# Evaluation of ClO+ $HO_2$ -> HOCl + $O_2$ reaction in the atmosphere by SMILES observations

7th Atmospheric Limb Conference
LIMB-13
This presentation participates in the student award contest

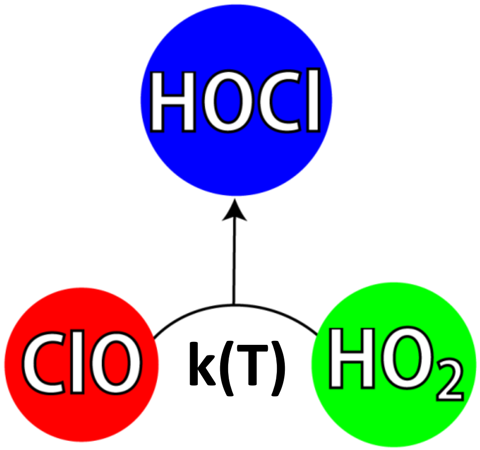
K. Kuribayashi[1,2], H. Sagawa[2], R. Lehmann[3], T. O. Sato[1,2], and Y. Kasai[1,2]

[1]Tokyo Institute of Technology
[2]National Institute of Information and Communications Technology
[3]AlfredWegener Institute for Polar and Marine Research

The 7th International Atmospheric Limb Conference and Workshop, 17-19, 6, 2013

# The role of $ClO + HO_2 \rightarrow HOCl + O_2$ reaction in the stratospheric chemistry

**Short-lived reservoir**



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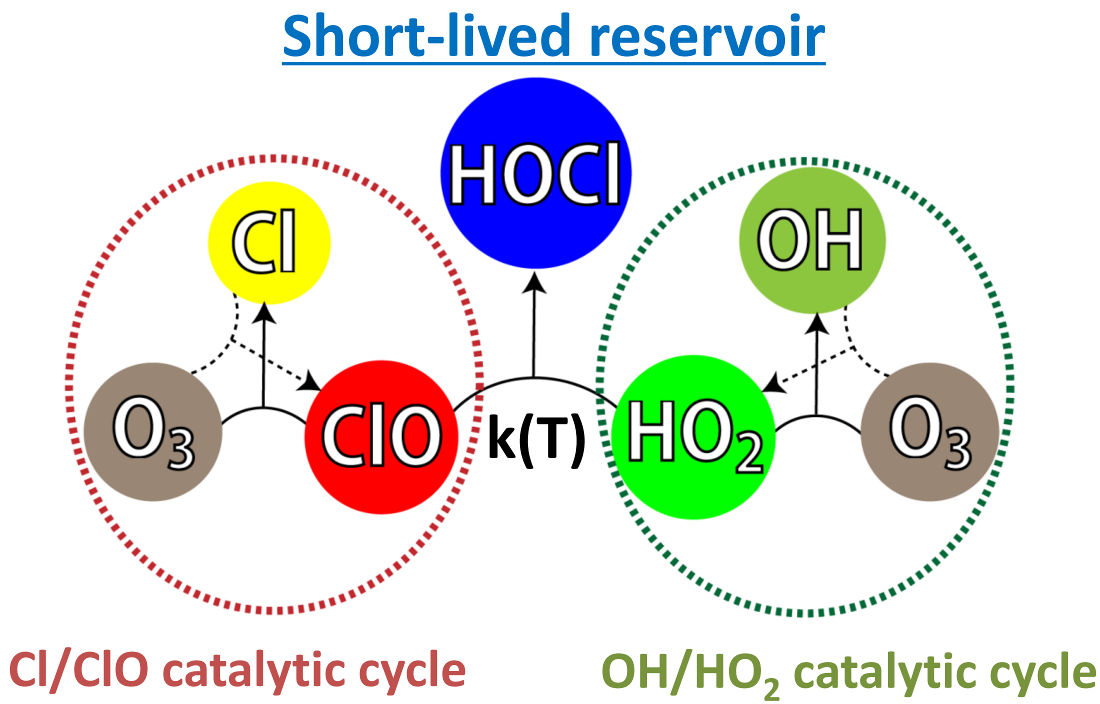

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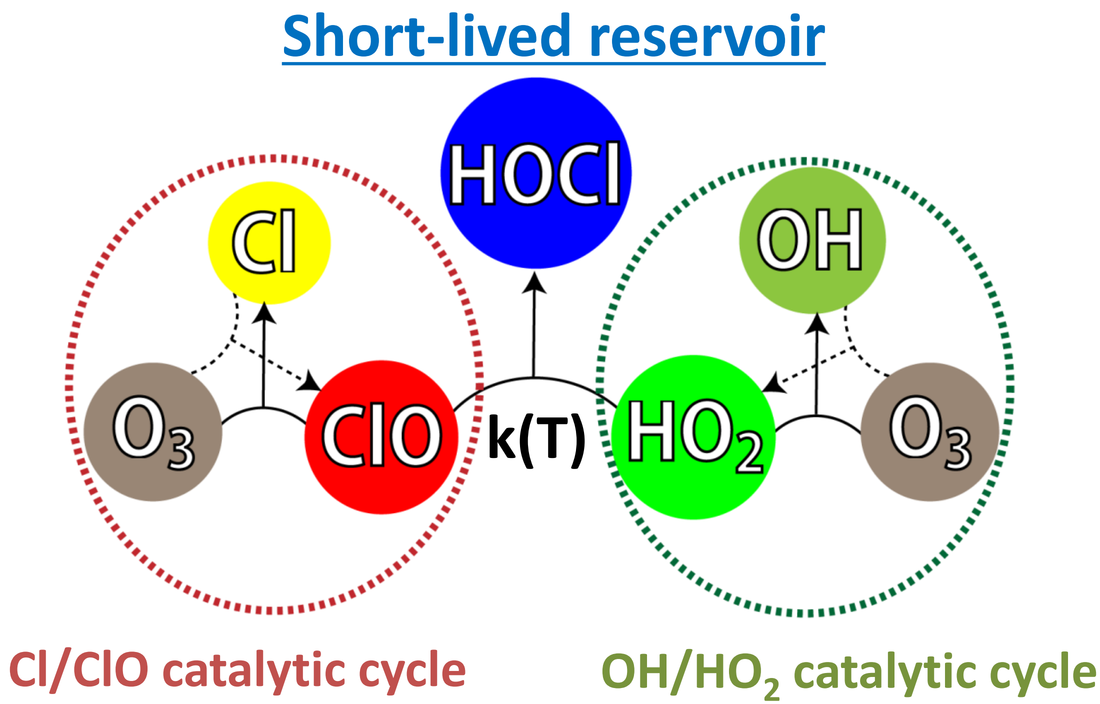
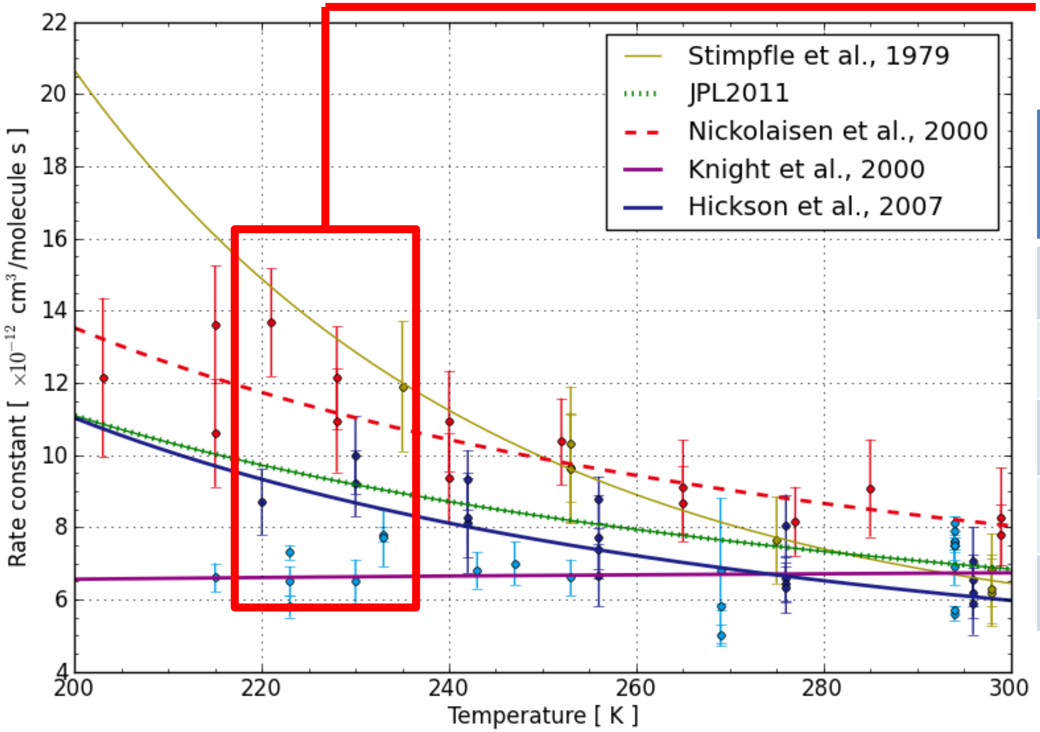



The quantitative understanding of the rate constant of $ClO + HO_2 \rightarrow HOCl + O_2$ is essential for the understanding of the effect of HOCl.

# Current summary of *k*(T) of $ClO + HO_2 \rightarrow HOCl + O_2$ reaction




**Large discrepancies of *k***
in mid-latitude middle stratosphere.

| Laboratory measurements | *k*(225K)[a] | 1σ[a] |
|---|---|---|
| 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 |
| JPL 2011 | 9.44 | 1.41 |

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

**Approximately two times different!!**

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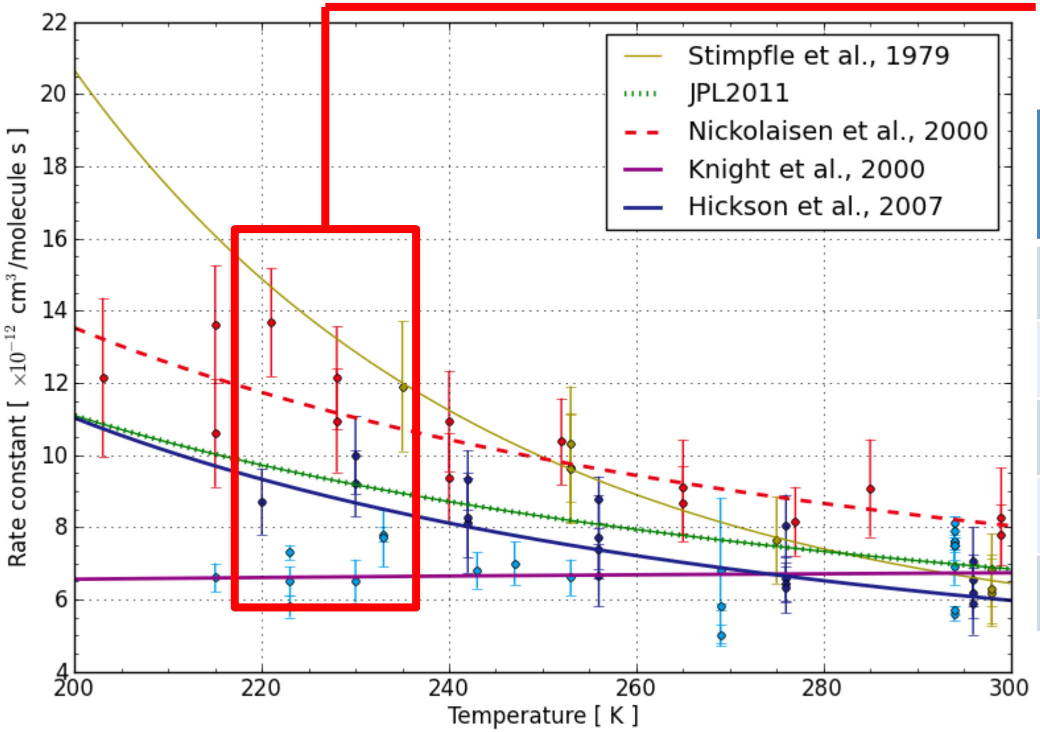


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These large discrepancies in laboratory measurements are caused by the difficulty of the radical (ClO) – radical ($HO_2$) reaction in larboratory

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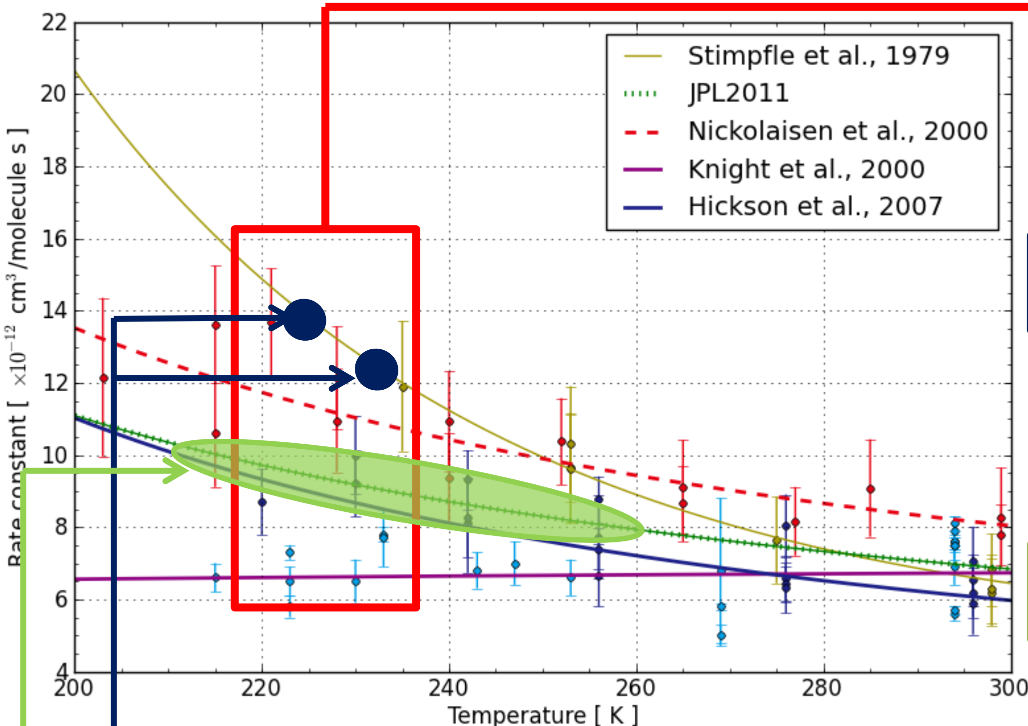


FIRS-2 and MkIV observation (Kovalenko et al., 2007)

MIPAS observation (von Clarmann et al, 2012)

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**Two *k*(T) supported from stratospheric observations are different!!**

The … ory r…

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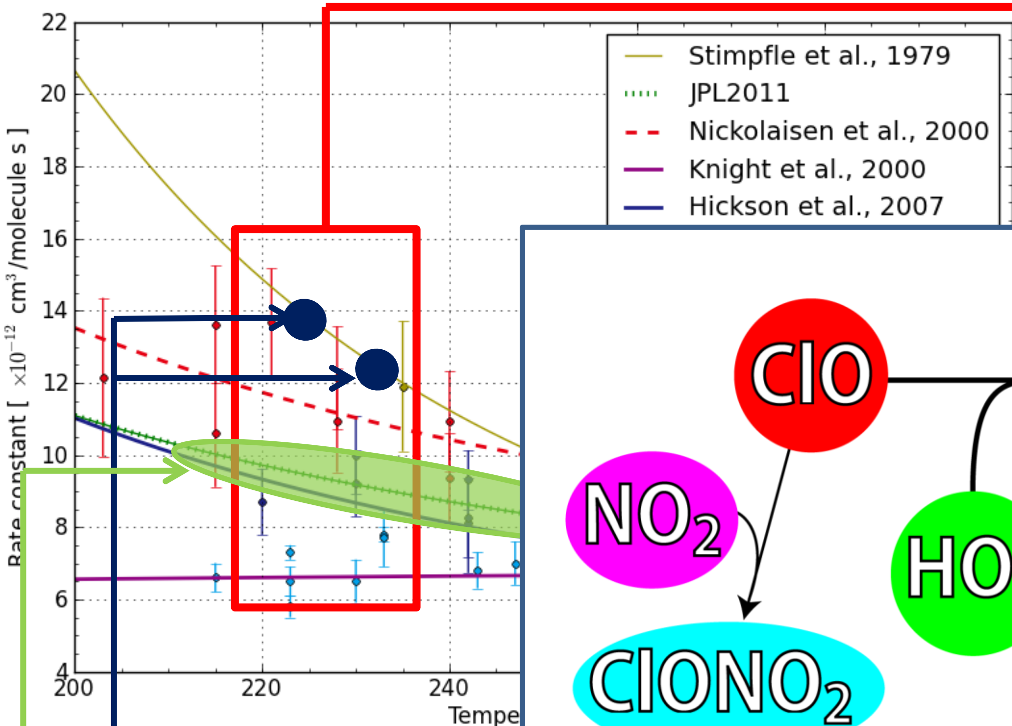


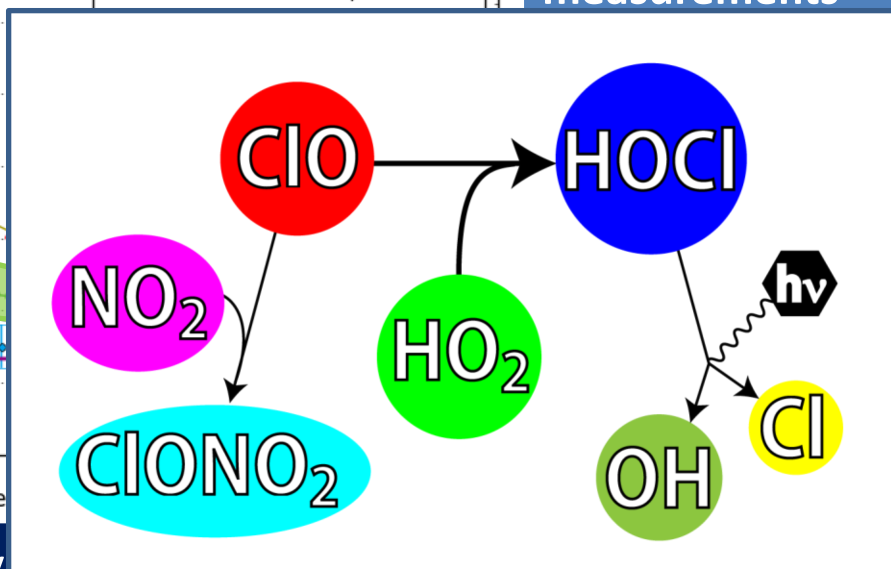


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# "Purity" of $ClO + HO_2 \rightarrow HOCl + O_2$ reaction

The "Purity" means that only $ClO + HO_2 \rightarrow HOCl + O_2$ reaction modifies the concentration of ClO and HOCl, and no competitive reaction exists.

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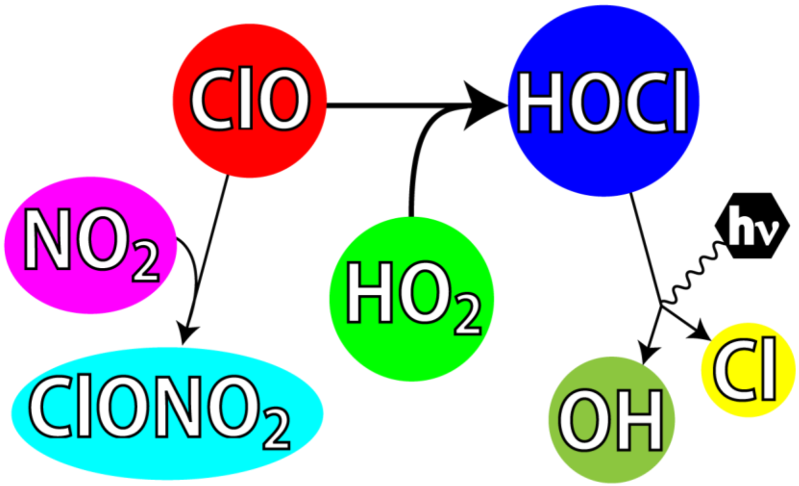
"Is there the pure $ClO + HO_2 \rightarrow HOCl + O_2$ reaction period in actual atmosphere? "



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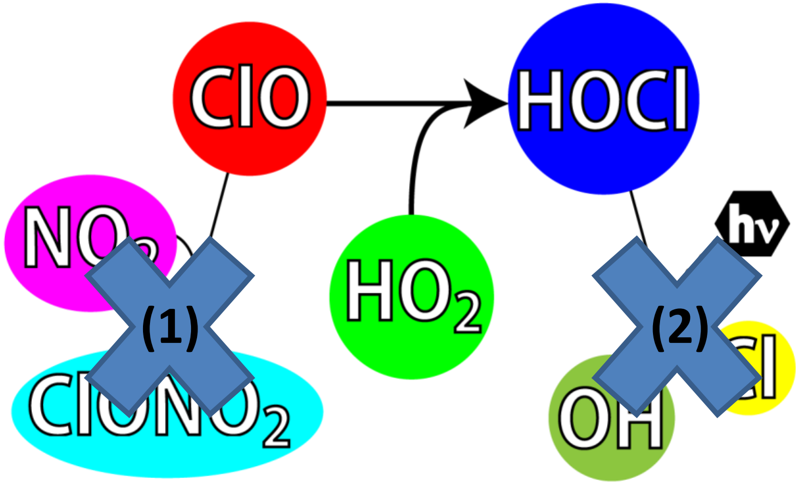


1) Lower mesosphere! 2)Nighttime!

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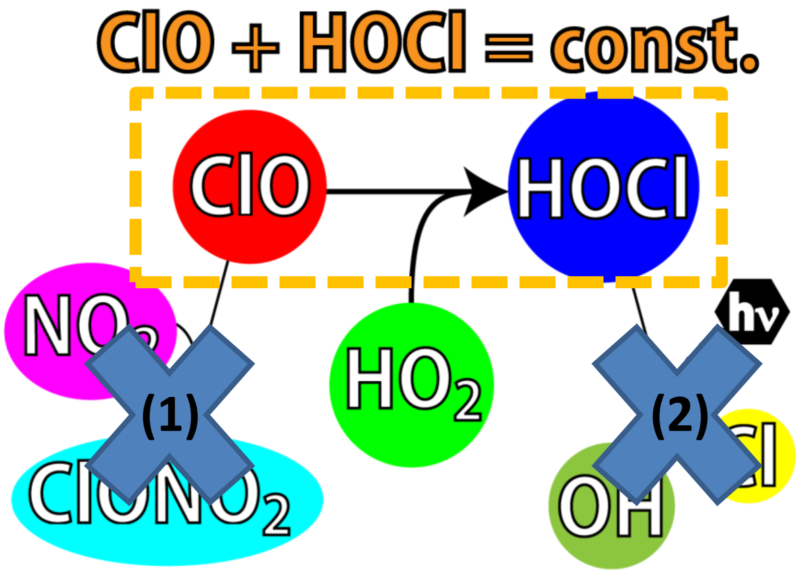


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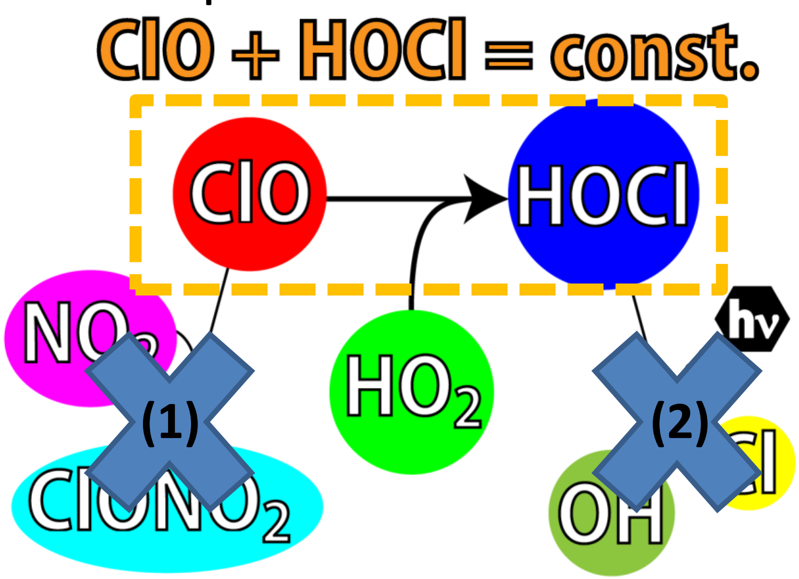
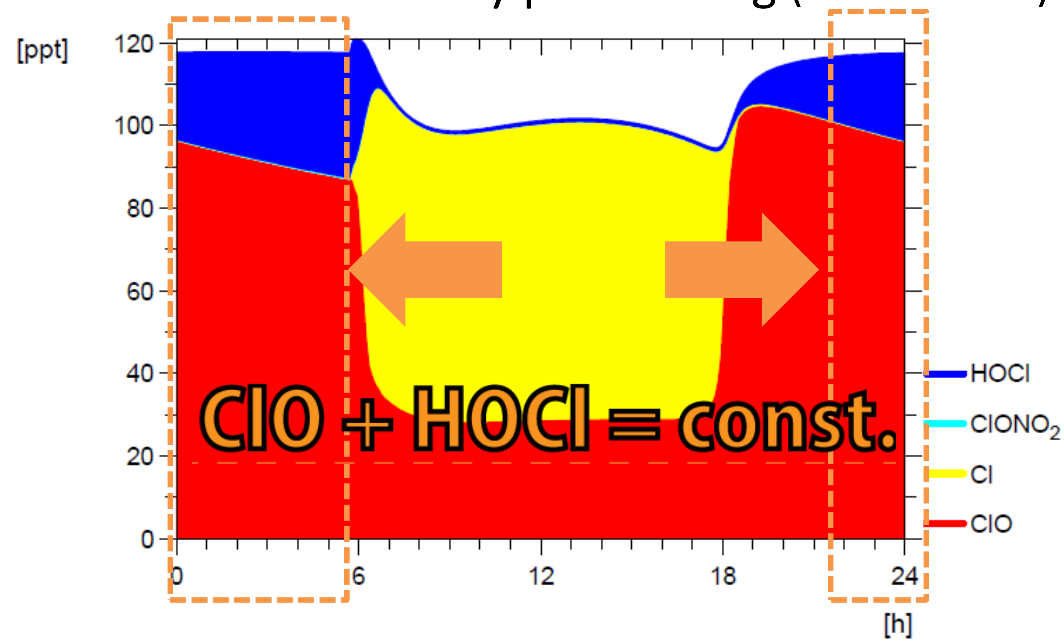



1) Lower mesosphere! 2)Nighttime!

Model calculation of Cly partitioning (HCl omitted)




Latitude : 30°S , Height: 58km, Period: 31, March

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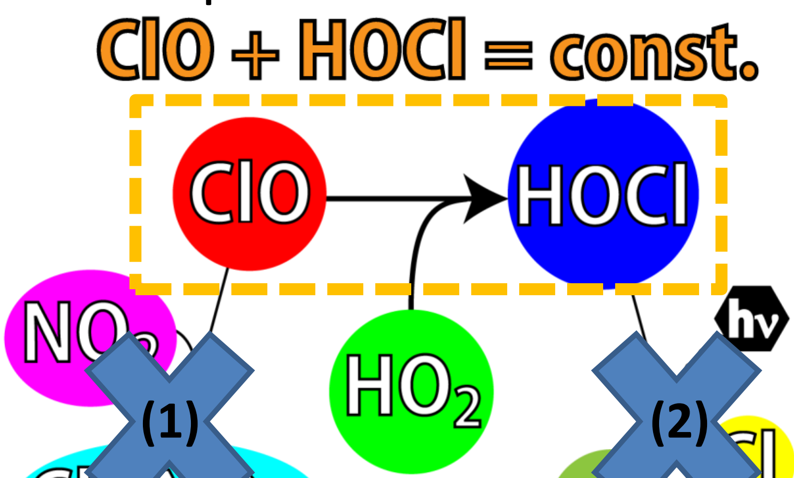


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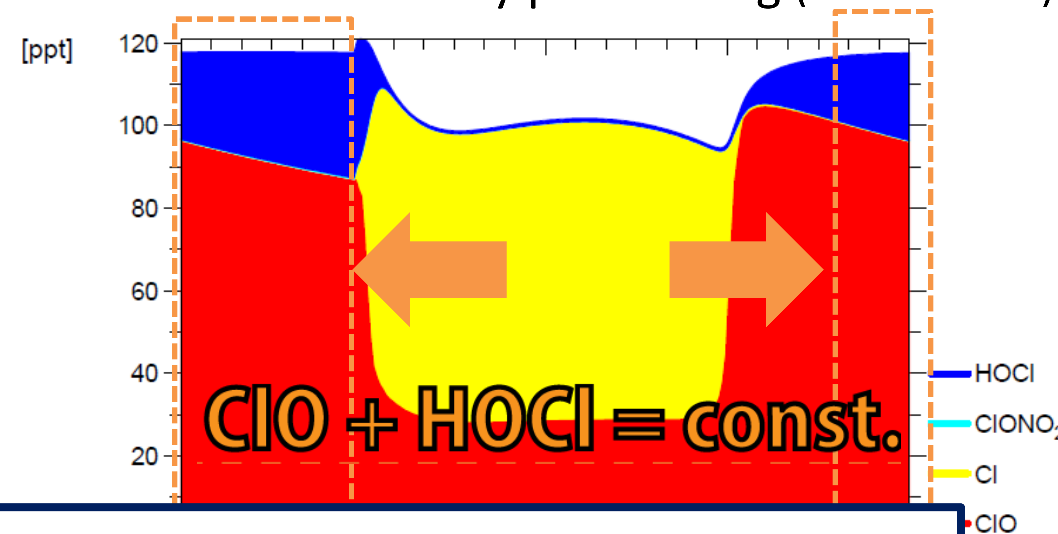
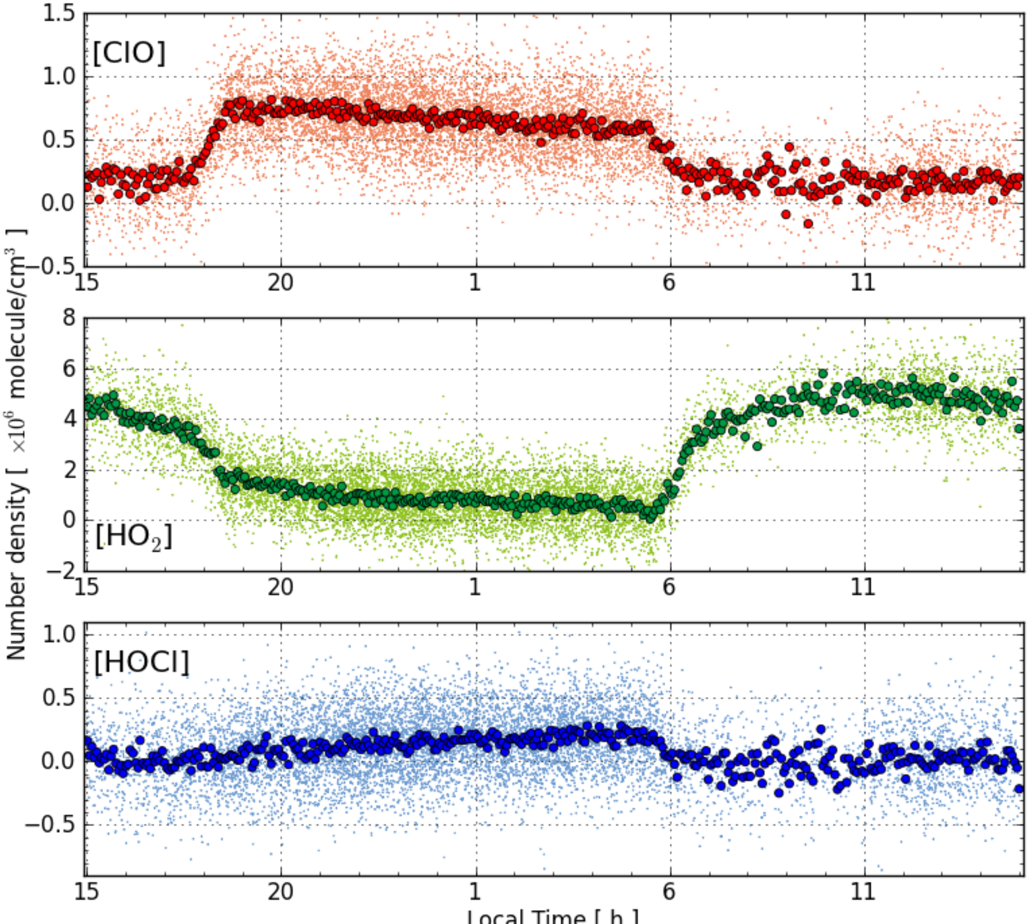



**<u>There is possibility to exist the "pure" reaction period during nighttime in lower mesosphere</u>**

# Diurnal variation of ClO, $HO_2$, and HOCl by SMILES observations

SMILES is the only instrument to reveal the observation of the diurnal variation of ClO, $HO_2$, and HOCl simultaneously by its high-sensitivity.




Data condition

Latitude : 20°S - 40°S
Height : 0.28 hPa (58 km)

Period : Feb. - Apr., 2010

Temperature : 245.0 ± 1.3 (1σ) K

Data product :

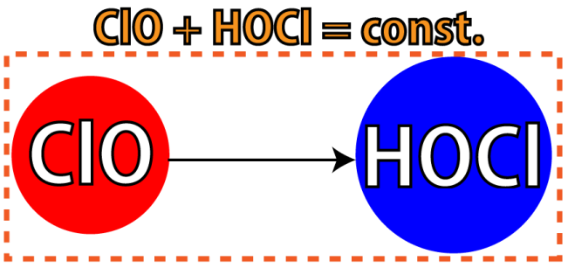
SMILES NICT level-2 product v2.1.5

Small dots : Raw observation data

Large dots : bin of 3.75 minutes

# Method of evaluation of the "pure" reaction period from SMILES observation

In the "pure" $ClO + HO_2 \rightarrow HOCl + O_2$ reaction period




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

Necessary condition in actual atmosphere

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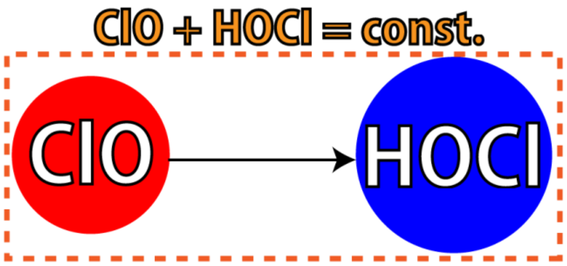


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**Consistency between two rate constants, HOCl production and ClO loss**

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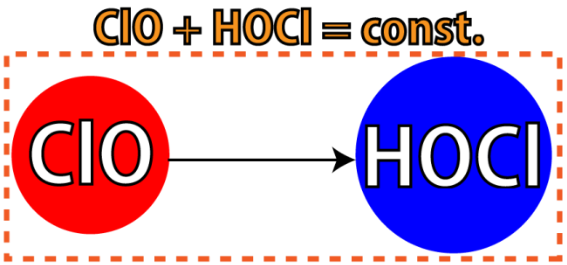


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**Consistency between two rate constants, HOCl production and ClO loss**

**Rate constant of HOCl production, $k_1$**

$$\frac{d[\mathrm{HOCl}]}{dt} = k_1[\mathrm{ClO}][\mathrm{HO2}] \quad (2)$$

**Rate constant of ClO loss, $k_1'$**

$$\frac{d[\mathrm{ClO}]}{dt} = -k_1{}'[\mathrm{ClO}][\mathrm{HO2}] \quad (3)$$

**$\Delta k = |k_1 - k_1'| = 0$**

⇩

$\frac{d[ClO]}{dt} + \frac{d[HOCl]}{dt} = 0$ **is fulfilled.**

# Calculation of the rate constant of HOCl production, $k_1$

Rate constant of HOCl production, $k_1$

$$\frac{d[\mathrm{HOCl}]}{dt} = k_1[\mathrm{ClO}][\mathrm{HO2}]$$

Example of the numerical analysis

**Time interval: LT20:00 ~ LT04:00**

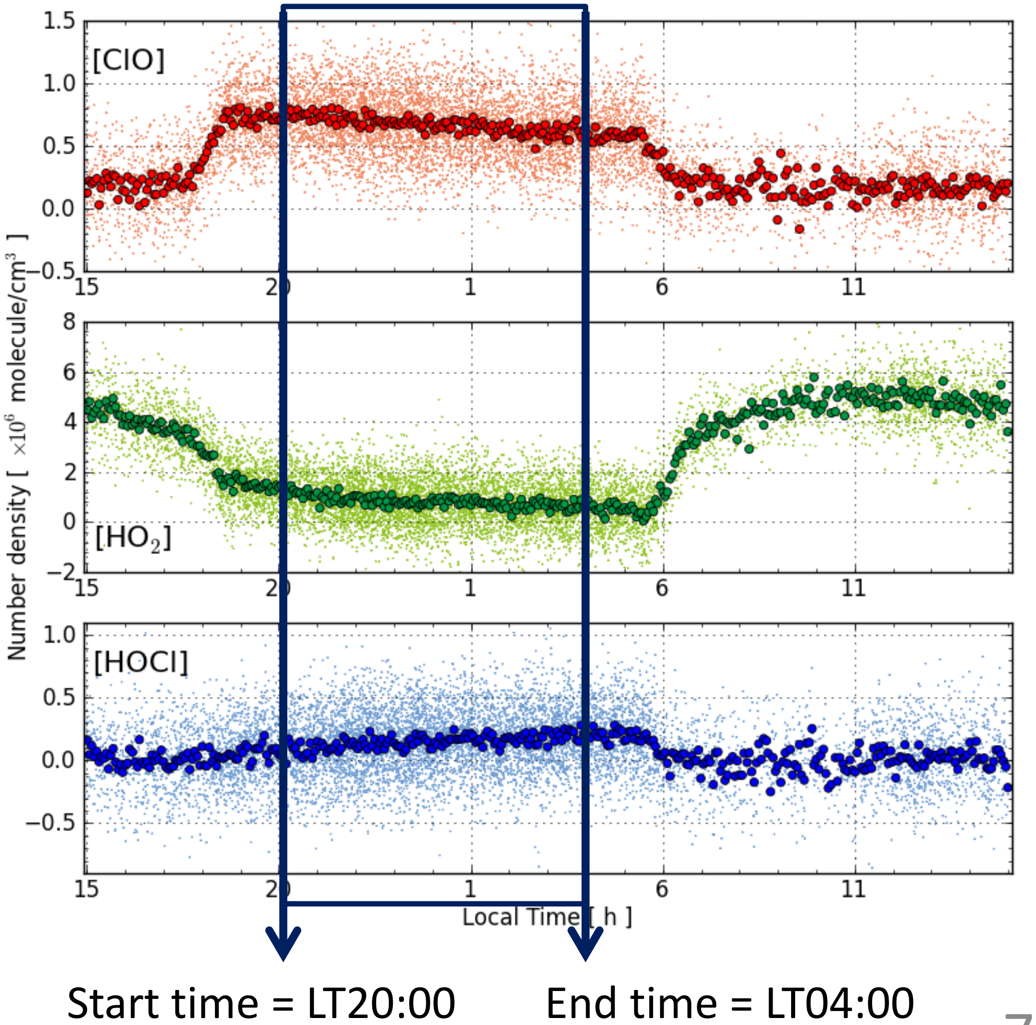
Calculation function

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

$$[\mathrm{HOCl}]_{m+1}^{calc} = [\mathrm{HOCl}]_m^{calc} + \frac{k_1}{2}\left(([\mathrm{ClO}]_m^{obs}[\mathrm{HO_2}]_m^{obs}) + ([\mathrm{ClO}]_{m+1}^{obs}[\mathrm{HO_2}]_{m+1}^{obs})\right) \times (t_{m+1}^{obs} - t_m^{obs})$$

Evaluation function

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



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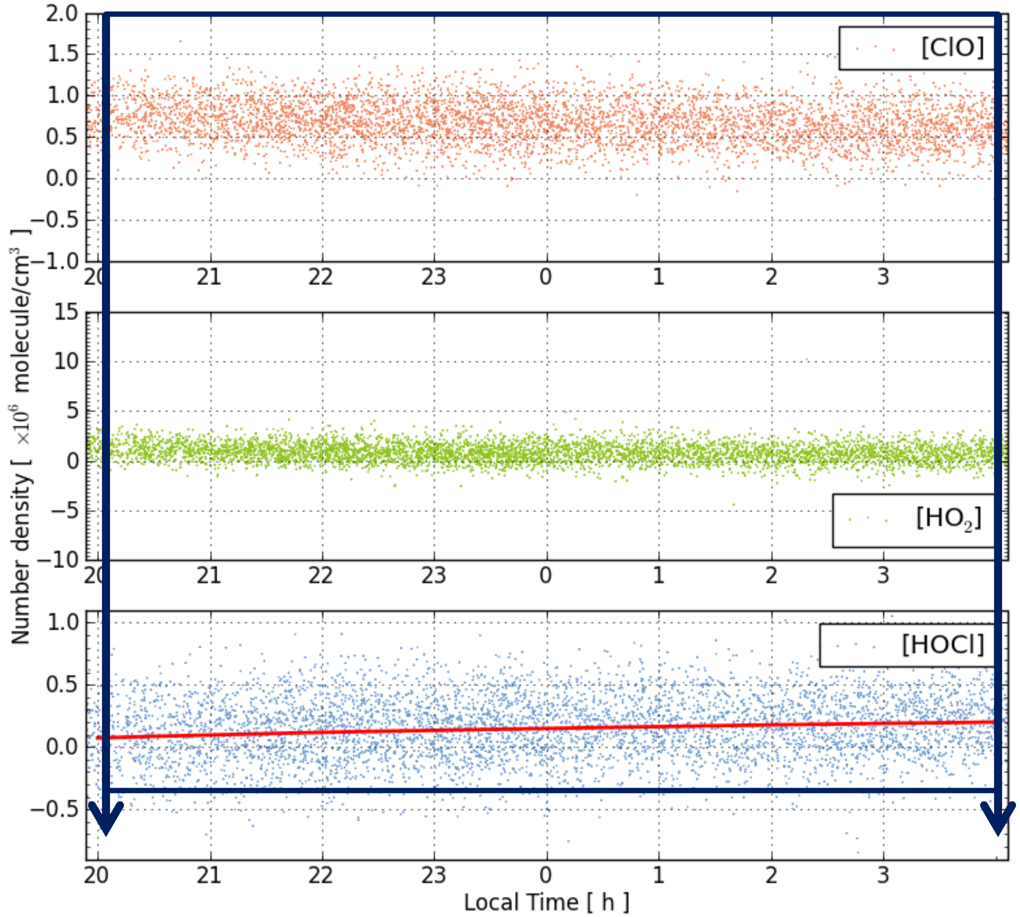


$Y_0$ and $k_1$ are optimized to minimize $\chi$.
We calculated each time interval.

# Time dependence of the rate constant of HOCl production, $k_1$

Rate constant of HOCl production, $k_1$

$$\frac{d[\mathrm{HOCl}]}{dt} = k_1[\mathrm{ClO}][\mathrm{HO2}]$$

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Evaluation function

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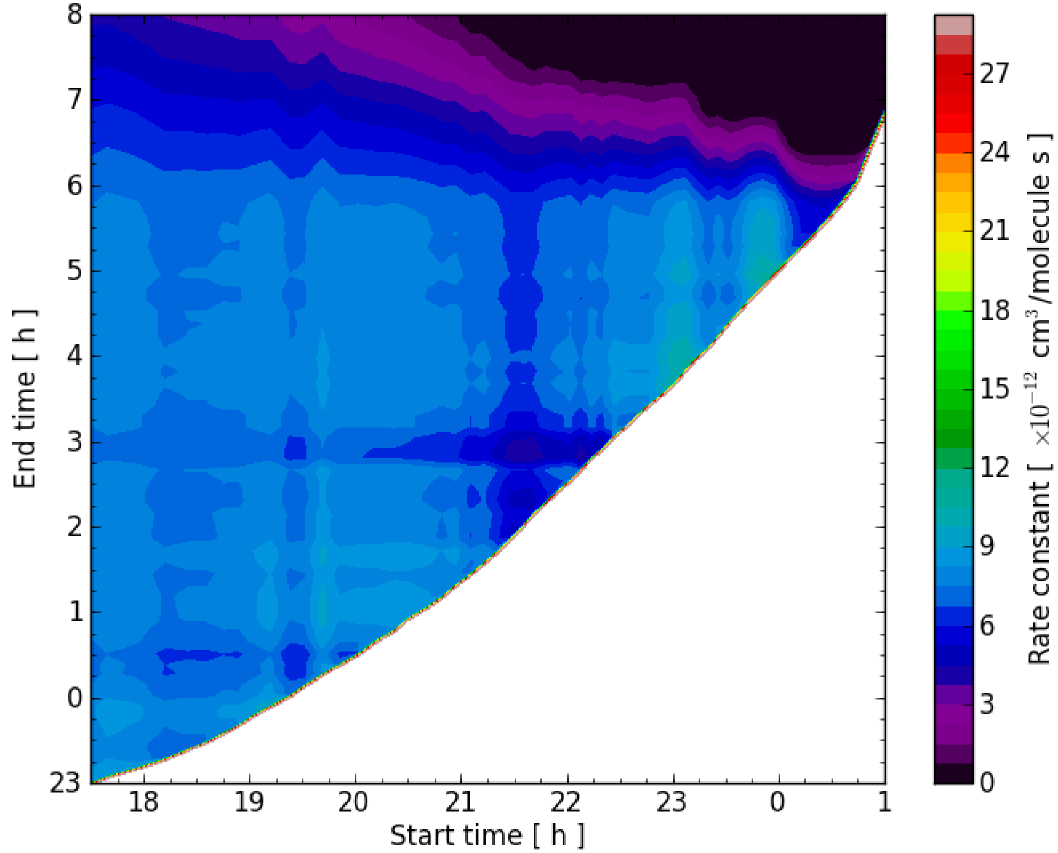

# Time dependence of the rate constant of ClO loss, $k_1'$

Rate constant of ClO loss, $k_1'$

$$\frac{d[\mathrm{ClO}]}{dt} = -k_1'[\mathrm{ClO}][\mathrm{HO2}]$$

Calculation function

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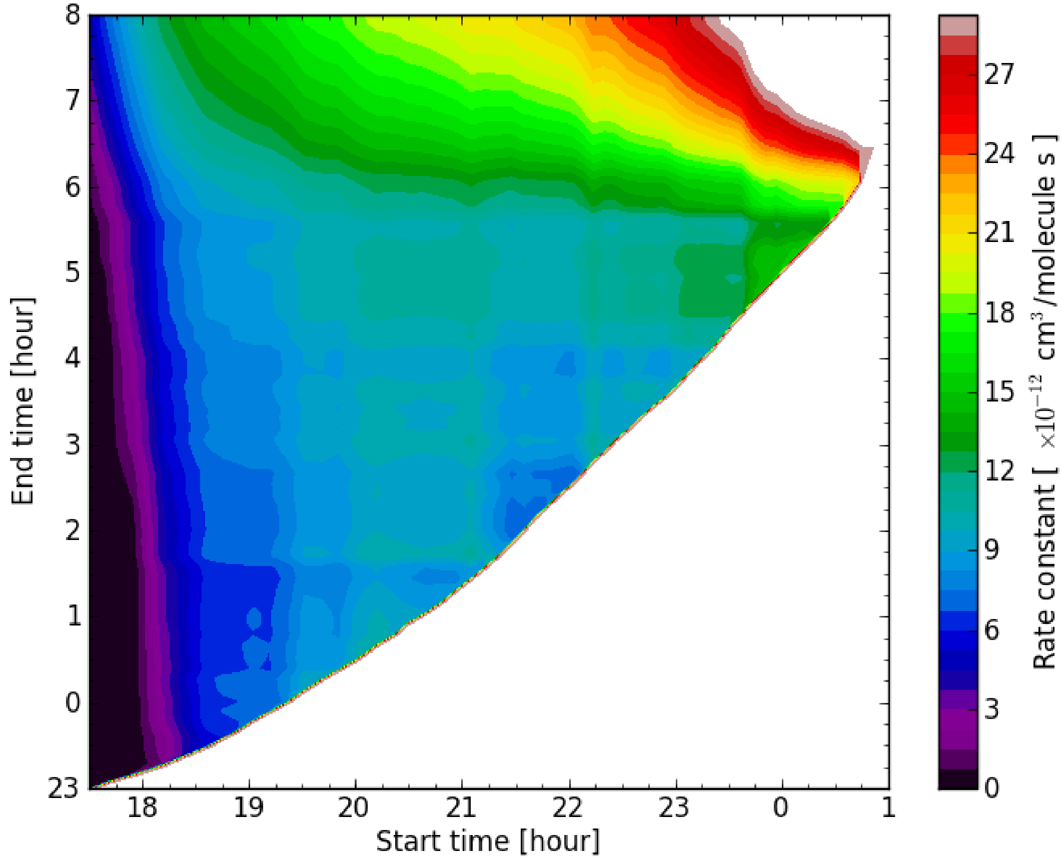


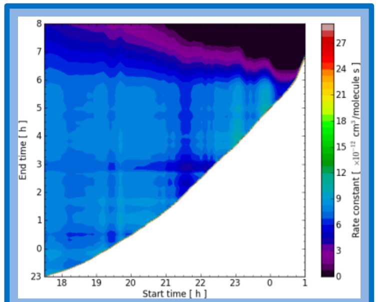
# Time dependence of the difference of two rate constants, $k_1$ and $k_1'$

Difference between $k_1$ and $k_1'$

$$\Delta k = |k_1 - k_1'|$$

Rate constant of HOCl production, $k_1$

$$\frac{d[\mathrm{HOCl}]}{dt} = k_1[\mathrm{ClO}][\mathrm{HO2}]$$

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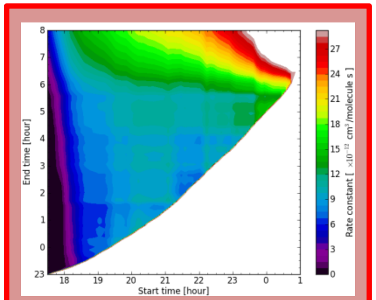


Rate constant of ClO loss, $k_1'$

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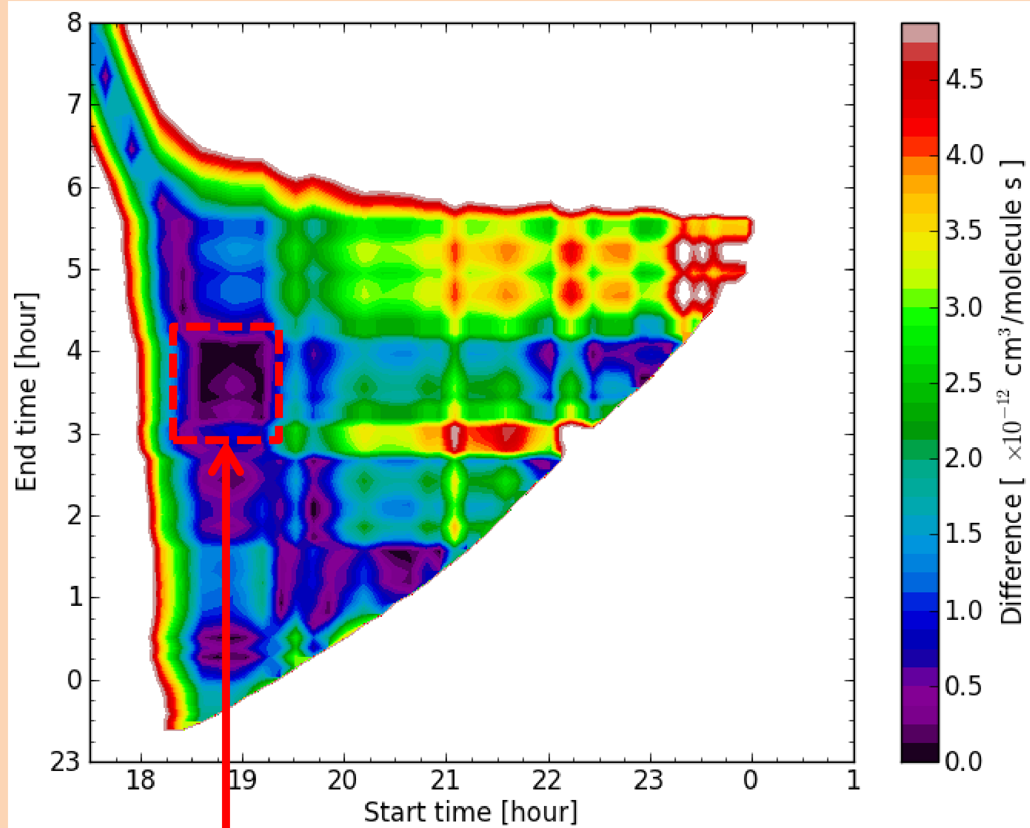
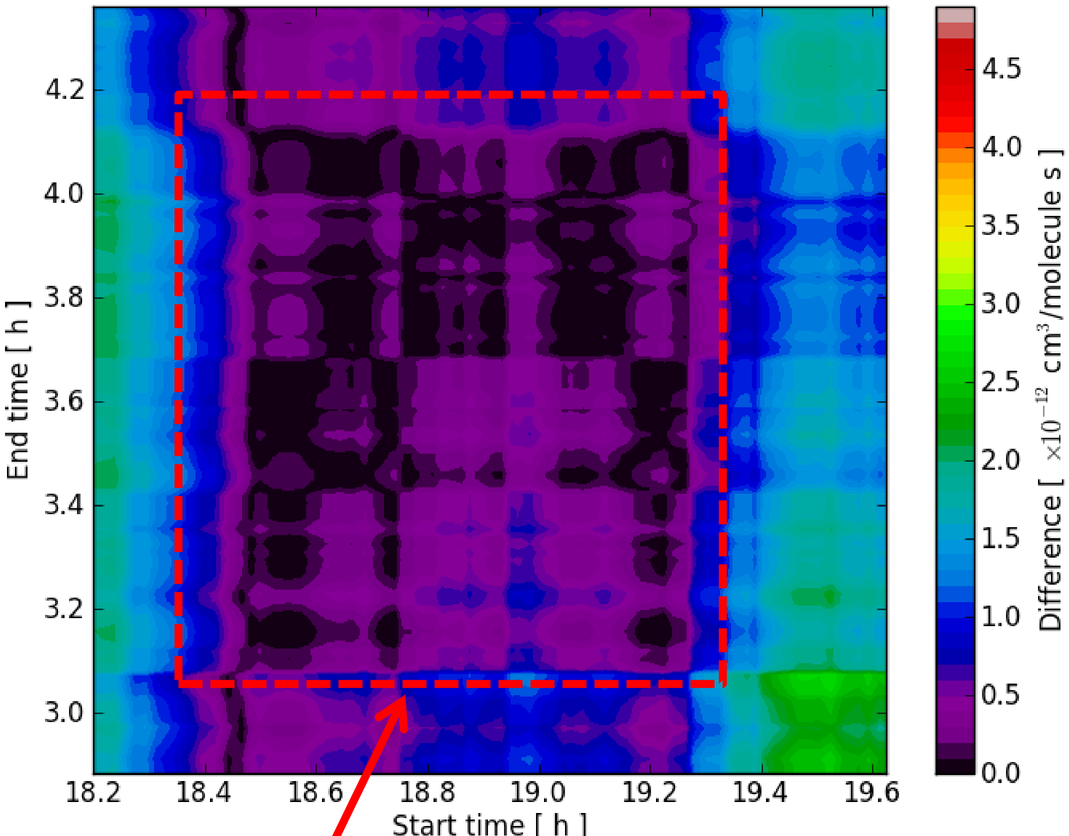



$\Delta k \simeq 0$

$$\frac{d[\mathrm{ClO}]}{dt} + \frac{d[\mathrm{HOCl}]}{dt} \cong 0$$

# Determination of the “pure” $ClO + HO_2 \rightarrow HOCl + O_2$ reaction period

Time dependence of $\Delta k = |k_1 - k_1'|$




$\Delta k \simeq 0$ $\quad \dfrac{d[ClO]}{dt} + \dfrac{d[HOCl]}{dt} \cong 0$

Data condition

- Latitude : 20°S - 40°S
- Height : 0.28 hPa (58 km)
- Period : Feb. - Apr., 2010
- Temperature : 245.0 ± 1.3 (1σ) K
- Data products : NICT v2.1.5

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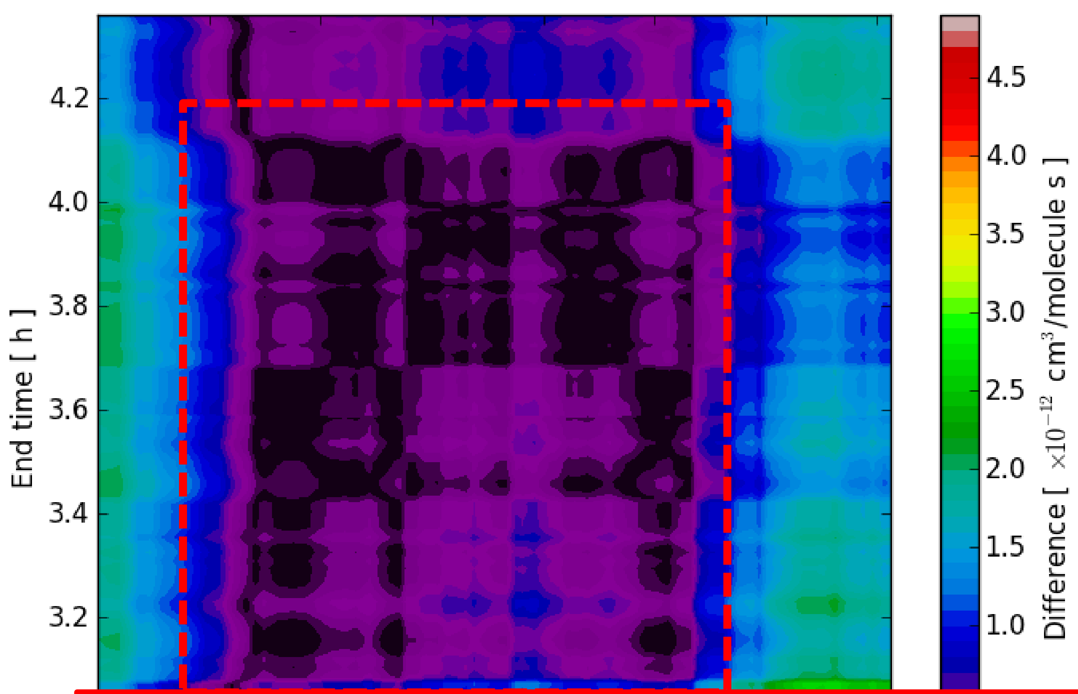


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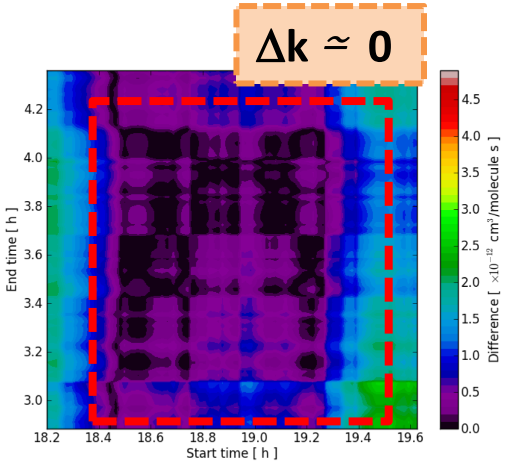
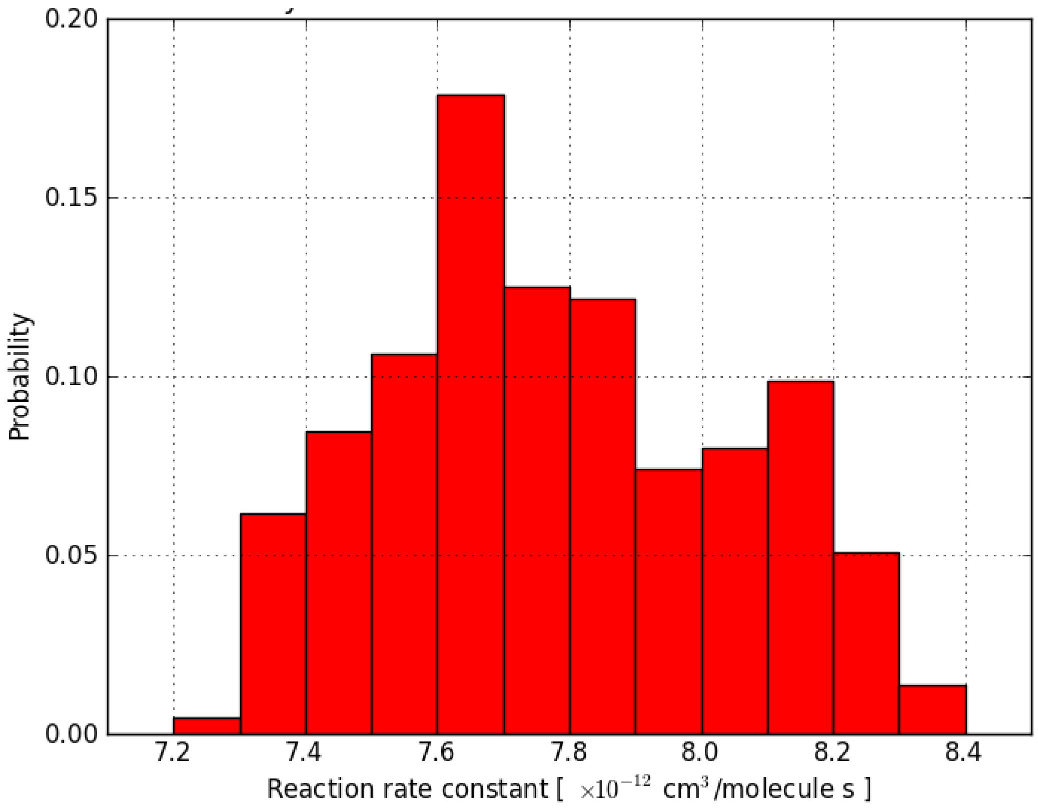
- Temperature : 245.0 $\pm$ 1.3 (1$\sigma$) K
- Data products : NICT v2.1.5

We determined that there was "pure" reaction period.
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 Cly chemistry in the lower mesosphere.

# Determination of the rate constant of $ClO + HO_2 \rightarrow HOCl + O_2$ reaction

Probability of $k_1$ in the "pure" reaction period in $\Delta k \leq 0.1$ [ $\times 10^{12}$ cm3/molecule s]



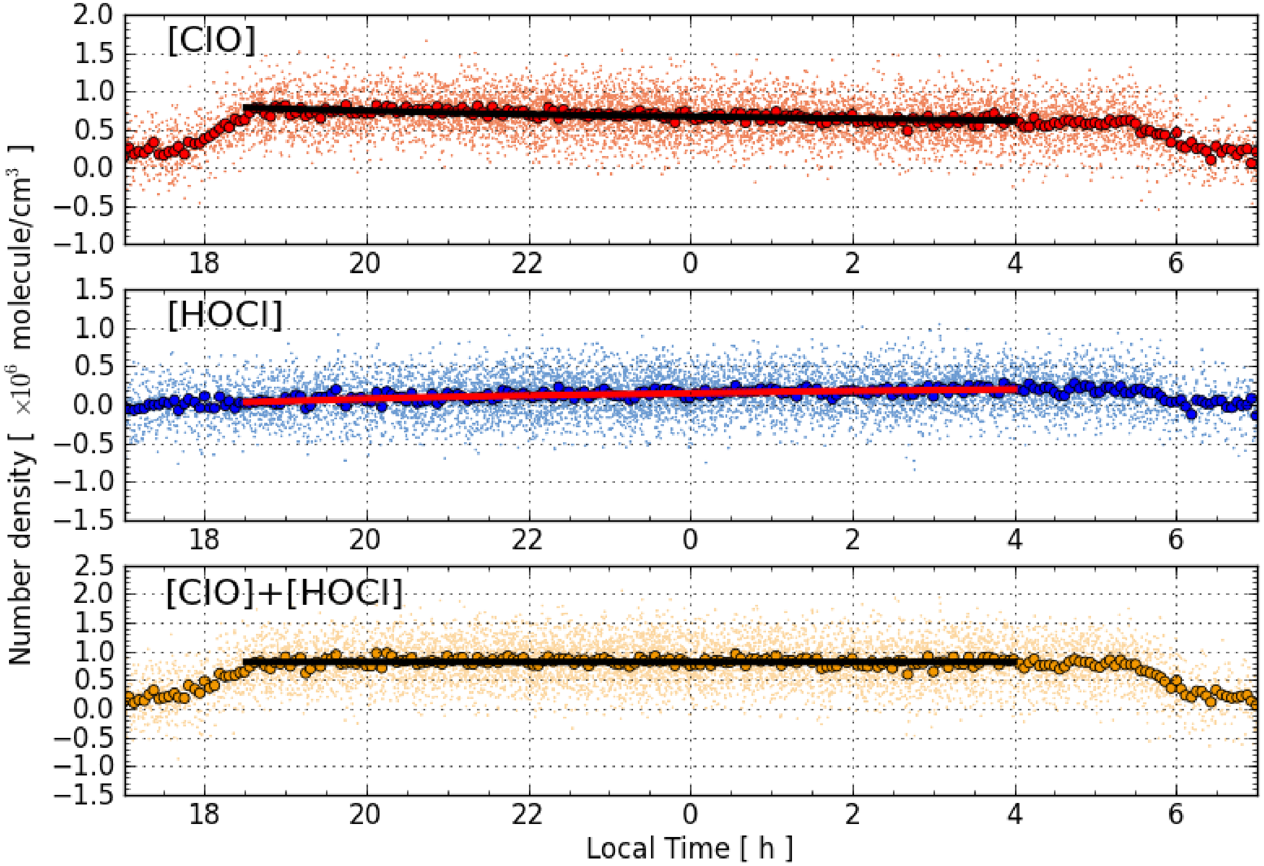

Average value;
7.73 [ $\times 10^{12}$ cm$^3$/molecule s]
Standard deviation;
0.26 [ $\times 10^{12}$ cm$^3$/molecule s]

$k_1$ is obtained to be
$k_1$(245K) = 7.73 $\pm$ 0.26(1$\sigma$)
[ $\times 10^{12}$ cm$^3$/molecule s]

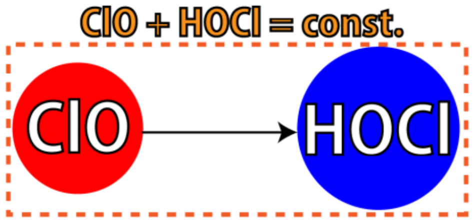
# Diurnal variation of calculated ClO, HOCl, and ClO + HOCl by SMILES observations

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

Time interval : LT 18:30 ~ LT 04:00




Small dots : Raw observation data
Large dots : bin of 3.75 minutes
Solid line: Calculated value



# Comparison with previous works

## Pressure dependence of $ClO + HO_2 \rightarrow HOCl + O_2$ reaction

Xu et al. (2003) pointed from ab initio calculations;

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

$ClO + HO_2 + M \rightarrow HOOOCl + M$ (R2)

reaction intermediate

| P = 0.28 [hPa] (0.21 [Torr])<br>T = 245.0 [K] | Rate constant<br>[ $\times 10^{12}$ $cm^3$/molecule s] |
|---|---|
| Xu et al. (2003) | |
| $ClO + HO_2 \rightarrow HOCl + O_2$ (R1) | **7.51** |
| $ClO + HO_2 + M \rightarrow HOOOCl + M$ (R2) | 0.0021 |
| SMILES $k_1$ | $7.73 \pm 0.26 (1\sigma)$ |

The value of $k_1$ from SMILES is consistent with that of from Xu et al. (2003) within $1\sigma$.

# Summary of k(T)of ClO + $HO_2$ → HOCl + $O_2$ reaction with pressure dependence

Pressure condition in laboratory measurements

| Laboratory measurements | P [Torr] |
|---|---|
| Stimpfle et al. (1979) | 0.8 - 3.4 |
| Nickolaisen et al. (2000) | 50 – 700 |
| Knight et al. (2000) | 1.1 - 1.7 |
| Hickson et al. (2007) | 1.5 |

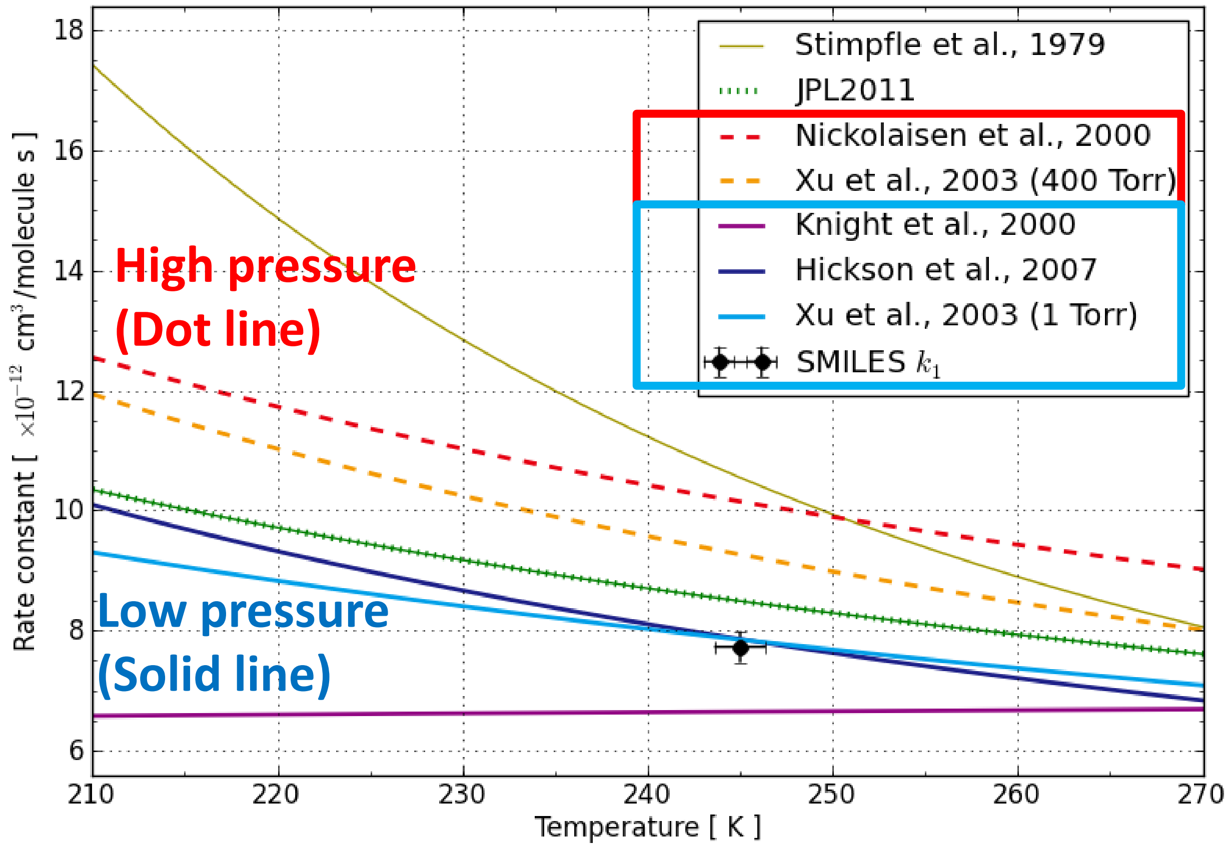
+ ab initio calculations
Xu et al. (2000)

1 Torr

400 Torr

+ SMILES $k_1$

0.21 Torr



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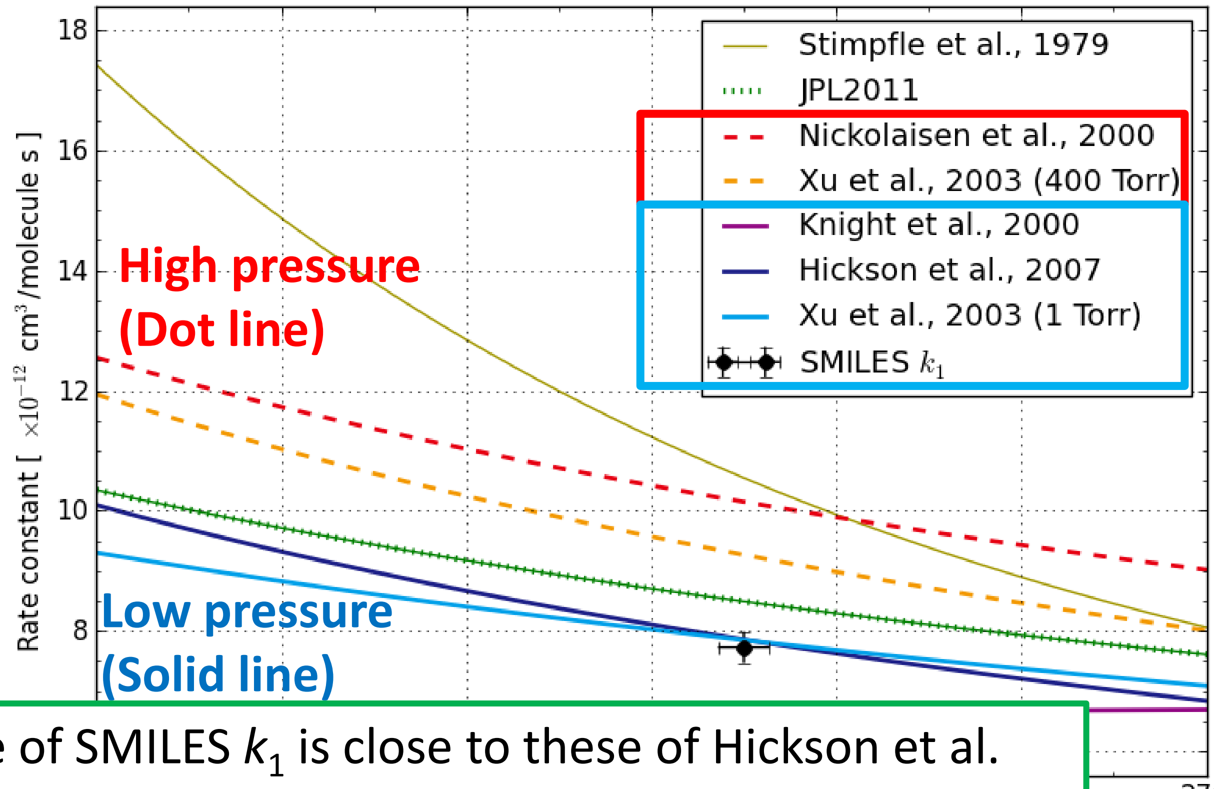


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Xu et al. (2000)

1 Torr

400 Torr

+ SMILES $k_1$

0.21 Torr

The value of SMILES $k_1$ is close to these of Hickson et al. (2007) and Xu et al. (2000) of 1Torr at 245K.
The large discrepancies of $k$(T) might be caused by the pressure dependence.

# Conclusion

- We evaluated the purity of ClO + $HO_2$ -> HOCl + $O_2$ reaction using two rate constants, HOCl production and ClO loss.
- The condition was in the mid-latitude between 20°S and 40°S at a temperature range 5 of 245 +- 1.4(1$\sigma$) 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 + $HO_2$ -> HOCl + $O_2$ purely happens in the Cly chemistry in the lower mesosphere.
- The rate constant of the reaction, ClO + $HO_2$ -> HOCl + $O_2$ , is obtained to be k1 = 7.73 +- 0.26(1$\sigma$)[ $\times 10^{12}$ $cm^3$/molecule s] at 245 K from SMILES observation data.
- The large discrepancies of *k*(T) might be caused by the pressure dependence.