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Interactive comment on “Understanding the kinetics of the ClO dimer cycle” *by* M. von Hobe et al.

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Even though our paper has been rejected and the open discussion is closed, we choose to respond to the additional review given in the Editor comment by John Crowley. We want to clarify some points made in our ACPD paper that have obviously been misunderstood, and to argue against some statements in the review that we feel are not correct.

Before we address the points raised by the reviewer one by one, we would like to comment on one issue that we regard as central to this discussion: the use of atmospheric observations to infer or constrain kinetic and thermodynamic properties, or as the reviewer puts it: "the atmosphere is not a laboratory for the measurement of rate coefficients because too many factors cannot be controlled". Certainly one should not

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(and we *do* not) confuse atmospheric observations and process studies with controlled laboratory experiments. Field studies can neither replace nor compete with the important work carried out in the laboratories. However, we strongly believe that the use of atmospheric observations can *complement* laboratory measurements, particularly if these display significant disagreement suggesting that the controlled conditions in the laboratory experiments may not have been fully understood. We would argue that, with the formalism for approaching the problem of ClO dimer kinetics described in our paper, we have advanced the science further than yet another laboratory study would have done. Although we probably all agree that ultimately the discrepancies will indeed need to be resolved in the laboratory.

The reviewer correctly states at the beginning of his review that the "goal of this paper is to *compare* field measurements…". It was not by any means our goal or intention to make new *recommendations*, and we believe that nowhere in the paper we give the impression that we intend to do so. Certainly, we would have been happy had we found out that the JPL or IUPAC recommendations for the combination of K_{eq}, k_{rec} and J had fitted the atmospheric observations of ClO and Cl_2O_2. We could have closed the chapter and state that we understand the kinetics of the ClO dimer cycle. Unfortunately, our results indicated that we have not yet reached this understanding. As discrepancies of laboratory studies with each other and with theoretical calculations (as noted previously by Golden, 2003) clearly point to a lack of understanding, we chose to take an unbiased look at *all* the available information to identify these discrepancies and the questions that need to be answered.

With respect to our discussion on k_{rec} in Section 4, the review states that our paper "rejects the Bloss et al. …on the grounds that the values from the latter two studies are inconsistent with theory". Although we do point out this inconsistency ("A value for $k_{\mathrm{rec},0}$ higher than the derived $k^{sc}_{\mathrm{rec},0}$ (i.e. $\beta_c = 1.0$) is difficult to rationalize: …"), we do not "reject" any laboratory measurement! The reason for using the chosen value (Nickolaisen et al., 1994) in Section 5 was that, in our opinion, it presented the least discrepancies for the suite of parameters discussed in Section 2, 3 and 4. A similar comparison of field observations with many different laboratory kinetic parameters (including Bloss et al. k_{rec}) has been published before by Stimpfle et al. (2004). We have in fact carried out our steady state calculations and box model runs for Bloss et al. (2001), coming to the same conclusion that Stimpfle et al. reached: Bloss et al. (2001) is consistent only with J(Burkholder)! Furthermore, unless all Cl_2O_2 and many ClO observations are erroneous beyond the given error margins, Bloss et al. (2001) is *not* consistent with J(Huder and DeMore) now recommended by IUPAC and likely to be confirmed by Pope et al.. We are aware that the Bloss et al. (2001) study in a way supersedes the Nickolaisen et al. (1994) study made earlier by the same laboratory. Bloss et al. do point out potential problems with the earlier low temperature results, but do not present a convincing case why the older results need to be discarded altogether. As the reviewer points out, Bloss et al. (2001) state that the discrepancy with Nickolaisen et al. (1994) at low temperatures arises from the ClO cross section used: “This extrapolation [i.e. by Nickolaisen et al., 1994] probably underestimated the true value of σ_{ClO} at temperatures below 220 K.” If we understood the descriptions of σ_{ClO} in the two papers correctly, the earlier study uses absolute cross sections at 275.2 nm while Bloss et al. look at differential cross sections (peak at 275.2 nm, trough at 276.4 nm). We assume that this is the reason, why the cross sections calculated by the two formulae for temperature dependence of σ_{ClO} (both given in the Bloss et al. paper) are in fact always lower in Bloss et al. compared to Nickolaisen et al. for $T > 155$ K. The steeper increase of σ_{ClO} towards lower temperatures observed by Bloss et al. would then be explained by the significant increase of peak-to-valley ratios with decreasing temperature observed by Sander and Friedl. (J. Phys. Chem. 93, 4764, 1989), the study on which the cross sections used in Nickolaisen et al. are based. While the use of differential cross sections has certainly advantages, it does not in our opinion provide conclusive evidence that the Bloss et al. results are correct and the Nickolaisen et al. ones are not, especially considering the significant scatter in the various σ_{ClO} determinations from different chemical systems described in the Bloss et al. paper.

Concerning our application of rate theory using Troe calculations for $k_{\mathrm{diss},0}$ and $k_{\mathrm{rec},0}$ there still seems to be a severe misunderstanding. We are not deriving a "recommendation" from the Troe equation. We are using it in the same way the NASA data evaluation panel does: to "raise a flag" for some values measured in the laboratory. Bloss et al. raise this flag themselves, using essentially the same calculations as in our paper, but rationalising their measured results with $\beta_c = 1$. In the case of $k_{\mathrm{diss},0}$ measured by Bröske and Zabel (2006) we also raise a "green" flag: within uncertainties their results agree well with the Troe calculations. Unfortunately they span only a very limited temperature range, so we further use the Troe expression to extrapolate these results to lower temperatures. By the end of Section 4, we have found one consistent combination of $measured$ values for K_{eq}, k_{rec} and k_{diss} in good agreement with rate theory calculations. We choose to use only this combination in Section 5 of the paper in order to test whether consistency with field observations can also be shown in combination with a realistic (i.e. within the measured range) choice of J.

There also seems to be some misunderstanding as to how the values and uncertainties given in Table 2 were derived. While the $\Delta_{\mathrm{r}}H^{\circ}$ and corresponding $\Delta_{\mathrm{f}}H^{\circ}$ values as well as the uncertainty given for Plenge et al. are taken from their paper, the numbers given for the laboratory studies have been newly derived using third law analysis based on entropies and thermal corrections with Cl_2O_2 vibrational frequencies given in Table 1. The exact derivation is described in our paper, with the important point to note that we fix $\Delta_{\mathrm{r}}S^{\circ}$ and d($\Delta_{\mathrm{f}}H^{\circ}$)/d$T$ within uncertainties resulting from Table 1 (because here one could argue that the uncertainties are optimistic, we describe in the footnotes to Table 1 how they are constrained), so the only unknown variable in Eq. 3 is $\Delta_{\mathrm{r}}H^{\circ}$ (0 K). We now try to obtain this parameter by logarithmic fit to laboratory values for K_{eq}, namely Cox and Hayman (1988) and Nickolaisen et al. (1994). Only one parameter is fitted, so the uncertainty (accounting for uncertainties in both the unmeasured parameters and the error bars of the laboratory measurements) does become rather small (i.e. 0.2 kJ/mol). Also, because we have only one unknown variable in Eq. 3, it is possible to calculate $\Delta_{\mathrm{r}}H^{\circ}$ (0 K) directly from an observation of K_{eq} at a single temperature. We agree with the reviewer that $\Delta_r H^\circ$ (0 K) should certainly not be derived from a single and possibly outdated K_{eq} observation. We only chose to reference the works by Basco and Hunt (1979) and Ellerman et al. (1995) and perform this calculation for their K_{eq} values for completeness and to show that, irrespective of the potential problems named by the reviewer, these studies agree well with Cox and Hayman (1988). The differences between the values for $\Delta_r H^\circ$ derived from various studies may be small, but the resulting differences in K_{eq} at stratospheric temperatures are sizable, and the potential impact on the prediction of night time ClO_x partitioning can be severe (von Hobe et al., 2005). K_{eq} values inferred from field measurements are only used as one of many arguments in support of Cox and Hayman (1988) and Plenge et al. (2005) over Nickolaisen et al. (1994).

We do not take K_{eq} values inferred from field measurements any further than Section 2 in our paper. The reviewer states "the atmosphere is not a laboratory for the measurement of rate coefficients because too many factors cannot be controlled". We strongly disagree with the notion that we are using the atmosphere in this manner: we seek to define consistency, or lack thereof, between various laboratory measurements (which in some cases disagree by large amounts!) and field observations. This has been a central component of advancing our knowledge of atmospheric chemistry since the advent of modern instrumentation. We could cite many cases where such comparisons have led to the recognition of a need to reduce uncertainties in key laboratory parameters, such as the absorption cross section for ClOOCl! The fact that field observations in darkness support Plenge et al. (2005) and Cox and Hayman (1988), and that these values for K_{eq} are used in Section 5 in the context of modeling daylight field observations with different J values is in our opinion an important scientific finding and far from a circular argument, as implied by the reviewer, because: 1. the choice of K_{eq} is by no means based solely on field observations, and 2. for most zenith angles the results presented in Section 5 are insensitive to the choice of K_{eq}.

The statement in the review that our paper assumes that there are no uncertainties associated with the field measurements of Cl_2O_2 and ClO is simply not true. Rather large error bars based almost entirely on the measurement uncertainties (as described in Section 5.1) are drawn in Figs. 7 and 9, and the reader is referred to the papers by Stimpfle et al. (2004) and von Hobe et al. (2005) for a detailed discussion of the uncertainties and the laboratory calibration of the Cl_2O_2 measurements (von Hobe et al., 2005).

The MPIC spectrum of Cl_2O_2 cross sections had been created before our paper was written, and at one point had been considered to be presented to the scientific community by the NASA Data Evaluation panel as a recommendation. Indeed, members of the NASA Data Panel encouraged use of this cross section during the preparation of early drafts of the WMO/UNEP 2006 Ozone Assessment Report. In our paper – and we cannot stress this point often enough – we do not intend to present these cross sections as a “recommendation”. We chose to include the MPIC cross sections to better illustrate that most field observations are best reproduced with J between JPL and Burkholder et al. (1990). Seeing the strong opposition to the MPIC cross sections by some reviewers, maybe it would have been wiser not to include MPIC and simply state that in our studies JPL is on the low side and Burkholder slightly high. Nevertheless, we doubt readers would quote and use these cross sections for “decades to come”: i.e., we all know of the impending Pope et al. study, which has been presented publically on several occasions. The vast majority of modellers (e.g., those who provide calculations to the ozone assessments) use the kinetics from the JPL or IUPAC evaluations, and certainly would continue to do so regardless of what would have been stated in our paper, had it been published in ACP. In the context of Cl_2O_2 cross sections, an interesting reference has been added for the first time in JPL 2006: Toniolo et al. (J.Phys.Chem.A, 104, 7278, 2000) have calculated a theoretical photoabsorption spectrum of ClOOCl. While one should be careful using quantitative information from such ab initio calculations, it is nevertheless interesting to note that these authors predict a two electronic excited states producing small absorption bands centered at about 340 nm. The existence of these bands may explain the structure observed by Burkholder et al. (1990)

and DeMore and Tschuikow-Roux (1990) in the wavelength region between 310 and 400 nm and implies that one needs to be careful to simply extrapolate the spectrum in this region from shorter wavelengths as done by Huder and DeMore (1995).

In conclusion, based on the statements in our paper and our replies to this and the earlier reviews, we can not see "the main problems" identified in the concluding paragraph of this review:

1. "The discussion of $k_{\rm rec}$ largely repeats the analysis in Golden (2003) and the NASA/JPL data evaluations."

Our paper repeats to some extent earlier analyses – probably even more for Bloss et al. (2001) than Golden (2003) – but it also extends considerably beyond the past literature. Unlike the previous discussions, we suggest that the uncertainty in the temperature dependence of $k_{\rm rec,0}$ should be lower than the uncertainty in $k_{\rm rec,0}$ itself derived from Troe calculations. Also, for the first time we discuss $k_{\rm rec}$ in the context of independent measurements of $k_{\rm diss}$ (Bröske and Zabel, 2006).

2. "There are key points in several laboratory papers that are missed in the discussion, causing incorrect conclusions to be drawn about the results."

Our discussions were not intended to be an exhaustive review of the literature. However, we strongly object to the notion that we have missed key points and drawn incorrect conclusions. No doubt, sources of error associated with many laboratory studies and the older ones in particular have been identified and pointed out in the literature. However, to our knowledge none of the results cited in our paper has been falsified beyond doubt by later studies. The value of our study is that, for the first time, we have sought to document consistency, or lack thereof, between a myriad of studies using different experimental techniques to study the ClO and ClO dimer system. Some of the past studies pointed out by the reviewer as being "suspect" happen to have results that agree closely with later, apparently more "reputable studies" (according to the reviewer). Our paper shows that $k_{\rm rec,0}$ from Nickolaisen et al. (1994) agrees better with theory and other experiments than the more recent results from Bloss et al. (2001) and Boakes et al. (2005). We believe this finding is based on sound intellectual synthesis of available information that goes considerably beyond what is available in the present literature. We have attempted to extend the present state of knowledge by pointing out discrepancies and inconsistencies within the entire ClO/Cl_2O_2 kinetic system arising from certain combinations of rate constant and thermodynamic data, and indicate a combination of parameters that seems to provide best overall agreement. We are deeply disappointed that the reviewer does not find value in this analysis.

3. “The paper lacks a clear analysis of the propagation of uncertainties from the laboratory parameters and their impact on model calculations of ClOOCl and ClO in the atmosphere. There is also no discussion of uncertainties in the atmospheric measurements of ClOOCl and ClO, and how these compare with uncertainties propagated through the model calculations to answer the question of whether there are indeed missing steps in the assumed mechanism of polar stratospheric ozone depletion. The paper has a strong bias in its recommendations toward those lab measurements which result in agreement with the field measurements, which is not the way the problem should be analyzed.”

This criticism seems unwarranted. First, uncertainties in the atmospheric measurements have been considered in Section 5. As stated above, a detailed discussion of all instrumental errors of the ClO and Cl_2O_2 is beyond the scope our paper but this information is readily available in referenced papers. The primary goal of our paper is to examine self consistency (or lack thereof) among a host of laboratory observations, followed by an analysis designed to discern which laboratory measurements are in best agreement with field observations. We examined uncertainties in a clear manner throughout the analysis. However, as noted by the reviewer, we did not examine the propagation of these uncertainties to the “question of whether there are indeed missing steps in the assumed mechanism of polar stratospheric ozone depletion”. We do not understand why this issue was noted in the concluding paragraph of the review; while clearly important, it is simply not the subject matter of the paper! It seems like proper theoretical, laboratory, and field measurement understanding (or lack thereof!) is a prerequisite for addressing whether there are missing steps in the assumed mechanism of polar stratospheric ozone depletion. We are surprised that the reviewer would apparently not appreciate this sequencing and would not find value in our attempts to define the level of quantitative understanding of the ClO dimer cycle based on the current state of knowledge.

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