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Direct estimation of the rate constant of the reaction ClO + $HO_2 \rightarrow$ HOCl + O_2 from SMILES atmospheric observations

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Abstract

Diurnal variations of ClO, HO_2, and HOCl were simultaneously observed by the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES) between 12 October 2009 and 21 April 2010. These were the first global observations of the diurnal variation of HOCl in the upper atmosphere. A major reaction to produce HOCl is ClO + HO_2 →HOCl + O_2 (R1) in extra polar region. A model study suggested that in the mesosphere during night this is the only reaction influencing the amount of HOCl and ClO. The evaluation of the pure reaction period, where only reaction (R1) occurred in Cl_y chemical system, was performed by the consistency between two reaction rates, HOCl production and ClO loss, from SMILES observation data. It turned out that the SMILES data at the pressure level of 0.28 hPa (about 58 km) during night (between local time 18:30 and 04:00) in the autumn mid-latitude region (20–40° S February–April 2010) were suitable for the estimation of k_1. The rate constant was obtained to be $k_1(245\,\mathrm{K}) = 7.73 \pm 0.26(1\sigma)[\times 10^{-12}\,\mathrm{cm^3/molecule\,s}]$ from SMILES atmospheric observations. This result was consistent with that from both the laboratory experiment and the ab initio calculations for similar low-pressure conditions. The 1σ precision of k_1 obtained was 2–10 times better than those of previous laboratory measurements.

1 Introduction

The Reaction (R1) converts active chlorine monoxide (ClO) into hypochlorous acid (HOCl) as a short-lived reservoir in the atmosphere:

$$ClO + HO_2 \rightarrow HOCl + O_2 \qquad (R1)$$

The Reaction (R1) is the rate-limiting step of a catalytic ozone depletion cycle that contributes about 7 % to the ozone loss in the extratropical lower stratosphere (Lee et al., 2002).

Several laboratory studies on the rate constant of the Reaction (R1), k_1, have been reported (Stimpfle et al., 1979; Knight et al., 2000; Nickolaisen et al., 2000; Hickson et al., 2007). k_1 has relatively larger uncertainties compared with the rate constants of other major reactions in the atmospheric chemistry. For example, k_1 value from Hickson et al. (2007) has about a 25 % error ($k_1(296\ \text{K}) = (6.4 \pm 1.6) \times 10^{-12}$ [cm^3/molecule s]), while the rate constant of the $\text{Cl} + \text{O}_3 \rightarrow \text{ClO} + \text{O}_2$ reaction, k, has about a 10 % error ($k(298\ \text{K}) = (1.21 \pm 0.13) \times 10^{-11}$ [cm^3/molecule s] (Seely et al., 1996). Table 1 shows k_1 and the error (1σ) calculated based on previous laboratory studies at 225 K, which corresponds to the typical temperature of the lower stratosphere. k_1 has two-fold discrepancies between values from Stimpfle et al. (1979) and Knight et al. (2000). There is as yet no accurate estimation of k_1 in previous laboratory studies. Large uncertainties and discrepancies of k_1 lead to uncertainties of the estimation of the ozone loss in the extra polar region.

k_1 values from laboratory studies have been discussed using atmospheric observations and model calculations of HOCl. Several atmospheric observations of HOCl in the lower/middle stratosphere have been reported (Kovalenko et al., 2007; von Clarmann et al., 2012). Kovalenko et al. (2007) reported that their HOCl measurements by balloon-borne infrared spectrometers FIRS-2 and MkIV better agreed with the k_1 value based on Stimpfle et al. (1979) than that of the JPL 2006 recommendation (Sander et al., 2006). von Clarmann et al. (2012) confirmed that the k_1 of the JPL 2009 recommendation (Sander et al., 2010) better explained the middle stratospheric HOCl abundance measured by the Envisat/MIPAS instrument.

A high-sensitive remote sensing instrument named the Superconducting Submillimeter-Wave Limb-Emission Sounder (SMILES) on the International Space Station (ISS) performed the first observation of diurnal variations of HOCl, ClO, and HO_2 simultaneously in the middle atmosphere. The observation period was between 12 October 2009 and 21 April 2010. The latitude and altitude coverage of the SMILES observation was roughly 38° S–65° N and 16–90 km, respectively. An overview of SMILES is given in Kikuchi et al. (2010). Detail of the observation of O_3 and ClO are described in Kasai et al. (2013); Sato et al. (2012); Sagawa et al. (2013).

In this paper, we directly derived k_1 from the diurnal variations of HOCl, ClO, and HO_2 observed by SMILES in the lower mesosphere. We evaluated the "puriry" of the Reaction (R1) using both of the rate of HOCl production and the rate of ClO loss. The "purity" means that only the Reaction (R1) modifies the concentration of ClO and HOCl, and no competitive reaction exists. The "pure" condition is essential for the accurate estimation of k_1. It was difficult to obtain such condition in the laboratory experiment and in the stratospheric observation. In the laboratory, a radical(ClO)-radical(HO_2) reaction experiment has a problem of the purity of the target species because of active contaminations (many other active radical species) generated simultaneously in the system. In the stratosphere, many competitive reactions exist to modify the amount of HOCl and ClO. A photolysis of HOCl occurs during daytime, and ClO is consumed by the reaction $ClO + NO_2 \rightarrow ClONO_2$ during night time.

2 Model calculation of Cly chemistry in the lower mesosphere

In order to derive the rate constant of a chemical reaction from the observations of the concentrations of chemical species in the atmosphere, two basic approaches are possible:

(a) Steady-state approach: If the reaction of interest is involved in the production or destruction of a chemical species that is in steady state, then the corresponding balance equation (chemical production = destruction) may be exploited. It can be solved for the unknown rate constant, if the rate constants of all other involved reactions and the concentrations of all the reactants are known. The disadvantage of this method is that, besides the reaction of interest, at least one more reaction is involved in the chemical equilibrium. That is why assumptions on the corresponding reaction rate constant(s) must be made.

(b) Exploitation of the temporal evolution of the concentration of a chemical species: An estimate of the rate constant of the reaction of interest can be obtained from the rate of change of the concentration of a reactant or product of this reaction. This approach is especially useful if it is applied under conditions when the concentration of a certain species is affected only by the reaction of interest, because then no assumptions on the rate constants of other reactions are needed.

We used approach (b) for the calculation of k_1 from the SMILES HOCl, ClO, and HO_2 observations. In order to find out under which conditions the temporal evolution of HOCl can be expected to be determined solely by the Reaction (R1), we ran the AWI (Alfred Wegener Institute) chemical box model at different altitudes. This model simulates 175 reactions between 48 chemical species in the stratosphere and mesosphere. We performed 3d-runs, the last 24 h of which were used for the analysis. SMILES observations (bi-monthly mean data within latitude and altitude bins) were used for the initialization of these runs. For the species which were not observed by SMILES initial mixing ratios were taken from Brasseur et al. (1999), Appendix C, with the exception of water vapour. Its initial mixing ratio was adjusted such that the diurnally varying mixing ratio of ClO repeated every 24 h in the simulation.

These model runs yielded the following results:

1. Daytime conditions are not suitable for the application of method (b), because the photolysis of HOCl counteracts the Reaction (R1).

2. Nighttime conditions in the lower and mid stratosphere are not suitable, because the reaction (R1) nearly stops shortly after sunset, when the concentration of HO_2 almost vanishes (the production of $[HO_x] = [OH] + [HO_2]$ by photolysis and reactions involving $O(^1D)$ stops after sunset, HO_x is converted to reservoir species by several reactions, e.g. $OH + NO_2 + M \rightarrow HNO_3 + M$).

3. Nighttime conditions in the mesosphere are suitable for the analysis.

HOCl is produced only by the reaction (R1) in the mesosphere during nighttime, and there is no competing production or destruction reaction. The Reaction (R1) occurs throughout the night: both reactants (ClO and HO_2) are present, because the concentrations of their reaction partners in the loss reactions are smaller than those in the stratosphere due to the lower air pressure.

Figure 1 shows the corresponding model results for 0.28 hPa (58 km). After sunset Cl is quickly converted to ClO. Then, a slow conversion of ClO to HOCl occurs. As mentioned above, this is caused by the reaction of interest, $ClO + HO_2 \rightarrow HOCl + O_2$.

As the daytime loss reactions of HOCl (photolysis and reaction with atomic oxygen O) stop after sunset, the Reaction (R1) is the only reaction affecting HOCl after about local time (LT) 18:30 in the present model run. That is why, after that time, the rate of the increase of [HOCl] together with the concentrations of ClO and HO_2 may be used to estimate k_1.

After sunset there is a slow ClO production by $HCl + OH \rightarrow Cl + H_2O$, and $Cl + O_3 \rightarrow ClO + O_2$. This slows down significantly until 20:00 and almost completely decays until midnight. This means that after 18:30 the rate of change of [ClO] is determined to an increasing degree by the reaction (R1), until this is the only relevant reaction for ClO and, consequently, [ClO] + [HOCl] is nearly constant. That is why it is possible to derive an alternative estimate of k_1 from the rate of the decrease of [ClO] together with the concentrations of ClO and HO_2. Here two effects compete: The later this analysis starts, the smaller is the effect of the counteracting HCl–to–ClO conversion. The earlier this analysis starts, the more data enter the analysis, making it more robust.

The alternative calculation of k_1 may be helpful to detect and exclude effects in the data that are not caused by chemistry: for example, as the data corresponding to different local times may be from different months (see Fig. 2), a seasonal variation of the data may result in a variation with local time not caused by chemistry.

3 Diurnal variation by SMILES observation

We obtained concentrations of ClO, HO_2 and HOCl from the SMILES NICT level-2 product version 2.1.5 (Sato et al., 2012; Sagawa et al., 2013; Kasai et al., 2013). VMRs (volume mixing ratios) of the species of interest were retrieved from the spectra observed in the stratosphere and the mesosphere. Two months data are required to obtain all local time at night in the case of the SMILES observation because of the ISS orbit.

The 0.28 hPa pressure level (~58 km) was used to investigate the lower mesosphere. We selected the latitude range between 20 and 40° S and the seasons between February and April 2010 for our analysis by by the following reasons: (1) Reduce the effect of seasonal and latitudinal variability of the atmosphere, (2) The amount of HOCl was abundant in the mid-latitude autumn season (von Clarmann et al., 2012), and (3) SMILES has a denser data sampling in 20-40° S region. We extracted observations at a temperature within $245 \pm 1.4(1\sigma)$ K in order to reduce the variability of the calculated k_1 caused by the variability of the temperature.

The number density at that specific altitude was calculated by vertically interpolating the original data of level-2 VMR profiles. The vertical resolutions were about 6 km, 5 km, and 12 km for ClO, HO_2, and HOCl respectively. The 1σ error precision of the derived number density was estimated to be ~ 35 %, 90 %, and 120 % at 0.28 hPa (~58 km) for the single measurement of ClO, HO_2, and HOCl in the nighttime, respectively.

The number of data was about 6,000 points during the nighttime (LT 18:00–LT 06:00), which number is large enough for statistical analysis. The variance of the number density was roughly 40 %, 110 %, and 170 % for ClO, HO_2, and HOCl, respectively. These variances are larger than the 1σ error precision of the individual measurement.

Figure 2 shows the diurnal variations of ClO, HO_2, and HOCl in the lower mesosphere (0.28 hPa). Individual observations and data in averages of 3.75 min are presented. The lowest panel in Fig. 6 is the local time dependence of the number of our extracted SMILES data for each month. For the local time of each measurement, we used the elapsed time after the sunset (i.e., solar zenith angle = 90 deg) by fixing the sunset time as LT 18:00. This correction reduces the error due to merging data from different latitudes and seasons which have different relation between local times and solar zenith angles.

4 Estimation of k_1

4.1 Method of the estimation

The results of our model calculation suggested that [ClO] + [HOCl] increases rapidly until about 18:30 and undergoes only a small increase (10 %) afterwards. The sum [ClO] + [HOCl] become to be constant after that as shown in Fig. 1. This relation is equivalent to the following relation:

$$\frac{d[\mathrm{ClO}]}{dt} + \frac{d[\mathrm{HOCl}]}{dt} = 0 \qquad (1)$$

We consider the Eq. (1) as a necessary condition to prove the purity of Reaction (R1) in the actual atmosphere.

The Reaction (R1) is a second-order reaction of ClO and HO_2. Its reaction velocity is represented with the help of the number densities of relevant species as:

$$\frac{\mathrm{d}[\mathrm{HOCl}]}{\mathrm{d}t} = k_1[\mathrm{ClO}][\mathrm{HO_2}] \qquad (2)$$

Eq. (1) is equivalent to:

$$\frac{d[\mathrm{ClO}]}{dt} = -\frac{d[\mathrm{HOCl}]}{dt} \qquad (3)$$

Equation (3) can be rewritten as follows using Eq. (2):

$$\frac{d[\mathrm{ClO}]}{dt} = -k_1[\mathrm{ClO}][\mathrm{HO_2}] \qquad (4)$$

The calculation of k_1 in Sects. 4.2 and 4.3 will be based on Eqs. (2) and (4), respectively. In order to distinguish the results, the rate constant determined on the basis of Eq. (4) will be denoted by k_1'. To fulfill the condition of Eq. (1), k_1 and k_1' must be identical. If other reactions affect either the increase in HOCl or the decrease in ClO, there can be some difference between k_1 and k_1'.

4.2 Calculation of k_1 based on increase in HOCl

We performed the numerical analysis from Eq. (2) for the calculation of k_1 based on the increase in HOCl. Using the midpoint method scheme, the numerical solution of the differential Eq. (2) is given as:

$$[\mathrm{HOCl}]_0^{\mathrm{calc}} = Y_0 \tag{5}$$

$$\begin{aligned}[\mathrm{HOCl}]_{m+1}^{\mathrm{calc}} = {} & [\mathrm{HOCl}]_m^{\mathrm{calc}} \\ & + \frac{k_1}{2}\Big(([\mathrm{ClO}]_m^{\mathrm{obs}}[\mathrm{HO_2}]_m^{\mathrm{obs}}) \\ & + ([\mathrm{ClO}]_{m+1}^{\mathrm{obs}}[\mathrm{HO_2}]_{m+1}^{\mathrm{obs}})\Big) \\ & \times (t_{m+1}^{\mathrm{obs}} - t_m^{\mathrm{obs}})\end{aligned} \tag{6}$$

The calculation is performed for various local time intervals from different start time to end time. The observation values of ClO and $\mathrm{HO_2}$ were extracted for each time interval for the calculation of Eq. (6). $[\mathrm{ClO}]_m^{\mathrm{obs}}$, $[\mathrm{HO_2}]_m^{\mathrm{obs}}$ are the m-th observed number densities of ClO, $\mathrm{HO_2}$. t_m^{obs} is the m-th elapsed time from the calculation start time for each time interval. The intervals of $t_{m+1}^{\mathrm{obs}} - t_m^{\mathrm{obs}}$ is about 7 s. Y_0 is the initial value of HOCl at the calculation start time.

The temporal evaluation of HOCl, $[\mathrm{HOCl}]_m^{\mathrm{calc}}$, is computed from the observed ClO and $\mathrm{HO_2}$ using k_1 and Y_0 as variable parameters. The reason for not fixing Y_0 is that there is a variability of the SMILES observation data of HOCl at the calculation start time for each time interval. k_1 and Y_0 are determined by minimizing the following function χ:

$$\chi = \frac{1}{N}\sum_{m=0}^{N}\left(\frac{\left([\mathrm{HOCl}]_m^{\mathrm{calc}} - [\mathrm{HOCl}]_m^{\mathrm{obs}}\right)^2}{\left(\sigma_m^{\mathrm{HOCl}}\right)^2}\right) \tag{7}$$

The observation values of HOCl and the observation error of HOCl were extracted in the same time interval as in the calculation of Eq. (6). $[\mathrm{HOCl}]_m^{\mathrm{obs}}$ is the m-th observed number density and σ_m^{HOCl} is the m-th observation error of HOCl. N is the number of data for each time interval. To reduce the effect of random errors from SMILES measurements, we ignored time intervals which data numbers are less than 3000 (half of the total data numbers at night).

4.3 Calculation of k_1' based on decrease in ClO

We also conducted a numerical analysis from Eq. (4) for the calculation of k_1' based on the decrease in ClO. As in the case of Eq. (6), the numerical solution of the differential Eq. (4) is shown as follows:

$$[\mathrm{ClO}]_0^{\mathrm{calc}} = Y_0 \tag{8}$$

$$\begin{aligned}[\mathrm{ClO}]_{m+1}^{\mathrm{calc}} = {} & [\mathrm{ClO}]_m^{\mathrm{calc}} \\ & -\frac{k_1'}{2}\Big(([\mathrm{ClO}]_m^{\mathrm{obs}}[\mathrm{HO_2}]_m^{\mathrm{obs}}) \\ & +([\mathrm{ClO}]_{m+1}^{\mathrm{obs}}[\mathrm{HO_2}]_{m+1}^{\mathrm{obs}})\Big) \\ & \times(t_{m+1}^{\mathrm{obs}} - t_m^{\mathrm{obs}})\end{aligned} \tag{9}$$

This temporal evaluation of ClO, $[\mathrm{ClO}]_m^{\mathrm{calc}}$, is computed from the observed ClO and HO_2. We also used the evaluation function for the least squares fitting of Eq. (9). k_1'

and Y_0 are determined by minimizing the following function χ:

$$\chi = \frac{1}{N}\sum_{m=0}^{N}\left(\frac{\left([\mathrm{ClO}]_m^{\mathrm{calc}}-[\mathrm{ClO}]_m^{\mathrm{obs}}\right)^2}{\left(\sigma_m^{\mathrm{ClO}}\right)^2}\right) \quad (10)$$

The condition of the minimization of the evaluation function is the same as described in Sect. (4.2).

4.4 Results

Figure 3 shows the calculated k_1 and k'_1 values in each local time interval. In addition, the difference between k_1 and k'_1, $\Delta k = |k_1 - k'_1|$ is presented. The horizontal and vertical axes are the start and end time of the considered time intervals, respectively. The blank area represents the time intervals where the data numbers are less than our threshold or Δk values are greater than 5.0 [$\times 10^{-12}$ cm^3/molecule s].

5 Discussion

5.1 Evaluation of the purity of Reaction (R1) by Δk

As already described in Sect. 4.1, Δk is an indicator of the purity of the Reaction (R1). $\Delta k = 0$ is necessary that the relation (2) is fulfilled.

Our results in Fig. 3 show the following typical distributions of Δk in the nighttime.

1. Range $\Delta k \sim 0$: the conditions of the start time of LT 18:30– LT19:30 and any end time. Note that the Δk is not zero ($\sim$1.0 [$\times 10^{-12}$ cm^3/molecule s]) when the end time is set at LT 00:45–1:45 and LT 4:00–06:00.
2. Range $\Delta k > 3.0$ [$\times 10^{-12}$ cm^3/molecule s]: the conditions of the start time later than LT 20:00 and the end time around LT 03:00

3. Another range $\Delta k > 3.0$ [$\times 10^{-12}$ cm^3/molecule s]: the conditions of the start time later than LT 20:00 and the end time later than LT 04:00.

We considered that the result 2 may be caused by two problems. One is the unknown strange behavior observed in the ClO data around LT 02:40. In Fig. 2, the ClO data around this local time show a relatively smaller number density compared to other local times (0.5×10^6 molecule/cm^3 at LT 02:40 while it is around 0.7×10^6 molecule/cm^3 at neighboring local times). Another is the inhomogeneous local time sampling of SMILES in our extracted February–April dataset. As shown in Fig. 2, the data for LT 21:00–00:00 was mixed well homogeneously between February, March, and April, 2010 while that of LT 02:00–03:00 mostly coming from March 2010. The problem in the result 1 between LT 00:45–01:45 is also considered due to the inhomogeneous sampling.

The effect of photochemistry in the morning time causes problems of the result 3 and the result 1. During sunrise ClO and HOCl started to decrease, and HO_2 starts to increase. This time range should be excluded from our analysis in order to ensure conservative discussion of the purity of the Reaction (R1).

As a conclusion, we derived from the SMILES dataset that the local time interval of LT 18:30–LT 04:00 is the time in which the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ purely happens in the Cl_y chemistry in the lower mesosphere. The condition of the SMILES dataset used here is the pressure level of 0.28 hPa in the mid-latitude region (20–40° S) in February–April 2010, having a temperature of 245 K.

5.2 Estimation of the rate constant of Reaction (R1)

Under the time interval of LT 18:30–LT 04:00, the derived k_1 ranges between 1.1 [$\times 10^{-12}$ cm^3/molecule s] and 11.3 [$\times 10^{-12}$ cm^3/molecule s]. It is clear that this variability of k_1 includes the errors as discussed in Sect. 5.1. To estimate k_1 more accurately, we discuss Δk in the time range between start time of LT 18:10–19:40 and end time of LT 02:50–04:20 where the Δk value is closest to zero in Fig. 3. Figure 4 shows a magnified figure of Δk in Fig. 3 in this time range.

The start time LT18:30 has nearly zero value of Δk, but there is a variability in the values of Δk shown in Fig. 4, which is likely due to the measurement errors. The threshold was determined for the case that the probability distribution of k_1 became close to a Gaussian distribution, which gives us an expectation that the variability of k_1 in this $\Delta k \le 0.1[\times 10^{-12}\,\mathrm{cm}^3/\mathrm{molecule\,s}]$ fairly represents the error due to the SMILES measurements errors. Therefor, we considered this standard deviation of k_1 as the 1σ precision of the k_1 derived in this study. Figure 5 shows the probability distribution plot of k_1 under the condition of $\Delta k \le 0.1$ in the time range between start time of LT 18:10–19:40 and end time of LT 02:50–04:20.

The median and the standard deviation of k_1 shown in Fig. 5 are used for the SMILES k_1 and the 1σ. The k_1 provided by SMILES observation is:

$$k_1(245\mathrm{K}) = 7.73 \pm 0.26(1\sigma)[\times 10^{-12}\,\mathrm{cm}^3/\mathrm{molecule\ s}]$$

Figure 6 shown the time dependences of [HOCl] and [ClO]. both for observation and calculation using the SMILES k_1 for LT 18:30–LT 04:00. The lowest panel in Fig. 6 is the sum of observations ([HOCl] + [ClO]) and optimized Y_0 (Eq. 7 and Eq. 10). Both of them show good agreement with each other.

5.3 Comparison of k_1 with previous studies

We estimated the SMILES k_1 using the atmospheric remote sensing data with the good sensitivity of the SMILES receivers and longer line-of-sight limb measurement from space. Comparison was performed between our derived k_1, previous laboratory studies, an ab initio calculation study (Xu et al., 2003), and JPL 2011 recommendation (Sander et al., 2011).

Table 2 shows k_1 values calculated at 245 K from our and previous works with 1σ errors. The value of the SMILES k_1 is consistent with the one from Hickson et al. (2007) and the ab initio value at 1 Torr from Xu et al. (2003) within the margin of error. The 1σ error of k_1 from the SMILES observation data is 2–10 times smaller than that of previous laboratory experiments at 245 K. This can be attributed to the fact that the

SMILES k_1 was derived from the dataset in which only the Reaction (R1) happened and no other competitive radical reactions contaminated. Such a condition is very difficult for laboratory experiments to realize.

Figure 7 shows the temperature dependence of k_1 from the previous laboratory studies, the ab initio calculations (Xu et al., 2003), JPL 2011 recommendation (Sander et al., 2011), and the SMILES k_1 value. The error of the temperature, σ_T, for our derived k_1 is set as 1.4 K as described in Sect. 3. Variability of k_1 at the room temperature is smaller than that at 215 K (lower temperature in stratosphere). k_1 varies between 6–8 and 6–16 [$\times 10^{-12}$ cm^3/molecule s] at 300 K and 215 K, respectively. It should be noticed that values of the k_1 from Hickson et al. (2007) and Xu et al. (2003) are nearly identical in the range between 300 K and 215 K.

A pressure dependence was noticed by Xu et al. (2003) due to the longer lifetime of the reaction intermediate HOOOCl. A higher pressure provides a larger k_1 (Xu et al., 2003) as shown in Fig. 7 at 400 Torr and at 1 Torr; for example, the value of k_1 at 215 K is 9 and 11 [$\times 10^{-12}$ cm^3/molecule s] at 1 Torr and 400 Torr, respectively.

As shown in Table 2, the measurement of Nickolaisen et al. (2000) performed under the higher pressure condition (50–700 Torr) and the temperature dependence of k_1 are larger value than the other values which were performed under the condition of 0.21–1.7 Torr (excepting Stimpfle et al. (1979)). The values of k_1 from Hickson et al. (2007) and SMILES, which were derived under the condition of 1.5 Torr and 0.21 Torr (0.28 hPa) respectively, were consistent with that of the ab initio calculation at 1 Torr of Xu et al. (2003).

6 Conclusions

The model calculation of the chlorine partitioning suggests that the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ is the only reaction affecting HOCl and ClO after about LT 18:30 in the lower mesosphere. This provides an opportunity for determining the rate constant k_1 of this reaction from diurnal variations of ClO, HO_2, and HOCl.

The SMILES NICT Level-2 product version 2.1.5 was used for our study. We evaluated the purity of the Reaction (R1) at the 0.28 hPa pressure level (58 km) by the consistency between two reaction rates estimated HOCl production and ClO loss using SMILES observation data. The condition was in the mid-latitude between 20° S and 40° S at a temperature range of 245 ± 1.4(1σ) K, in the period from February to April 2010. We derived from the SMILES dataset that the local time interval of LT 18:30–LT 04:00 is the time in which the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ purely happens in the Cl_y chemistry in the lower mesosphere.

We used the condition of $\Delta k \leq 0.1[\times 10^{-12}\ cm^3/molecule\ s]$ (Δk is the difference between two reaction rates) as a threshold for the estimation of k_1 in the derived pure reaction period. The rate constant of the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ is obtained to be $k_1 = 7.73 \pm 0.26(1\sigma)[\times 10^{-12}\ cm^3/molecule\ s]$ at 245 K, which was 2–10 times better precision than those from laboratory measurements. The SMILES k_1 was directly estimated using the remote sensing data with the long line of sight under the condition that the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ purely happened in the Cl_y chemistry. This condition could not have been achieved in the previous laboratory measurements and the previous HOCl measurements. The SMILES k_1 has an advantage over the results of previous studies, while it is valid only for one temperature (245 K) and one pressure (0.28 hPa).

The SMILES k_1 was consistent with that from both the laboratory experiment and the ab initio calculations for similar low-pressure conditions. On the other hand, k_1 from high pressure region shows a larger value. The large variability for pressure dependence in k_1 might be caused by the lifetime of the reaction intermediate HOOOCl as mentioned in Xu et al. (2003). It may be worth to use pressure dependent k_1 value for atmospheric chemical model calculations.

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Table 1. k_1 and the error (1σ) calculated based on previous laboratory studies at 225 K.

Laboratory measurements	k_1(225K)*	1σ *
Stimpfle et al. (1979)	13.80	None
Nickolaisen et al. (2000)	11.36	3.03
Knight et al. (2000)	6.61	0.66
Hickson et al. (2007)	8.98	3.20

* Units: [$\times 10^{-12}$ cm^3/molecule s.]

Table 2. Comparison with previous studies.

Measurement method	k_1(245K)[a]	1σ [a]	P [Torr]
-Atmospheric measurement			
SMILES	7.73	0.26	0.21
-Laboratory measurement			
Stimpfle et al. (1979) [b]	10.55	None	0.8–3.4
Nickolaisen et al. (2000)	10.15	2.49	50–700
Knight et al. (2000)	6.65	0.63	1.1–1.7
Hickson et al. (2007)	7.86	2.60	1.5
JPL 2011 [c]	8.49	2.87	None
-Ab initio calculation			
Xu et al. (2003)			
400 Torr	9.27	None	400
1 Torr	7.85	None	1

[a] Units 10^{-12} cm^3/molecule s.
[b] Kovalenko et al. (2007) supported.
[c] von Clarmann et al. (2012) supported

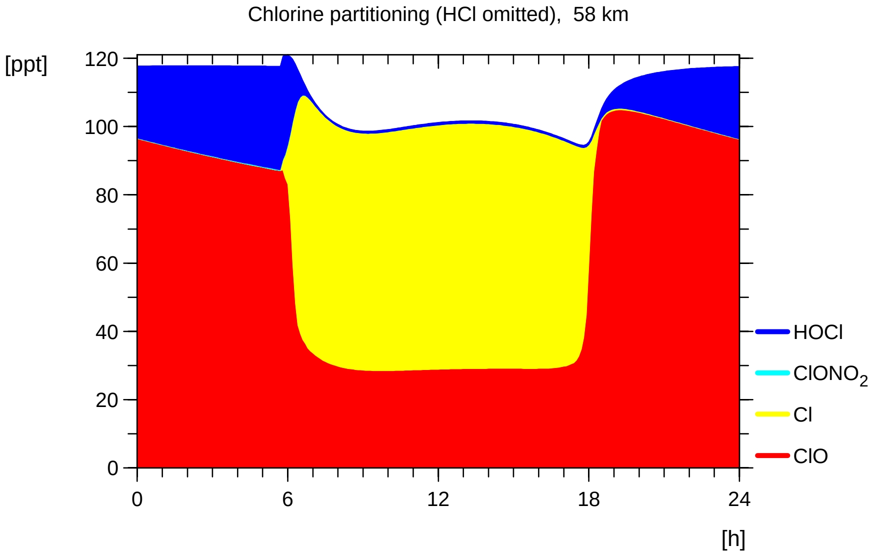

Fig. 1. Diurnal variation of the chlorine partitioning (HCl omitted) at 0.28 hPa altitude according to model calculations for 30° S, 31 March.

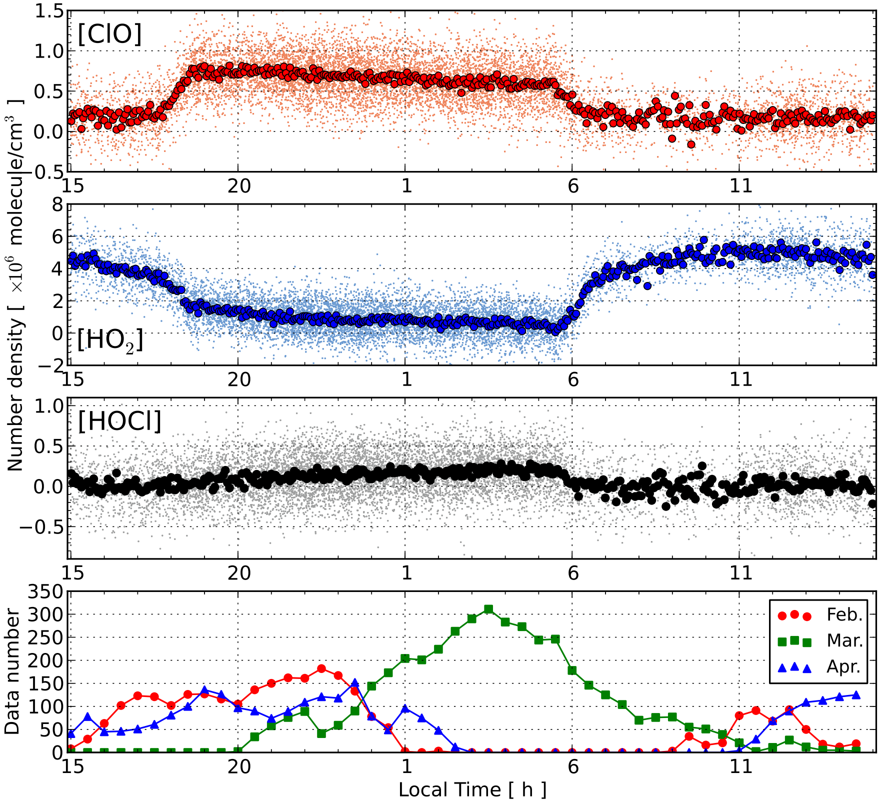

Fig. 2. Diurnal variation of the number density of ClO, HO_2, HOCl in 0.28 hPa region obtained by SMILES. The data from 20–40° S between February and April 2010 are used in this study. Data shown in small dots represent the results from each single measurement of SMILES. Large dots are the smoothed temporal evolution with an average over 3.75 min. Local time dependence of the number of data is shown in the bottom panel. The number of data is integrated over every 0.5 h for February (red), March (green), and April (blue) separately.

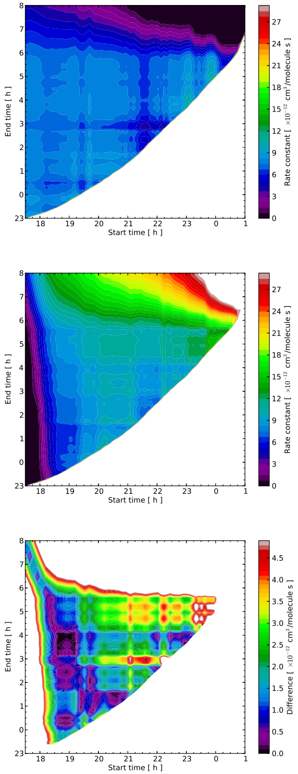

Fig. 3. Contour plots of k_1 (top), k_1' (middle) Δk (bottom) calculated from SMILES observation dataset. k_1 and k_1' are calculated in time periods from each start to each end time.

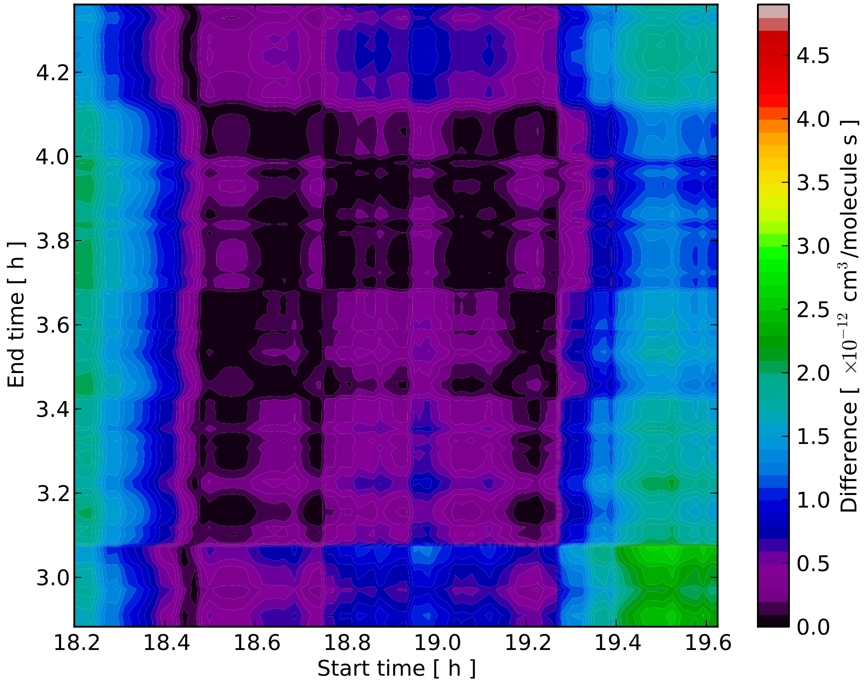

Fig. 4. The contour plot of Δk calculated from the SMILES observation data set between LT 18:10–19:40 and LT 02:50–04:20.

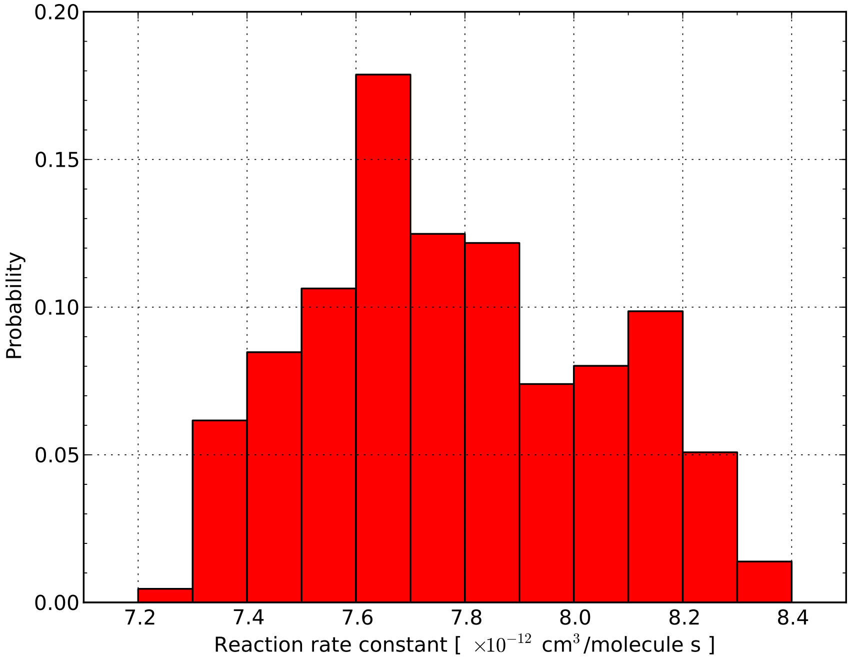

Fig. 5. Probability distribution plots of k_1 under the condition of $\Delta k \leq 0.1[\times10^{-12} cm^3/\text{molecule s}]$ in the time range between start time of LT 18:10–19:40 and end time LT 02:50–04:20.

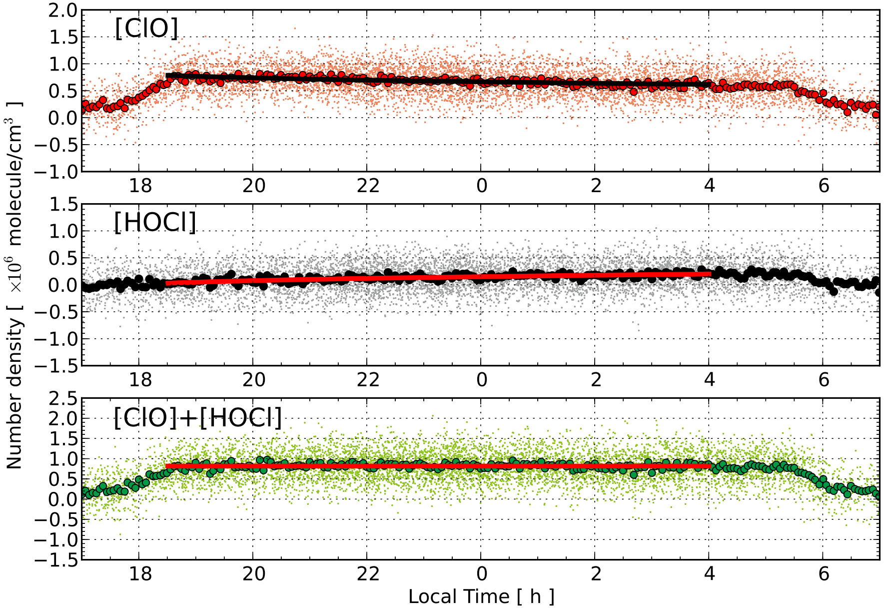

Fig. 6. Diurnal variation plot of ClO with average values (red) and calculation values using the rate constant of this work (black) in 0.28 hPa region (top). Diurnal variation plot of HOCl with average values (black) and calculation values using the rate constant of this work (red) in 0.28 hPa region (middle). Diurnal variation plot of the sum of ClO + HOCl with average values (green) and the sum of calculation values.

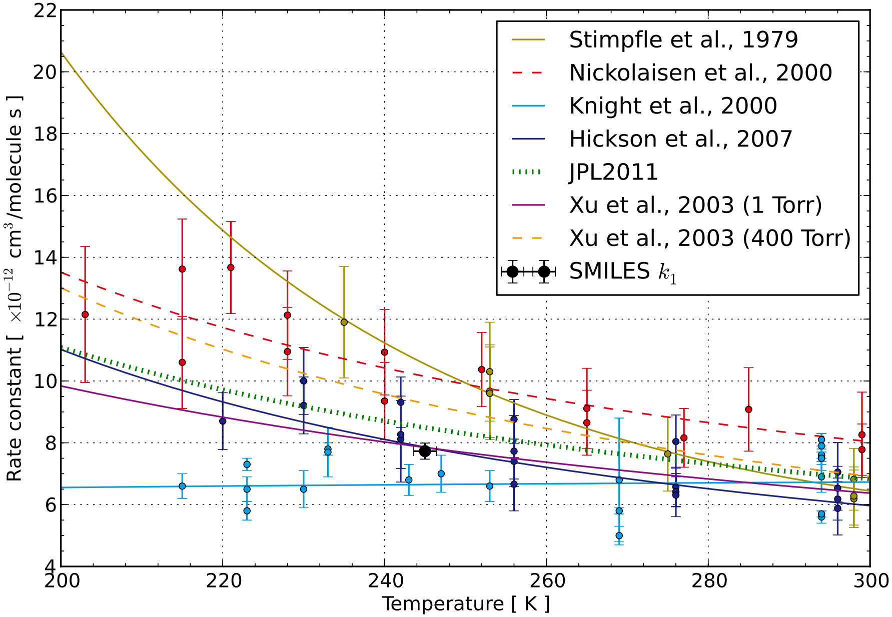

Fig. 7. Comparison with previous work. Each scatter plots and lines are the experimental values from Stimpfle et al. (1979) (yellow), Knight et al. (2000) (red), Nickolaisen et al. (2000) (cyan), and Hickson et al. (2007) (blue). Each lines are the calculation values from JPL 2011 recommendation (Sander et al., 2011) (green) and the ab initio calculation (Xu et al., 2003) (purple (1 Torr) and orange (400 Torr)). The black dot is the value of the SMILES k_1. Solid and dashed lines are k_1 values at higher pressure region (50–700 Torr) and lower pressure region (≤ 5.0 Torr), respectively.