

## ***Interactive comment on “The potential impact of $\text{ClO}_x$ radical complexes on polar stratospheric ozone loss processes” by B. Vogel et al.***

**B. Vogel et al.**

Received and published: 6 June 2006

### **Reply to the Reviewer 1 and 2 Comments**

We thank the reviewers for a very thorough and very helpful review. Because referee 2 was taking the freedom of agreeing or disagreeing on some issues raised in the report of referee 1, we answered by one author comment referring to both reviews. Following the reviewers advice, we discuss some topics in more detail. Figure 4 was corrected and in Figures 1, 5, and 6 the  $\text{Cl}_2\text{O}_2$  and  $\text{ClO}_x$  mixing ratios were added.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

## Specific Comments:

### 1. Possible photolysis reactions of ClOx radical complexes (p. 990)

Reviewer 1 asked why photolysis is not considered as a possible loss process for the complexes considered. He suspects that it is because the thermal dissociation rates are so fast that any reasonable photolysis rate is too low in comparison to affect the concentrations. Reviewer 2 made the following comment on that: "If there is a built-up of complex concentration as modeled in some runs, than these complexes could photolyze, regardless of their thermal lifetime. The UV/VIS chromophore of the complex absorption would probably be the same as in the bare radical - leading to almost identical electronic absorption spectra; the H<sub>2</sub>O- and O<sub>2</sub>-radical bond is way too weak to have significant influence. The position of the vibrational absorption features will certainly shift but not dramatically. With respect to photolysis, the complexes should thus basically do what the bare radicals do."

In contrast to Reviewer 2 the authors are no experts in laboratory chemistry, therefore we are very grateful about the comment by Reviewer 2. In section 3.2, we added the following statement: "Photolysis reactions of ClOx radical complexes play a minor role in stratospheric chemistry, because it is assumed that UV/VIS chromophore of the complex radical absorption would probably be the same as in the bare radical - leading to almost identical electronic absorption spectra. Calculations of Coxon et al. [Coxon, J.A., W.E. Jones, and D.A. Ramsey, 12th International Symposium on Free Radicals, 1976, Laguna Beach, California] and Langhoff et al. [Langhoff, S.R., L. Jaffe, and J.O. Arnold, 1977, J. Quant. Spectrosc. Radiant. Transfer, 18, 227] indicate that photodecomposition of the bare ClO radical accounts for almost 2 to 3% of the total destruction rate of ClO in the stratosphere, therefore the photolysis of ClO (ClO + hv → Cl + O) and ClO radical complexes are not considered in our model calculations."

## 2. Inorganic chlorine budget (p. 993)

Reviewer 1 wrote: “The authors have used  $K_{eq}$  for  $ClOOC\dot{Cl}$  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 into the discussion constraints presented by the state of the inorganic chlorine budget. How much room is there for the possibility of other exotic  $ClO_x$  species given what we already know from in situ and remote observations of  $ClO$ ?”

An analysis of the inorganic chlorine budget ( $Cl_y$ ) in the stratosphere should be ideally based on simultaneous measurements of the primary inorganics ( $HCl$ ,  $ClONO_2$ ,  $ClO$ , and  $Cl_2O_2$ ). A model study [Grooß et al., JGR, 2002] based on in situ measurements of  $HCl$ ,  $ClONO_2$ ,  $ClO$ ,  $Cl_2O_2$  performed on board the ER-2 aircraft in the Arctic winter 1999/2000 found that the simulated tracer mixing ratios are in good agreement with the measurements, but it was not possible to reproduce the exact details of the inorganic chlorine compounds. Further, if we assume that the total amount of stratospheric inorganic chlorine ( $Cl_y$ ) is 3.7 ppbv [e.g. WMO2003] and assume an error of 10% for  $Cl_y$  then we obtain an amount of 370 pptv  $Cl_y$  what is within the uncertainties of the measurements. In our study the simulated mixing ratios for  $ClO_x$  radical complexes for cases where  $K_{eq}$  is used as criteria to rule out some model results are below or in the same magnitude of this assumed error range of  $Cl_y$ . There are also cases where the simulated  $ClO_x$  radical complexes mixing ratios are much smaller than 370 pptv, but the partitioning between  $ClO$  and  $Cl_2O_2$  is so much shifted that we have to rule out these cases with the  $K_{eq}$  criteria (e.g.  $ClO-O_2$  case 6,  $ClO-H_2O$  case 3). Thus we think that the  $K_{eq}$  criteria are the better criteria to rule out some model cases, because the simulated  $ClO_x$  radical complexes mixing ratios are more or less within the uncertainty range of the measured  $Cl_y$  species.

Furthermore, recent results from the remote sensing experiment ACE (as presented during the CMOS congress in Toronto, 2006) that measures practically all relevant chlorine species except  $Cl_2O_2$ , indicate no substantial imbalance of the polar strato-

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

spheric chlorine budget that would support the idea of other exotic ClOx species.

### 3. Error in Figure 4? (p. 994)

Figure 4 was corrected. In the revised figure the model data are shown for SZA lower than 90 degree and averaged over all temperatures.

### 4. Show additionally Cl<sub>2</sub>O<sub>2</sub> and ClOx in Figures 1, 5, and 6 (p. 996)

Reviewer 1 wrote: “In the section considering the ClO-H<sub>2</sub>O complex, Cl<sub>2</sub>O<sub>2</sub> and total ClOx are discussed in the text but not shown in the figures. Since in some of these cases ClOx/Cl<sub>y</sub> 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 O<sub>3</sub> loss, it would be useful to show the modeled ClO dimer concentrations for the various cases.”

We added in Figures 1, 5, and 6 the Cl<sub>2</sub>O<sub>2</sub> and ClOx mixing ratios.

### 5. Model - MATCH disagreement (p. 998)

Reviewer 1 wrote: “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 underpinning the MATCH

results, unknown mixing effects, or some heterogeneous effects? I think this is worth mentioning and exploring a bit.“

We added the following discussion in the introduction of our paper:

The discrepancies between model results and Match results, especially during cold Arctic Januaries, is a open question currently discussed in the literature [e.g., Rex et al. 2003, Feng et al. 2006]. Rex et al. [2003] suggested the existence of a currently unknown ozone loss process that is related to ClOx and/or PSCs. They found that the observed ozone loss later during the winter is in good agreement with model results based on observed ClO, suggesting that the unknown ozone loss mechanism is most important at high SZA and low temperatures typical of January conditions. A recently published model study by Frieler et al. [GRL, 2006] shows that with faster rates of photolysis and thermal decomposition of ClOOCl and higher stratospheric bromine concentrations than previously assumed a model closely reproduces observed Arctic ozone loss while being consistent with observed levels of ClO and ClOOCl. Thus they suggested that previous discrepancies between measured and modeled polar ozone loss rates might be resolved by greater efficiency of known catalytic cycles, rather than by the introduction of new chemical loss processes. The consistency of faster rates of photolysis and thermal decomposition of ClOOCl are currently discussed in a study by von Hobe et al. [2006, Understanding the kinetics of the ClO-dimer cycle, to be submitted to ACPD]. Moreover, further atmospheric observations of BrO are needed to better define levels of stratospheric BrOx and Bry. Finally the model simulations by Frieler et al. are only performed for certain level of potential temperature and in general for early winter conditions with maximum chlorine activation ( $\text{ClOx} = \text{Cl}_y = 3.7 \text{ ppbv}$ ). Thus a full resolution of the discrepancies between simulated and Match deduced ozone losses requires an explanation of the causes of the previously noted discrepancies throughout the lower stratosphere consistent with our understanding of global stratospheric ozone chemistry.

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

## 6. Discrepancies regarding the equilibrium constant of ClOOCl (p. 1002)

Reviewer 1 wrote: “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. We believe that there are no discrepancies, at least there are 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–ClO 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 discrepancies exists.

Reviewer 2 wrote on this point:” I can only support the comment of referee 1 about the discrepancies regarding the equilibrium constants. At least from what is presented in paper there certainly is no such discrepancy.”

We are in agreement with Reviewer 1 and 2 that the in situ measurements conducted by Stimpfle et al. 2004 and by von Hobe et al., 2005 are within the error limits of Plenge et al., 2005, however small discrepancies between field measurements and Plenge et al. 2005 exist. The equilibrium constant of ClOOCl formation is a crucial quantity with respect to the importance of stratospheric ozone and chlorine chemistry, therefore at present reasons for these small discrepancies between field measurements and Plenge et al. 2005 are discussed [Plenge et al., 2005].

We refined our statement in the conclusions as following: “The equilibrium constant of ClOOCl formation is a crucial quantity with respect to the importance of stratospheric ozone and chlorine chemistry. Although stratospheric measurements of the equilibrium constant of ClOOCl formation are within the uncertainty range of recent laboratory measurements, still small differences exist between laboratory and stratospheric

[Full Screen / Esc](#)[Printer-friendly Version](#)[Interactive Discussion](#)[Discussion Paper](#)

measurements, whereas reasons for this are discussed in present [Plenge et al. 2005, von Hobe et al., 2006, Understanding the kinetics of the ClO-dimer cycle, to be submitted to ACPD]. The present findings show that the existence of ClOx radical-molecule complexes could possibly explain these discrepancies.”

#### 7. Agreement between in situ ClO and mm-wave techniques? (p. 1000)

Reviewer 1 wrote: “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-O<sub>2</sub> 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-O<sub>2</sub> 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.”

Reviewer 2 wrote to this issue: “Referee 1 made a very strong comment concerning the two measurement techniques (ClO to Cl conversion by NO and mm-wave measurements). As I said, I simply don’t know these techniques well enough. However, if the NO method would indeed be unspecific and if the uncertainties in both measurement techniques are small enough and if there is broad agreement between the two techniques than there are no complexes in appreciable amounts out there: The rotational spectrum of a complex should indeed differ from that of the bare molecule (depending on which lines are measured). To me it looks extremely interesting to experimentally verify/falsify this proposal.”

Above (6.) we mentioned that small discrepancies between laboratory and stratospheric in situ measurements of the equilibrium constant of ClOOCl formation exist. A

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

recent paper based on nighttime ClO measurements conducted by the Sub-Millimeter Radiometer (SMR) instrument on board the Odin satellite also studied the nighttime thermal equilibrium between ClO and its dimer [Berethet, G. et. al, 2005, GRL, 32, L11812, doi:10.1029/2005GL022649]. They found that the value of Keq currently recommended by JPL [Sander et al., 2003] leads to a large underestimation of the observed nighttime ClO amounts, and that a realistic estimation of Keq must lie between the values determined by Cox and Haymann [1988] and von Hobe et al. [2005]. An intermediate value of Keq that falls in this range is obtained by taking the lowest possible value allowed by the estimated uncertainty of the Sander et al. [2003] recommendation. CTM simulations using this JPL lower limit agree best with Odin/SMR observations. These findings are in very good agreement with the laboratory measurements of Keq by Plenge et al. [2005], especially for stratospheric temperatures. Thus the Keq values based on laboratory and mm-wave measurements are in excellent agreement, while Keq values based on stratospheric in situ measurements based on the chemical-conversion resonance-fluorescence technique underestimate Keq (von Hobe et al., 2005) or scatter in a wide range (Stimpfle et al., 2004). These results support our assumption that ClOx radical-molecule complexes possibly have a potential impact on stratospheric in situ measurements. The authors agree with Reviewer 2 that it looks extremely interesting to experimentally verify/falsify this assumption.

In the paper we added the discussion above to Section 4.3.

## 8. ClOx radical-molecule complex formation channel via heterogeneous reactions on PSCs? (p. 1002)

The last sentence in Section 5 states, “However if another ClOx radical-molecule complex formation channel for instance via heterogeneous reactions on polar stratospheric



clouds would exist [McKeachie et al., 2004], the ozone destroying cycles discussed here could have an important impact on stratospheric polar ozone loss processes, especially under cold mid-winter conditions.”

Reviewer 1 wrote: “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  $\text{Cl}_y$  to  $\text{Cl}_x$  conversion, and subsequent ozone loss. Secondly, if the  $\text{ClO}_x$  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  $\text{ClO}$ .”

Reviewer 2 comment on that: “In that light referee 1 is right in stating that it appears not to be defensible that additional ‘heterogeneous’ reactions could impact on the ozone budget through the ‘homogeneous’ cycles discussed in the present paper (last comment, page S87). If I am not mistaken, then the cited paper (McKeachie et al.) does not built on homogeneous gas phase cycles but rather investigates radical complex driven heterogeneous chemistry. And the result there is not elevated  $\text{ClOOCl}$  in the gas phase.

To continue: I do not understand the remaining part of the above referee comment. First, I am judging the present state of knowledge about heterogeneous chlorine chemistry simply as being incomplete – the heterogeneous chemistry of  $\text{ClOOCl}$  is an example to start with. I can’t see why there should not exist other very fast and saturated reactions in the condensed phase involving chlorine chemistry. Second, the  $\text{ClO}_x$  complexes as modeled in the present paper appear to be unimportant for homogeneous chemistry (enhancing the concentration of  $\text{ClOOCl}$ ). However,  $\text{ClO}$  induced heterogeneous chemistry could generate species that are not even discussed in the present paper.”

The authors agree that our statement above is bit speculative. In fact McKeachie et al. found in experiments a heterogeneous source of  $\text{OCIO}$  and  $\text{ClClO}_2$  from  $\text{ClO}$

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper

radicals passed over water-ice surfaces at low pressures. To explain these findings, they proposed that a ClO-H<sub>2</sub>O complex is formed in a rapidly established equilibrium between ClO monomers and gas-phase H<sub>2</sub>O. The existence of this complex as well as a surface-enhanced ClO-recombination process is assumed to be responsible for the observed efficient reactive uptake of ClO radical onto the ice surface. Thus the results of McKeachie et al. are first a very good example that our knowledge about heterogenous chlorine chemistry is incomplete and second confirm the assumption that ClO<sub>x</sub> complex radicals could be possibly formed via heterogenous reactions on ice surfaces. Further examinations of this feature would be worthwhile. Therefore, from our point of view the statement above (the last sentence in Section 5) is a bit speculative, but not unlikely.

We refined our statement above: “We assume that if another ClO<sub>x</sub> radical-molecule complex formation channel for instance via heterogeneous reactions on polar stratospheric clouds would exist [McKeachie et al., 2004], the ozone destroying cycles discussed here could possibly have an important impact on stratospheric polar ozone loss processes, especially under cold mid-winter conditions.”

Full Screen / Esc

Printer-friendly Version

Interactive Discussion

Discussion Paper