**Atmospheric
Chemistry
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Discussions

EGU

Interactive comment on "Mechanism of ozone loss under enhanced water vapour conditions in the mid-latitude lower stratosphere in summer" *by* Sabine Robrecht et al.

Anonymous Referee #2

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General comments:

The paper by Robrecht et al. investigates a potential ozone loss mechanism in the mid-latitude lower stratosphere under enhanced water vapour conditions and low temperatures, initiated by heterogeneous chlorine activation on liquid aerosol particles. For that purpose the authors conducted box model simulations along 7(19)-days backward trajectories with the CLamS model. Besides a detailed chemical analysis of their standard case, they investigated the sensitivity of the proposed ozone loss mechanism to water vapour, mixing ratios of Cly, NOy, and Bry, sulphate content and temperature.

Overall, I have no doubts that the applied methods and presented findings are valid

and of wider interest for the scientific community, and therefore, I recommend this paper for publication in ACP. However, the paper is rather lengthy and the presentation of so many different case studies and sensitivity simulations does not increase the readability of the manuscript. Below I tried to make some suggestions for clarifications. Furthermore, I would like to encourage the authors to address or discuss the overall importance of the discussed ozone depletion mechanism. At the very end it is written that for observed conditions no ozone depletion was simulated, but it would be great to put the presented results more into a global and climatological perspective.

Specific comments:

- Abstract: It is a bit weird that the abstract does not clearly mention that the discussed ozone loss mechanism is initiated by heterogeneous chlorine activation on binary (ternary?) solution droplets. There are only "hints" in this direction, namely the impact of volcanic eruptions, geoengineering etc.

- Introduction: Again, it would be good to clearly state that the ozone loss process proposed by Anderson et al. involves sulphate aerosol particles. This would put the subsequent description of heterogeneous chlorine activation and catalytic ozone loss cycles much more into perspective.

- P2, l 15: Is the ClOx definition used here not a bit odd? Why is Cl2 not included? This would also facilitate the understanding of Fig.4f, because then it would be clear where the chlorine released from HCl during the first phase did go. Alternatively, one could also show Cl2 in Fig. 4.

- P3, l17/18: By how much has water vapour to be enhanced to allow Cl activation at higher temperatures? Can you provide a number?

- Model set-up: Why do you neglect NAT and ice in this study? NAT is probably not an issue, but how about ice? Especially since you mention a potential impact of ice particles on the water vapour threshold for Cl activation on liquid aerosol particles due

to different heterogeneous reactivities (p32, l3-5).

- Model set-up: Could provide a short description of the treatment of liquid aerosol particles in your model? In Table 1 you provide the gas phase equivalent H_2SO_4 mixing ratio and Fig. 4 ff show the surface area density, but some more information would be great. For example, which H_2SO_4 wt% in the liquid aerosol particles is reached under the assumed high water vapour/low temperature conditions?

- P5, l32/33: What was the overall background H_2O mixing ratio for the calculated trajectories? And temperature? By how much are the selected trajectories colder?

- Sect. 2.3 Initialization: In Table 1 it is mentioned that the ClOx species were initialized with 0. Ok, in the mid-latitude lower stratosphere most chlorine is deactivated, but I am wondering how your initial phase in Fig. 4 would look like, if the trajectories had started with non-zero ClOx? Maybe you could add a short discussion.

- Sect. 2.3.3: I do not really see the point of discussing the MACPEX case. In my view it is just another special case that could be covered by the sensitivity simulations. For the sake of clarity, I would suggest to leave it away.

- Fig. 2: What is the rationale behind the chosen H_2O mixing ratios of 5 and 15 ppmv? This choice seems a bit arbitrary to me. Why do you not use the 10.6 ppmv H_2O of your standard case?

- P10, discussion of Fig. 3: In line 3-5 the water vapour threshold is defined as H_2O mixing ratio "at which the end ozone value clearly falls below the end ozone that is reached for low water vapour amounts." What is meant by "clearly"? That sounds a bit vague. Can you be a bit more quantitative? Furthermore, it is stated that "by 12 ppmv of water vapour, the system is clearly in an ozone destruction regime." But is 12 ppmv not just the water vapour mixing ratio at which the transition between ozone production to ozone destruction occurs? At lower H_2O values, end ozone is higher than initial ozone.

- Fig. 4b: Where does the first sharp peak in the light blue line (ClONO2+HCl) come from?

- P13, l20ff: Shouldn't this sentence read: "Dependent on temperature and water vapour content, the HNO3 formed remains in the condensed phase."? And further down: "... 64% of the HNO3 remains in the condensed phase on the day with the lowest temperature, while at higher temperatures... 85% of HNO3 are released to the gas phase...". Is the HNO3 shown in Fig. 4d gas-phase only or total HNO3?

- P18/19 cycles C7 and C8: I have a hard time to follow the construction of these reaction cycles. My impression is that the authors combined different reactions until they ended up with the intended net reaction. For example: In R29 NO2 is formed, which in the next step photolyzes (R15). Lower down another NO2 is formed (R32), but this time it reacts with ClO to ClONO2 (R22).

- P20, l 14-16: I think it would be helpful to mention the reason for the lower H2O threshold under enhanced sulphate conditions, namely the increased SAD. In general, the presentation of the model results would benefit from some more explanation of the underlying processes. This holds also for Sect. 4.2 and the sensitivity of the uptake coefficient to H2O or temperature. By the way, why is the 10xH2SO4 case not shown in Fig. 7?

- P20, discussion of Fig. 6b: I do not understand the statement that similar conclusions as for the SEAC4RS trajectory hold for the MACPEX trajectory. For almost all cases final O3 is higher than initial O3. And why is there only a subset of sensitivities shown for the MACPEX trajectory? Why not also +1K and 10xH2SO4?

- Fig. 6: What is the rationale for the 3xH2SO4 case?

- P25, l3-5: I do not fully understand this argumentation. Do you mean that there is no longer enough ClONO2 available to react with the HCl taken up by the condensed particles and that therefore the enhanced HCl uptake does not lead to further chlorine

activation and ozone loss?

- Fig. 8: This figure nicely shows the different ozone regimes as a function of temperature and H2O for two different sulphate conditions. Would it possible to provide such figure also for Cly, Bry, NOy sensitivities? I am aware that this is a multi-dimensional problem, but I think it would be really helpful to get an overview under which conditions ozone formation and ozone depletion occurs. This would also help to get a better understand of the importance of this mechanism on larger scales.

- Sect. 5: As mentioned above I think the case studies are too much and do not help to provide further insights into the main chemical mechanism. It's rather confusing to distinguish the various atmospheric compositions assumed for the individual model simulations. In particular the 19-days case seems trivial to me: longer time under cold and humid conditions, more ozone loss.

Technical corrections:

- P3, l19: hypothesis hat -> hypothesis that

- P4, l8: ans -> and

- P4, l20: HNO3+2N2O5

- P8, l3: N2O, 2 should be subscript

- P9, l28: ClOx, x should be subscript

- P16, l3: simultanous -> simultaneous

- P17, l29: HCl-formating -> HCl-forming

- P34, l19: and extreme -> an extreme

- Units: The text is a mixture of ppb/ppt and ppbv/pptv. I assume it is always volume mixing ratio?

- Chemical reactions: It would be nice to mark heterogenous reactions as such.

- Table 1: I would suggest to add Cly and NOy for completeness. And are 0.6 ppbv and 2.0 ppbv H2SO4 not also sensitivity simulations?

- Fig 1. It would be nice to mark the time of measurement by a red square or a vertical line also to the left panels. And maybe the tropopause altitude at the location of the air parcel could also be added to the left panel.

- Fig. 4, 9, 10, 11, 12: Which time of day do the x-axis tick marks refer to? One can infer night-/day-time from the reactions with OH, but it would be helpful to provide this information, e.g., in the caption.

- Fig. 7: units (y-axis) are missing