

# Answers for comments from Dr. D. G. Johnson,

We appreciate you very much the careful peer review and constructive comments on this study. All the comments are very valuable for us to improve the quality of this study. We would like to address your comments as follows. Page numbers and line numbers of the text denote these of the revised manuscript.

In the answer, we use following notations about rate constant:

- ${}^c k_1$ : Rate constants calculated from HOCl production. The symbol of  ${}^c$  means calculated.
- ${}^c k'_1$ : Rate constants calculated from ClO loss. The symbol of  ${}^c$  means calculated.
- $k_1$ : Rate constant of Reaction (R1) estimated from  ${}^c k_1$  and  ${}^c k'_1$  using the threshold of  $\Delta k = |{}^c k_1 - {}^c k'_1|$ .

## Specific Comments

### 1 Threshold, $\Delta k = |{}^c k_1 - {}^c k'_1|$

Your first question is about the threshold,  $\Delta k = |{}^c k_1 - {}^c k'_1|$  as follows:

**Q1** I have two concerns with the discussion of uncertainties in this paper. The Authors have estimated the rate constant  $k_1$  using HOCl, ClO, and HO<sub>2</sub> ( $k_1$ ), and using only ClO and HO<sub>2</sub> ( $k'_1$ ). They look at  $\Delta k = |k_1 - k'_1|$ , select a time period where the  $\Delta k$  is small, then further select only data for which  $\Delta k$  is less than a threshold value before looking at the distribution of remaining  $k_1$  values to estimate the statistical error. It is not clear to me that after already selecting for small  $\Delta k$  one will not be biased towards a small spread in the remaining  $k_1$  and wind up underestimating the statistical uncertainty

**A1:** We used the threshold  $\Delta k \leq 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  to estimate the rate constant of Reaction (R1), and the deviation of  ${}^c k_1$  and  ${}^c k'_1$  under this threshold was considered as the  $1\sigma$  precision of the derived rate constant in the manuscript. We agree that the values of the rate constant of Reaction (1) and the  $1\sigma$  depend on the value of the threshold (See Fig. 3). The usage of this threshold is essential to derive a reliable rate constant in our analysis.

As described in the manuscript, we focused to the modified local time range of  $19.0 \pm 0.7 - 3.6 \pm 0.7$  hr at which we consider that the purity of Reaction (1). This time range was roughly determined for convenience sake, therefore there exist many data which  ${}^c k_1$  and  ${}^c k'_1$  are not identical (see Fig. 1). In fact, the probability distributions of  ${}^c k_1$  and  ${}^c k'_1$  within this time range show quite (without any data selection with respect to  $\Delta k$ ) inhomogeneous distribution (Fig. 2): values of  $7.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  or less are only composed of  ${}^c k_1$ , and values of  $8.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  or more are only composed of  ${}^c k'_1$ .

The mean value of all the  ${}^c k_1$  and  ${}^c k'_1$  collected from this modified local time range (without any data selection with respect to  $\Delta k$ ) is  $7.80 \pm 0.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ . However, we consider that this standard deviation  $0.45 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  certainly overestimates the precision of the derived reaction rate because of the contamination of such inconsistent  ${}^c k_1$  and  ${}^c k'_1$ .

What we consider is that the reasonable estimate for the precision of the derived reaction rate can be obtained from the uncertainty of "each"  ${}^c k_1$  and  ${}^c k'_1$  derivation. This uncertainty is calculated via the chi square functions of Eq (8) and (12) of the manuscript. The  $\sigma_{\text{HOCl}_m}$  at Eq (8) and  $\sigma_{\text{ClO}_m}$  at Eq (12) yield the uncertainty of the derived  $\sigma_{\text{HOCl}_m}$ , respectively (hereinafter denoted as  $\sigma_{{}^c k_1}$  and  $\sigma_{{}^c k'_1}$ ). The mean values of  $\sigma_{{}^c k_1}$  and  $\sigma_{{}^c k'_1}$  for the local time range of  $19.0 \pm 0.7 - 3.6 \pm 0.7$  hr are:

$$\sigma_{{}^c k_1} = 1.15 \pm 0.09(1\sigma)[\times 10^{-12} \text{ cm}^3 / \text{molecule}^{-1} \text{ s}^{-1}] \quad (1)$$

$$\sigma_{{}^c k'_1} = 0.26 \pm 0.03(1\sigma)[\times 10^{-12} \text{ cm}^3 / \text{molecule}^{-1} \text{ s}^{-1}] \quad (2)$$

1  $\sigma_{c_{k_1}}$  becomes larger than  $\sigma_{c_{k'_1}}$  because SMILES has less sensitivity to HOCl compared to ClO. In order  
 2 to take full advantage of SMILES high sensitivity, we considered using  $\sigma_{c_{k'_1}}$  for the precision of the  
 3 reaction rate estimation instead of using  $\sigma_{c_{k_1}}$ . Then the  $\Delta k$  threshold was determined with the value  
 4 that gives the “ variation ” of  $c_{k_1}$  and  $c_{k'_1}$  equal to the mean uncertainty of individual  $c_{k'_1}$  derivation  
 5 ( $\sigma_{c_{k'_1}}$ ).

6 Figure 3 shows the threshold dependence of the mean value and variation of  $c_{k_1}$  and  $c_{k'_1}$  in the  
 7 modified local time range of  $19.0 \pm 0.7$  -  $3.6 \pm 0.7$  hr. The value of  $\Delta k$  threshold was to be  $0.1 \times 10^{-12}$   
 8  $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  from Fig. 3.

9 In summary, the criteria on  $\Delta$  is required to evaluate a more reliable reaction rate in our analysis,  
 10 and its threshold is determined to have a reasonable extent of  $c_{k_1}$  and  $c_{k'_1}$  variation. We added the  
 11 detail explanation on the manuscript (page 7, line 62 - 8, 2).

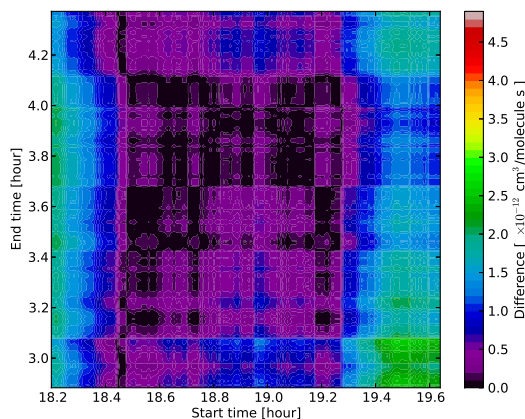


Figure 1: The contour plot of  $\Delta k$  calculated in from the SMILES observation data set between MLT 18:10 - 19:40 and MLT 02:50 - 04:20.

## 12 2 Systematic error analysis

13 Your second question is about the systematic error as follows:

14 **Q2** My bigger concern is that the authors have not considered other sources of bias in their estimate  
 15 of  $k_1$ . Anything that causes a bias in the measurement of ClO, HOCl, or HO<sub>2</sub> number density  
 16 will cause a bias in the estimate of  $k_1$ . Potential sources of bias include errors in the assumed  
 17 atmospheric temperature profile, antenna elevation angle, line strength parameters, interfering  
 18 species, and instrument calibration. The total systematic uncertainty (bias) in the constituent  
 19 profiles needs to be included in the analysis and added to the statistical uncertainty in  $k_1$  before  
 20 the results presented here can be compared to previous work.

21 **A2:** We agree that the discussion about the accuracy of the analysis is very important. We updated  
 22 the manuscript with including new paragraphs (at page 3, line 70–78) to clarify our thought about the  
 23 accuracy. The systematic error (bias uncertainty) of SMILES NICT ClO data for the single measurement  
 24 has been estimated by Sagawa et al. (2013). It is about 3% at 0.28 hPa for the mid-latitude nighttime  
 25 condition by the maximum. Using the same method with the ClO error analysis, we newly estimated  
 26 the systematic errors for HOCl and HO<sub>2</sub>: 10% and 9%, respectively, at 0.28 hPa for the mid-latitude

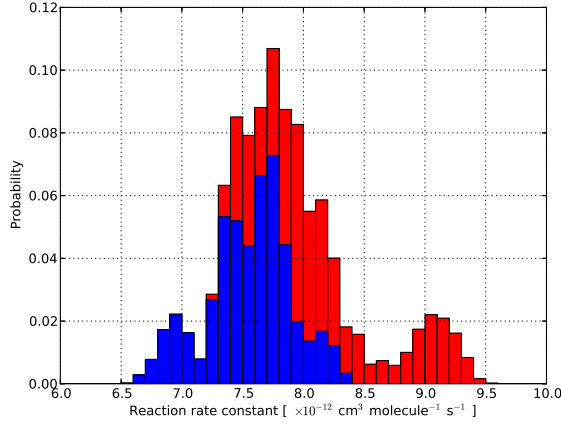


Figure 2: The probability plot of  $k_1$ (blue) and  $k'_1$ (red) in the modified local time range of  $19.0 \pm 0.7 - 3.6 \pm 0.7$  hr.

1 nighttime condition by the maximum. It should be noted here that this systematic error estimation is  
 2 carried out based on forward model simulations without taking the SMILES actual instrumental noise  
 3 into account. For the real SMILES measurements, the individual retrieval of HOCl and HO<sub>2</sub> contains  
 4 random errors (such as  $\sigma_{\text{HOCl}_m}$ ) much larger than these estimated systematic errors. It is considered  
 5 that the way how systematic errors appears in our reaction rate derivation is not that simple. If we  
 6 mechanically consider the systematic errors of ClO, HOCl, and HO<sub>2</sub> of 3%, 10%, and 9%, then it turned  
 7 out that there are no dataset which satisfy  ${}^c k_1 \simeq {}^c k'_1$ : this breaks the premise of our analysis, and we  
 8 consider it is not appropriate to employ such a case for the accuracy evaluation. Contrary to HOCl and  
 9 HO<sub>2</sub>, ClO has been measured by SMILES with a relatively high signal to noise ratio ( $S/N \sim 4$ ) and is  
 10 more sensitive to the systematic error. In this study, we consider that the systematic errors of HOCl  
 11 and HO<sub>2</sub> are sufficiently smaller than the systematic error of the ClO.

12 The impact of the systematic errors of ClO, HOCl, and HO<sub>2</sub> is evaluated as follows:

$${}^b[\text{ClO}] = [\text{ClO}]^{\text{obs}} \times (1 + a) \quad (3)$$

$${}^b[\text{HO}_2] = [\text{HO}_2]^{\text{obs}} \times (1 + b) \quad (4)$$

$${}^b[\text{HOCl}] = [\text{HOCl}]^{\text{obs}} \times (1 + c) \quad (5)$$

13 In these equation,  $a$ ,  $b$ , and  $c$  are the systematic errors of ClO, HO<sub>2</sub>, and HOCl, respectively. We  
 14 denoted  ${}^b[\text{ClO}]$ ,  ${}^b[\text{HO}_2]$ , and  ${}^b[\text{HOCl}]$  as values including the systematic errors, respectively.

15 The numerical solution for the calculation of the rate constant based on the HOCl production using  
 16 Eq. (5) is given as;

$${}^b[\text{HOCl}]_0^{\text{calc}} = [\text{HOCl}](0) \quad (6)$$

$${}^b[\text{HOCl}]_{m+1}^{\text{calc}} = {}^b[\text{HOCl}]_m^{\text{calc}} + \frac{{}^b k_1}{2} \left( ({}^b[\text{ClO}]_m \cdot {}^b[\text{HO}_2]_m) + ({}^b[\text{ClO}]_{m+1} \cdot {}^b[\text{HO}_2]_{m+1}) \right) \times (t_{m+1}^{\text{obs}} - t_m^{\text{obs}}) \quad (7)$$

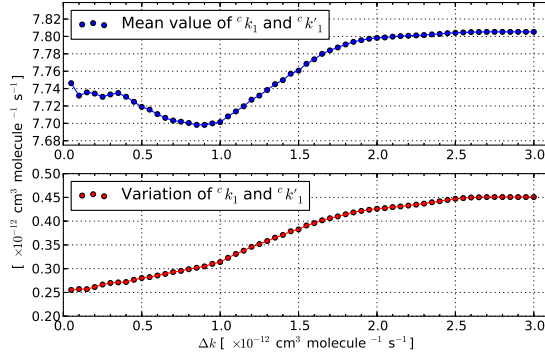


Figure 3: The threshold dependence of the mean value of  ${}^c k_1$  and  ${}^c k'_1$  (top) and the variation of  ${}^c k_1$  and  ${}^c k'_1$  (bottom) in the modified local time range of  $19.0 \pm 0.7 - 3.6 \pm 0.7$  hr.

- 1 In this equation, we denote the rate constant of HOCl increase using Eq. (5) as  ${}^b k_1$ .  ${}^b k_1$  and  $[\text{HOCl}](0)$   
 2 are determined by minimizing the following function  $\chi^2$ :

$$\chi^2 = \frac{1}{N} \sum_{m=1}^N \left( \frac{({}^b[\text{HOCl}]_m - {}^b[\text{HOCl}]_m^{\text{calc}})^2}{(\sigma_m^{\text{HOCl}})^2} \right) \quad (8)$$

- 3 Also the calculation function of the ClO decrease and evaluation function are performed using Eq.  
 4 (5) as following equations;

$$\begin{aligned} {}^b[\text{ClO}]_0^{\text{calc}} &= Y_0 \\ {}^b[\text{ClO}]_{m+1}^{\text{calc}} &= [\text{ClO}]_m^{\text{calc}} \\ &\quad - \frac{{}^b k'_1}{2} \left( ({}^b[\text{ClO}]_m \cdot {}^b[\text{HO}_2]_m) + ({}^b[\text{ClO}]_{m+1} \cdot {}^b[\text{HO}_2]_{m+1}) \right) \times (t_{m+1}^{\text{obs}} - t_m^{\text{obs}}) \end{aligned} \quad (9)$$

$$(10)$$

$$\chi^2 = \frac{1}{N} \sum_{m=1}^N \left( \frac{({}^b[\text{ClO}]_m^{\text{calc}} - {}^b[\text{ClO}]_m)^2}{(\sigma_m^{\text{ClO}})^2} \right) \quad (11)$$

- 5 In this equation, we denote the rate constant of ClO decrease using Eq. (5) as  ${}^b k'_1$ .  
 6 We calculated two rate constants,  ${}^b k_1$  and  ${}^b k'_1$ , using following value as the systematic error;

$$a = 3\% \quad (12)$$

$$b = 1\% \quad (13)$$

$$c = 1\% \quad (14)$$

$$(15)$$

- 7 The value of the systematic error of ClO is the maximum value obtained from the error analysis. Also  
 8 the values of the systematic errors of  $\text{HO}_2$  and HOCl are determined by the reason that we consider

1 that the systematic errors of HOCl and HO<sub>2</sub> are sufficiently smaller than the systematic error of the  
 2 ClO.

3 The difference between  ${}^b k_1$  and  ${}^b k'_1$ ,  ${}^b \Delta k = |{}^b k_1 - {}^b k'_1|$ , is shown in Fig. 4. The horizontal and  
 4 vertical axes are the start and end time of the considered time intervals, respectively. The blank area  
 5 represents the time intervals where the data numbers are less than our threshold.

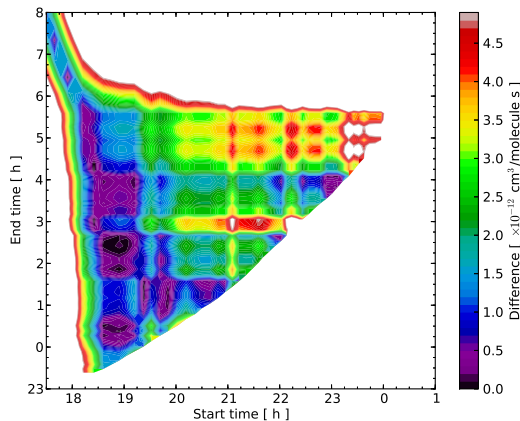


Figure 4: The contour plot of the difference between  ${}^b k_1$  and  ${}^b k'_1$ ,  $\Delta k = |{}^b k_1 - {}^b k'_1|$  in each local time interval.

6 We estimated the rate constant of the Reaction (R1) from Fig. 4 obtained using values of Eq. (15).  
 7 To estimate the rate constant of the Reaction (R1), we used following conditions:

- 8 1. Time range of 18.5 - 4.0 (same with our estimated pure reaction period)
- 9 2. Threshold of  $\Delta k = |{}^b k_1 - {}^b k'_1| \leq 0.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$  (same with our estimated  
 10 threshold)

11 The rate constant of the Reaction (R1) was obtained to be  $\bar{k}_1 = 7.49 \pm 0.73(1\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$   
 12  $\text{s}^{-1}$  at 245 K. To distinguish the rate constant of the Reaction (R1) including the systematic errors,  
 13 we denoted  $\bar{k}_1$ . Also the SMILES  $k_1$  was obtained to be  $k_1 = 7.73 \pm 0.26(1\sigma) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$   
 14  $\text{s}^{-1}$ . The value of  $\bar{k}_1$  is consistent with one of  $k_1$  within the  $1\sigma$  error of  $k_1$ . There is the effect of the  
 15 systematic errors in Eq. (15) within the range of  $\sigma_k$  of  $k_1$ .

16 The conclusion of this section is as follows: The maximum systematic error from the single scan  
 17 spectrum of SMILES was estimated to be 3%, 10%, and 9% for ClO, HO<sub>2</sub>, and HOCl, respectively  
 18 in the night time at 0.28 hPa by using theoretical error analysis based on forward model simulations  
 19 without taking account the actual random noise component. On the other hand, the signal to noise ratio  
 20 of the single scan spectrum of SMILES was about 4, 1, and 1 for ClO, HO<sub>2</sub>, and HOCl, respectively  
 21 in the night time at 0.28 hPa. We consider that the systematic error estimated is sufficiently apparent  
 22 only for ClO but HOCl and HO<sub>2</sub>, since ClO has been measured by SMILES with a relatively high signal  
 23 to noise ratio. The impact of the systematic errors of ClO, HOCl, and HO<sub>2</sub> is estimated using values of  
 24 3% of ClO, 1% of HO<sub>2</sub>, and 1% of HOCl as the systematic errors with taking account the signal to noise  
 25 ratio. The estimated rate constant of the Reaction (R1) including the systematic errors is consistent  
 26 with  $k_1$  within  $1\sigma$ . We added the detail explanation on the manuscript (page 8, line 11–28).

1 **Technical comments**

2 **Page 12800, line 4: "Purity" should be "purity" Page 12803**

3 We changed the manuscript as you mentioned (Page.2, Line30)

4 **Page 12803, line 10: change "by by" to "by"**

5 We changed the manuscript as you mentioned (Page.3, Line44)

6 **Page 12803, next to last paragraph: the authors talk about the variance**  
7 **being larger than the "1-sigma error precision" This statement is confusing,**  
8 **since the variance is the square of the standard deviation (usual meaning of**  
9 **1-sigma precision.)**

10 We changed the manuscript as you mentioned (Page.3 ,Line65)

11 **Page 12806, Eq. 7: While I don 't object to this being called the function**  
12 **chi, it is more commonly called the reduced chi-square. I also believe the**  
13 **sum should run from 1 to N, not 0 to N**

14 We changed the manuscript as you mentioned (Page.4, Line81)

15 **Page 12807, Eq. 10 See comment above for Eq. 7**

16 We changed the manuscript as you mentioned (Page.6, Line14)