

Interactive comment on “Heterogeneous reaction of ClONO₂ with TiO₂ and SiO₂ aerosol particles: implications for stratospheric particle injection for climate engineering” by M. J. Tang et al.

Anonymous Referee #1

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This study reports room temperature uptake coefficients of chlorine nitrate (ClONO₂) on TiO₂ and SiO₂ aerosol particles as well as on a macroscopic Pyrex surface. ClONO₂ is implicated in the chlorine activation cycles sustaining stratospheric ozone loss and the formation of the polar ozone hole. This study is motivated by the proposals to use the injection of highly refractive nanomaterials, such as TiO₂, into the stratosphere as a climate engineering measure to reduce solar radiation on the ground. Adding a substantial amount of TiO₂ to the stratosphere is directly increasing the surface area for those heterogeneous processes normally occurring on polar stratospheric clouds or sulfuric acid particles of volcanic origin. ClONO₂ hydrolysis is one of the key processes therein. Therefore, this study is addressing a highly relevant topic. The po-

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tential adverse (chemical) effects of solar radiation management schemes need careful attention. Apart from the laboratory measurement of the uptake coefficients, a global chemistry-climate model is used to assess the impact of TiO₂ on stratospheric ozone in comparison to the sulfuric acid particle injection following the eruption of Pinatubo by tuning the TiO₂ injection to have the same radiative properties as the Pinatubo sulfuric acid particles.

The results demonstrate uptake coefficients on TiO₂ in the range of 1e-3 in the lower relative humidity range, which is significantly lower than hydrolysis on liquid sulfuric acid. For SiO₂, uptake coefficients remained in the few 1e-4 range, about an order of magnitude larger than those observed on Pyrex, indicating the importance of representing the material of interest in the form most relevant for the atmosphere. The model work showed that injecting TiO₂ into the stratosphere leads to two partially counteracting effects due to the altitude dependence of the efficiency of different species families involved in catalytic ozone loss: While the uptake of ClONO₂ on TiO₂ leads to less chlorine activation than would occur on sulfuric acid, the concomitantly smaller N₂O₅ uptake on TiO₂ than on sulfuric acid results in lower ozone levels in the middle stratosphere. Therefore, within the constraints of a still not sufficiently established heterogeneous chemistry scheme, the effect of TiO₂ on column ozone abundances remained similar to those of an equivalent sulfuric acid injection.

This study is well designed and performed and uses state of the art methods to address the kinetics of heterogeneous reactions. ClONO₂ is an inherently difficult species to work with, and the efforts of the authors to synthesize, measure and calibrate it are appreciated. Only a few minor issues may remain as additional discussion topics with respect to the experimental part of the work. The model runs appear to be well designed, even though this reviewer is not familiar enough with modelling to judge the details. The manuscript is generally well written. A few comments below indicate where the structure could be improved.

Specific comments 1. Introduction section: the authors should somewhere address

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the fact that TiO₂ is a well-known photocatalyst, which may trigger radical production and chemical conversions, both oxidation and reduction. Are there estimates whether this could be relevant? Also, the photochemical activity is strongly size dependent and restricted to the size range used in this study. The authors should clarify whether the type of material studied here would be the one foreseen for the solar-radiation management purpose.

2. section 4.1: since the measured uptake coefficient were rather close to the diffusion limit, the relevance of these values is rather limited. This section could therefore be condensed a bit. I suggest to add either the effective (uncorrected) uptake coefficients or the correction factor to table 1, so that the magnitude of correction becomes immediately apparent.

3. page 17, lower paragraphs: while I agree that the local diffusion around the particles is not having an effect, I wonder whether the obviously strong radial gradients have an impact on the measured uptake coefficient. The effective first order wall loss rate coefficient is only acting on the average concentration.

4. page 20, top paragraph: it is not surprising that ClONO₂ hydrolysis behaves differently than N₂O₅ hydrolysis. However, from the discussion given here, it is not becoming apparent in what way the authors think the two mechanisms are operating such that ClONO₂ hydrolysis behaves as observed. Both processes are likely initiated by OH groups, and both require adsorbed water. Is it maybe because for N₂O₅ two steps are required?

5. page 20, section 4.4 first paragraph: if Molina et al. have not done any control experiments in absence of HCl, I suggest to reduce this comparison to a minimum. It is rather trivial that the uptake on TiO₂ in absence of HCl is different to that on alumina in presence of HCl. So there would be simply no data to compare with. In turn, the temperature dependence may indeed be important and should be carried into the modelling study as a big uncertainty.

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6. page 23, top paragraph: somewhere here the authors should address the sensitivity of the model runs to the temperature dependence of the uptake coefficient. I am not convinced that the studies cited for other species are giving a good indication for the potential T dependence for ClONO₂.

7. page 24, last part of discussion of modelling section: it is not clear to this reviewer what level of detail is included for the treatment of polar ozone, the occurrence and composition of PSCs etc. A few times, particularly strong effects at high latitudes are mentioned. It might be insightful to learn about the reasons for differences at high latitudes.

8. section 6: this section is not written as a conclusion. This is more a reiteration of the discussion and is partially repetitive. I suggest to integrate the important points to the previous sections and condense the rest into a real conclusion section. And since this rest contains quite a bit of statements and suggestions, I would entitle it as 'conclusions and outlook'.

Technical comments

Page 2, abstract, line 20: revise sentence: 'Introduction of ...would scatter solar radiation'; it is the particles that have an effect, not the introduction! Page 7, line 160: ...was then passed through... Page 9, line 208: ...served as a dry atmosphere... Page 18, line 421: ...The heterogeneous reaction ...was studied... Page 19, line 456: ...adsorbed water on the SiO₂ surface... Page 22, line 527:... has a much smaller impact ... than...(not 'reduced impact') Page 23, line 558: In contrast, ...

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