

Kinetic Model for Reaction of ClONO₂ with H₂O and HCl and HOCl with HCl in Sulfuric Acid Solution

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Updated kinetic models for ClONO₂+H₂O, HCl and HOCl + HCl reactions in binary sulfuric acid solution are presented in the attached tables, based on the latest experimental results of *Robinson et al.* [1997], *Donaldson et al.* [1997] and *Hanson* [1998]. This new formulation is valid from 185K to 260K, spanning the range of laboratory and stratospheric conditions. Compared to the most recent formulations, there are several significant changes:

- The mechanism for reaction of HCl with both ClONO₂ and HOCl includes protonation (HClONO₂⁺ and H₂OCl⁺), as was suggested for the reaction of HOCl + HCl by *Donaldson et al.* [1997]. Hydrolysis of ClONO₂, includes both direct and protonated reaction channels with H₂O, as suggested by *Robinson et al.* [1997]. The inclusion of the protonation channels significantly improves “global” fitting to experimental data sets. In the stratosphere, ClONO₂ processing rates above 205K are increased in more concentrated H₂SO₄ solution.
- Complete temperature and composition dependencies are included for Henry’s law solubilities (H), liquid diffusion (D_l) and reaction rate coefficients. This follows the framework introduced by *Robinson et al* [1997] and includes updated diffusion coefficients [*Klassen et al, 1998*]. These more complete formulations should improve extrapolation of laboratory derived rates to colder (<195K) and to warmer (>205K) temperatures, as well as providing more accurate altitude dependence in the stratosphere.
- There is a new formulation to estimate HCl depletion in the aerosol due to reaction with (excess) ClONO₂. This is important at low HCl levels (i.e. p_{HCl} ≤ p_{ClONO2}), when reaction of HCl occurs faster than thermodynamic equilibrium can be maintained, reducing the steady state HCl concentration in the aerosol. This has the effect of decreasing HCl reaction rates and increasing the ClONO₂ hydrolysis rate at cold temperatures below 195K.

The complete formulation has been fit to all experimental data sets, spanning the range of 195 to 260K. The formulation is listed in Tables 1 to 4, followed by a text listing that can easily be pasted into computational code. Table 5 lists example output data for three stratospheric altitudes (30, 55 and 100 mbar), each for two HCl/ClONO₂ scenarios (typical: 1.5ppb HCl; 0.5 ppb ClONO₂; low HCl: 0.5ppb HCl; 1.0 ppb ClONO₂). Two figures are also included, showing (1) the comparison of this formulation for ClONO₂ and HOCl reactivity, at 55 mbar with that of *Hanson* [1998] and *Donaldson et al* [1997], respectively, and (2) the effect of low HCl on ClONO₂ reactivity. The computer code and output data (Tables 1 through 5) are downloadable as the text file <http://www.aerodyne.com/ClNO3code.txt>.

The overall formulation combines the kinetic frameworks presented by *Hanson* [1998] and *Robinson et al* [1997]. In particular, the competition between surface and liquid reactivity of ClONO₂ with HCl and H₂O follows *Hanson* [1998]. The formulation of solubilities in terms of Setchenow coefficients and reaction coefficients with exponential temperature dependencies, including protonation channels, follows *Robinson et al.* [1997]. Note that the protonated

channels assume equilibrium concentrations for the protonated species (HClONO_2^+ and H_2OCl^+), so that the rate coefficients for the acid catalyzed channels (k_{H} for $\text{ClONO}_2 + \text{H}_2\text{O}$, k_{HCl} for $\text{ClONO}_2 + \text{HCl}$, and $k_{\text{HOCl}_\text{HCl}}$ for $\text{HOCl} + \text{HCl}$) actually include equilibrium constants for protonation, which cannot be explicitly evaluated. Properties and chemical activities in H_2SO_4 solution are parameterized from more exact formulations: wt% and water activity, a_{w} , as in *Tabazadeh et al*, [1997]; acidity, a_{H} , this work derived from *Michelsen* [1998], which based on the work of *Carslaw et al*, [1995]; viscosity and liquid diffusion, this work, derived from *Klassen et al*, [1998].

Specific changes and updates from previous formulations are noted below:

- The Setchenow coefficient used in calculating the Henry's law constant for HOCl (H_{HOCl}) is assumed to be dependent on molarity of H_2SO_4 rather than molality as originally suggested by *Huthwelker et al*. [1995]. The new expression for the Henry's law constant for HOCl in Table 3 agrees better with previous HOCl solubility data [*Hanson and Ravishankara*, 1993] and recent data in *Donaldson et al*. [1997].
- Based on this molarity dependent solubility and new experimental data in *Hanson* [1998], the formulation for ClONO_2 hydrolysis has been updated from *Robinson et al*, [1997].
- The formulation of surface reactivity of $\text{ClONO}_2 + \text{HCl}$ (Γ_{s}) is temperature dependent through the inclusion of H_{ClONO_2} as a measure of the surface ClONO_2 isotherm and a temperature dependent rate coefficient that was matched to aerosol experiments at 250K that showed no evidence of the surface reaction channel [*Hanson and Lovejoy*, 1995]
- Expressions for HOCl and ClONO_2 diffusion coefficients are given by *Klassen et al*. [1998]. However, the parameterization of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ solution viscosity is a new fit that combines the viscosity of supercooled water [as noted in *Jayne et al*, 1996] with the formulation discussed in *Klassen et al* [1997]. The new formulation reduces the "singularity" in viscosity at stratospheric temperatures <190K, which is an extreme extrapolation of laboratory data.
- The new formulation of HOCl + HCl reactivity (Table 4) assumes a diffusion limited reaction between $\text{H}_2\text{OCl}^+ + \text{Cl}^-$, analogous to that for $\text{ClONO}_2 + \text{HCl}$ (see discussions in *Donaldson et al*, 1997, and *Hanson*, 1998). The rate coefficient ($k_{\text{HOCl}_\text{HCl}}$) is fitted to experimental data between 200 and 250K [*Zhang et al*, 1994; *Hanson and Lovejoy*, 1996; *Donaldson et al*, 1997], with updated composition and temperature dependent formulations for H_{HOCl} and D_1 included (see $\Gamma_{\text{HOCl}}^{\text{rxn}}$ in Table 4). Reactivity of HOCl + HCl reactivity explicitly depends on a_{H} (see $k_{\text{HOCl}_\text{HCl}}$ in Table 4), in contrast to the previous formulation which was parameterized in terms of H_2SO_4 wt% [*Donaldson et al*, 1997].
- The formulation of F_{HCl} accounts for the depletion of HCl in the aerosol when reaction rate of ClONO_2 with HCl exceeds the flux of HCl to the particle surface. The F_{HCl} expression is based on scaling HCl reaction and accommodation fluxes. This flux correction is not exact (i.e. it does rigorously calculate the HCl surface or bulk concentration) but provides a good approximation to expected reduction in HCl + $\text{ClONO}_2/\text{HOCl}$ reactivity and, just as importantly the effective increase in $\text{ClONO}_2 + \text{H}_2\text{O}$ reactivity, when $p_{\text{ClONO}_2} > p_{\text{HCl}}$ (see Figure 2). This will be particularly relevant during cold Cl activation events when HCl can be virtually removed (for example, see *Jaegle et al*, 1997).

Tables 1-4 present the formulations needed to calculate the reaction probability

coefficients for $\text{ClONO}_2 + \text{H}_2\text{O}$, HCl , and $\text{HOCl} + \text{HCl}$ under stratospheric conditions. Table 1 is taken from *Tabazadeh et al.* [1997] and used to calculate the H_2SO_4 weight percentage for a specified temperature, T , and water vapor partial pressure, $p_{\text{H}_2\text{O}}$. Table 2 is used to calculate H_2SO_4 solution parameters: H_2SO_4 molarity (M_{SO_4}), mole fraction (X), viscosity (η), and acid activity (a_{H}). Table 3 contains the complete uptake formulation for the reaction of $\text{ClONO}_2 + \text{H}_2\text{O}$ and HCl , and Table 4, the formulation for the reaction of $\text{HOCl} + \text{HCl}$. Following the formatted tables, there is a text listing of the tables that is designed to be directly pasted into computer code.

The figures attached at the end elucidate the significant features of the new formulation for the 55 mbar case in Table 5. Figure 1 compares those results for $\text{ClONO}_2 + \text{H}_2\text{O}$, $\text{ClONO}_2 + \text{HCl}$ and $\text{HOCl} + \text{HCl}$ with recent formulations in the literature [*Hanson et al.*, 1994; *Hanson*, 1998]. The formulations agree best at 195-205K, overlapping the most extensive experimental data sets.

In the new formulation, ClONO_2 reactivity increases above 205K, particularly with H_2O , a direct consequence of including the k_{H} and k_{HCl} acid catalyzed reaction channels. The new formulation is also slightly faster for $\text{ClONO}_2 + \text{HCl}$ reaction at 192K, due to the added temperature dependence in the surface reaction channel. Below 190K, the new formulation drops slightly below *Hanson* [1998], not quite reaching unit reaction probability for $\text{ClONO}_2 + \text{HCl}$. This is due to the correction for the reduction in HCl density in the aerosol (F_{HCl}). The effect on $\text{ClONO}_2 + \text{H}_2\text{O}$ reactivity is more pronounced, with the reaction probability plateauing at $\sim 10^{-2}$ below 195K, where the HCl flux correction accounts for incomplete reaction of ClONO_2 with HCl . This is further shown in Fig. 2, which plots $\text{ClONO}_2 + \text{H}_2\text{O}$ and HCl channels for the “high” (as in Fig. 1) and “low” HCl case listed in Table 5. In the “low” HCl case, where $p_{\text{HCl}} < p_{\text{ClONO}_2}$, the $\text{ClONO}_2 + \text{HCl}$ reaction probability plateaus at ~ 0.4 below 190K while that for $\text{ClONO}_2 + \text{H}_2\text{O}$ increases above 0.02.

In the lowest panel of Fig. 1, the new formulation for $\text{HOCl} + \text{HCl}$ reactivity below 210K is about a factor 2 lower than that of *Donaldson et al* [1997] due to differences in extrapolation to low temperatures. Differences above 210K reflect the detailed formulations of composition and temperature dependent solubility, diffusion and reactivity, in contrast to *Donaldson et al* [1997] which parameterized $\text{HOCl} + \text{HCl}$ reaction rates in terms of H_2SO_4 wt%. Below about 195K, the $\text{HOCl} + \text{HCl}$ reaction drops steeply due to the F_{HCl} flux correction, since the fast surface reaction for $\text{ClONO}_2 + \text{HCl}$ at cold temperatures effectively depletes the HCl bulk density for reaction with HOCl .

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Table 1: Calculations of H₂SO₄ wt% from T and p_{H2O}. (from Tabazadeh et al., 1997)

Parameters and Expression		Note
p _{0H2O}	$\exp(18.452406985-3505.1578807/T-330918.55082/T^2+12725068.262/T^3)$	saturation water vapor, mbar
aw	p_{H2O}/p_{0H2O}	water activity
m	$y1+(T-190)(y2-y1)/70$	H ₂ SO ₄ molality, mol/kg
y1	$a1*aw^{b1}+c1*aw+d1$	
y2	$a2*aw^{b2}+c2*aw+d2$	
	if aw<=0.05	if 0.85>aw>0.05
	a1=12.37208932	a1=11.820654354
	b1=-0.16125516114	b1=-0.20786404244
	c1=-30.490657554	c1=-4.807306373
	d1=-2.1133114241	d1=-5.1727540348
	a2=13.455394705	a2=12.891938068
	b2=-0.1921312255	b2=-0.23233847708
	c2=-34.285174607	c2=-6.4261237757
	d2=-1.7620073078	d2=-4.9005471319
		if aw>=0.85
		a1=-180.06541028
		b1=-0.38601102592
		c1=-93.317846778
		d1=273.88132245
		a2=-176.95814097
		b2=-0.36257048154
		c2=-90.469744201
		d2=267.45509988
wt	$9800m/(98m+1000)$	Weight percentage, %

Table 2: Parameters for the H₂SO₄ Solution

Parameter	Value or Expression	Units	References and Note
M _{SO4}	$\rho wt/9.8$	mol/l	H ₂ SO ₄ molarity
ρ	$1+Z_1m+Z_2m^{1.5}+Z_3m^2$	g/cm ³	H ₂ SO ₄ solution density,
Z ₁	$0.12364-5.6x10^{-7}T^2$		Huthwelker et al., 1995
Z ₂	$-0.02954+1.814x10^{-7}T^2$		
Z ₃	$2.343x10^{-3}-1.487x10^{-6}T-1.324x10^{-8}T^2$		
X	$wt/(wt+(100-wt)98/18)$		H ₂ SO ₄ mole fraction
η	$AT^{-1.43}\exp(448/(T-T_o))$	cp	Viscosity of H ₂ SO ₄ solution, this work
A	$169.5+5.18wt-0.0825wt^2+3.27x10^{-3}wt^3$		
T _o	$144.11+0.166wt-0.015wt^2+2.18x10^{-4}wt^3$		
a _H	$\exp[60.51-0.095wt+0.0077wt^2-1.61x10^{-5}wt^3-(1.76+2.52x10^{-4}wt^2)T^{0.5}+(-805.89+253.05wt^{0.076})/T^{0.5}]$		Acid activity in molarity, this work

Note: If T and wt% are known, water activity can be calculated as (this work):

$$aw=\exp[(-69.775X-18253.7X^2+31072.2X^3-25668.8X^4)/(1/T-26.9033/T^2)].$$

Table 3. Uptake Model Parameters for the Reactions of ClONO₂ + H₂O and ClONO₂+HCl

Parameter	value or Expression	Units	References and Note
$\Gamma_b^{H_2O}$	$4H_{ClONO_2}RT (D_{ClONO_2}k_{hydr})^{0.5}/ C_{ClONO_2}$		$R=0.082 \text{ atm K}^{-1} \text{ M}^{-1}$
C_{ClONO_2}	$1474T^{0.5}$	cm/s	$cbar=\text{sqrt}(8RT/\pi MW)$
H_{ClONO_2}	$1.6 \times 10^{-6} \exp(4710/T) \exp(-S_{ClONO_2}MSO_4)$	M atm^{-1}	This work
S_{ClONO_2}	$0.306+24.0/T$	M^{-1}	Setchenow coefficient, this work
D_{ClONO_2}	$5 \times 10^{-8} T/\eta$	cm^2/s	Klassen et al., 1998
k_{hydr}	$k_{H_2O}a_w + k_H a_{H_2O}$	s^{-1}	This work
k_{H_2O}	$1.95 \times 10^{10} \exp(-2800/T)$	s^{-1}	''
k_H	$1.22 \times 10^{12} \exp(-6200/T)$	$\text{M}^{-1} \text{s}^{-1}$	''
k_{HCl}	$7.9 \times 10^{11} a_H D_{ClONO_2} M_{HCl}$	s^{-1}	''
M_{HCl}	$H_{HCl} P_{HCl}$	M	$p_{HCl} \text{ (atm)}$
H_{HCl}	$(0.094-0.61X+1.2X^2) \exp(-8.68+(8515-10718X^{0.7})/T)$		M atm^{-1} , This work
ℓ_{ClONO_2}	$(D_{ClONO_2}/(k_{hydr}+k_{HCl}))^{0.5}$	cm	reacto-diffusive length
f_{ClONO_2}	$1/\tanh(r/\ell_{ClONO_2}) - \ell_{ClONO_2}/r$		r : aerosol size, cm
$\Gamma_{ClONO_2}^{rxn}$	$f_{ClONO_2} \Gamma_b^{H_2O} (1+k_{HCl}/k_{hydr})^{0.5}$		Hanson, 1998
Γ_b^{HCl}	$\Gamma_{ClONO_2}^{rxn} k_{HCl}/(k_{HCl}+k_{hydr})$		''
Γ_s	$66.12 \exp(-1374/T) H_{ClONO_2} M_{HCl}$		This work
F_{HCl}	$1/(1+0.612(\Gamma_s+\Gamma_b^{HCl})p_{ClONO_2}/p_{HCl})$		This work, $0.612=(MW_{HCl}/MW_{ClONO_2})^{1/2}$
Γ_s'	$F_{HCl} \Gamma_s$		
Γ_b^{HCl}	$F_{HCl} \Gamma_b^{HCl}$		
Γ_b	$\Gamma_b^{HCl} + \Gamma_{ClONO_2}^{rxn} k_{hydr}/(k_{HCl}+k_{hydr})$		
γ_{ClONO_2}	$1/(1+1/(\Gamma_s' + \Gamma_b))$		
$\gamma_{ClONO_2_HCl}$	$\gamma_{ClONO_2} (\Gamma_s' + \Gamma_b^{HCl})/(\Gamma_s' + \Gamma_b)$		Hanson, 1998
$\gamma_{ClONO_2_H_2O}$	$\gamma_{ClONO_2} - \gamma_{ClONO_2_HCl}$		''

Note: We have assumed $\alpha = 1$ in Tables 3 and 4, which is appropriate in the stratosphere. F_{HCl} accounts for depletion of HCl concentration in the particles due to reaction with ClONO₂ inside/on the surface of particles. In light of low stratosphere levels of HOCl, the effect of HOCl + HCl reaction on HCl concentration has been neglected. However, the depletion of HCl concentration in the particles due to reaction with ClONO₂ affects the HOCl + HCl reaction probability, which is taken into account by F_{HCl} in Table 4 (see γ_{HOCl}).

Table 4. Uptake Model Parameters for the Reaction of HOCl + HCl

Parameter	value or Expression	Units	References and Note
$\Gamma_{\text{HOCl}}^{\text{rxn}}$	$4H_{\text{HOCl}}RT(D_{\text{HOCl}}k_{\text{HOCl_HCl}})^{0.5}/C_{\text{HOCl}}$		$R=0.082 \text{ atm K}^{-1}\text{M}^{-1}$
C_{HOCl}	$2009T^{0.5}$	cm/s	$\text{cbar}=\text{sqrt}(8RT/\pi\text{MW})$
H_{HOCl}	$1.91 \times 10^{-6} \exp(5862.4/T) \exp(-S_{\text{HOCl}}\text{MSO}_4)$	M atm^{-1}	This work
S_{HOCl}	$0.0776 + 59.18/T$	M^{-1}	Setchenow coefficient, this work
D_{HOCl}	$6.4 \times 10^{-8} T/\eta$	cm^2/s	Klassen et al., 1998
$k_{\text{HOCl_HCl}}$	$1.25 \times 10^9 a_{\text{H}} D_{\text{HOCl}} M_{\text{HCl}}$	s^{-1}	This work
ℓ_{HOCl}	$(D_{\text{HOCl}}/k_{\text{HOCl_HCl}})^{0.5}$	cm	reacto-diffusive length
f_{HOCl}	$1/\tanh(r/\ell_{\text{HOCl}}) - \ell_{\text{HOCl}}/r$		r : aerosol size, cm
γ_{HOCl}	$1/(1+1/(f_{\text{HOCl}}\Gamma_{\text{HOCl}}^{\text{rxn}}F_{\text{HCl}}))$		This work

Note: The factor F_{HCl} here, as shown in Table 3, accounts for depletion of HCl concentration in the particles due to reaction with ClONO_2 inside/on the surface of particles.

Table 5 Formulation Output for listed conditions.

H₂O=4.5 ppm		<u>HCl (ppb) ClONO₂(ppb)</u>			<u>HCl (ppb) ClONO₂(ppb)</u>		
r_a= 10⁻⁵ cm		1.5	0.5		0.5	1.0	
P=30 mbar							
T (K)	H ₂ SO ₄ Wt%	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}
185	38.29	0.821	0.00747	0.0515	0.431	0.0339	0.00951
190	50.37	0.168	0.0113	0.0444	0.0609	0.0149	0.0147
195	58.00	0.00181	0.00375	0.00171	0.000612	0.00391	0.000572
200	63.53	6.31e-05	0.00107	9.45e-05	2.12e-05	0.00109	3.15e-05
205	67.82	5.01e-06	0.000361	8.05e-06	1.67e-06	0.000362	2.68e-06
210	71.20	6.46e-07	0.000153	1.02e-06	2.16e-07	0.000153	3.41e-07
215	74.09	9.99e-08	7.9e-05	1.59e-07	3.33e-08	7.9e-05	5.32e-08
220	76.63	1.68e-08	4.62e-05	2.78e-08	5.6e-09	4.62e-05	9.28e-09
225	78.89	3.01e-09	2.84e-05	5.22e-09	1e-09	2.84e-05	1.74e-09
230	80.91	5.75e-10	1.75e-05	1.03e-09	1.92e-10	1.75e-05	3.44e-10
235	82.72	1.17e-10	1.05e-05	2.13e-10	3.89e-11	1.05e-05	7.1e-11
240	84.34	2.49e-11	5.98e-06	4.55e-11	8.31e-12	5.98e-06	1.52e-11

55 mbar

T (K)	H ₂ SO ₄ Wt%	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}
185	21.34	0.821	0.0114	0.00123	0.423	0.0591	0.000288
190	42.67	0.778	0.00607	0.181	0.4	0.0234	0.0415
195	52.69	0.0414	0.009	0.0238	0.0145	0.0108	0.00799
200	59.53	0.000843	0.0028	0.00106	0.000288	0.00292	0.000355
205	64.58	5.03e-05	0.000877	7.27e-05	1.69e-05	0.000887	2.42e-05
210	68.54	5.29e-06	0.000327	7.48e-06	1.77e-06	0.000328	2.49e-06
215	71.73	7.77e-07	0.000153	1.07e-06	2.59e-07	0.000153	3.58e-07
220	74.47	1.32e-07	8.46e-05	1.84e-07	4.39e-08	8.46e-05	6.14e-08
225	76.89	2.41e-08	5.16e-05	3.48e-08	8.02e-09	5.16e-05	1.16e-08
230	79.06	4.69e-09	3.25e-05	7.04e-09	1.56e-09	3.25e-05	2.35e-09
235	81.00	9.71e-10	2.04e-05	1.49e-09	3.24e-10	2.04e-05	4.98e-10
240	82.74	2.13e-10	1.24e-05	3.3e-10	7.09e-11	1.24e-05	1.1e-10

100 mbar

T (K)	H ₂ SO ₄ Wt%	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}	γ _{ClONO₂+HCl}	γ _{ClONO₂+H₂O}	γ _{HOCl+HCl}
190	30.34	0.824	0.00808	0.0241	0.431	0.0419	0.00476
195	45.89	0.562	0.00816	0.211	0.253	0.0196	0.0658
200	54.55	0.0141	0.00663	0.0132	0.005	0.00775	0.00443
205	60.78	0.000537	0.00215	0.000704	0.000185	0.00224	0.000235
210	65.42	4.5e-05	0.000737	5.84e-05	1.52e-05	0.000745	1.95e-05
215	69.12	5.62e-06	0.000303	7.01e-06	1.88e-06	0.000304	2.34e-06
220	72.14	9.1e-07	0.000154	1.12e-06	3.04e-07	0.000154	3.73e-07
225	74.76	1.67e-07	9.01e-05	2.08e-07	5.55e-08	9.02e-05	6.94e-08
230	77.08	3.29e-08	5.67e-05	4.24e-08	1.1e-08	5.67e-05	1.41e-08
235	79.16	6.91e-09	3.64e-05	9.17e-09	2.3e-09	3.64e-05	3.06e-09
240	81.03	1.54e-09	2.32e-05	2.08e-09	5.13e-10	2.32e-05	6.92e-10

C Stratospheric Reaction Coefficients of ClONO2 and HOCl
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C INSTRUCTIONS FOR USE:

C *INPUT*
 C The user must provide Temperature(K); Aerosol radius (cm);
 C Water vapor partial press (mbar);
 C HCl and ClONO2 partial pressure (atm).
 C These are symbolized in the following code, respectively, as:
 C T, r, PH2O, PHCl, PClONO2

C *OUTPUT*
 C Heterogeneous reaction probabilities for:
 C ClONO2 reacting with HCl and H2O;
 C HOCl reacting with HCl.
 C These are symbolized in the following code as:
 C gClONO2_HCl, gClONO2_H2O, gHOCl

C //Table 1: H2SO4 wt% from T and pH2O

p0H2O = exp(18.452406985-3505.1578807/T-330918.55082/T^2+12725068.262/T^3)

aw = pH2O/ p0H2O

if (aw<=0.05)
 a1=12.37208932
 b1=-0.16125516114
 c1=-30.490657554
 d1=-2.1133114241
 a2=13.455394705
 b2=-0.1921312255
 c2=-34.285174607
 d2=-1.7620073078
 endif

if (aw>0.05)
 a1=11.820654354
 b1=-0.20786404244
 c1=-4.807306373
 d1=-5.1727540348
 a2=12.891938068
 b2=-0.23233847708
 c2=-6.4261237757
 d2=-4.9005471319
 endif

if (aw>=0.85)
 a1=-180.06541028
 b1=-0.38601102592
 c1=-93.317846778
 d1=273.88132245
 a2=-176.95814097
 b2=-0.36257048154
 c2=-90.469744201
 d2=267.45509988
 endif

y1 = a1*aw^b1+c1*aw+d1
 y2 = a2*aw^b2+c2*aw+d2
 m = y1+(T-190)*(y2-y1)/70
 wt = 9800*m/(98*m+1000)

C //Table 2: Parameters for H2SO4 Solution

```

z1 = 0.12364-5.6e-7*T^2
z2 = -0.02954+1.814e-7*T^2
z3 = 2.343e-3-1.487e-6*T-1.324e-8*T^2
rho = 1+z1*m+z2*m^1.5+z3*m^2
MSO4 = rho*wt/9.8
X = wt/(wt+(100-wt)*98/18)
A = 169.5+5.18*wt-0.0825*wt^2+3.27e-3*wt^3
To = 144.11+0.166*wt-0.015*wt^2+2.18e-4*wt^3
h = A*T^(-1.43)*exp(448/(T-To))
aH = exp(60.51-0.095*wt+0.0077*wt^2-1.61e-5*wt^3-(1.76+2.52e-4*wt^2)*T^0.5
+(-805.89+253.05*wt^0.076)/T^0.5)

```

C //Table 3. ClONO2 + H2O and ClONO2+HCl

```

c_ClONO2 = 1474*T^0.5
SClONO2 = 0.306+24.0/T
HClONO2 = 1.6e-6*exp(4710/T)*exp(-SClONO2*MSO4)
DClONO2 = 5e-8*T/h
kH2O = 1.95e10*exp(-2800/T)
kH = 1.22e12*exp(-6200/T)
khydr = kH2O*aw + kH*aH*aw
GbH2O = 4*HClONO2*0.082*T*(DClONO2*khydr)^0.5/c_ClONO2
HHCl = (0.094-0.61*X+1.2*X^2)*exp(-8.68+(8515-10718*X^0.7)/T)
MHCl = HHCl *PHCl
KHCl = 7.9e11*aH*DClONO2*MHCl
lClONO2 = (DClONO2/(khydr+kHCl))^0.5
fClONO2 = 1/tanh(r/lClONO2)- lClONO2/r
GClONO2rxn = fClONO2*GbH2O *(1+kHCl/khydr)^0.5
GbHCl = GClONO2rxn* KHCl/( KHCl+ khydr)
Gs = 66.12*exp(-1374/T)*HClONO2*MHCl
FHCl = 1/(1+0.612*(Gs+GbHCl)* pClONO2/ pHCl)
Gsp = FHCl*Gs
GbHClp = FHCl*GbHCl
Gb = GbHClp + GClONO2rxn* khydr/( KHCl+ khydr)
gClONO2 = 1/(1+1/(Gsp + Gb))
gClONO2_HCl = gClONO2 *(Gsp + GbHClp)/(Gsp + Gb)
gClONO2_H2O = gClONO2 - gClONO2_HCl

```

C //Table 4. HOCl + HCl

```

c_HOCl = 2009*T^0.5
SHOCl = 0.0776+59.18/T
HHOCl = 1.91e-6*exp(5862.4/T)*exp(-SHOCl*MSO4)
DHOCl = 6.4e-8*T/h
kHOCl_HCl = 1.25e9*aH*DHOCl*MHCl
GHOClrxn = 4*HHOCl*0.082*T*(DHOCl*kHOCl_HCl)^0.5/c_HOCl
lHOCl = (DHOCl/kHOCl_HCl)^0.5
fHOCl = 1/tanh(r/lHOCl)- lHOCl/r
gHOCl = 1/(1+1/ ( fHOCl*GHOClrxn*FHCl))

```

Figure 1 Comparison of Uptake Coefficient of ClONO₂ and HOCl Using Different Formulations

(55 mbar, $r_a=10^{-5}$ cm, 4.5 ppm H₂O, 1.5 ppb HCl, 0.5 ppb ClONO₂)

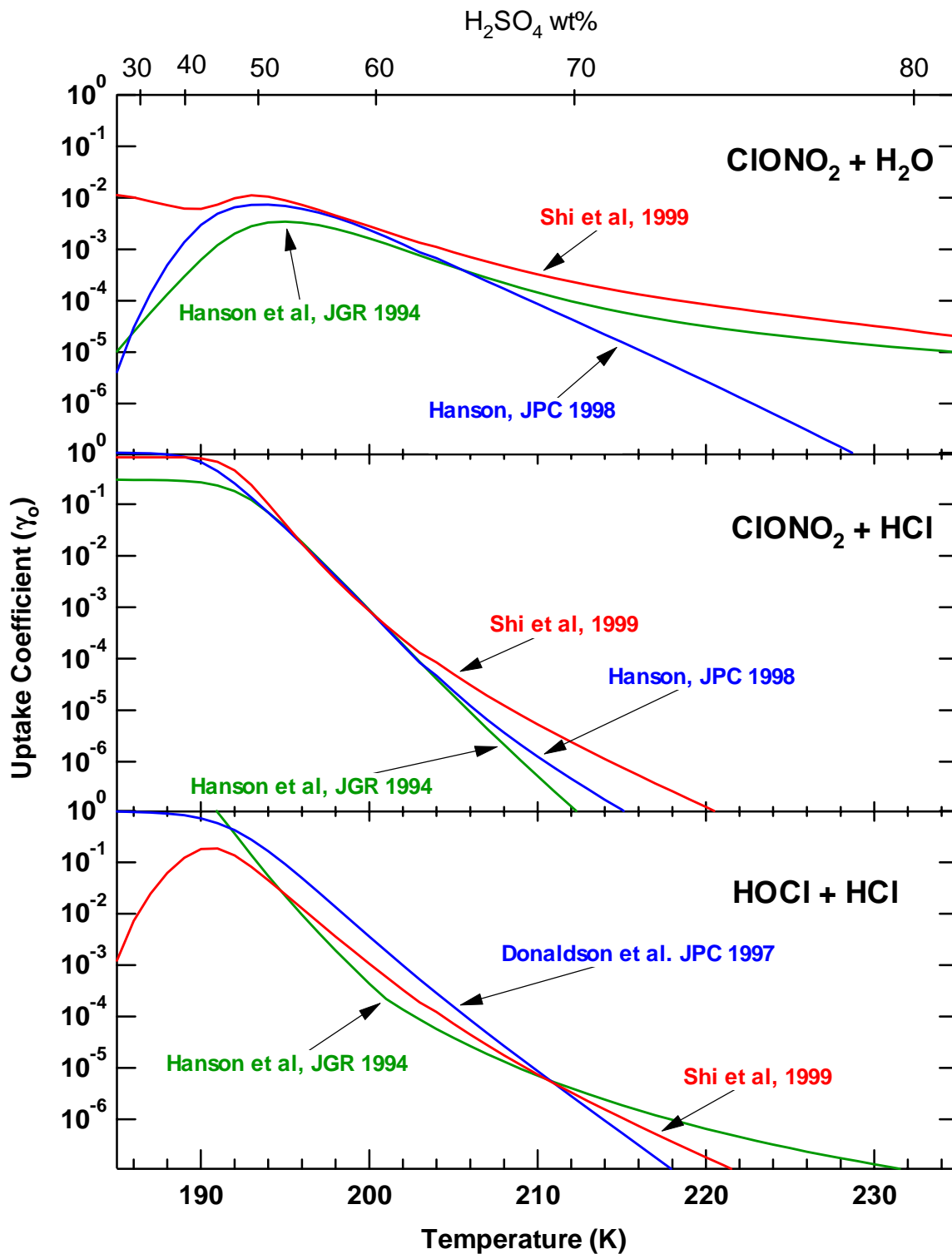


Figure 2 Uptake Coefficient of ClONO₂ under two Stratospheric HCl and ClONO₂ Concentrations.

