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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Heterogeneous reaction of $ClONO_2$ with TiO_2 and SiO_2 aerosol particles: implications for stratospheric particle injection for climate engineering" *by* M. J. Tang et al.

Anonymous Referee #2

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Summary. Due to its high refractive index, TiO2 has been considered as a geoengineering material that could be deliberately injected into the upper atmosphere for the purpose of scattering incoming solar radiation. However, the consequences of this added aerosol mass on heterogeneous reactions that impact ozone levels in the stratosphere are unknown. Tang et al. present a combined experimental and modeling studied aimed at understanding the effects of injected TiO2 particles on stratospheric chemistry, with a focus on heterogeneous hydrolysis of chlorine nitrate (ClONO2), a process known to activate Cl and lead to stratospheric ozone depletion.

Tang at al. use an aerosol flow tube technique with chemiluminescence detection of ClONO2 (and associated aerosol sizing / number measurements) to study the loss

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of ClONO2 on TiO2 particles. For comparison, losses onto SiO2 aerosols are also studied, in addition to the adsorption of ClONO2 to the flow tube walls. Ambient temperature uptake coefficients for ClONO2 are reported over a limited relative humidity range.

It is clear to this reviewer that a lot of hard work that went into making these measurements; they are not easy. Generating a flow of ClONO2 that is free of impurities, the constant supply of uniformly sized aerosols that is required, and the method of indirectly detecting ClONO2 via catalytic decomposition followed by chemiluminescence detection are complex and present multiple challenges. The methods appear to be appropriately chosen and the experiments executed in the best possible way. The main weakness in the experiments is that wall uptake was so high that in some cases, wall losses masked uptake onto the aerosol particles; this likely contributed to the limited scope of the data presented.

A unique aspect of the work is its use of modeling to evaluate the impact of the measured ClONO2 uptake coefficients on a hypothetical event where TiO2 or sulfate aerosols are injected into the stratosphere. A vertically resolved global chemistry-climate model (UKCA) indicated that less ozone destruction occurred as a result of reactions of ClONO2 and N2O5 on injected TiO2 particles vs. on aerosols formed from the Mt. Pinatubo eruption (under conditions where both injection events had the same solar radiation scattering). My comments are listed below.

General Comments. The description of ClONO2 generation and detection is detailed in the methods section, but at times it is difficult to reconcile with Figure 1. I recommend that more detail be added to Figure 1 to show the aerosol cyclone mentioned, two diffusion driers, and the reactor that converts ClONO2 to NO, etc. In addition, it would benefit the reader, especially when reading section 2.1.3, to include a diagram of the ClONO2 detection scheme.

I feel that the rationale for choosing the ClONO2 uptake coefficients used in the model

was not made sufficiently clear. Uptake coefficients for both N2O5 and ClONO2 hydrolysis on stratospheric TiO2 particles are set to 0.0015. The N2O5 value of 0.0015 is taken from the group's prior work (Tang et al. 2014d). It is not clear why the authors assume the uptake coefficient for ClONO2 is the same as that of N2O5. The values for gamma(ClONO2) listed in Table 2 for TiO2 are 0.001, so I am assuming that given the error in the measurements the authors are just assuming that the uptake coefficients are the same within error for the two processes?

I feel that the TiO2 uptake coefficient for ClONO2 may be underestimated, meaning the ozone loss predicted by the model may be underestimated. The studies here were conducted at room temperature and lower temperatures expected for the stratosphere could result in higher gamma-values. The authors discuss this near line 549 and argue that the measured room temperature gamma-values may be within a factor of 2 or 3 of those at lower temperatures. More important may be the concentration effect. A concentration dependence of the uptake coefficient for the reaction of ClONO2 on TiO2 surfaces is an important consideration that should be addressed in a revised manuscript. One would expect significant surface saturation at the high concentrations (hundreds of ppb) used in this study. This effect would result in correspondingly low uptake coefficients. ClONO2 levels in the stratosphere are 2-3 orders of magnitude lower than the concentrations used in this study. Therefore, it is likely that the uptake coefficients under atmospheric conditions of lower ClONO2 concentrations would be higher than those reported. Related to this, I feel it is important to list specific ClONO2 concentrations used in each experiment listed in Table 1 and 2.

How relevant is it to consider adsorption to a TiO2 surface, which at room temperature and at 7-33 % relative humidity would contain a monolayer (or less) of adsorbed water? In the stratosphere, I would think that injected TiO2 particles would be rapidly coated in NAT, HCl, H2SO4, etc. If that is true, should not the model be treating the TiO2 as simply a seed particle? Or does it already? In that case, would it not be more accurate to assume that the uptake coefficients would be those for ClONO2 uptake onto PSC

components, which could be one or two orders of magnitude higher than what was measured in this work on TiO2?

Lastly, I am aware of the meaning of the word “nudged” in the context of atmospheric models. However it is ambiguous and could be misinterpreted by a non-scientist who could think “nudging” a model means to coax it into giving you the results you want to see (thinking of “Climategate here). I would encourage the authors to consider replacing a phrase like, “. . .simulations were nudged. . .” with something more accurate; for example, “. . .initial conditions were set to. . .”

Specific Comments: line 279: replace “spectroscopy” with “spectrometry.”

line 540-542: It is not clear to me how the presented “measurements suggest that the uptake coefficient onto TiO2 is smaller than that for sulphate below ∼215K.” This comment is related to the discussion above regarding the relevance of treating TiO2 as pure TiO2 surface or one that coated and has surface properties more in line with a PSC.

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