

Interactive comment on “The potential impact of ClO_x radical complexes on polar stratospheric ozone loss processes” by B. Vogel et al.

Anonymous Referee #1

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General Comments.

This is an interesting paper. It is a worth while to take a look at some possible consequences if these ClO_x complexes could be produced and lost with the rate constants assumed in the various cases. While I agree with the basic conclusion that there is no evidence that these species play an important role in the atmosphere, I have some substantial comments.

Specific Comments.

P. 990. The authors should mention why photolysis is not considered as a possible loss process for the complexes considered. I suspect it is because the thermal dissociation

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rates are so fast that any reasonable photolysis rate is too slow in comparison to affect the concentrations. It would be useful to include in the tables the first order loss rates due to thermal dissociation, i.e., $k(\text{Reverse}) = k(\text{Forward}) / K(\text{Equilibrium})$) to make this clear. However, even if photolysis can't affect the concentrations of the complexes, there might be a photolysis product that could alter Cly chemistry which could be important in those cases where the model predicts large daytime concentrations of a complex. Of course estimating possible photolysis products and J values presents another level of conjecture, but this topic should at least be mentioned. Perhaps, since as a conclusion it seems unlikely that these complexes exist in large quantities for other reasons, the authors could simply state there is no need to go into a more detailed discussion of what additional photochemical reactions are possible.

P. 993. The authors have used K Eq for ClOOCl derived from in situ observations as a measure to rule out some of the model results. I think it would also be useful to bring in to the discussion constraints presented by the state of the inorganic chlorine budget. How much room is there for the possibility of other exotic ClOx species given what we already know from in situ and remote observations of ClO?

P. 994. Is there an error in Figure 4? I thought Case 1 resulted in less O₃ loss compared to the standard model, Case 2 and Case 3 showed no additional O₃ loss, and Case 5 showed a lot more loss. Yet in Figure 4, the right side panel shows all cases having additional O₃ loss, if not zero additional O₃ loss, compared to the standard loss. Shouldn't Case 1 be positive on this plot instead of negative?

P. 996. In the section considering the ClO-H₂O complex, Cl₂O₂ and total ClOx are discussed in the text but not shown in the figures. Since in some of these cases ClOx/Cly changes, as one might expect to see in the most dramatic cases, it would be useful to show this in the figure. Also, since one might simplify the situation here by noting that if you make more dimer you will get more O₃ loss, it would be useful to show the modeled ClO dimer concentrations for the various cases.

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P. 998. I think it is interesting to note from Figures 3 and 7, that changes in the photochemistry of the model do not change the shape of the modeled results much compared to the shape of the MATCH results. One might have hoped that some change in the model photochemistry might have led to a better agreement with regard to the shape mismatch. Does this imply that the model - Match disagreement is more likely dependent on a poor wind field or transport description in deriving the MATCH results, unknown mixing effects, or some heterogeneous effects? I think this is worth mentioning and exploring a bit.

P. 1000. The conjecture that the in situ ClO measurements, that are based on $\text{ClO} + \text{NO} \rightarrow \text{Cl} + \text{NO}_2$ reaction, might be insensitive to whether “ClO” exists as ClO or ClO-O₂ or one of the other complexes is interesting. But there is broad agreement between the in situ ClO observations and all of the mm-wave based observations of ClO by satellite, balloon-borne, and from the ground. The mm-wave technique is most likely very sensitive to the spectroscopy of ClO and would not detect ClO-O₂ as ClO. Given the agreement between in situ and mm-wave techniques, it seems unlikely that the ClO detected by the in situ techniques is not ClO. The discussion in the text is quite speculative and it might be labeled as such more deliberately if not dropped.

P 1002. In the conclusions and in the abstract, statements are made regarding the equilibrium constant for ClOOCl, about a discrepancy between Plenge laboratory result and the in situ observations. From the abstract, “However the existence of ClOx radical-molecule complexes could possible explain discrepancies for the equilibrium constant of the ClO dimer formation found between recent laboratory and stratospheric measurements.” However, there are no discrepancies, at least none pointed out in this paper. Figure 2 shows excellent agreement between the Plenge et al. 2005 laboratory result based on the bond strength of ClO-OCl and the Stimpfle et al. 2004 in situ measurements. The von Hobe et al, 2005 in situ results are within the error bounds of Plenge and the scatter of Stimpfle et al. 2004 results. Given the scatter in all previous laboratory based determinations, one cannot say any discrepancy exists. What is the

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basis for this statement?

The last sentence states, “However, if another ClOx radical-molecule complex formation channel for instance via heterogeneous reactions on polar stratospheric clouds would exist, the ozone destroying cycles discussed here could have an important impact on stratospheric polar ozone loss processes, especially under cold mid-winter conditions.” This statement doesn’t seem likely or defensible. First, the heterogeneous reaction mechanism we know of are so fast and saturated that it is hard to imagine any additional process that might promote even faster Cly to Clx conversion, and subsequent ozone loss. Secondly, if the ClOx complexes are not important in the atmosphere as modeled here, I don’t see why they would be important if they were formed from a heterogeneous reaction and then quickly converted to ClO.

Technical corrections There are numerous minor grammatical issues that could be cleared up with a careful reading.

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