

Interactive comment on “Heterogeneous reaction of N₂O₅ with airborne TiO₂ particles and its implication for stratospheric particle injection” by M. J. Tang et al.

T. Bartels-Rausch (Referee)

thorsten.bartels-rausch@psi.ch

Received and published: 5 May 2014

Dear Tang et.al. Thank you for your contribution to ACP. Unfortunately one Referee did not submit a report in time, so I provide a quick review to substitute a report of one Referee. The manuscript describes the uptake of N₂O₅ to TiO₂ aerosol and the impact of this on stratospheric N₂O₅ and ozone budgets. Such studies are highly relevant and needed to understand the consequences of recently proposed approaches of solar-radiation management. The study is carefully done and analysed, conclusions are well justified and limitations are highlighted. Even though it is not a complete study, I accept this manuscript for publication in ACP after some minor changes. There

C2076

are three main aspects that I ask you to discuss in more detail: * Could you give more details on the humidity and temperature conditions in the stratosphere for the altitude that shows highest TiO₂ concentrations after injection. This would help the reader to relate your experimental study to the relevant environmental conditions. I feel that currently the relevance of the experimental settings is addressed rather late in the manuscript and the reader keeps wondering why you did experiments at RT and whether or not the RH are appropriate for the stratosphere. * You nicely show and discuss the dependence of N₂O₅ uptake on relative humidity and conclude that the water at the TiO₂ surface is relevant. Taken that temperature is lower in the stratosphere than at RT (where I assume the Goodman, 2001, data were derived); how would the water coverage look like at stratospheric temperatures; is that known? * What is the effect of N₂O₅ ↔ NO₃ + NO₂ equilibrium on your results. Removing N₂O₅ by uptake might lead to re-formation from NO₃ and NO₂. Did you by-pass the 100 °C reaction chamber occasionally to observe changes in NO₂? Further, I hope you'll find the following detailed comments helpful: P4424 l15ff: Re- word: This implies a connection between low stratospheric ozone and decrease in surface temperature. P4428, l 20 ff: Could you include some more details about the experimental set-up such as concentration. What does "largely reduce NO₂" mean exactly. P 4430 l10: Wagner described this synthesis first, didn't they? Could you add a reference? P4433 l9: "The difference of kw measured before and after introducing TiO₂ aerosols in the AFT was insignificant, indicating that the N₂O₅ wall loss did not change significantly during the uptake experiment." How much did it change usually, could you specify. P4433 l15. It is not clear what "true loss rate" means in this context, could you specify?

P4433 l 18+19: Change to Author (year) P 4433 l25: define gamma and gamma(eff) and gamma(exp) P4437l10: Why "Another"? P4439l24 I don't understand this: "and this may be a result of an overestimate of surface area densities caused by extrapolation over the poles" P4440l10: "Whilst we acknowledge that there are limitations to these simulations, most notably the inclusion of only a single heterogeneous process on the TiO₂, but also due to factors such as the omission of the TiO₂ aerosols from

C2077

the photolysis calculation, we believe the qualitative conclusions from them are valid." This sounds a little vague. Could you summarize why you believe this? P4441115: At what concentration did Molina 1997 study the uptake? Are those atmospherically relevant? P4442: What is QBC? P4445, Caption fig 4: could you add experimental settings? Section 3.1 and 3.2: What is the surface coverage of N₂O₅ and of H₂O? How important is the thermal N₂O₅ → NO₂ equilibrium as source of uncertainties? Did you observe NO₂ upon N₂O₅ uptake, or do your data suggest that N₂O₅ is completely taken up (as 2 HNO₃) by the aerosol? Did this depend on humidity? Introduction or Discussion: Are there other important loss processes in the stratosphere, i.e. photolysis that might be changed by TiO₂ (and the induced changes on radiation). Could you elaborate on this?

Interactive comment on Atmos. Chem. Phys. Discuss., 14, 4421, 2014.

C2078