Geophysical Research Abstracts, Vol. 8, 06977, 2006
SRef-ID:
© European Geosciences Union 2006

Constrains on the Photolysis Rate of ClOOCl

M. von Hobe (1), Jens-Uwe Grooß (1), Rolf Müller (1), Ross Salawitch (2), and Fred Stroh (1)

(1) Institut für Chemie und Dynamik der Geosphäre I: Stratosphäre (ICG-I), Forschungszentrum Jülich, Jülich, Germany, (2) Jet Propulsion Laboratory, California Institute of Technology, Pasadena, CA, USA (m.von.hobe@fz-juelich.de / Fax: +49 2461-614620 / Phone: +49 2461-614620)

One of the most important catalytic cycles destroying ozone in the polar vortices in late winter/early spring is the ClO dimer cycle:

ClO + ClO + M $\rightarrow$ ClOOCl + M k_f

ClOOCl + $h\nu$ $\rightarrow$ 2 Cl + O_2 ***J***

2 (Cl + O_3 $\rightarrow$ ClO + O_2)

Net: 2 O_3 $\rightarrow$ 3 O_2

The rate at which this cycle destroys ozone is determined by the rates of dimer formation k_f and photolysis$J$. The latter depends directly on the actinic flux and the absorption cross section σ_{ClOOCl}.

Of all parameters governing the ClO dimer cycle kinetics, σ_{ClOOCl} holds the largest uncertainty. It has been determined in a number of laboratory studies, which are complicated by spectral impurities particularly in the most interesting spectral region between 350 and 450 nm. The photolysis rates based on the most commonly used cross sections (Burkholder et al., 1990; Huder and De More, 1995) differ by a factor of about 2, with the current recommendation by JPL (Sander et al., 2003) falling about halfway in between. Simultaneous observations of ClO and ClOOCl made by (Stimpfle et al., 2004) were best reproduced by a model with the higher J values based on the (Burkholder et al., 1990) cross sections, while a new model study (Pope et al., 2005) supports the lower value given by (Huder and De More, 1995).

Here we constrain J using photochemical steady state calculations on simultaneous

observations of ClO and ClOOCl made during the EUPLEX campaign in the Arctic winter 2002/03 and during a single flight into the Arctic vortex in March 2005. The results are tested for consistency comparing model simulations to a number of ClO observations. Finally, implications of the results on ozone loss are discussed.

Burkholder, J. B., Orlando, J. J., and Howard, C. J.: Ultraviolet-Absorption Cross-Sections of Cl_2O_2 Between 210 and 410 Nm, J. Phys. Chem., 94 (2), 687-695, 1990.

Huder, K. J., and De More, W. B.: Absorption Cross-Sections of the Clo Dimer, J. Phys. Chem., 99 (12), 3905-3908, 1995.

Pope, F., Hansen, J., Bayes, K., Friedl, R., and Sander, S.: Re-determination of the UV Absorption Cross Sections of ClOOCl, Eos Trans. AGU, 86 (52), Fall Meet. Suppl., Abstract A13D-0970, 2005.

Sander, S. P., Friedl, R. R., Golden, M. M., Kurylo, M. J., Huie, R. E., Orkin, V. L., Moortgat, G. K., Ravishankara, A. R., Kolb, C. E., Molina, M. J., and Finlayson-Pitts, B. J.: Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, in Evaluation Number 14, Jet Propulsion Laboratory, Pasadena, 2003.

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.-Atmos., 109 (D3), 2004.