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Polar stratospheric chlorine kinetics from a self-match flight during SOLVE-II/EUPLEX

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[1] In-situ measurements of ClO made onboard the Geophysica aircraft on 30 January 2003 in the Arctic afford a novel approach to constrain the kinetic parameters governing polar stratospheric chlorine chemistry using atmospheric observations. The self-match flight pattern, i.e. sampling individual air masses twice at different zenith angles, was utilized by simulating the evolution of ClO mixing ratios between two 'matching' points using a photochemical model and optimizing the model parameters to fit the observations within a retrieval framework. Our results suggest a ClO/ClOOCl thermal equilibrium constant K_{eq} a factor of 5 smaller and a ratio J/k_f a factor of 2 larger than the values based on the JPL recommendations. This concurs with other studies based on observed ClO_x partitioning and corroborates that our understanding of stratospheric chlorine chemistry is incomplete, particularly in the light of the most recent laboratory experiments pointing to a J/k_f ratio almost an order of magnitude below the JPL recommendation.

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1. Introduction

[2] Ozone loss in the cold polar stratosphere is largely attributed to the chlorine catalytic cycle involving ClO dimer formation [*Molina and Molina*, 1987]:

$$\mathrm{ClO + ClO + M \underset{k_b}{\overset{k_f}{\rightleftharpoons}} ClOOCl + M} \tag{1}$$

$$\mathrm{ClOOCl} + h\nu \xrightarrow{J} \mathrm{Cl + ClOO} \tag{2}$$

$$\mathrm{ClOO + M \rightarrow Cl + O_2 + M} \tag{3}$$

$$\frac{2 \times [\mathrm{Cl + O_3 \rightarrow ClO + O_2}]}{\mathrm{2O_3 \rightarrow 3O_2}} \tag{4}$$

with the thermal equilibrium constant given by $K_{eq} = k_f/k_b$. K_{eq} is temperature dependent - at lower temperatures the equilibrium shifts towards ClOOCl. J is primarily controlled by the solar zenith angle (SZA).

[3] Measurements of ClO by in-situ and remote sensing methods have been used to test our understanding of the kinetics of this catalytic cycle. Table 1 summarizes these studies in terms of scale factors relative to current JPL06 laboratory based recommendations [*Sander et al.*, 2006]. To explain existing ClO measurements it is required that J/k_f (essential for determining ozone loss) be equal to or greater than JPL06 and K_{eq} be between 0.15–0.5 × JPL06.

[4] The recent laboratory measurements of K_{eq} and k_b by *Plenge et al.* [2005] and *Bröske and Zabel* [2006], respectively, are consistent with a smaller value of K_{eq}. On the other hand, the most recent laboratory studies of k_f by *Boakes et al.* [2005] and the ClOOCl photolysis cross-section measured by *Pope et al.* [2007] indicate a larger value of k_f and a smaller value of J compared to JPL06 and thus seem to contradict the larger J/k_f ratios implied by the atmospheric studies listed in Table 1. These discrepancies suggest that our quantitative understanding of the chemical mechanisms controlling chlorine partitioning in the polar stratosphere is incomplete, compromising our ability to quantitatively account for observed ozone depletion [*von Hobe et al.*, 2007].

[5] Here we present a novel approach to constrain these kinetic parameters made possible by the 'self-match' flight during SAGE III Ozone Loss and Validation Experiment (SOLVEII)/European Polar Stratospheric Cloud and Lee Wave Experiment (EUPLEX). The flight design, photochemical model, and retrieval algorithm used to obtain J/k_f and K_{eq} are described in section 2. In section 3 the results and uncertainties are discussed and compared to previous studies.

2. Data and Analysis

[6] The Geophysica aircraft flew on 30 January 2003 out of Kiruna, Sweden (11:44–14:37 UTC). This airplane flew isentropically, sampling airmasses twice in a self-match pattern (Figure 1). For each airmass ClO was measured at two distinct SZAs near sunset, for otherwise constant conditions. The photolysis of ClOOCl slows as the Sun sets, altering the partitioning between ClO and ClOOCl. No

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Table 1. Scale Factors Relative to JPL06 for Previous Observation/Model Comparisons, Under the Conditions of the Match Flight[a]

Reference	Range	Study Temperature	Platform (Mission) Latitude
Brune et al. [1990]	$0.25K_{eq}$	200 K	NASA ER-2 (AASE I) 68°N
Pierson et al. [1999]	$<0.3K_{eq}$	200 K	Balloon (SESAME/AASE I) 68°N
Avallone and Toohey [2001]	$<0.47-0.49K_{eq}$	188–209 K	NASA ER-2 (AASE I and II) 68°N
Stimpfle et al. [2004]	$\sim 0.5K_{eq}$	189–202 K	NASA ER-2 (SOLVE/THESEO-2000) 68°N
von Hobe et al. [2005]	$0.04-0.48K_{eq}$	192–216 K	M55-Geophysica (EUPLEX) 68°N
Berthet et al. [2005]	$0.15-0.5K_{eq}$	200–220 K	Satellite (ODIN) < 80°N
This work	$0.2^{+0.4}_{-0.1}K_{eq}$	200–207 K	M55-Geophysica (EUPLEX) 68°N
Shindell and de Zafra [1996]	$0.9-1.8J/k_f$	190 K	Ground-based Microwave 78°S (1993)
Solomon et al. [2002]	$1.0-1.7J/k_f$	-	Ground-based Microwave 77°S
Vogel et al. [2003]	$\sim 1.08J/k_f$	190–210 K	Balloon (SOLVE/THESEO-2000) 68°N
Stimpfle et al. [2004]	$\sim 1.4-1.8J/k_f$	189–202 K	NASA ER-2 (SOLVE/THEOSEO-2000) 68°N
von Hobe et al. [2007]	$\sim 1.2-1.7J/k_f$	198–208 K	M55-Geophysica (March 2005) 48–58°N
This work	$(1.9-3.9J/k_f)^{+1.8}_{-0.9}$	200–207 K	M55-Geophysica (EUPLEX) 68°N

[a] Conditions of the match flight are SZA = 83°–94°, T = 200–207 K, and θ = 430 K.

polar stratospheric clouds or large dynamical disturbances capable of significantly altering ClO_x (ClO + 2ClOOCl) occurred along the air mass trajectories.

2.1. ClO Observations

[7] The in-situ ClO measurements were made by the HALOX instrument [*von Hobe et al.*, 2005], based on the chemical conversion resonance fluorescence technique [*Brune et al.*, 1989]. Precision, resulting mainly from random noise, varied from 4 to 8%. The accuracy is estimated to be ~16%; 12.5% constant and up to 10% sloping (varying with time) error components.

2.2. Trajectory Calculation and Match Identification

[8] Trajectories were calculated (for details see *Wohltmann and Rex* [2007]) backwards for 48 hours and forward for 24 hours for each individual ClO measurement along the outgoing flight path. Trajectories were generated using a 4th order Runge-Kutta method applied to ECMWF operational data as input for wind and temperature with a 1 minute integration step. An isentropic vertical coordinate was used, assuming no diabatic motion. Wind and temperature were linearly interpolated to the position of the trajectory.

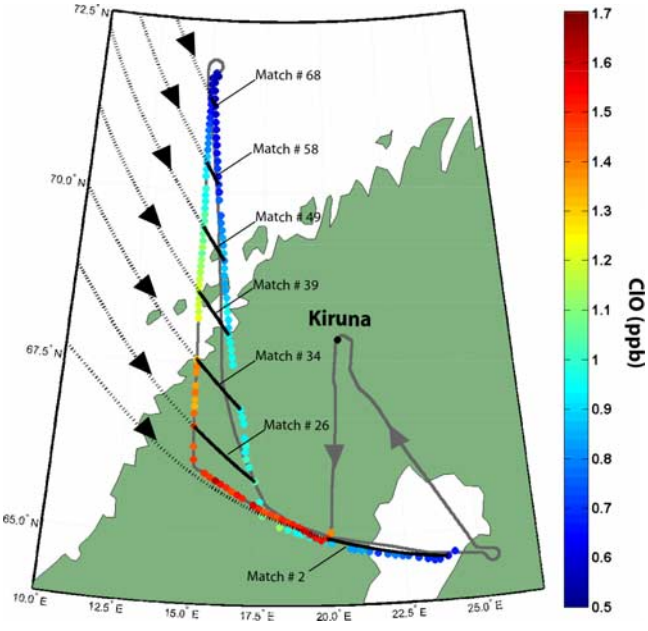

Figure 1. Map of the self-match flight path (grey curve). Colored points: all 72 match pairs ($\theta \sim 430$ K) (colorscale: ClO value). Dotted black lines: back trajectories for seven of the match pairs for this flight. Solid black lines: trajectories linking the outbound and inbound match points.

[9] A match point [*Rex et al.*, 1998] was found by minimizing the distance between the trajectory and inbound flight measurement points in time (1 minute intervals). This distance, the match radius, was never larger than 20 km (see Figure 2). The outbound leg was 85 minutes long, enabling 72 matches to be identified.

2.3. Photochemical Box Model

[10] The photochemical box model described in detail by *Salawitch et al.* [1993] formed the basis of the forward model function, simulating the diurnal variation of ClO, ClOOCl, OClO, BrO, BrCl and atomic O. The model was initialized for 24 hours with ClO_x assigned a priori and Br_y from the AER 2D model (only long-lived species). The chemical model was run along the trajectory for 48 hours (1 minute steps) until the first match point was reached (the outbound ClO value). The chemistry was calculated further along the trajectory until the second match point (the inbound ClO value) was reached.

2.4. Retrieval

[11] The state vector (**x**) describing what we wish to retrieve from the 72 ClO matches (**y**) was constructed with the kinetic parameters describing K_{eq} (log A and B as given by JPL06), and a multiplicative scale factor for J relative to the J value calculated with JPL06 ClOOCl cross-sections (J_{scale}). Additionally **x** contained the ClO_x value for each match pair. ClO_x was assumed to be constant for a given match, but allowed to vary between matches. The state space was explored by fixing k_f between 0.35 and 1.8 × k_f JPL06.

[12] The forward model function $\boldsymbol{F}$ finds ClO at the match points when supplied with the state vector kinetic parameters and ClO_x (section 2.3). The sensitivity of the modeled ClO to the state vector was explored by calculating weighting functions **K** numerically as the response in the forward model to perturbing the parameter of interest ($d\boldsymbol{F}/d\mathbf{x}$) (see auxiliary material).[1]

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[1] Auxiliary materials are available in the HTML. doi:10.1029/2007GL031740.

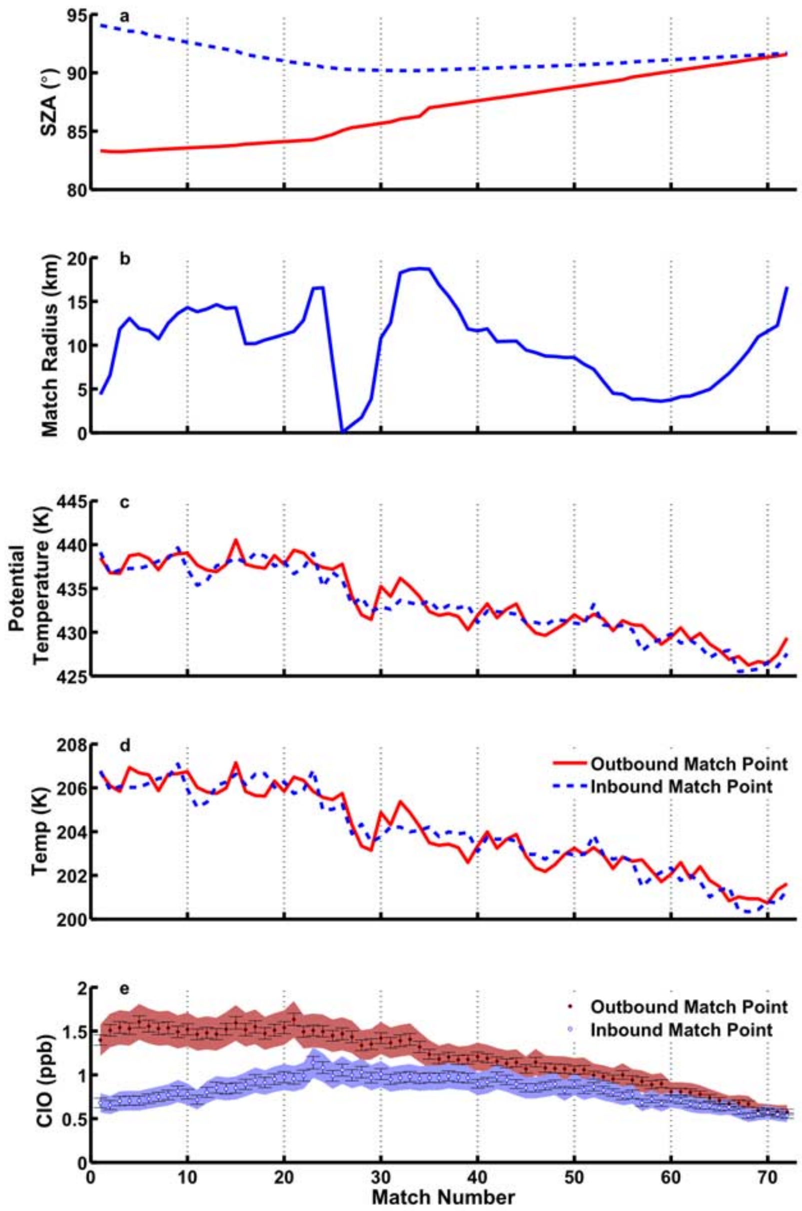

Figure 2. The (a) SZA, (b) match radius, (c) potential temperature, and (d) temperature for the outbound (solid red line) and inbound (dotted blue line) flight legs for each match pair. (e) The ClO observational data with error-bars indicating the precision error and the shaded region the total error (precision plus systematic).

[13] An iterative solution to Bayes Theorem minimized the root mean square difference between the model and the measured values of ClO [*Rodgers*, 2000]:

$$\hat{\mathbf{x}}_{i+1} = \mathbf{x}_a + \left(\mathbf{S}_a^{-1} + \mathbf{K}_i^T \mathbf{S}_\epsilon^{-1} \mathbf{K}_i\right)^{-1} \mathbf{K}_i^T S_\epsilon^{-1} \cdot \left[\mathbf{y} - F(\hat{\mathbf{x}}_i) + \mathbf{K}_i(\hat{\mathbf{x}}_i - \mathbf{x}_a)\right] \qquad (5)$$

This inversion weights the state vector solution according to the measurement precision covariance (S_ϵ) and the a priori state ($\mathbf{x}_a$) covariance ($\mathbf{S}_a$).

[14] Air masses were sampled over sunset, for which the ClO_x system was neither at thermal nor photolytic equilibrium. Therefore, interdependence is high between the parameters describing K_{eq}, J and ClO_x (and forward model parameter k_f). For example, without reaching a daytime equilibrium the same diurnal slope can be explained with more ClO_x but a slower photolysis. Similarly, k_f and J are related; a stronger rate of dimer formation can be balanced by faster photolysis. Thus a priori information was required to constrain the retrieval.

[15] A priori values for K_{eq} and J_{scale} were taken from JPL06. For ClO_x we retrieved for two a priori constraint cases. First; ClO_x = 2.0 ppb, obtained considering the dimer measurements of HALOX [*von Hobe et al.*, 2005] scaled by 1.4 as suggested by *von Hobe et al.* [2007] (see auxiliary material).

[16] For the second a priori case: ClO_x = 2.7 ppb approximating 'complete activation' of all available Cl_y (total chlorine). We estimate a mean value of $Cl_y \simeq 2.7$ ppb for the matches, based on the relation between Cl_y

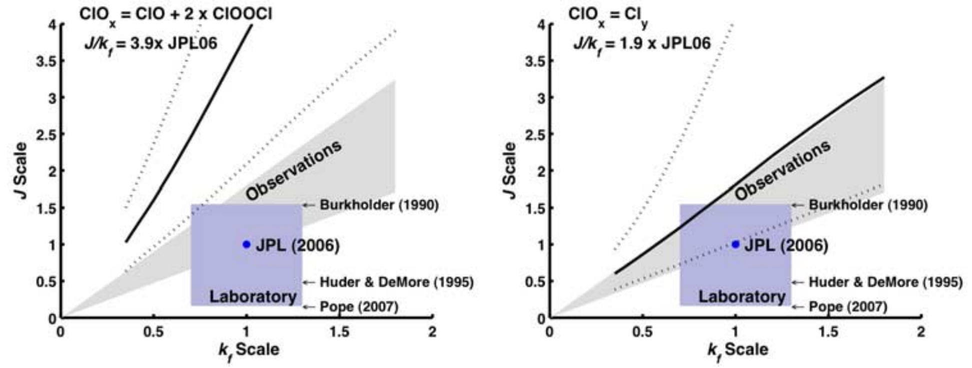

Figure 3. (left) The match-retrieved scale factors for k_f and J given the ClO_x a priori 'dimer' assumption (see text). (right) Same but assuming ClO_x 'total activation' assumption a priori. Black lines: self-match flight. Dashed lines: uncertainties (upper) plus systematic and (lower) minus systematic, respectively. Light grey area: region consistent with previous observational/modeling studies. Light blue area: region consistent with laboratory studies.

and θ inferred from HAGAR measurements (see auxiliary material).

[17] $\mathbf{S_a}$ was constructed using the following uncertainties: JPL06 error for K_{eq}, 0.9 for J_{scale} and 0.5 ppb for ClO_x. The retrievals resulted in an a priori weighting for K_{eq} and J_{scale} of 2% and 7% respectively from averaging kernel considerations. The uncertainties on the retrieved quantities were calculated by repeating the analysis with the measurements modified by their systematic uncertainties. These uncertainty limits represent bounds outside which the model is in no way consistent with the measurements.

3. Results and Discussion

[18] The SZA, match radius, potential temperature, and temperature for the outbound and inbound flight legs are displayed for each match in Figure 2. The ClO measurements with their precision and systematic errors are also displayed for the outbound and inbound flight legs.

3.1. Retrieved Kinetic Parameters

[19] Retrievals were run as outlined in section 2.4. For each retrieval the measurements were well described by the model, with absolute residuals less than 0.15 ppb (see auxiliary material).

[20] Figures 3 and 4 display the results from all retrievals expressed as scale factors of JPL06 kinetic parameters. Figure 3 displays the retrieved values for J against k_f. Only when the 'total activation' a priori constraint where $ClO_x \simeq Cl_y$ is applied does the slope approach that of previous studies using atmospheric observations, with best agreement seen at the lower uncertainty range of our work. This 'total activation' case (Figure 3, right) provides the lower limit constraint on J/k_f of 1.0 × JPL06. When ClO_x is constrained using the ClOOCl measurements (a priori $ClO_x = 2.0$ ppb), then a lower limit for J/k_f of 2.1 × JPL06 is found. The results for the 2 cases shown in Figure 3 give estimates for J/k_f of 1.9 and 3.9 × JPL06, respectively. This lies outside the range of values derived previously from observational/modeling studies. Note that neither this work nor any previous work is consistent with the combination of the most recent laboratory studies of *Pope et al.* [2007] ($0.16 \times J_{\mathrm{JPL06}}$) and *Boakes et al.* [2005] ($k_f = 1.3 \times k_f$ JPL06) giving a ratio of $0.13 \times J/k_f$ JPL06.

[21] Figure 4 displays the retrieved relationship between K_{eq} and k_f with respect to JPL06. The error range is valid for all values of ClO_x. This figure illustrates the $K_{eq} = 0.2^{+0.4}_{-0.1} \times$ JPL06 result that is found when k_f is constrained to lie within the laboratory estimates. This range of K_{eq} is independent of the dimer measurements which have been used in previous estimates of K_{eq} from observations [*Stimpfle et al.*, 2004; *von Hobe et al.*, 2005]. Additionally, if the dimer measurements are considered (a priori = 2.0 ppb for ClO_x), the values retrieved for J_{Scale} are given by the colors on the central curve (refer to Figure 3 for clearer k_f vs J information illustration). The error limits (dashed lines) consider the systematic error in the measurements. Even considering measurement errors, the retrieved K_{eq} and k_f do not agree with JPL06. The relationship of K_{eq} and k_f is virtually unaltered with the 'total activation' assumption, however the relationship between k_f and J is dramatically different (see Figure 3).

4. Conclusions

[22] Using ClO measurements from the self-match flight carried out during the SOLVE II/EUPLEX campaign, the match technique was combined with a retrieval formalization to study the chlorine dimer catalytic cycle in the activated polar stratosphere. Using JPL06 as a normalizing standard, the relationship between K_{eq}, k_f and J was retrieved.

[23] We found no combination of retrieved kinetic parameters (within measurement errors) consistent with JPL06 for K_{eq} and k_f. When k_f is constrained within limits from previous laboratory work then K_{eq} is a factor of $0.2^{+0.4}_{-0.1} \times K_{eq}$ JPL06. This result, independent of the dimer measurement, supports the conclusions of previous analyses of atmospheric observations [*Brune et al.*, 1990; *Pierson et al.*, 1999; *Avallone and Toohey*, 2001; *Stimpfle et al.*, 2004; *von Hobe et al.*, 2005; *Berthet et al.*, 2005] and the recent laboratory observations of K_{eq} and k_b [*Plenge et al.*, 2005; *Bröske and Zabel*, 2006] of a smaller K_{eq} than the current JPL06 recommendations. Furthermore, we determined a lower limit for the ratio of J/k_f of $1.0 \times J/k_f$ JPL06 when simply limiting ClO_x to be below Cl_y. Additionally, when the dimer measurements were used to constrain ClO_x this lower limit becomes $2.1 \times J/k_f$ JPL06, higher than other

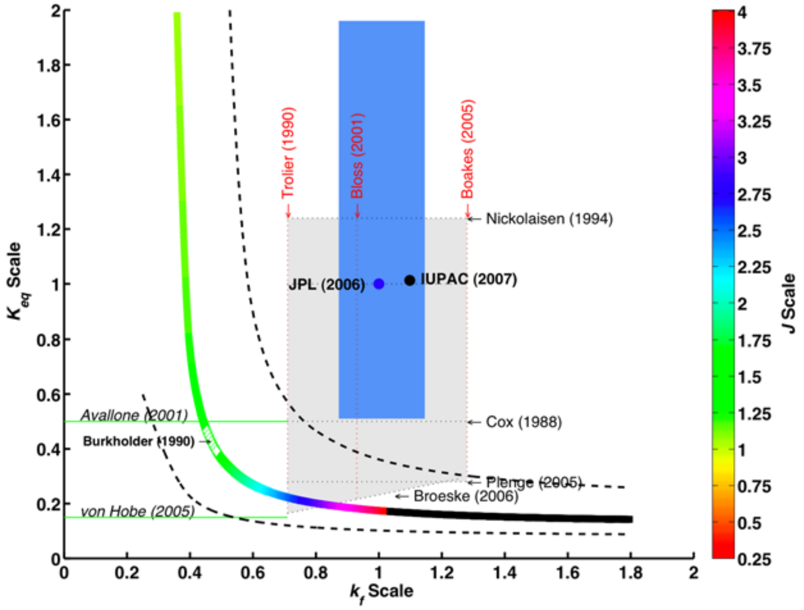

Figure 4. Thick colored curve: match-retrieved scale factors (relative to JPL06) for K_{eq} for varying k_f. The color scale: J_{Scale} for the a priori constraint ClO_x = 2.0 ppb (‘dimer’ case) (J_{Scale} above 4 is black). Dashed curves: the addition (lower), and subtraction (upper) of measurement systematic error. Grey shaded region: region consistent with laboratory studies. Green lines: observationally based K_{eq} estimates (see Table 1 for more details). Blue shaded region: uncertainty range for current JPL06 recommendations. IUPAC (2007) refers to *Atkinson et al.* [2007].

observational estimates. In all cases we find no combination of kinetic parameters that can simultaneously explain our observations of ClO and a value of *J* found using the *Pope et al.* [2007] cross-sections.

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