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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 for the production of HOCl is ClO + HO_2 →HOCl + O_2 (Reaction (R1)) in extra-polar regions. A model study suggested that in the mesosphere, this is the only reaction influencing the amount of HOCl during the night. The evaluation of the pure reaction period, when only Reaction (R1) occurred in the Cl_y chemical system, was performed by checking the consistency of the HOCl production rate with the ClO loss rate from SMILES observation data. It turned out that the SMILES data at the pressure level of 0.28 hPa (about 58 km) in the autumn mid-latitude region (20–40° S, February–April 2010) during night (between modified local time 18:30 and 04:00) were suitable for the estimation of the rate constant, k_1. The rate constant obtained from SMILES observations was $k_1(245\,\mathrm{K}) = (7.75 \pm 0.25) \times 10^{-12}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$. This result is consistent with results from a laboratory experiment and ab initio calculations for similar low-pressure conditions.

1 Introduction

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

$$ClO + HO_2 \rightarrow HOCl + O_2. \qquad \text{(R1)}$$

The Reaction (R1) is the rate-limiting step of a catalytic ozone depletion cycle that causes about 7 % and 10 % of the ozone loss in the extra-tropical lower stratosphere and in the Arctic stratospheric vortex, respectively (Lee et al., 2002; Chipperfield et al., 1994).

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 large uncertainties compared with the rate constants of other major reactions in the atmospheric chemistry. For example, the k_1 value from Hickson et al. (2007) has an error of about 25 % ($k_1(296\,\mathrm{K}) = (6.4 \pm 1.6) \times 10^{-12}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$), while the rate constant of the Cl + O_3 →ClO + O_2 reaction, k, has an error of about 10 % ($k(298\,\mathrm{K}) = (1.21 \pm 0.13) \times 10^{-11}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$) (Seely et al., 1996). Table 1 shows k_1 and the error (1σ) calculated from previous laboratory studies at 225 K (which corresponds to the typical temperature of the lower stratosphere). A discrepancy of a factor of 2 between the k_1 values from Stimpfle et al. (1979) and Knight et al. (2000) can be noticed. There is no consistency in the previous laboratory studies. One reason for this is that the quantification of the production of HO_2 and ClO in laboratory experiments is difficult. Large uncertainties and discrepancies of k_1 lead to uncertainties of the estimation of the ozone loss in the extra-tropical lower stratosphere and in the Arctic stratospheric vortex.

The validity of 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

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: 10^{-12} cm^3 $molecule^{-1}$ s^{-1}.

(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 agreed better with the k_1 value based on Stimpfle et al. (1979) than that recommended by the Jet Propulsion Laboratory (JPL) 2006 (Sander et al., 2006). von Clarmann et al. (2012) confirmed that the k_1 of the JPL 2009 recommendation (Sander et al., 2010) explained the middle stratospheric HOCl abundance measured by the Envisat/MIPAS instrument better than the k_1 of the JPL 2006 recommendation (Sander et al., 2006).

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

In this paper, we directly derive k_1 from the diurnal variations of HOCl, ClO, and HO_2 observed by SMILES in the lower mesosphere. We evaluate the "purity" of Reaction (R1) using both of the rate of HOCl production and the rate of ClO loss. Here "purity" means that only the Reaction (R1) modifies the concentration of ClO and HOCl, and the effect of competitive reactions does not appear in the observation. This "purity" condition is essential for the accurate estimation of k_1. It is difficult to obtain such a condition in stratospheric observations. In the stratosphere, several competitive reactions exist that modify the amount of HOCl and ClO. The photolysis of HOCl occurs during daytime, and ClO is consumed by the reaction $ClO + NO_2 + M \rightarrow ClONO_2 + M$ during nighttime.

2 Model calculation of Cl_y 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 at steady state, then the corresponding balance equation (chemical production = depletion) 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 about 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 in which the concentration of a certain species is affected only by the reaction of interest, because then no assumptions about 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 that 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]

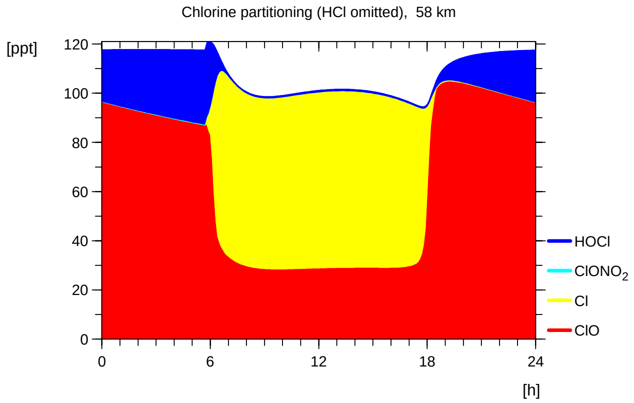

Fig. 1. Diurnal variation of the chlorine partitioning (HCl omitted) at 0.28 hPa altitude according to model calculations for 30° S, 31 March.

+ [HO_2] by photolysis, and reactions involving $O(^1D)$ stop 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 by the Reaction (R1) on 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.

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 18:30 local time (LT) 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 can 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 by 20:00 and almost completely decays by 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 the effect of the counteracting HCl-to-ClO conversion is. The earlier this analysis starts, the more data enter the analysis (making the analysis more robust).

The alternative calculation of k_1 may be helpful in detecting and excluding 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 observed by SMILES

We obtained concentrations of ClO, HO_2 and HOCl from the SMILES NICT (National Institute of Information and Communications Technology) 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. Data for at least two months are required to obtain all local times at night 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° S and 40° S and the season from February to April 2010 for our analysis for the following reasons: (1) the effect of the seasonal and latitudinal variability of the atmosphere is reduced, (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 around the 38° 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 extracted SMILES data are from different latitudes and seasons, for which there are different relations between local times and solar zenith angles (SZA). This is why, throughout this study, a modified local time (MLT) of the SMILES observations is used. It is defined as follows: modified local time (MLT) = local time − local time corresponding to a SZA of 90° + 18:00. According to this definition, the sunset at the Earth's surface (solar zenith angle = 90°) always occurs at 18:00 MLT independently of latitudes and seasons.

The number density at a 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 precision of the derived number density was estimated to be ∼ 35 %, 90 %, and 120 % at 0.28 hPa (∼ 58 km) for single measurements of ClO, HO_2, and HOCl in the nighttime, respectively. 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 precision of the single measurements because they include variabilities of the number density in the atmosphere.

The number of data was about 6000 during the nighttime (18:00–06:00 MLT). This number is large enough for statistical analysis.

Figure 2 shows the diurnal variations of ClO, HO_2, HOCl, and the sum of [ClO] and [HOCl] in the lower mesosphere (0.28 hPa). Individual observations and averages over 3.75 min are presented. The horizontal and vertical axes are the modified local time and the number density of each molecule, respectively. The lowest panel in Fig. 2 is the modified local time dependence of the number of the extracted SMILES data for each month.

The systematic error (bias) of SMILES NICT ClO data was estimated in a theoretical manner by Sato et al. (2012) and Sagawa et al. (2013). Theoretical estimations of the systematic errors are done by a forward-model simulation using a certain reference atmospheric state, and they do not include the actual measurement noise of SMILES observations in order to estimate the maximum impact of each error factor on the bias uncertainties. According to Sagawa et al. (2013), the systematic error for ClO is up to about 3 % at 0.28 hPa for the mid-latitude nighttime. In this study, we adopt the systematic error of 3 %, which is derived from the theoretical systematic error analysis of ClO, for all the considered species. The SMILES ClO, HO_2, and HOCl products have been compared to other satellite measurements (Khosravi et al., 2013). However, due to the limitation in the number of compared instruments and due to the large difference in the sensitivity and observation local time of each instrument, it is not possible to determine which instrument has positive/negative bias errors. Despite such technical difficulties, the diurnal variation of the SMILES ClO, HO_2, and HOCl show general agreement both in the quantity and shape (Khosravi et al., 2013). It is noted that more robust evaluation on the systematic error of our analysis will be addressed when further validation works of SMILES products are completed.

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. As shown in Fig. 1, the sum of [ClO] + [HOCl] is nearly constant after that. This relation is equivalent to the following relation:

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

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

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

$$\frac{d[\mathrm{HOCl}]}{dt}=k_1[\mathrm{ClO}][\mathrm{HO_2}] \tag{2}$$

Eq. (1) is equivalent to:

$$\frac{d[\mathrm{ClO}]}{dt}=-\frac{d[\mathrm{HOCl}]}{dt} \tag{3}$$

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

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

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 constants determined on the basis of Eqs. (2) and (4) will be denoted by ${}^{c}k_1$ and ${}^{c}k'_1$, respectively. Here the superscript ^{c} means "calculated". To fulfill the condition of Eq. (1), ${}^{c}k_1$ and ${}^{c}k'_1$ must be identical. If other reactions affect either the increase of HOCl or the decrease of ClO, there can be some difference between ${}^{c}k_1$ and ${}^{c}k'_1$.

4.2 Calculation of ${}^{c}k_1$ based on increase of HOCl

To calculate ${}^{c}k_1$ based on the increase of HOCl, we start from Eq. (2). After substituting k_1 by ${}^{c}k_1$, the integration equation of Eq. (2) yields

$$[\mathrm{HOCl}](t)=[\mathrm{HOCl}](t_0)+{}^{c}k_1\cdot\int_{t_0}^{t}[\mathrm{ClO}](\tau)\cdot[\mathrm{HO_2}](\tau)d\tau. \tag{5}$$

Using the trapezoidal rule, we obtain the following approximate solution of the integration Eq. (5):

$$[\mathrm{HOCl}]_0^{\mathrm{calc}}=[\mathrm{HOCl}](t_0) \tag{6}$$

$$\begin{aligned}[\mathrm{HOCl}]_{m+1}^{\mathrm{calc}}=&[\mathrm{HOCl}]_m^{\mathrm{calc}}\\&+\frac{{}^{c}k_1}{2}\Big([\mathrm{ClO}]_m^{\mathrm{obs}}[\mathrm{HO_2}]_m^{\mathrm{obs}}\\&+[\mathrm{ClO}]_{m+1}^{\mathrm{obs}}[\mathrm{HO_2}]_{m+1}^{\mathrm{obs}}\Big)\\&\times(t_{m+1}^{\mathrm{obs}}-t_m^{\mathrm{obs}}).\end{aligned} \tag{7}$$

In these equations, $[\mathrm{ClO}]_m^{\mathrm{obs}}$ and $[\mathrm{HO_2}]_m^{\mathrm{obs}}$ are the mth observed number densities of ClO and HO_2. t_m^{obs} is the mth elapsed time from the calculation start time. The intervals of $t_{m+1}^{\mathrm{obs}}-t_m^{\mathrm{obs}}$ are about 7 s. $[\mathrm{HOCl}](t_0)$ is the initial value of HOCl at the calculation start time. The calculation is performed for various modified local time intervals from different start time to end time. The observation values of ClO and HO_2 were extracted for each time interval for the calculation of Eq. (7).

The rate constant of interested, ${}^{c}k_1$, and also $[\mathrm{HOCl}](t_0)$ are considered as variable parameters. The reason for not fixing $[\mathrm{HOCl}](t_0)$ is that there is a variability of the SMILES observation data of HOCl at the calculation start time for each time interval. ${}^{c}k_1$ and $[\mathrm{HOCl}](t_0)$ are determined by the minimization of the following function χ^2 using the least-squares method:

$$\chi^2=\frac{1}{N}\sum_{m=1}^{N}\left(\frac{\left([\mathrm{HOCl}]_m^{\mathrm{calc}}-[\mathrm{HOCl}]_m^{\mathrm{obs}}\right)^2}{\left(\sigma_m^{\mathrm{HOCl}}\right)^2}\right). \tag{8}$$

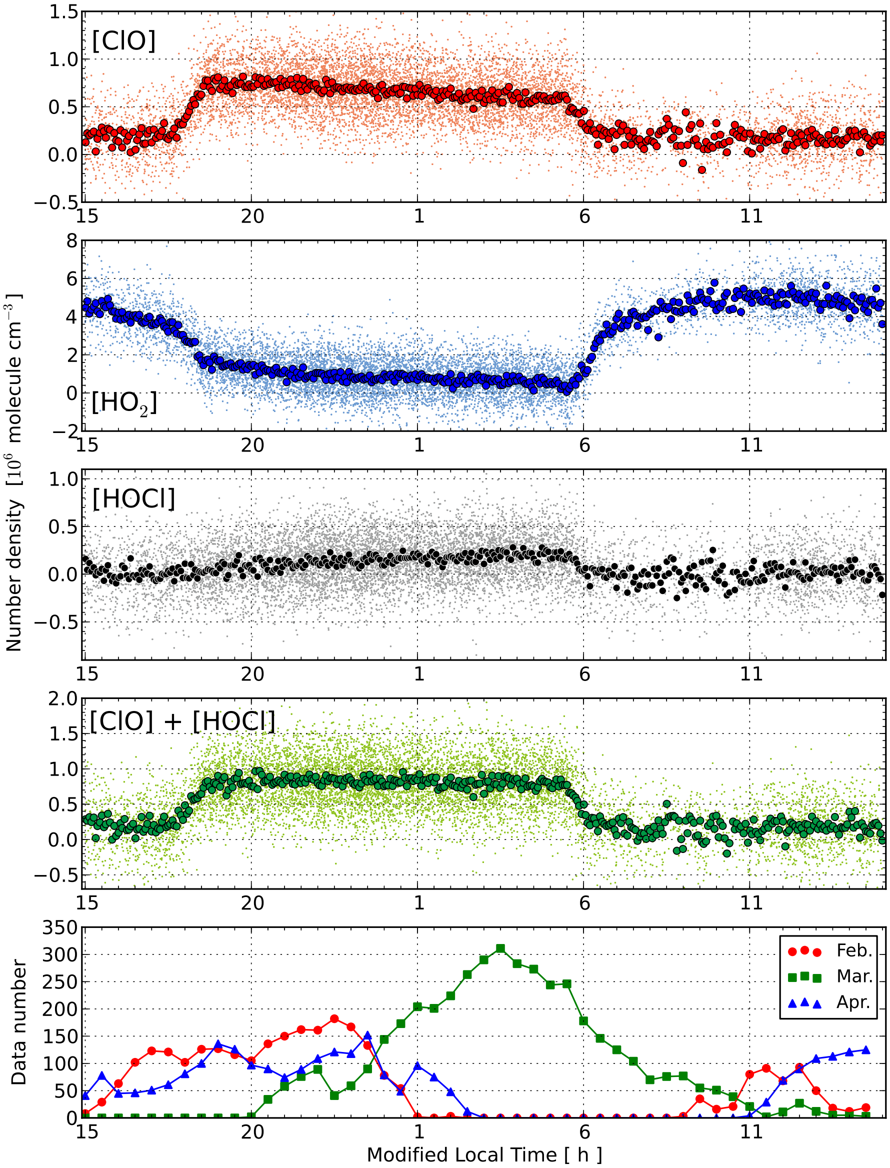

Fig. 2. Diurnal variation of the number density of ClO, HO_2, HOCl, and the sum of [ClO] and [HOCl] at 0.28 hPa obtained by SMILES. Data from 20–40° S from February to April 2010 are used in this study. Small dots represent the results from each single measurement of SMILES. Large dots show the smoothed temporal evolution with an average over 3.75 min. The modified 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.

The observation values of HOCl and the observation error of HOCl were extracted in the same time interval as in the calculation of Eq. (7). $[\mathrm{HOCl}]_m^{\mathrm{obs}}$ is the mth observed number density and σ_m^{HOCl} is the mth 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 with a data volume less than 3000 (half of the total data number at night). We also obtained the calculated error (fitting error) of ${}^{\mathrm{c}}k_1$ from the optimization of ${}^{\mathrm{c}}k_1$ and $[\mathrm{HOCl}](t_0)$.

4.3 Calculation of ${}^{\mathrm{c}}k_1'$ based on decrease of ClO

To calculate ${}^{\mathrm{c}}k_1'$ based on the decrease of HOCl, we start from Eq. (4). After substituting k_1 by ${}^{\mathrm{c}}k_1'$, the integration equation of Eq. (4) yields

$$[\mathrm{ClO}](t) = [\mathrm{ClO}](t_0) - {}^{\mathrm{c}}k_1' \cdot \int_{t_0}^{t} [\mathrm{ClO}](\tau) \cdot [\mathrm{HO_2}](\tau)\,\mathrm{d}\tau. \qquad (9)$$

Using the trapezoidal rule, we obtain the following approximate solution for the integration Eq. (9):

$$[\mathrm{ClO}]_0^{\mathrm{calc}} = [\mathrm{ClO}](t_0) \tag{10}$$

$$\begin{aligned}[\mathrm{ClO}]_{m+1}^{\mathrm{calc}} &= [\mathrm{ClO}]_m^{\mathrm{calc}} \\ &\quad -\frac{{}^{\mathrm{c}}k_1'}{2}\Big([\mathrm{ClO}]_m^{\mathrm{obs}}[\mathrm{HO_2}]_m^{\mathrm{obs}} \\ &\quad +[\mathrm{ClO}]_{m+1}^{\mathrm{obs}}[\mathrm{HO_2}]_{m+1}^{\mathrm{obs}}\Big) \\ &\quad \times(t_{m+1}^{\mathrm{obs}}-t_m^{\mathrm{obs}}).\end{aligned} \tag{11}$$

In these equations, the rate constant of interest, ${}^{\mathrm{c}}k_1'$, and also $[\mathrm{ClO}](t_0)$ are considered as variable parameters. ${}^{\mathrm{c}}k_1'$ and $[\mathrm{ClO}](t_0)$ are determined by the minimization of the following function, χ^2, using the least-squares method:

$$\chi^2 = \frac{1}{N}\sum_{m=1}^{N}\left(\frac{\left([\mathrm{ClO}]_m^{\mathrm{calc}}-[\mathrm{ClO}]_m^{\mathrm{obs}}\right)^2}{\left(\sigma_m^{\mathrm{ClO}}\right)^2}\right) \tag{12}$$

Similarly, calculated errors of ${}^{\mathrm{c}}k_1'$ were obtained in parallel with the optimization of ${}^{\mathrm{c}}k_1'$ and $[\mathrm{ClO}](t_0)$.

4.4 Results

Figure 3 shows the calculated ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k_1'$ values in each modified local time interval.

In addition, the difference between ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k_1'$ is presented. We denote this difference by

$$\Delta k = |{}^{\mathrm{c}}k_1 - {}^{\mathrm{c}}k_1'|. \tag{13}$$

The horizontal and vertical axes are the start and end times of the considered time intervals, respectively. The blank area represents the time intervals where the data numbers are less than the threshold of 3000 or Δk values are greater than $5.0\times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$.

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 for the relation expressed in Eq. (1) to be fulfilled.

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

1. Range $\Delta k \sim 0\ \times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$: for the start time of 18:30–19:30 MLT and the end time of 01:45–04:00 MLT.
2. Range $\Delta k \sim 1.0\ \times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$: for the start time of 18:30–19:30 MLT the end time of 00:45–01:45 MLT or 04:00–06:00 MLT.
3. Range $\Delta k > 3.0\ \times10^{-12}\,\mathrm{cm^3\,molecule^{-1}\,s^{-1}}$: for the start time later than 20:00 MLT and the end time around 03:00 MLT.

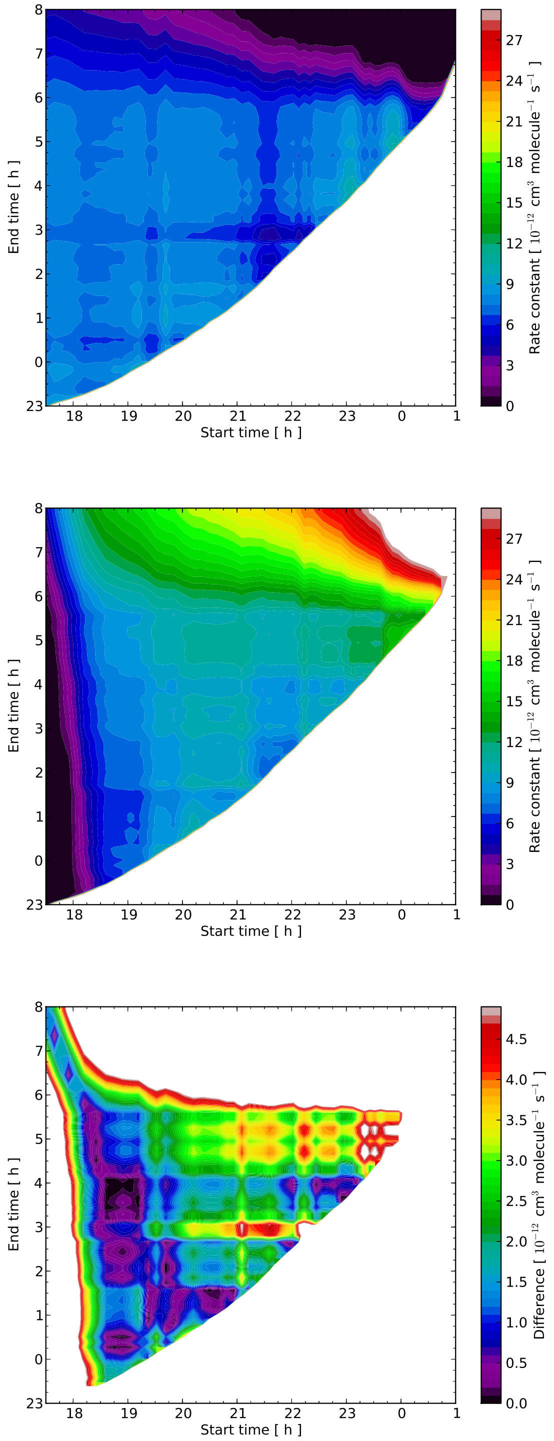

Fig. 3. Contour plots of ${}^{\mathrm{c}}k_1$ (top), ${}^{\mathrm{c}}k_1'$ (middle), and Δk (bottom) calculated from the SMILES observation data set. ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k_1'$ are calculated in time periods from each start time (horizontal axis) to each end time (vertical axis).

4. Another range $\Delta k > 3.0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}: for the start time later than 20:00 MLT and the end time later than 04:00 MLT.

Result 3 may be caused by two problems. One is the variability observed in the ClO data around 02:40 MLT. In Fig. 2, the ClO data around this modified local time show a relatively smaller number density compared to neighbouring modified local times (0.5×10^6 molecule cm^{-3} at 02:40 MLT while it is around 0.7×10^6 molecule cm^{-3} at neighbouring modified local times). Another one is the inhomogeneous local time sampling of SMILES in the extracted February–April data set. As shown in Fig. 2, the data for 21:00–00:00 MLT was quite evenly distributed throughout February, March, and April 2010, while that for 02:00–03:00 MLT mostly is from March 2010. Such a problem in result 2 between 00:45–01:45 MLT is also considered to be due to the inhomogeneous sampling.

The effect of photochemistry in the morning time causes relatively large Δk in the result 4 and the result 2. During sunrise ClO and HOCl start to decrease, and HO_2 starts to increase. This time range should be excluded from our analysis in order to ensure the purity of the Reaction (R1).

A good possibility exists that the modified local time interval of 18:30–04:00 MLT was the time in which the reaction $ClO + HO_2 \rightarrow HOCl + O_2$ predominantly occurred in the Cl_y chemistry. The sum of [ClO] and [HOCl] was near constant after 18:30 MLT in Fig. 2. However, as shown in Sect. 2, the model calculation suggested that the ClO production by HCl + OH $\rightarrow$ Cl + H_2O and Cl + O_3 $\rightarrow$ ClO + O_2 affected the sum of HOCl and ClO until 20:00 LT. The sum of HOCl and ClO in Fig. 1 increased by about 11 % after 18:30 LT. Thus, a noticeable difference occurred between the numerical analysis result using the SMILES observation data and the model calculation result. We considered this difference as caused by the following reason: although we used the modified local time to reduce effects of variabilities from latitude and season, some variabilities (e.g. water vapour) are still left. The ClO production by HCl + OH $\rightarrow$ Cl + H_2O and Cl + O_3 $\rightarrow$ ClO + O_2 might still remain between 18:30 and 19:30 MLT, but did not appear in the SMILES observations.

As a conclusion, we derived from the SMILES data set that the modified local time interval of 18:30–04:00 MLT 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 data set 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)

In the modified local time interval of 18:30–04:00 MLT, the derived ${}^{c}k_1$ and ${}^{c}k_1'$ range between 1.1 and 11.3×10^{-12} cm^3 molecule^{-1} s^{-1}. This variability includes the irrelevant results as discussed in Sect. 5.1. To reduce the effect of this variability on the estimation of k_1, for the following calculation we use the time range between start time of 18:30–19:30 MLT and end time of 03:00–04:00 MLT where the Δk according to Eq. (13) value is closest to zero in Fig. 3. Figure 4 is a magnified figure of the Δk shown in Fig. 3 in this time range. Δk is close to zero for start times near 18:30 MLT.

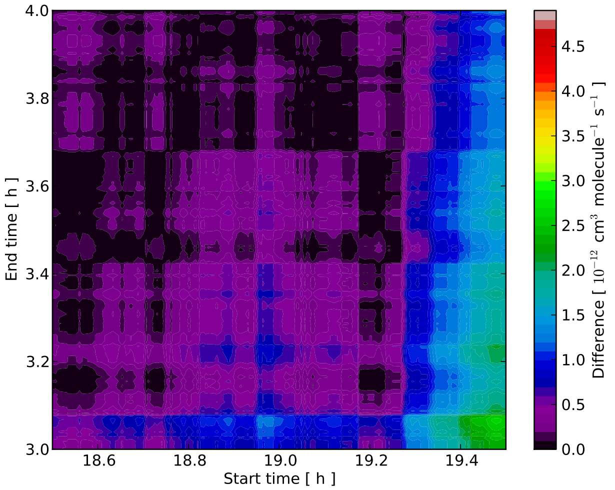

Fig. 4. The contour plot of Δk calculated from the SMILES observation data set between 18:30–19:30 and 03:00–04:30 MLT.

To estimate k_1 under the condition that Δk approaches zero, we calculated average values of ${}^{c}k_1$ and ${}^{c}k_1'$ under the condition of $\Delta k \leq x$, where x is a variable threshold ranging from 0.01 to 2.5×10^{-12} cm^3 molecule^{-1} s^{-1} in increments of 0.01×10^{-12} cm^3 molecule^{-1} s^{-1}. The average values of ${}^{c}k_1$ and ${}^{c}k_1'$ under the condition of $\Delta k \leq x$ are denoted as ${}^{c}\bar{k}_1(x)$ and ${}^{c}\bar{k}_1'(x)$, respectively. The calculation of the standard deviation, $\sigma_{{}^{c}\bar{k}_1(x)}$ and $\sigma_{{}^{c}\bar{k}_1'(x)}$, of ${}^{c}\bar{k}_1(x)$ and ${}^{c}\bar{k}_1'(x)$ was performed simultaneously.

Figure 5 shows the dependence of ${}^{c}\bar{k}_1(x)$, ${}^{c}\bar{k}_1'(x)$, $\sigma_{{}^{c}\bar{k}_1(x)}$, and $\sigma_{{}^{c}\bar{k}_1'(x)}$ on x. The values of ${}^{c}\bar{k}_1(x)$ and ${}^{c}\bar{k}_1'(x)$ and the values of $\sigma_{{}^{c}\bar{k}_1(x)}$ and $\sigma_{{}^{c}\bar{k}_1'(x)}$ converge in a case in which x approaches zero. We estimated the following limits:

$$\bar{k}_1(0) = \lim_{x \to 0} {}^{c}\bar{k}_1(x), \tag{14}$$

$$\bar{k}_1'(0) = \lim_{x \to 0} {}^{c}\bar{k}_1'(x), \tag{15}$$

$$\sigma_{\bar{k}_1(0)} = \lim_{x \to 0} \sigma_{{}^{c}\bar{k}_1(x)}, \tag{16}$$

$$\sigma_{\bar{k}_1'(0)} = \lim_{x \to 0} \sigma_{{}^{c}\bar{k}_1'(x)}. \tag{17}$$

In this estimation, we linearly extrapolated the results shown in Fig. 5 to $x = 0 \times 10^{-12}$ cm^3 molecule^{-1} s^{-1}. The dependence of $\bar{k}_1(0)$ and $\sigma_{\bar{k}_1(0)}$ on how to take the value of increments of x or to extrapolate is much smaller than 1 % of $\bar{k}_1(0)$ and $\sigma_{\bar{k}_1(0)}$, respectively. The differences between the results of Eqs. (14) and (15) and between the results of Eqs. (16)

and (17) are much smaller than 1 % of these limits. We used $\bar{k}_1(0)$ and $\sigma_{\bar{k}_1(0)}$ as the k_1 and 1σ provided by the SMILES observations, respectively:

$$k_1(245\,\mathrm{K})=(7.75\pm0.25)\times10^{-12}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}. \qquad (18)$$

Moreover, a comparison between the derived 1σ of k_1 and the uncertainties of ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$ calculated in Sects. 4.2 and 4.3 was performed. As described in Sect. 4, the uncertainties (calculated errors) of ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$ were calculated simultaneously with ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$, respectively. These uncertainties are denoted as $\sigma_{{}^{\mathrm{c}}k_1}$ and $\sigma_{{}^{\mathrm{c}}k'_1}$ hereafter. The average values of $\sigma_{{}^{\mathrm{c}}k_1}$ and $\sigma_{{}^{\mathrm{c}}k_1}$ in the time range between start time of 18:30–19:30 MLT and end time of 03:00–04:00 MLT are

$$\sigma_{{}^{\mathrm{c}}k_1} = 1.15 \pm 0.09(1\sigma)\ \times 10^{-12}\mathrm{cm}^3/\mathrm{molecule}^{-1}\ \mathrm{s}^{-1}, \qquad (19)$$

$$\sigma_{{}^{\mathrm{c}}k'_1} = 0.26 \pm 0.03(1\sigma)\ \times 10^{-12}\mathrm{cm}^3/\mathrm{molecule}^{-1}\ \mathrm{s}^{-1}. \qquad (20)$$

$\sigma_{{}^{\mathrm{c}}k_1}$ is larger than $\sigma_{{}^{\mathrm{c}}k'_1}$ because SMILES has less sensitivity to HOCl compared to ClO. If both $\sigma_{{}^{\mathrm{c}}k_1}$ and $\sigma_{{}^{\mathrm{c}}k'_1}$ are the standard deviations of a Gaussian distribution and ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$ are assumed to be statistically independent, then the joint distribution of ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$ is the product of two Gaussian distributions. A short calculation shows that the selection of ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k'_1$ according to the condition $\Delta k \leq x$ for $x \to 0$ yields a Gaussian distribution with the following standard deviation σ_{G}:

$$\frac{1}{\sigma_{\mathrm{G}}^2} = \frac{1}{\sigma_{{}^{\mathrm{c}}k_1}^2} + \frac{1}{\sigma_{{}^{\mathrm{c}}k'_1}^2}. \qquad (21)$$

σ_{G} was calculated to be $0.25 \times 10^{-12}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$, and is consistent with 1σ of k_1 given in Eq. (18). This confirms that a reasonable estimate for the precision of the derived reaction rate constant was obtained.

The derived 1σ error of k_1 is attributable to the 1σ precisions of [ClO], [HOCl], and [HO_2] which are caused by the random errors in the single-scan spectrum of SMILES. There are systematic errors in [ClO], [HOCl], and [HO_2] observed by SMILES. As described in Sect. 3, the systematic errors of ClO, HO_2, and HOCl are another error source of the derived k_1. The total impact on the rate constant of Reaction (R1) was estimated to be 4.3 % at maximum using 3 % for [ClO], [HO_2], and [HOCl] as the systematic errors (cf. Appendix A). Thus, the impact of systematic errors was slightly larger than that of the 1σ precision (3.3 %) of the derived k_1 in Eq. (18).

Figure 6 shows the time dependence of [HOCl] and [ClO] both for observations and calculations using the derived k_1 in Eq. (18). The lowest panel in Fig. 6 is the sum of observations ([HOCl] + [ClO]) and the sum of the optimized [HOCl](t_0) and [ClO](t_0). Both of them show good agreement with each other.

5.3 Comparison of k_1 with previous studies

We estimated k_1 using the SMILES atmospheric remote sensing data, which have advantages owing to the high instrumental sensitivity and the long line-of-sight of the limb measurement from space. We compared our derived k_1, hereafter denoted "SMILES k_1", with previous laboratory experiments (Stimpfle et al., 1979; Knight et al., 2000; Nickolaisen et al., 2000; Hickson et al., 2007), an ab initio calculation (Xu et al., 2003), and JPL 2011 recommendation (Sander et al., 2011).

Table 2. Comparison with previous studies.

Measurement method	k_1 (245 K)[a]	1σ[a]	P [Torr]
– Atmospheric measurement			
SMILES	7.75	0.25	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 $10^{-12}\,\mathrm{cm}^3\,\mathrm{molecule}^{-1}\,\mathrm{s}^{-1}$.
[b] Kovalenko et al. (2007) supported.
[c] von Clarmann et al. (2012) supported.

Figure 7 shows the comparison of k_1 from our work and that from previous works. To see the detail number at 245 K, which we analyse in the presented study, we summarized the k_1 values with 1σ errors in Table 2. 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 measurement of Nickolaisen et al. (2000) was performed under higher pressure (50–700 Torr), and the value of k_1 is larger than the other values which were performed under the condition of 0.21–1.7 Torr (except Stimpfle et al., 1979). A pressure dependence of the Reaction (R1) was noticed by Xu et al. (2003) due to the long lifetime of the reaction intermediate HOOOCl. As mentioned in Xu et al. (2003), the large value of Nickolaisen et al. (2000) might be caused by the pressure dependence.

The 1σ error of k_1 from the SMILES observation data is 2–10 times smaller than those of previous laboratory experiments at 245 K. In the laboratory experiments, the radical amount calibration is difficult because of the light source of the photolysis. The smaller 1σ error of the SMILES k_1 can be attributed to the fact that the SMILES k_1 was derived from the data set in which only the Reaction (R1) happened and other competitive radical reactions did not appear in the observation.

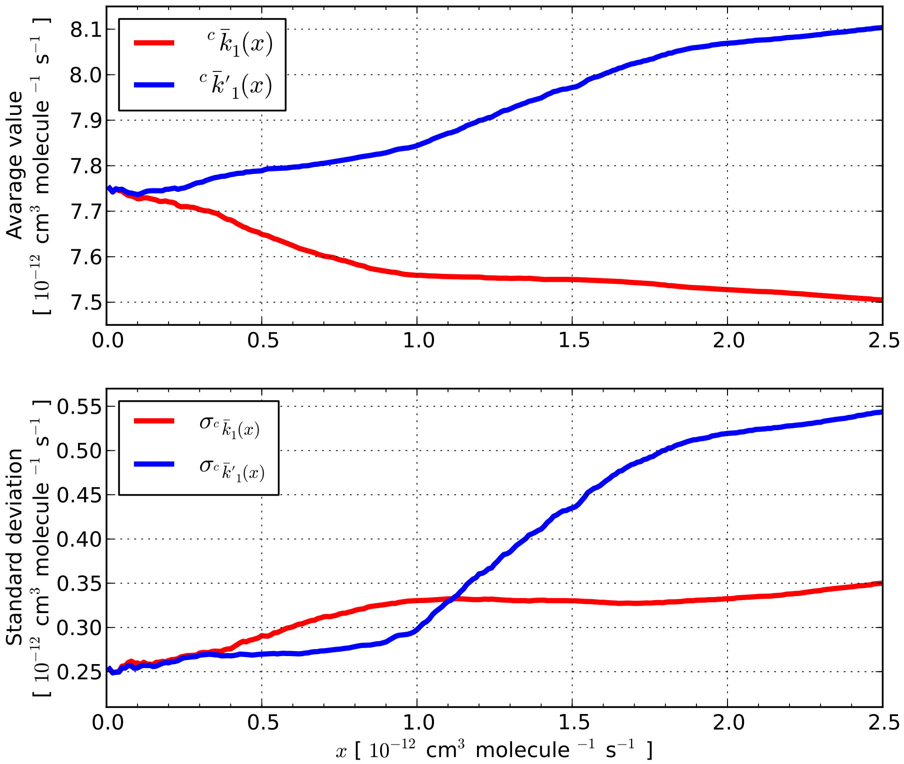

Fig. 5. The plot of the dependence of ${}^{c}\bar{k}_1(x)$ (blue) and ${}^{c}\bar{k}'_1(x)$ (red) on x in the time range between start time of 18:30–19:30 MLT and end time of 03:00–04:00 MLT (top). The plot of the dependence of $\sigma_{\bar{k}_1(0)}$ (blue) and $\sigma_{\bar{k}'_1(0)}$ (red) on x in the same time range (bottom).

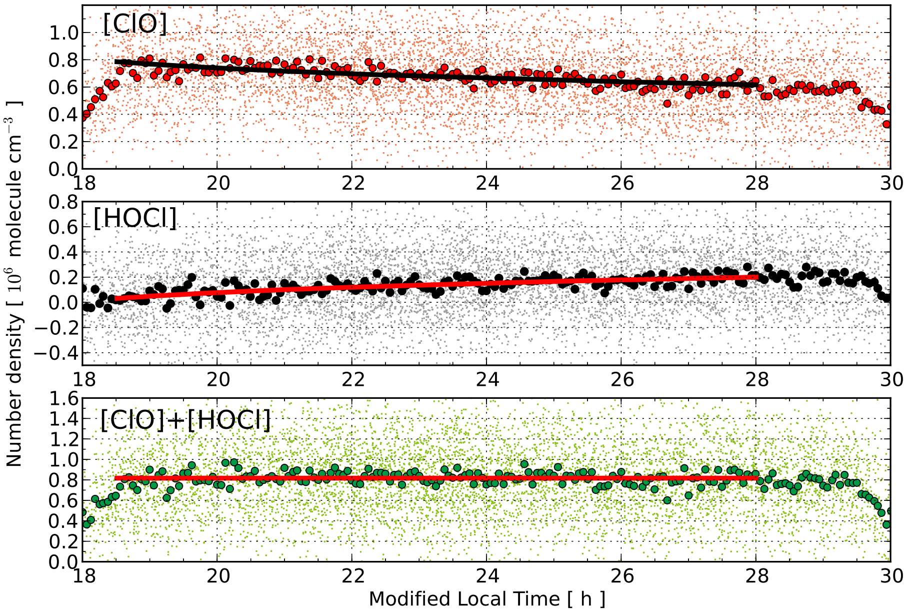

Fig. 6. Diurnal variation plot of ClO with average values (red) and calculation values using the rate constant of this work (black) in 0.28 hPa region (top). Diurnal variation plot of HOCl with average values (black) and calculation values using the rate constant of this work (red) in 0.28 hPa region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

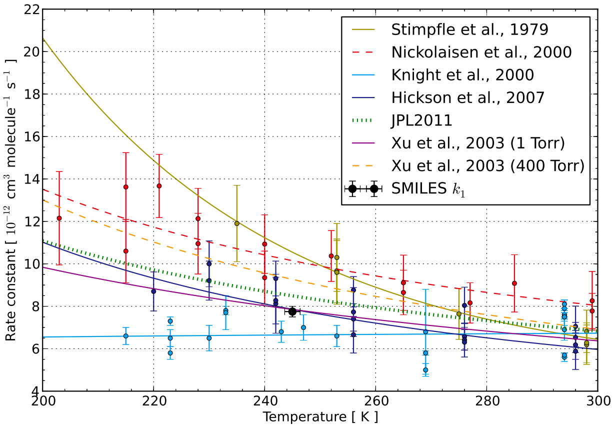

Fig. 7. Comparison with previous works. The dots and lines represented the experimental values from Stimpfle et al. (1979) (yellow), Knight et al. (2000) (red), Nickolaisen et al. (2000) (cyan), and Hickson et al. (2007) (blue). Further lines show the calculation values recommended by JPL 2011 (Sander 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 pressures (50–700 Torr) and lower pressures (≤ 5.0 Torr), respectively.

6 Conclusions

The model calculation of the chlorine partitioning suggests that the reaction ClO + HO_2 → HOCl + O_2 is the only reaction affecting HOCl after about 18:30 LT 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 in the mid-latitude between 20° S and 40° S at a temperature range of $245 \pm 1.4 (1\sigma)$ K, in the period from February to April 2010 was used for our study. We evaluated the purity of the Reaction (R1) at the 0.28 hPa pressure level (58 km) by checking the consistency between two reaction rates estimated from HOCl production and ClO loss using SMILES observation data. From the SMILES data set, we derived that the modified local time interval of 18:30–04:00 MLT is the time in which the reaction ClO + HO_2 → HOCl + O_2 purely happens in the Cl_y chemistry in the lower mesosphere. The SMILES k_1 was directly estimated using the remote sensing data with a long line-of-sight under the condition that the reaction ClO + HO_2 → HOCl + O_2 purely happened in the Cl_y chemistry. This condition could not have been achieved in the previous laboratory experiments and the previous stratospheric HOCl measurements. Based on these facts, we consider the SMILES k_1 to have an advantage over the results of previous studies, even though it is valid only for one temperature (245 K) and one pressure (0.28 hPa).

The rate constant of the reaction ClO + HO_2 → HOCl + O_2 is found to be $k_1 = (7.75 \pm 0.25) \times 10^{-12}$ cm^3 molecule^{-1} s^{-1} at 245 K. This is a 2–10 times better precision than that from laboratory measurements. The SMILES k_1 is consistent with that from the laboratory experiment of Hickson et al. (2007) and the ab initio calculations of Xu et al. (2003) for similar low-pressure conditions.

Appendix A

Estimation of the impact of systematic errors

In this Appendix, we describe the estimation of the impact of the systematic observation errors on the calculation of k_1.

We considered two different ways of implementing the systematic error: treating it as a constant offset term, or treating it as a term positively/negatively proportional to the amount of considered molecules. These two effects are expressed as follows:

$$[\mathrm{X}]^{\mathrm{bias}} = [\mathrm{X}]^{\mathrm{obs}} \times (1 \pm 0.03 \times B) \pm [\bar{\mathrm{X}}] \times 0.03 \times (1 - B), \qquad \text{(A1)}$$

where X is ClO, HO_2, or HOCl.

In this equation, $[\mathrm{X}]^{\mathrm{bias}}$ is the number density including the additional systematic errors of 3 %, $[\mathrm{X}]^{\mathrm{obs}}$ is the number density obtained from SMILES observations, B is the contribution ratio of the proportional term and the offset term, and $[\bar{\mathrm{X}}]$ is the average value of $[\mathrm{X}]^{\mathrm{obs}}$ in the time range between 18:30–04:00 MLT.

We estimated the total impact of the systematic errors on k_1 in the two cases of $B = 1$ (only the slope term) and $B = 0$ (only the base line term) by the following method: we calculated two rate constants, ${}^{\mathrm{c}}k_1^{\mathrm{bias}}$ and ${}^{\mathrm{c}}k_1^{\prime\mathrm{bias}}$, including the systematic errors given in Eq. (A1) using the same method as for the calculations of ${}^{\mathrm{c}}k_1$ and ${}^{\mathrm{c}}k_1^{\prime}$ in Eqs. (6)–(8) and (10)–(12) with respect to each molecule. The rate constant, k_1^{bias}, including the systematic errors given in Eq. (A1) was estimated from ${}^{\mathrm{c}}k_1^{\mathrm{bias}}$ and ${}^{\mathrm{c}}k_1^{\prime\mathrm{bias}}$ using the same method as for the estimation of the k_1 in Eq. (18). The impact of including the systematic errors given in Eq. (A1) was calculated from the difference between k_1^{bias} and the k_1 in Eq. (18) with respect to each molecule. The total impact of including the systematic errors was calculated from the root-sum-square of impacts of the systematic errors for each molecule. Table A1 shows the impacts of the systematic errors. The total impact for the rate constant of Reaction (R1) was estimated to be up to 4.3 % using 3 % for [ClO], [HO_2], and [HOCl] as the systematic errors.

Table A1. Impacts of the systematic errors.

	systematic errors	Proportional term ($B = 1$)	Offset term ($B = 0$)
ClO	3 %	2.2 %	2.9 %
HO_2	3 %	3.0 %	3.0 %
HOCl	3 %	2.2 %	0.0 %
Total		4.3 %	4.2 %

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