. After significant revision and improvement of the presentation of the data, discussion of results, and the conclusions that follow, this manuscript may be suitable for publication in ACP.

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Major issues:

I frequently was confused as to what data was being discussed – Knudsen cell or DRIFTS. Please be sure to make it clear which experimental technique was used to measure the data under discussion, particularly when data from both techniques are discussed in the same sentence. On a related note, the authors seem to assume, without any discussion, that the Knudsen cell and DRIFTS data are directly comparable. However, the two instruments operate under widely different pressure ranges, and also extremely different OCS reactant concentrations were used in the two experiments. [OCS] = 7 ppb for KCMS and 1000 ppm for DRIFTS yet there is NO discussion of this dramatic difference or the effect it might have on the uptake kinetics. This is really rather shocking. I realize that different concentrations are required for the two techniques, but the possible ramifications must be discussed. Reactant concentration has frequently been found to affect the uptake kinetics of reactant gases on mineral dust surfaces due to saturation effects (e.g. Hanisch and Crowley 2003; Sullivan et al. 2004). Furthermore, there should be a discussion of the comparability of the observed reaction probability between the two experiments for as similar as possible reaction conditions (e.g. zero water vapor). If such reactions have not been conducted they should and be included in the revised manuscript. Only four water vapor mixing ratios were used to test the effect of water vapor on the uptake kinetics measured by KCMS. Four conditions is the bare minimum to observe any significant trend. Given the shallow slope (Fig. 4) and scatter in the data more experiments at different conditions, over a wider range of water vapor (if possible) should be included. It also does not appear that any of the experiments were ever repeated so there is no sense of the variability or reproducibility in the experimental data. Similarly, I did not see a discussion of how the measurement uncertainties were derived. Since the effect of water on the KCMS kinetics was small, the reaction probabilities should always be stated with their associated uncertainties, in the Abstract for example. Given the controversy and large differences in kinetics derived based on which surface area available for reaction is assumed, it is important that the authors always clearly state which surface area

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(geometric, BET, pore diffusion, etc.) they have used to calculate the given reaction probability for a particular set of experiments. Different terms to discuss the water vapor mixing ratios used in the KCMS and DRIFTS experiments than “low” and “high” relative humidity should be used. These do not accurately reflect the several orders of magnitude difference in water vapor partial pressure used in the two experiments. The different effects of water on the kinetics for MgO and Al₂O₃ in the KCMS and DRIFTS experiments need to be made clear. In KCMS gamma increased as water vapor partial pressure increased, while gamma decreased for Al₂O₃. However, at the high RH used in DRIFTS, gamma decreased with increasing RH for both surfaces, albeit by different degrees. I don't think that “liquid membrane” is the appropriate term for mineral particles surrounded by water. Membrane usually refers to a specific structure. Perhaps water coating or thick water layer could be used. A brief Table listing the reaction probabilities (instantaneous and steady-state) obtained from the two experiments and two surfaces for various conditions would be very useful. The Discussion could often benefit if the specific experimental values being discussed were stated, rather than discussing them in relative terms. I have noted just a few such occasions below. The uptake kinetics derived from these experiments should be compared to those obtained from other systems to put the potential significance of this reaction for the atmospheric sink of OCS in perspective.

Specific comments:

p. 12486 line 5: these References are not appropriate for typical tropospheric RH, but no Reference is really required for these values. p. 12493, line 2, this sentence is difficult to follow: “These contrary phenomena could be explained by the differential signals detected by QMS in the ñÇow system and the integrated signal of DRIFTS in the closed system; however, the characteristic absorption band of -SH was also not observed.” p. 12493: How do the product concentrations differ for the two surfaces as a function of temperature? Does MgO produce more H₂S per reactant? p. 12496: “Additionally, H₂S and CO₂ were observed as the gaseous products for the catalytic

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hydrolysis of OCS on -Al₂O₃ at ambient temperature (Rhodes et al., 2000; West et al., 2001). Therefore, we conclude that, similar to reaction on the surface of MgO, heterogeneous hydrolysis of OCS on the surface of -Al₂O₃ also occurs at ambient temperature.” This is confusing and misleading, it sounds as though you observed the H₂S and CO₂ products from reactions on Al₂O₃ but you are citing other work. Make it clear that these are not your results by saying “Work by Rhodes et al. (2000) and West et al. (2001)...” or similar, and make it clear which products were observed in YOUR experiments. p. 12497, lines 19-25: Give the rate constants when comparing the results. Could the desorption rate be determined? p. 12500, lines 22-25: Can you estimate the concentration of surface groups (A) on the two surfaces in your experiments? p. 12501, lines 16-18: Give the values reported by Goodman et al. The differences between their and your results should not be discounted so quickly. The preparation and state of the surfaces used in these types of reactions has a large impact on the measured kinetics. If such a large difference for water adsorption exists between your and previous work, further investigation is required. p. 12502, line 7: what does “typical relative humidity” mean, what RH value are you referring to? This term is frequently used later in the manuscript as well. p. 12502, lines 24-30: How did MgO behave at “low” RH? p. 12503, line 19: state the RH(ML).

Technical corrections:

There are several grammatical or syntax errors, including: p. 12484, line 14: “corresponding” not “which corresponding” p. 12486 line 11: “gas” not “gases” p. 12492 line 2: “literature” not “literatures” p. 12493, line 16: “data” not “date” p. 12503, line 4: “atmosphere” not “atmospheric”

Figure 3: List the ions being measured at the three m/z ratios. Figure 8: State what instrument the uptake coefficients were measured in.

Cited References:

Hanisch, F. and Crowley, J. N. (2003). Ozone decomposition on Saharan dust: an ex-

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perimental investigation. *Atmos. Chem. Phys.* 3:119-130 Sullivan, R. C., Thornberry, T. and Abbatt, J. P. D. (2004). Ozone decomposition kinetics on alumina: effects of ozone partial pressure, relative humidity and repeated oxidation cycles. *Atmos. Chem. Phys.* 4:1301-1310

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