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Understanding the kinetics of the ClO dimer cycle

M. von Hobe[1], R. J. Salawitch[2], T. Canty[2], H. Keller-Rudek[3],
G. K. Moortgat[3], J.-U. Grooß[1], R. Müller[1], and F. Stroh[1]

[1]Forschungszentrum Jülich GmbH, Institute for Chemistry and Dynamics of the Geosphere (ICG-1), Jülich, Germany

[2]Jet Propulsion Laboratory, California Institute of Technology, Pasadena, California, USA

[3]Max-Planck-Institute for Chemistry, Atmospheric Chemistry Division, Mainz, Germany

Abstract. Among the major factors controlling ozone loss in the polar vortices in winter/spring is the kinetics of the ClO dimer catalytic cycle. Here, we propose a strategy to test and improve our understanding of these kinetics by comparing and combining information on the thermal equilibrium between ClO and Cl_2O_2, the rate of Cl_2O_2 formation, and the Cl_2O_2 photolysis rate from laboratory experiments, theoretical studies and field observations. Concordant with a number of earlier studies, we find considerable inconsistencies of some recent laboratory results with rate theory calculations and stratospheric observations of ClO and Cl_2O_2. The set of parameters for which we find the best overall consistency – namely the ClO/Cl_2O_2 equilibrium constant suggested by Plenge et al. (2005), the Cl_2O_2 recombination rate constant reported by Nickolaisen et al. (1994) and Cl_2O_2 photolysis rates based on absorption cross sections in the range between the JPL 2006 assessment and the laboratory study by Burkholder et al. (1990) – is not congruent with the latest recommendations given by the JPL and IUPAC panels and does not represent the laboratory studies currently regarded as the most reliable experimental values. We show that the incorporation of new Pope et al. (2007) Cl_2O_2 absorption cross sections into several models, combined with best estimates for other key parameters (based on either JPL and IUPAC evaluations or on our study), results in severe model underestimates of observed ClO and observed ozone loss rates. This finding suggests either the existence of an unknown process that drives the partitioning of ClO and Cl_2O_2, or else some unidentified problem with either the laboratory study or numerous measurements of atmospheric ClO. Our mechanistic understanding of the ClO/Cl_2O_2 system is grossly lacking, with severe implications for our ability to simulate both present and future polar ozone depletion.

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