

## ***Interactive comment on “Evidence for***

# **heterogeneous chlorine activation in the tropical UTLS” by M. von Hobe et al.**

**M. von Hobe et al.**

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Thanks Ross for the constructive review and interesting comments. See our response and two additional figures below.

As mentioned in the response to reviewer 1, a more detailed discussion on the possible supply of  $\text{Cl}_y$  from VSLs and sea salt will be included in the revised manuscript.

The observation of high  $\text{ClO}$  in the presence of high  $\text{NO}_2$  is puzzling indeed, and there have been long discussions on this issue among the authors. We certainly have taken extra care in the analysis of these observations and data artifacts can be ruled out to

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the best of our knowledge. You are of course correct that  $\text{NO}_2$  will quickly react with  $\text{ClO}$  into  $\text{ClONO}_2$ . But as long as the heterogeneous surfaces are there, “the game is not over”! Much on the contrary, chlorine activation is preserved or even amplified (as long as there is still more  $\text{HCl}$  than  $\text{ClONO}_2$ ) until at some point it is “game over” for  $\text{NO}_x$ , which via  $\text{ClONO}_2$  is removed into  $\text{HNO}_3$  on the particles on a time-scale of about 1 day. So the  $\text{NO}_x$  measured by SIOUX would have to be produced or transported within a few hours preceding the flight. We will take more care to explain this mechanism and point to the “very fresh in-mixing condition” with a timescale  $< 1$  day as the only plausible explanation for the co-existence of observed amounts of  $\text{ClO}$  and  $\text{NO}_x$ .

SZA will be added in Figure 6. We have looked into the issue of elevated night-time  $\text{ClO}$  in much more detail and found that the night-time reservoirs and the rates of conversion strongly depend on the prescribed conditions, in particular the amount of  $\text{Bry}$  in the CLaMS simulations. At high  $\text{Bry}$  levels, mainly  $\text{OCIO}$  is formed, while at low  $\text{Bry}$ ,  $\text{Cl}_2\text{O}_2$  is dominating. However, even though the rate constant  $k_f$  of the dimer formation reaction,  $\text{ClO} + \text{ClO} + \text{M} \rightarrow \text{ClOOCl}$ , is fast at these low temperatures, the reaction proceeds much slower in the tropical UTLS than for example in the activated polar vortices due to the quadratic dependence of the reaction rate on the  $\text{ClO}$  concentration. For the conditions found on 30 November, the lifetime of  $\text{ClO}$  with respect to dimer formation is too long for quantitative conversion overnight. This will be addressed quantitatively in the revised manuscript. Most of the minor points and technical corrections have been addressed as suggested. Some points are addressed below.

The notion that “super-high-altitude means different things to different people” (point 4) is absolutely correct. In fact, “super-high-altitude” was chosen because for some people high altitude does not even encompass the tropical UTLS. But the exact altitude range is of course the most unambiguous and we have changed the manuscript accordingly.

The 10 ppm  $\text{H}_2\text{O}$  as initialization for the CLaMS\_BT runs (point 12) were chosen so that the observed total water measured by FISH at the end of the simulation is reproduced.

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10 ppm does not seem so unrealistic taking into account the tropospheric character of the air masses and the presence of ice particles expected to lead to considerable dehydration over the course of the simulation. The latter is supported by the CLaMS\_CTM simulations. A significantly lower initial  $\text{H}_2\text{O}$  mixing ratio in the CLaMS\_BT runs would significantly reduce particle formation. This will be stated in the revised manuscript.

For the relation of enhanced  $\text{ClO}/\text{Cl}_y$  with low  $\text{O}_3$  and low temperature (point 13), we will add a sentence on the non-yellow points at higher temperatures (which were one of the reasons for the more detailed investigation that led to Figure 5). Figure 1 below shows a simple plot of  $\text{ClO}/\text{Cl}_y$  plotted against temperature. We do not think that this plot adds so much more information than is in the paper, so we tend towards not including it in the revised manuscript.

A short description of Figures 6 and 7 will be added prior to the discussion of these plots in the revised text. In Figures 7 and 8, the observations will be added to facilitate comparison between the simulation results and the actual data (point 14).

The “uncertainty of about a factor 3” (point 16) refers to the ratio of activation over deactivation rates determined by equation (7). It contains the uncertainties for the three reaction rates of  $\text{ClO}$ ,  $\text{BrO}$ , and  $\text{O}_3$  with  $\text{NO}$  from the reported rate coefficient uncertainties by the JPL assessment. It does not yet include the uncertainty of the photolysis rate or the uncertainty of any of the chemical species concentrations. The sentence will be rephrased to clarify this.

A discussion on the plausibility of up to 5 ppt of  $\text{BrO}$  in the tropical UTLS will be added in Section 4 (point 18).

Adding representative error bars for  $\text{X}(\text{ClO})/\text{X}(\text{Cl}_y)$  in Figure 5 (point 20) is problematic. First, the figure is rather busy and intricate to interpret with the different symbol sizes and colours as it is. Second, the uncertainty depends on both the  $\text{ClO}$  measurement error that varies greatly with concentration and the uncertainty in the  $\text{Cl}_y$  estimate that is > 100 % for the lowest  $\text{O}_3$  mixing ratios where many of the points with

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high  $X(\text{ClO})/X(\text{Cl}_y)$  ratios fall. Thus the error bars would be rather different for the various points, and in the low  $\text{O}_3$  regime most of them would go up to 1.0 due to the  $\text{Cl}_y$  uncertainty. But we will include a comment on the uncertainties in the Figure caption.

A pictorial representation of the  $\text{NO}_x$  cycle (point 21) is shown in Figure 2 below this response but we decided against including it in the paper as is not its main focus. The key aspect for this study – namely the reaction of  $\text{NO}_2$  and  $\text{ClO}$  and its impacts on both the  $\text{NO}_x$  and the  $\text{Cl}$  cycles – can be described in the text.

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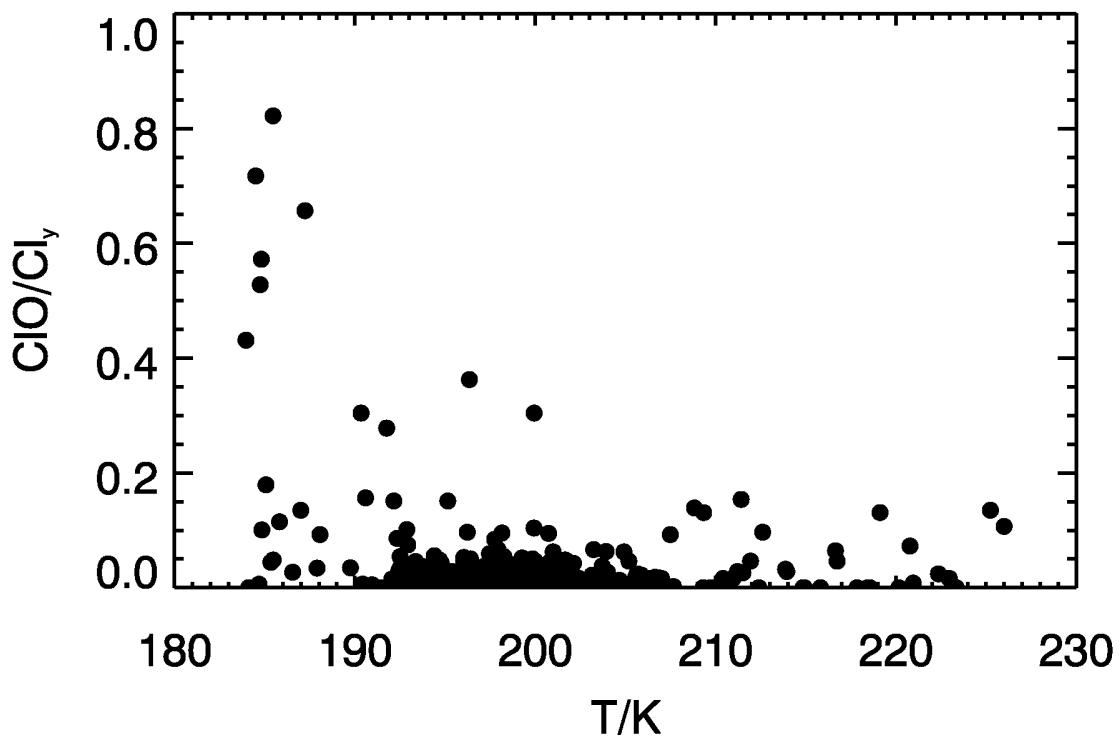
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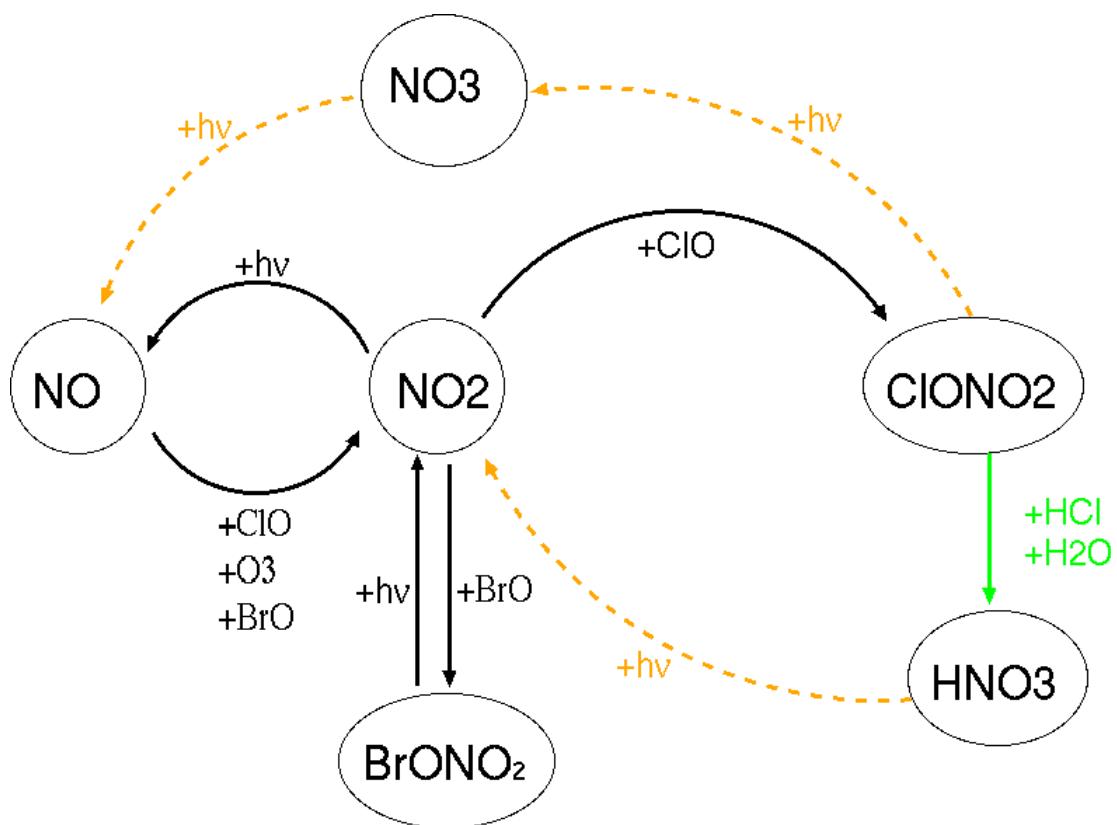


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**Fig. 1.**  $\text{ClO}/\text{Cly}$  vs. Temperature



**Fig. 2.** The chemical reaction system governing NOx