

Estimation of heterogeneous reaction rates for stratospheric trace gases with particular reference to the diffusional uptake of HCl and ClONO₂ by polar stratospheric clouds

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Abstract. The stratosphere holds a variety of particulates like polar stratospheric clouds (PSCs) and sulphate aerosols which catalyse chemical reactions. These reactions cause changes in the composition of the stratosphere, including the redistribution of active chlorine which might lead to ozone destruction. As a result during recent years a lot of effort has been directed towards the quantification of the uptake of trace gases like ClONO₂, HCl, etc. into these particulates. However, it has been observed that many of the two and three dimensional models used in such studies are constrained by the lack of adequate rate constant data. This paper describes a theoretical approach to estimate the reaction rate constants for 23 gases on both types of polar stratospheric clouds (type I and II). It is found that for gases like N₂O₅, ClONO₂ and HCl, diffusional uptake is important and contributes significantly to the heterogeneous reaction rate. A complete Lennard-Jones calculation is used to accurately compute the trace gas diffusion coefficients.

1 Introduction

Recent studies on the Antarctic ozone loss highlight the importance of heterogeneous reactions of trace gases on surfaces like polar stratospheric clouds (PSCs) and sulphate aerosols (Solomon *et al.*, 1986). The uptake of trace gases by these surfaces can be significant and a careful analysis of the time-dependent nature of the active surface is required in the evaluation of measured uptake kinetics (De More *et al.*, 1992). It is now well known that the surface adsorption and reactions of trace species such as HCl and ClONO₂ are crucial for the quantification of reaction rates for these heterogeneous processes (MacKenzie and Haynes, 1992). Therefore, we shall attempt to model the transfer rate of vapour molecules to particle surfaces. In many cases, reaction rates determine the net rates of mass transfer. We account for this effect by connecting

laboratory measurements of *sticking coefficients* (mainly from the measurements of Hanson and Ravishankara, 1991a, b) to fundamental parameters of surface chemistry.

2 Mass transfer rates and limiting conditions

Transport of a trace gas within the gas phase to a cloud droplet proceeds by turbulent and molecular diffusion. Far away from the droplet surface on scales much greater than molecular scales, eddy motions are responsible for mass transfer. While at the gas-liquid interface, mass transfer is governed by molecular dynamics. The mean free path of a molecule in air l_a is a key parameter which varies inversely with pressure and directly with temperature. The mean free path tends to decrease with molecular size, so that the free paths of HCl, ClONO₂ and other polyatomic species are somewhat lower than those of gases like O₂ and N₂. The molecular flux F_{ci} of a species i to a surface is controlled by molecular diffusion in the *continuum transport* regime where l_a is smaller than the particle radius a , i.e. $l_a < a$ (Turco *et al.*, 1989):

$$F_{ci} = 4\pi a D_i (n_i - n_{vi}), \quad (1)$$

where D_i is the molecular diffusivity of species i , n_i the ambient species concentration and n_{vi} the equilibrium vapour concentration on the particle. From Eq. (1) it becomes clear that an accurate estimation of D_i is crucial to the estimation of heterogeneous rates of mass transfer. However, in the *gas-kinetic* transport regime ($l_a > a$) the molecular flux is given by:

$$F_{ki} = \pi \alpha_i a^2 v_{th_i} (n_i - n_{vi}), \quad (2)$$

where α_i is the accommodation coefficient and v_{th_i} the mean kinetic velocity of the molecule. In this region therefore, the gas uptake is mainly collisional. The Knudsen number K_n which is defined as

$$K_n = l_a/a \quad (3)$$

is another important parameter because when $K_n \gg 1$, collisional uptake becomes significant, whereas when $K_n \ll 1$, it is diffusional uptake that is critical. Under typical stratospheric conditions where the pressure

~ 50 hPa and the temperature ~ 200 K the Knudsen number is small and the condensing flux in the *transition* regime is given by:

$$F_i = F_{ki}(1 + 3\alpha_i/4K_n)^{-1}. \quad (4)$$

Within a parcel of air containing a distribution of cloud particles, the total flux of molecules to the particles may be expressed as an integral over the particle size distribution. As an approximation, the total flux may be calculated as (Turco *et al.*, 1989):

$$F_i = \frac{1}{4} [S\alpha_i v_{th_i} (n_i - n_{vi})] / (1 + 3\alpha_i/4K_n) \quad (5)$$

where S is the total cloud particle surface area per unit volume of air. The above expression can be simplified further by letting $n_{vi} = 0$, since $n_{vi} \ll n_i$ and the time constant t_i for trace gas absorption by particles can be obtained as:

$$t_i = n_i/F_i = 4 \left(1 + \frac{3\alpha_i}{4K_n} \right) / S\alpha_i v_{th_i}. \quad (6)$$

If M is the total mass of particles per unit volume of air, then $S = 3M/a$ (assuming that all particles have a unit density and the same radius a), and also since $l_a = 3D_i/v_{th_i}$,

$$t_i = \left[\frac{4a}{3\alpha_i v_{th_i}} + \frac{a^2}{3D_i} \right] \frac{1}{M}. \quad (7)$$

Equation (7) can be re-written as

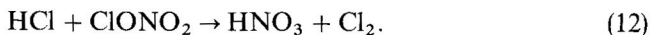
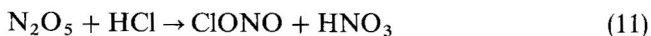
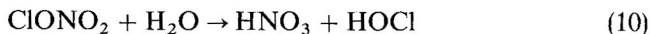
$$t_i = \left[\frac{4a}{3\alpha_i v_{th_i}} + \frac{a^2}{3D_i} \right] \frac{1}{M}. \quad (8)$$

where the first term within the square brackets in Eq. (8) corresponds to the *accommodation resistance* and the second to *diffusional transport resistance*.

The reaction rate K_L for a first-order process is then easily obtained as simply the reciprocal of t_i .

2.1 Limiting conditions

From Eq. (6) we find that the time constant (and hence the reaction rate) is controlled largely by the magnitudes of the mass accommodation coefficient α_i and the Knudsen number K_n , for given values of S . For very low values of α , the Knudsen number correction becomes unimportant. However α is often ~ 0.1 or even greater (De More *et al.*, 1992) for certain reactions that convert chlorine from the inert reservoir species to more active forms on PSCs like:



We shall first examine certain limiting cases for values of $\alpha \sim 0.1$ or more.

The above reactions can occur in early winter on type-I PSC particles and on sulphate aerosol droplets which are present all the year round, converting inert chlorine to active chlorine and active nitrogen to HNO_3 relatively quickly. An important role of type-I PSCs is that they can

absorb HNO_3 into solid solution, leading to the removal of HNO_3 by sedimentation (denitrification).

2.1.1 High Knudsen number limit

From Eq. (6) we obtain after dropping all subscripts:

$$t = \frac{4}{S\alpha v} \left(1 + \frac{3\alpha}{4K_n} \right). \quad (13)$$

For typical stratospheric conditions at 50 hPa, $T \sim 200$ K, for sulphate aerosol droplets ($a \sim 0.1 \mu$; $l \sim 1 \mu$) the Knudsen number $K_n \sim 1$. In this case (high Knudsen number limit) the term $3\alpha/4K_n$ is small and can be neglected. For reactions (10) and (12) on sulphate aerosols α -values are small ($\ll 0.1$), so that the above term is even smaller. For reaction (9) on sulphate aerosols, although the accommodation coefficient ~ 0.1 , because of the high Knudsen number the above-mentioned term can be neglected. Thus, in this case, we obtain:

$$t = \frac{4}{S\alpha v}, \quad (14)$$

which is the expression most often used to parameterise heterogeneous reaction rates in chemical models (e.g. Chipperfield *et al.*, 1993).

2.1.2 Small Knudsen number limit

For type-II PSCs however $K_n \sim 0.1$ and for typical stratospheric conditions the term $(3\alpha/4K_n) > 1$ and cannot be neglected for gases like HCl , ClONO_2 and N_2O_5 . The above is also true for gases like HNO_3 reacting on PSC I and in these cases:

$$t = \frac{3}{SvK_n}. \quad (15)$$

Since $l = 3D/v$

$$t = \frac{a}{SD} \quad (16)$$

indicating clearly that indeed the uptake is diffusion controlled.

From the above analysis we find that diffusional uptake becomes important for larger particles and for high values of accommodation coefficients. This was also pointed out by Schwartz (1986) in his analysis on gas uptake by water droplets. For the sake of completeness however, we have computed the reaction rates of 23 trace gases using the general expression (7) and using observations for α and γ (De More *et al.*, 1992) whenever available. Having established the importance of diffusional uptake for particular conditions we wish to emphasise that apart from the assumption of a potential no other approximations are made for the estimation of the diffusion coefficients D_i . A complete 6-12 Lennard-Jones calculation is used (Ghosh, 1993) to obtain D_i and a brief outline of the method is given in Sect. 3.

3 The Lennard-Jones method

The theory describing diffusion in binary gas mixtures at low-to-moderate pressure has been well developed

and the results are credited to Chapman and Enskog. Simplified versions can be found in standard textbooks of Physical Chemistry (e.g. Maitland *et al.*, 1982). Based on the kinetic theory, the diffusion coefficient may be expressed as (Reid *et al.*, 1987):

$$D_{AB} = \frac{0.00266 T^{3/2}}{P M_{AB}^{1/2} \sigma_{AB}^2 \Omega_D}, \quad (17)$$

where M_A, M_B = molecular weights of A and B , $M_{AB} = 2[(1/M_A + 1/M_B)]^{-1}$, T = temperature (K), P = pressure (bar), σ_{AB} = characteristic length (Å), Ω_D = diffusion collision integral, dimensionless D_{AB} = diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$).

The key to the use of Eq. (17) is the selection of an intermolecular force law and the evaluation of Ω_D . Reid and Sherwood (1958) emphasize that of all the available methods for correlating the intermolecular energy ψ between two molecules to the distance of separation r , the most accurate method is the one given by Lennard-Jones:

$$\psi = 4\epsilon \left[\left(\frac{\sigma}{r} \right)^{12} - \left(\frac{\sigma}{r} \right)^6 \right] \quad (18)$$

with ϵ and σ as the characteristic Lennard-Jones energy and length respectively. To use Eq. (17) some rule must be chosen to obtain σ_{AB} from σ_A and σ_B . Also, it can be shown that Ω_D is a function only of kT/ϵ_{AB} (k being the Boltzmann's constant), where again some rule must be selected to relate ϵ_{AB} to ϵ_A and ϵ_B . The simple rules shown below are usually employed:

$$\epsilon_{AB} = (\epsilon_A \epsilon_B)^{1/2}, \quad (19)$$

$$\sigma_{AB} = (\sigma_A + \sigma_B)/2. \quad (20)$$

Ω_D is tabulated as a function of kT/ϵ for the 6-12 Lennard-Jones potential and various analytical approximations are also available. We used the relation of Neufeld *et al.* (1972):

$$\Omega_D = \frac{A}{(T^*)^B} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)}, \quad (21)$$

where $T^* = kT/\epsilon_{AB}$, $A = 1.06036$, $B = 0.15610$, $C = 0.19300$, $D = 0.47635$, $E = 1.03587$, $F = 1.52996$, $G = 1.76474$ and $H = 3.89411$.

Application of the Chapman-Enskog theory to the viscosity of pure gases has led to the determination of many values of ϵ and σ (Reid *et al.*, 1987; Bzowski *et al.*, 1990). σ and ϵ/k were obtainable for most gases except for ClONO₂ (an important trace gas that participates in stratospheric heterogeneous reactions) where we used the relations (Reid *et al.*, 1987):

$$\sigma = 1.18 V_b^{1/3} \quad (22)$$

$$\epsilon/k = 1.15 T_b. \quad (23)$$

In Eqs. (22) and (23) V_b is the molar volume ($\text{cm}^3 \text{mol}^{-1}$) found from Tables 3–8 in Reid *et al.* (1987) and T_b is the normal boiling point (K). The normal boiling point was available experimentally from our centre at Cambridge (Harwood, private communication, 1993) and was found to be 295.16 K.

4 Results and discussions

Type-I PSCs are composed of an aerosol haze of micron sized nitric acid particles composed of HNO₃ and H₂O. Type-II PSCs are composed of water in ice crystals and appear to condense at colder temperatures ~ 187 K than type-I PSCs (at $T \sim 195$ K) consistent with the measured frost point of water vapour in the polar stratosphere (Poole and McCormick, 1988; Hamill *et al.*, 1988). It should be expected therefore that type-I haze would predominate cloud observations in the earliest part of the winter season. But the frequency of type-II clouds would increase with the progression of winter with cooling of upper air layers and as a result this would lead to a greater occurrence of heterogeneous reactions on type-II PSCs.

We present first results for the estimated reaction rates for the uptake of N₂O₅, ClONO₂ and HCl on type-II PSCs in Table 1.

The calculations shown correspond to the following input parameters: $a = 10 \mu$, $M = 10^{-10} \text{ g cm}^{-3}$, $T = 187 \text{ K}$, $P = 50 \text{ hPa}$.

Type-I PSCs are present at higher temperatures ($\sim 195 \text{ K}$) and appear earlier than type-II clouds. Diffusional uptake by type-I clouds although not as high as type-II clouds, contributes substantially to the overall reaction rates for the main heterogeneous reactions. This is clear in Table 2 where we show typical calculations for reaction rates on type-I PSCs for the following input parameters: $a = 1 \mu$, $M = 10^{-12} \text{ g cm}^{-3}$, $T = 195 \text{ K}$, $P = 50 \text{ hPa}$.

It is important to mention that in Tables 1 and 2, the α -values for the reaction of HCl were reported (De More *et al.*, 1992) as 0.3, irrespective of the type of surface involved. For ClONO₂ and N₂O₅, only the reaction probabilities γ -values have been reported (De More *et al.*, 1992). These have been assumed to be the same as the accommodation coefficients α . In the absence of further observational data, this is not an unreasonable approximation because the α -values are an upper limit to the γ -values. Also, for type-II PSCs, the same γ -values were reported for the reaction of ClONO₂ with both HCl and H₂O, and the same is true for N₂O₅.

From Table 1 it is clear that the contribution to the reaction rate by diffusional uptake is significant for type-II PSCs and can be as high as 64%. For type-I PSCs (Table 2), although the contribution diminishes, it is often not negligible. Thus it is important to include this contribution in heterogeneous reaction rate estimates. For the sake of completeness, we list in Table 3 the rate constants of other common trace gases reacting on PSCs calculated by the procedure just outlined. Accommodation coefficients for all of these gases were not available. A value of 0.05 has

Table 1. Uptake of HCl, ClONO₂ and N₂O₅ on PSC II

Species	D_g $\text{cm}^2 \text{s}^{-1}$	α	$V_{th} \times 10^4 \text{ cm s}^{-1}$	K_T, s^{-1}	% diff.
HCl	1.44	0.3	3.3	2.72×10^{-4}	63.25
ClONO ₂	0.86	0.3	2.02	1.64×10^{-4}	63.9
N ₂ O ₅	1.19	0.03	1.91	3.84×10^{-5}	10.77

Table 2. Uptake of HCl, ClONO₂ and N₂O₅ on PSC I

Species	$D_g, \text{cm}^2 \text{s}^{-1}$	α	$V_{th} \times 10^4 \text{cm s}^{-1}$	K_T, s^{-1}	% diff.
HCl	1.56	0.3	3.4	6.51×10^{-5}	13.94
ClONO ₂	0.93	0.3 (HCl)	2.06	3.97×10^{-5}	14.25
ClONO ₂	0.93	0.006 (H ₂ O)	2.06	9.23×10^{-7}	0.33
N ₂ O ₅	1.29	6×10^{-4} (H ₂ O)	1.96	8.8×10^{-8}	0.02
N ₂ O ₅	1.29	0.003 (HCl)	1.96	4.4×10^{-7}	0.11

Table 3. Rate constants for trace gas uptake on PSCs

Species	Surface type					
	PSC I			PSC II		
	α	K_T, s^{-1}	% diff.	α	K_T, s^{-1}	% diff.
NO	1.0×10^{-4}	2.78×10^{-8}	0.005	1.0×10^{-4}	2.72×10^{-7}	0.05
NO ₂	1.0×10^{-4}	2.25×10^{-8}	0.005	1.0×10^{-4}	2.2×10^{-7}	0.054
N ₂ O	1.0×10^{-6}	2.3×10^{-10}	0.00005	1.0×10^{-6}	2.25×10^{-9}	0.00057
O ₃	2.5×10^{-4}	5.5×10^{-8}	0.01	1.0×10^{-6}	2.15×10^{-9}	0.00053
HCl	0.3	6.5×10^{-5}	13.93	0.3	2.72×10^{-4}	63.26
HF	0.05	1.66×10^{-5}	2.84	0.05	1.27×10^{-4}	23.8
Br ₂	0.05	5.89×10^{-6}	2.19	0.05	4.7×10^{-5}	19.24
Cl ₂	0.05	8.87×10^{-6}	2.64	0.0001	1.78×10^{-7}	0.06
F ₂	0.05	1.21×10^{-5}	2.1	0.05	9.87×10^{-5}	18.5
H ₂ O	0.05	1.74×10^{-5}	3.1	0.05	1.31×10^{-4}	25.45
CO	0.05	1.41×10^{-5}	2.4	0.05	1.12×10^{-4}	20.67
CO ₂	0.05	1.11×10^{-5}	2.19	0.05	8.78×10^{-5}	22.01
CCl ₄	0.05	5.96×10^{-6}	2.89	0.05	4.57×10^{-5}	24.00
CCl ₂	0.05	6.78×10^{-6}	2.18	0.05	5.49×10^{-5}	19.11
CCl ₃	0.05	6.32×10^{-6}	2.55	0.05	4.97×10^{-5}	21.7
HCN	0.05	1.42×10^{-5}	3.45	0.05	1.04×10^{-4}	27.58
CH ₄	0.05	1.85×10^{-5}	29.88	0.05	1.41×10^{-4}	24.6
C ₂ H ₄	0.03	8.48×10^{-6}	1.93	0.05	1.05×10^{-4}	25.86
ClONO ₂	0.3 (HCl)	3.97×10^{-5}	14.25	0.3	1.64×10^{-4}	63.86
ClONO ₂	0.006 (H ₂ O)	9.23×10^{-7}	0.33	0.3	1.64×10^{-4}	63.86
HNO ₃	0.05	9.33×10^{-6}	28.22	0.03	4.76×10^{-5}	15.64
SO ₂	1.0×10^{-6}	1.91×10^{-10}	5.5×10^{-5}	0.05	7.2×10^{-5}	22.7
H ₂ O ₂	0.05	1.26×10^{-5}	3.22	0.05	9.46×10^{-5}	26.12
N ₂ O ₅	6×10^{-4} (H ₂ O)	8.8×10^{-8}	0.02	0.03	3.84×10^{-5}	10.77
N ₂ O ₅	0.003 (HCl)	4.4×10^{-7}	0.11	0.03	3.84×10^{-5}	10.77

been adopted for those gases for which the accommodation coefficients have not yet been reported. We have deliberately refrained from prescribing extreme (either too high or too low) values of α in order to see the importance of both diffusion and collision. In Tables 1, 2 and 3, the columns denoted by % diff. refer to the diffusional contribution to the reaction rates.

Figures 1 and 2 show the dependence of the rate constants (solid line) on droplet size on PSC I and II for HCl and ClONO₂, respectively. The diffusional contribution to the reaction rates is also indicated in these graphs (dashed line). We find that the diffusional contribution increases with particle size.

Finally, the effect of including diffusive transport into a single droplet was studied in an idealised box model run for an air parcel which encounters type-II PSCs, typical of air parcels in the Antarctic lower stratosphere during winter. The box model used for the idealised experiments is due to Lary (private communication, 1994) and contains a total of 208 reactions, 127 bimolecular reactions, 27 trimolecular reactions, 41 photochemical reactions and 13 heterogeneous reactions. The rate constants for the reactions were taken from Atkinson *et al.* (1992) and DeMore *et al.* (1992).

Figure 3 shows the results from part of the idealised experiment. The experiment started on 1 May and was for

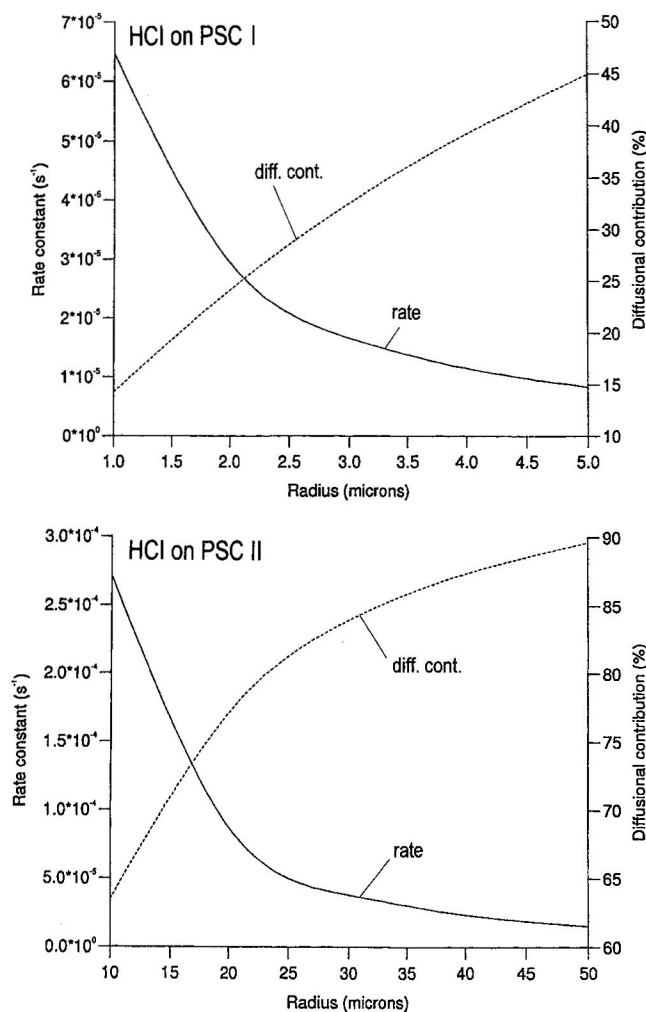


Fig. 1. Variation of rate constant (including diffusional contribution) with particle size for HCl on polar stratospheric clouds

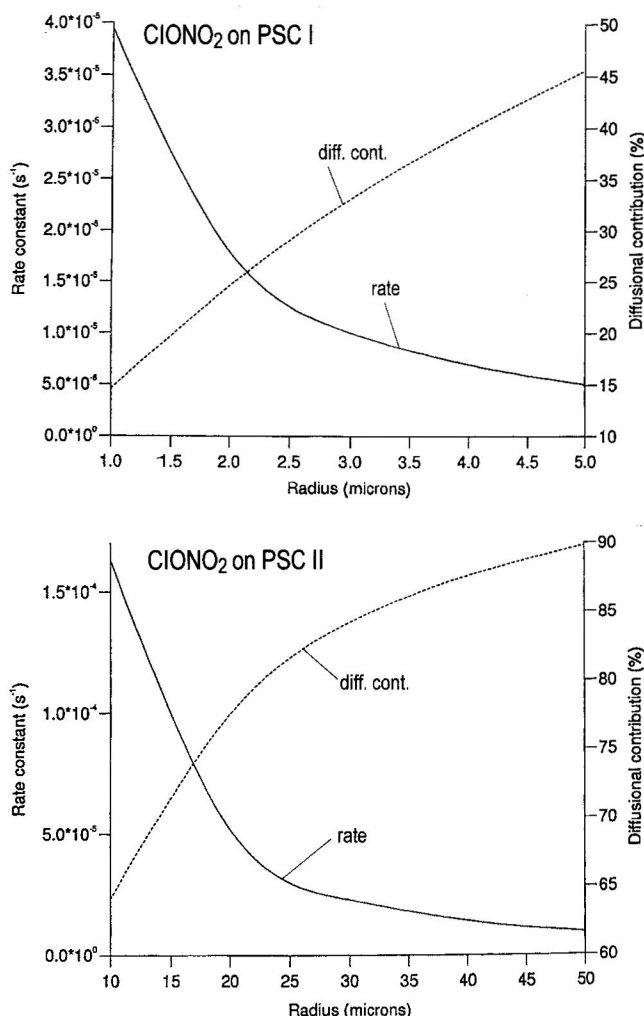


Fig. 2. Variation of rate constant (including diffusional contribution) with particle size for ClONO₂ on polar stratospheric clouds

a stationary box at a pressure of 42 hPa at 75°S. For the first 15 days the temperature was kept at 200 K, then for the next 20 days it was dropped to 185 K, during which time type-II PSCs were present.

Including the diffusional contribution increases the time constant for the heterogeneous reaction $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$. Consequently, when the diffusional contribution is included the calculated ClONO₂ concentration (dashed line in Fig. 3a) does not drop quite as rapidly as it does when the diffusional contribution is not included (solid line). The absolute rate of the reaction, $k_h [\text{HCl}][\text{ClONO}_2]$ (as opposed to the rate constant, k_h) is initially lower when the effect of diffusive transport into a single droplet is included. However, after a few days in a type-II PSC including the diffusional contribution means that the ClONO₂ concentration is higher and hence, so is the absolute rate of the heterogeneous reaction $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$ (Fig. 3).

The increased ClONO₂ concentration (of up to 120% in this idealised experiment) leads to more HOCl production via the heterogeneous reaction $\text{H}_2\text{O} + \text{ClONO}_2 \rightarrow$

HOCl + HNO₃. It should be noted that although the percentage increase in the ClONO₂ and HOCl concentrations can be very large it occurs at a time when the absolute values of these concentrations is small.

5 Conclusions

Trace gas uptake by polar stratospheric clouds is controlled by both molecular collision and diffusion. Most models consider only collisional uptake and estimate the first-order reaction rate as $K_T = \alpha v_{th} S/4$ (where the terms have their usual meanings) which implies that the rate constant is dependent only on molecular collision. However, the above is only true for low values of the mass accommodation coefficient α or for small particles. For gases like HCl, ClONO₂, N₂O₅ and HNO₃ which participate in heterogeneous processing on polar stratospheric clouds, this study shows that diffusional transport resistance is often the dominant mechanism or is at least comparable to the accommodation resistance. The reaction

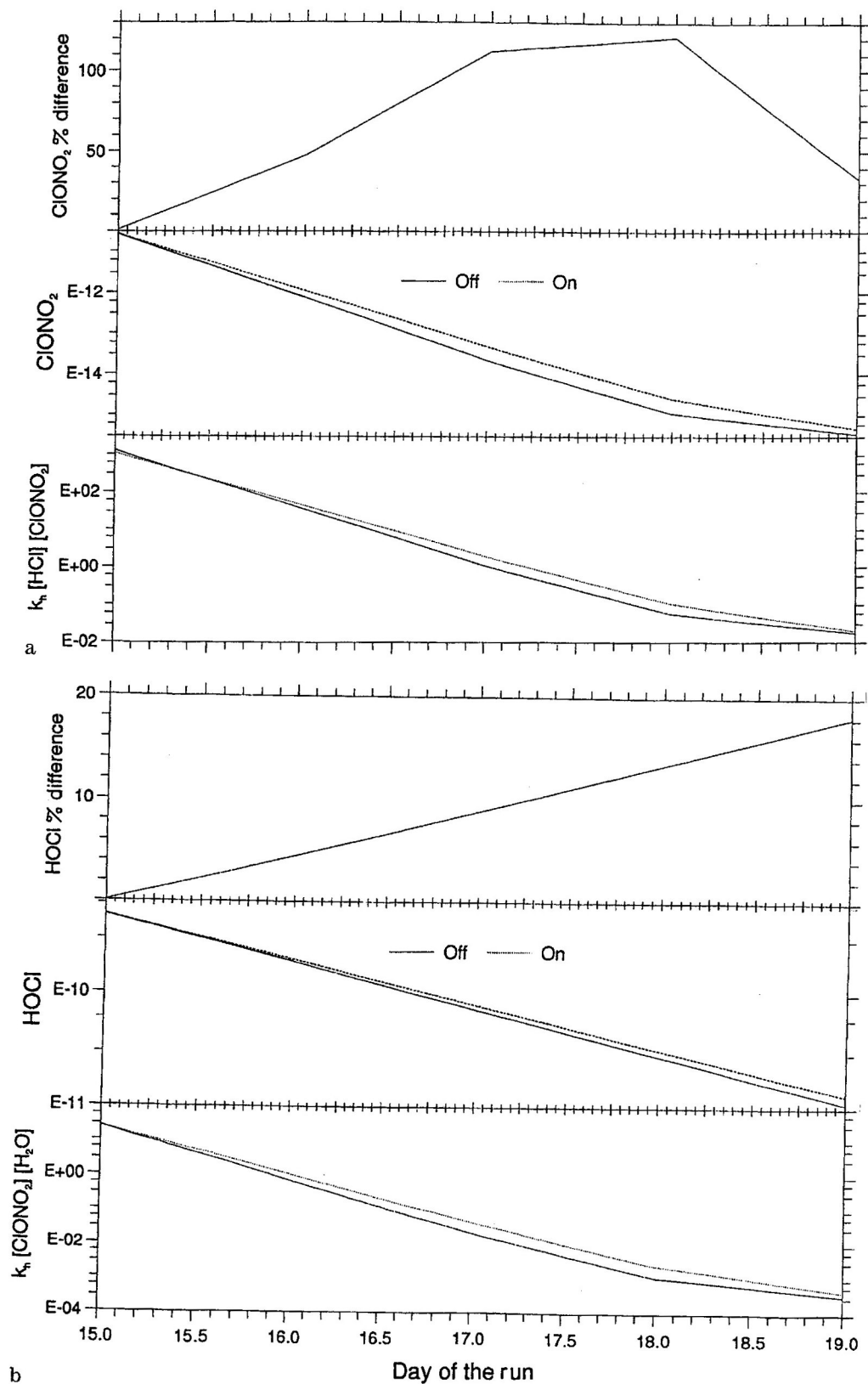


Fig. 3. Effect of including diffusional resistance in a box model run for an air parcel in a type-II PSC event, for **a** ClONO₂ and **b** HOCl. **a** shows the % change in the ClONO₂ concentration relative to a calculation which did not include the diffusional contribution, the ClONO₂ concentration (v.m.r.) and the absolute rate of the reaction (molecules cm⁻³ s⁻¹) $\text{HCl} + \text{ClONO}_2 \rightarrow \text{Cl}_2 + \text{HNO}_3$. **b** shows the % change in the HOCl concentration relative to a calculation which did not include the diffusional contribution, the HOCl concentration (v.m.r.) and the absolute rate of the reaction (molecules cm⁻³ s⁻¹) $\text{H}_2\text{O} + \text{ClONO}_2 \rightarrow \text{HOCl} + \text{HNO}_3$.

rates for heterogeneous reactions on polar stratospheric clouds have been estimated by including collisional and diffusional uptake. To model the latter process a full 6-12 Lennard Jones calculation is performed. It is expected

that this study will aid modellers concerned with heterogeneous chemistry (particularly on polar stratospheric clouds) and will significantly improve trace gas scavenging estimates.

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