Atmos. Chem. Phys. Discuss.,
https://doi.org/10.5194/acp-2018-1120-RC2, 2018

Atmospheric Chemistry and Physics Discussions

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

von Hobe (Referee)

m.von.hobe@fz-juelich.de

Received and published: 29 November 2018

The paper describes a well-designed laboratory study to measure the ClO/ClOOCl thermal equilibrium constant over a broad temperature range and includes a comprehensive analysis and comparison to earlier work. Based on the advanced methodology, broader temperature range and thorough thermodynamic analysis compared to earlier studies, I support publication in ACP.

Before submitting a final version for publication, I strongly recommend that the authors

to add some more information on their experiments and to drop the last sentence of the abstract because I don't think that the significant reduction of uncertainties is warranted. My reasoning for these suggestions is given below.

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 ClOOCl is actually 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, $T_{ReactionCell}, T_{ColdTrap}, T_{EquilibriumCell}$) and selected results (maybe even some raw spectra) could be provided as an electronic supplement that goes beyond the summary given in Table 1.

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 +/- 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 +/- 25 uncertainty in B 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.

Interactive comment on Atmos. Chem. Phys. Discuss., https://doi.org/10.5194/acp-2018-1120, 2018.