

# ***Interactive comment on “UV spectroscopic determination of the chlorine monoxide (ClO) / chlorine peroxide (ClOOC1) thermal equilibrium constant” by J. Eric Klobas and David M. Wilmouth***

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We would like to thank the referee for his detailed and constructive comments and have revised the manuscript accordingly. The reviewer's comments are presented below in **bold** text and our responses to the reviewer appear in plain text.

## **1. Add more experimental information**

**I have little doubt that the authors have carefully checked the conditions of each experiment to ensure that thermal equilibrium between ClO and ClOOC1 is ac-**

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tually established once the gas mixture passes into the absorption cell. Nevertheless, for the sake of transparency, it would be good to provide some actual numbers for flow rates and residence times in the different parts of the apparatus. Ideally, a complete set of experimental conditions (initial concentrations, pressure,  $T_{\text{ReactionCell}}$ ,  $T_{\text{ColdTrap}}$ ,  $T_{\text{EquilibriumCell}}$ ) and selected results (maybe even some raw spectra) could be provided as an electronic supplement that goes beyond the summary given in Table 1.

Table 1 has now been revised to include all of the experimental runs and not simply the binned data, and details on carrier gas flows and residence time have been added in section 2. We note that a critical element of the experimental design and operation was ensuring that ClO and ClOOCl were in equilibrium in the absorption cell when the measurements were made. As discussed in the manuscript, the kinetic model defined the experimental conditions (e.g., temperatures, pressures, concentrations) in which equilibrium would be achieved in the laboratory setup, and we operated experimentally across a range of conditions about the optimal starting conditions predicted by the model. In particular, we note that the same  $K_{eq}$  values were obtained when increasing or decreasing residence times in the equilibrium and absorption cells, providing confidence that ClO and ClOOCl were indeed in equilibrium.

## 2. Uncertainty assessment

I am not convinced that all potential sources of uncertainty are represented in the significantly reduced overall uncertainty presented in Figure 6. In particular, I'm thinking about the 17 % uncertainty in the ClOOCl reference cross sections that you mention on page 8, line 14. When I translate the uncertainty in the  $B$  parameter that accounts for this (given on page 8, line 17), I arrive at approximately  $\pm 40$  % uncertainty in  $K_{eq}$ , which is considerably larger than the uncertainty range given in Figure 6. There, it looks as if the blue uncertainty ranges only represent the statistical uncertainties in your experiment (i.e. the scatter between the individual white circles in that figure represented in the  $\pm 25$  uncertainty in  $B$

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given in Equation 3), and the statement about the trend to not explicitly include uncertainties from reference cross sections on page 6, line 21, seems to support that interpretation. In the work by Hume et al. (2015), there is a clear statement that the systematic uncertainties in cross sections to convert  $K_{abs}$  to  $K_{eq}$  are much more important than their experimental standard deviations, and their error propagation calculations arrive at an upper uncertainty limit from this is 36 % on the experimental  $K_{eq}$ , which appears to be a very realistic number. Note that the 17 % uncertainty in the ClOOCl cross section alone translates directly into a 17 % uncertainty in the ClOOCl concentration fitted to a particular spectrum, and in turn into a systematic 17 % uncertainty in  $K_{eq}$  via your Equation 1. The two studies by Papanastasiou et al. (2009, currently the JPL recommended value and used in both, your study and Hume et al.) and Lien et al. (2009; 17 % higher) used different methods to measure absolute cross sections: Papanastasiou et al. infer the absolute value from the reaction stoichiometry and the experimental absorbance at isosbestic wavelength, while Lien et al. use a known quantity of light to attenuate a molecular beam of ClOOCl. To date, no convincing evidence has been presented that proves either one of the results right or wrong. Therefore, the 17 % is not a statistical one or two sigma uncertainty, but a highly systematic one. As long as this is not resolved, it is therefore impossible to reduce the uncertainty in  $K_{eq}$  below this value with any method relying on the ClOOCl cross sections. And because it is systematic, it really has to be added to the blue ranges representing the statistical uncertainties in your Figure 6, because if the peak ClOOCl absorption cross section was 17 % higher than the value you actually used in your calculations, all your points and the ones from Hume et al. would simultaneously down by 17 %. Of course, if the uncertainties in the ClOOCl cross sections were reduced in future studies, this would immediately also reduce the uncertainty in  $K_{eq}$ , which I think would be a fair and valuable statement to make.

It is true that the ClOOCl cross section directly impacts  $K_{eq}$ , but to be clear, Hume

et al. actually did not incorporate the ClOOCl cross section uncertainty into their reported  $K_{eq}$ . Hume et al. used the larger uncertainty in the  $B$  parameter derived when considering the ClOOCl cross section uncertainty only when they assigned uncertainties to their enthalpy calculations. For consistency, we followed the same approach in our manuscript. Otherwise, we would be defining the uncertainty in  $K_{eq}$  in a manner that is inconsistent not only with the recent Hume paper but all other published laboratory ClOOCl  $K_{eq}$  papers that covered a range of temperatures, none of which include the uncertainty from the reference cross sections. We state on page 6 line 19 of the revised manuscript (page 6 line 21 of the original manuscript) that we are taking this approach, and on page 8 line 23 of the revised manuscript (page 8 line 17 of the original manuscript), we provide the larger uncertainty range in the  $B$  parameter found when including the ClOOCl cross section uncertainty. We have also now added additional detail to Table 1 such that if the ClOOCl or ClO cross sections are revised in the future, our  $K_{eq}$  values can be recalculated.

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