

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

Anonymous Referee #4

Received and published: 5 December 2018

This manuscript reports spectroscopic measurements of the concentrations of [ClO] and [ClOOCl] under conditions that should be very close to equilibrium, allowing the equilibrium constant to be determined as a function of temperature. There are several items, mentioned below, that should be addressed before this manuscript is accepted for publication.

The microwave discharge that generates atomic chlorine will also be a strong source of VUV radiation due to the strong Cl resonance lines. Since the ozone is introduced only 2.5 cm downstream, one would expect significant photolysis of the ozone, generating

C1

O(1D), O(3P), O₂(a¹Δ), etc. Also the discharge that generates ozone will also form copious amounts of the singlet states of O₂. Does the chemical modeling of this system show that none of these reactive species are causing trouble downstream? Typical gas flow rates or the velocities of the flows at the different pressures should be given.

Page 4, line 5: What is the resolution (FWHM) for this slit width?

Page 4, line 10: What are “dark spectra” and how are they used in subsequent spectra?

The two runs shown in Fig. 2 can be used to calculate two equilibrium constants: for 230K, $K = 1.84E(-11)$ which is 34% lower than Equation 3 predicts; for 300K, $K = 6.52E(-15)$ which is 34% higher than Eq.3. Are these typical deviations?

The treatment of the experimental data by “binning” is not the best use of the experimental data. If I understand this manuscript correctly, all values of K measured within a 5 K range of temperatures are averaged (average of K , or $\ln(K)$?) and then listed in Table 1 along with the averaged temperature (average T or $1/T$?). For example, if measurements were done at 250 and 255 K, one should get, according to Equation 3, $K(250) = 1.438E(-12)$ and $K(255) = 7.364E(-13)$. The average of $\ln(K)$ of these two K 's gives -27.602 or $K(\text{ave}) = 1.029E(-12)$, which is close to the value predicted by Eq. 3 for $T = 252.5$ K. But then using the deviations of these two values of K from the average K to get an estimate of the standard deviation of the measurements is not valid. There is no information about the random measurement errors in these two numbers. They are different because they were measured at two different temperatures. Supposed one has only two measurements in one bin that were at different temperatures but, due to random errors, gave almost the same value for K . The calculated “standard deviation” would now be very small and the weighting factor very large. That is not right. The numbers in the last column in Table 1 should be eliminated.

It would be better to do the least squares fitting using all 114 experimental measurements with equal weighting. Then the deviations of the experimental K values from the least squares fit would give information about the precision of the measurements. A

C2

plot of these 114 deviations vs. $1/T$ would be useful. As mentioned, this will probably show increasing deviations at both the upper and lower limits of temperature. Certainly the experimental values of the 114 measurements should be preserved, either in a table in the manuscript or as supplemental material.

With attention to the above comments, this manuscript should be accepted for publication.

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