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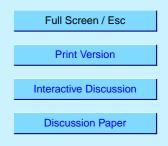
# *Interactive comment on* "Kinetics and mechanism of heterogeneous oxidation of sulfur dioxide by ozone on surface of calcium carbonate" *by* L. Li et al.

## Anonymous Referee #2

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## General comments

This paper explores the oxidation of SO2 on mineral dust in presence of ozone. Given the general importance of sulfate formation in atmospheric chemistry and climate, this topic is timely and of significant scientific relevance. Even though some previous studies have addressed the issue of SO2 oxidation by ozone on mineral dust surfaces, this work provides more insights into the stepwise oxidation process and also its humidity dependence on mineral dust. From an atmospheric chemistry relevance perspective, this work has been performed at very high ozone and SO2 concentrations, possibly



limited by the sensitivity constraints of the methods used, which reduces the direct relevance of the results. However, some of the conclusions can be extrapolated to atmospheric conditions. The paper is clearly structured and reasonably well written. Therefore, I recommend publication in ACP after revision according to the comments outlined below. The general concern is that while the title states that kinetics and mechanism for the sulfur dioxide oxidation by ozone are being explored, in the end the conditions during the experiments were such that the actual reaction of ozone with adsorbed sulfite was not the rate limiting step. From that perspective I suggest to formulate abstract and title a little more cautious and to more emphasize the evidence found for the mechanistic aspects. In the kinetic analysis section, the authors could derive lower bounds for the kinetics of the surface reaction. This aspect might also affect the atmospheric implications section, as eventually the oxidation step itself could also become the rate limiting process, depending on the gas phase concentrations of both ozone and SO2 in the atmosphere. Another general aspect might to mention and consider the fact that while CaCO3 is indeed an important dust constituent for certain sources, many dust aerosol types do not contain a lot of CaCO3.

#### Specific comments

The abstract contains too much introductory material, this should be reduced to a minimum.

P581, L7: specify the 'special' chemical properties (hydrate formation, others?). Also note that hydration occurs also in other mineral, but slower.

P581, L25: Recent work by Hoppel et al. in J. Geophys. Res. might be added.

P583: In order to understand how this experiment works, one should emphasize that the gas flow was forced through the powder, which seems to be the case based on the Figure. In relation to that point, the reader should learn what the probing depth of the IR beam is approximately: does it explore the uppermost few layers or rather the entire sample?

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P584: I wonder what happened when in absence of ozone SO2 was switched off. How much sulfite would have disappeared again? According to the text, ozone has been added at the moment SO2 has been switched off. Depending on the life time for desorption compared to that for reaction, the coverage by SO2 may not have been well defined. In addition, the time needed to equilibrate the signal with SO2 alone determined by the adsorption / desorption kinetics or by mass transport across the sample (to coat all the internal surface area). A switching on-off cycle of SO2 alone would help to clarify this.

P584, L5: this probably indicates that O3 just undergoes reversible adsorption in absence of a reactant.

P586, last paragraph: not that a reactive collision is not a well defined quantity. I would define the reaction probability as rate of product formation normalized to the collision rate of SO2. The problem is that the uptake coefficient of SO2 may be much larger at times, especially at the beginning, before the reaction quasi steady state is reached that is considered here.

P587, L15: is it important for this calibration that the two mixed powders have the same surface to volume ratio, because the DRIFTS basically probes the internal surface?

P588: Two issues seem appear from the reported uptake coefficients. A. Does using the term 'initial' uptake coefficient make sense in this context? Usually this term is used in experiments, in which the loss probability of the first collisions can really be resolved. It could well be that in these experiments the value of the uptake coefficient in the beginning is given by mass transport into the sample. B. Related to my questions regarding the probing depth of DRIFTS I wonder whether normalizing to the geometric surface makes sense at all in this context. The discussion around using the geometric versus the BET surface areas in analyzing Knudsen cell data are always related to a discussion of the probing depth, which is not the case here, as DRIFTS probably probes the entire BET surface?

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P588, L17: the discussion about the deposition velocity is not clear. What information can we get from the cited value, and where is that coming from, i.e. from what kind of measurement?

P590, last line: how does humidity affect this comparison with rigidity?

P591, L15: I suggest introducing the hydration of CaCO3 as a separate, explicit reaction; it is eventually the most important one, as it may determine the rate of sulfite formation.

P593, L5: it should be pointed out here that just because the experimental conditions were such, that the surface reaction with O3 was not rate determining, this does not necessarily mean that this is the case under all conditions.

P595: atmospheric implications: apart form the previous comment, also note that the uptake coefficient might be significantly higher at lower concentration. The interplay between relative concentrations at the surface of the dust particle will ultimately determine the removal rate of O3 and the formation rate of sulfate. Technical comments P580, L21: Particulate matter (PM) play...

P584, L9: ...exposure to SO2 and O3.

P586, L7: desorbed from the surface

P586, L9: Börensen

P587, L9: ...will be the geometric...

P588, L13: ...using Knudsen cell reactors; L15: ...in the order of 10-5 on China Loess...; L22: Knudsen; L23: measurement principles; L24: ...loss of the gaseous species...

P590, L6: ...water on the particle...; L18: ...about two times as fast as that in the experiment...

P591: L21: ...reaction, in which...

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P592: no kinetic parameters are available for the S(IV) oxidationĚ

P596, L19: Börensen

Figures: while the figures seem ok for presentation in ACPD, they might not be so when reduced to fit the column width in ACP. For that, most of them might need bigger fonts in the labels or in other text boxes.

Interactive comment on Atmos. Chem. Phys. Discuss., 6, 579, 2006.

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