

# ***Interactive comment on “UV spectroscopic determination of the chlorine monoxide (ClO) / chlorine peroxide (ClOOCI) 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. A quibble with the third-law analysis carried out in this paper is that it assumes that  $K_{eq}$  is a pure exponential function,  $K_{eq} = Aexp^{(B/T)}$ , while theoretical calculations predict that  $K_{eq}$  deviates slightly from a pure exponential. The**

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approach taken in this paper differs from the third-law analysis carried out by the NASA/JPL Panel for Data Evaluation. The Panel evaluates every individual data point to determine the reaction enthalpy change at 0 K,  $\Delta H_r(0)$ , extracted from the measured  $K_{eq}(T)$  at each temperature and then determines the average.  $\Delta H_r(298)$  is then computed from the calculated reaction entropies and average  $\Delta H_r(0)$ . From  $\Delta H_r(298)$ , one can then obtain the standard enthalpy of formation,  $\Delta H_f(298)$ , for ClOOCI. Although more laborious, the approach followed by the panel does not assume a pure exponential function and is thought to be more accurate. From the Panel's approach, the combined data set consisting of the new data from the present paper and the older data from Hume et al. (2015) gives  $\Delta H_r(298) = 130.1$  kJ/mol, which is 0.2 kJ/mol higher than the result reported in the manuscript, based on the pure exponential function.

We appreciate the approach described by the reviewer and the accuracy of this method for use in the NASA/JPL Data Panel Evaluation. However, to maintain consistency between our results and the method employed in prior papers (e.g., Hume et al. 2015), we have chosen to use the enthalpy values at 298 K for the calculations. Note that we now determine  $B$  from our unbinned data, and the calculated  $\Delta H_f(298$  K) for ClOOCI is 130.0 kJ/mol, now in even better agreement with the JPL-15 recommendation of 130.1 kJ/mol.

To facilitate alternate derivations of reaction enthalpies, all independent measurements are now reported in Table 1.

**2. In the abstract, it would be useful to state that the experimental errors are  $\pm 1\sigma$ .**

The abstract now reads: A third law fit of the equilibrium values determined from the experimental data provides the expression:

$$K_{eq} = 2.16 \times 10^{-27} e^{(8528 \pm 25K/T)} \text{cm}^3 \text{molecule}^{-1} (1\sigma \text{ uncertainty}).$$

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**3. In addition to the binned values for  $K_{eq}(T)$ , which are reported in Table 1, all of the individual  $K_{eq}$  measurements should be reported in Supporting Information.**

All independent measurements are now reported in Table 1.

**4. In Figures 4 and 6, the error bounds are functions of temperature. It would be useful to report the functional forms and parameters for the error bounds in Supporting Information.**

The error bounds of Figure 4 in the original manuscript (now Figure 5) are of the form:  $Ae^{(B \pm \epsilon/T)}$  from equation 2, where  $\epsilon$  is the appropriate uncertainty interval. We now explicitly mention the  $\epsilon$  value on page 7 line 9 of the revised manuscript.

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