



Inconsistencies in our Understanding of the ClO Dimer Cycle and Implications for polar Ozone Loss

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According to our current understanding, catalytic ozone destruction in the winter/spring polar vortices is mainly caused by the ClO/Cl₂O₂ and the ClO/BrO cycles. The rate of the ClO/Cl₂O₂ cycle is limited by Cl₂O₂ formation with the second order rate constant k_f , and by the Cl₂O₂ photolysis rate J . Overall ozone loss is more sensitive to J than to k_f , because more ClO formed at higher J also leads to a faster ClO/BrO cycle, while a faster ClO/Cl₂O₂ cycle induced by increasing k_{rec} is partly offset by the effect of reduced [ClO] on the ClO/BrO cycle. Discrepancies up to a factor of 2 exist between laboratory measurements of k_{rec} and J , and experiments determining the Cl₂O₂ dissociation rate constant k_{diss} and the equilibrium constant $K_{eq} = k_f/k_{diss}$ are also not in agreement. Some of these results are neither consistent with theoretical calculations nor can they be reconciled with atmospheric observations. Models using the combinations of K_{eq} , k_f , and J recommended by JPL 2006 (Sander et al., 2006) and IUPAC (Atkinson et al., 2006) fail to reproduce measurements of [ClO] and [Cl₂O₂] (e.g Stimpfle et al., 2004) and underestimate observed ozone loss (Frieler et al., 2006).

In an extensive study comparing different combinations of K_{eq} , k_f , and J with theoretical calculations and using models to check consistency with data from several Arctic field campaigns, we demonstrate that a combination of parameters from older laboratory studies is in much better agreement with theory and observations than newer studies that seem to have replaced the older results. If JPL 2006 and IUPAC recommendations for these constants are correct, then

1. our mechanistic understanding of the ClO self reaction to form Cl₂O₂ is incomplete;
2. additional (unknown) processes must exist that influence ClO_x partitioning and ozone destruction in the polar vortex.

Obviously, this will have severe implications for our ability to simulate and predict polar ozone loss. With future climate change leading to colder temperatures in the stratosphere (where the ClO dimer cycle proceeds fastest and discrepancies are greatest for k_f and K_{eq}) it is imperative to resolve these issues.

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Sander, S. P., et al.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation Number 15, JPL Publication 06-2, Jet Propulsion Laboratory, Pasadena, 2006.

Stimpfle, R. M., Wilmouth, D. M., Salawitch, R. J., and Anderson, J. G.: First measurements of ClOOCl in the stratosphere: The coupling of ClOOCl and ClO in the Arctic polar vortex, J. Geophys. Res. 109, doi: 10.1029/2003JD003811, 2004.