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# Modeling the heterogeneous reaction probability for chlorine nitrate hydrolysis on ice

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[1] We present a theoretical estimate of the reaction probability $\gamma$ for the chlorine nitrate ($ClONO_2$) hydrolysis on type II (water-ice) polar stratospheric cloud material. This estimate is based on high-level ab initio calculations in a supermolecule containing four molecules of water and one molecule of chlorine nitrate. To the best of our knowledge, this is the first estimate of $\gamma$ that makes no a priori use of experimental data at all. Instead, the rate constants for association, surface reaction, and surface desorption as calculated by variational transition state theory enter the model. At 180 K we estimate $\gamma \approx 0.10^{+0.20}_{-0.06}$, which is within the error bars of the agreeing recommendations of Jet Propulsion Laboratory and International Union of Pure and Applied Chemistry of $0.3^{+0.7}_{-0.1}$. The temperature dependence between 75 and 150 K agrees with results obtained from laser-induced thermal desorption. In particular, the temperature of 105 K above which $\gamma$ becomes less than unity is reproduced well. A negative temperature dependence between 180 and 210 K is found, which has not yet been confirmed in the laboratory for $ClONO_2$ hydrolysis but only for $BrONO_2$ on ice. This qualitative agreement of a gas-phase cluster calculation with experiments on hexagonal ice surfaces implies that a highly mobile and oxygen disordered ice surface rather than an ordered, immobile crystalline ice surface is experienced by chlorine nitrate molecules under polar stratospheric conditions.

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## 1. Introduction

[2] Heterogeneous chemistry is recognized to be a key factor involved in polar ozone depletion for about 15 years [*Solomon et al.*, 1986; *Molina et al.*, 1987; *Solomon*, 1990]. Polar stratospheric clouds (PSCs) are known to catalyze the conversion of chlorine and nitrogen reservoir species (HCl, $ClONO_2$ and $N_2O_5$) efficiently (for a recent review see [*Zondlo et al.*, 2000]) and to be an effective sink of nitric acid ($HNO_3$). Type Ia PSCs are composed of nitric acid trihydrate (NAT), type Ib PSCs are supercooled ternary solutions of $H_2SO_4/HNO_3/H_2O$ and type Ic PSCs are composed of small solid particles [*Zhang et al.*, 1993; *Tabazadeh et al.*, 1994; *Toon et al.*, 2000; *Tolbert and Toon*, 2001]. Because of the presence of acidic components in type I PSCs some experimental work has been devoted to studying the chemistry of chlorine nitrate with large ionic water clusters [*Schindler et al.*, 1996, 2000; *Gilligan et al.*, 2000; *Gilligan and Castleman*, 2001]. This study, however, focuses on type II PSCs, which are water-ice clouds occurring presumably as crystals of hexagonal ice.

[3] For chlorine reservoir species, three main activation reactions have been identified [*Kolb et al.*, 1995]. It has been shown that these three reactions likely occur efficiently also on the surface of cirrus clouds, thereby affecting the ozone depletion in the near-tropopause region [*Solomon et al.*, 1997]. Two out of these three are the conversion of HOCl or $ClONO_2$ by HCl on ice surfaces to molecular chlorine ($Cl_2$). This article, however, deals with equation (1), the hydrolysis of chlorine nitrate ($ClONO_2$) on water-ice surfaces:

$$ClONO_2(g) + H_2O(cond) \overset{\text{ice surface}}{\underset{\gamma}{\rightleftharpoons}} HOCl(g) + HNO_3(ad) \quad (1)$$

[4] As early as 1986 it was recognized that the heterogeneous reaction on generally inert surfaces is more than 50 times faster than the homogeneous reaction [*Rowland et al.*, 1986]. In the following years the hydrolysis has been studied extensively using various experimental techniques, e.g., flow tubes coupled to mass spectrometers, and employing different surfaces, e.g., nitric acid hydrates [*Moore et al.*, 1990; *Abbatt and Molina*, 1992; *Molina et al.*, 1993; *Zondlo et al.*, 1998], sulfuric acid hydrates [*Tolbert et al.*,

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1988; *Molina et al.*, 1993; *Zhang et al.*, 1994], supercooled ternary solutions of $H_2SO_4/HNO_3/H_2O$ [*Molina et al.*, 1993; *Zhang et al.*, 1995; *Del Negro et al.*, 1997], vapor-deposited ice [*Leu et al.*, 1991; *Berland et al.*, 1997], smooth ice [*Lee et al.*, 1999], and sodium chloride [see, e.g., *Finlayson-Pitts et al.*, 1989] or surfaces obtained from vapor codeposition on substrates [*Koch et al.*, 1997]. Concomitantly, also a lot of theoretical work has been done to resolve important details about the reaction mechanism [*Ying and Zhao*, 1997; *Bianco and Hynes*, 1998; *Bianco et al.*, 1998; *McNamara and Hillier*, 1999; *McNamara et al.*, 1999; *Xu and Zhao*, 1999; *McNamara and Hillier*, 2000; *Bianco et al.*, 2001; *McNamara and Hillier*, 2001; *Loerting and Liedl*, 2001; *Bianco and Hynes*, 2006]. These studies involved mainly molecular dynamics simulations and gas-phase cluster calculations by employing density functional theory or ab initio methods such as Møller-Plesset perturbation theory (MP2). Whereas the reactions are reasonably well understood from a phenomenological point of view due to the work in many research groups, there is still a vast amount of uncertainty in the microscopic view of the reaction mechanism. Especially the rates of the elementary steps in the overall process have not yet been characterized [*Molina et al.*, 1996]. However, a proper understanding of $\gamma$ and the various underlying chemical and physical processes is required for a sound basis of interpreting and predicting ozone losses [*Carslaw and Peter*, 1997; *Carslaw et al.*, 1997].

[5] We therefore contribute to bridge this gap by calculating the reaction probability $\gamma$ from first principles. Rate constants for the association, dissociation and reaction on the surface are determined from ab initio calculations and quantum transition state theory. This is, to the best of our knowledge, the first study that tries to model heterogeneous reaction probabilities without using experimental data at all. Experimental data is solely employed a posteriori for comparing with the theoretical prediction.

## 2. Methods

[6] The association rate constant $k_{\mathrm{ass}}(T)$ (in $\mathrm{Pa}^{-1}\mathrm{s}^{-1}$) is calculated from [*Tabazadeh and Turco*, 1993; *Adamson*, 1997]

$$k_{\mathrm{ass}}(T) = \frac{\alpha\sigma_0}{\sqrt{2\pi M k_B T}} \exp\left(-\frac{\Delta G^{\ddagger}_{\mathrm{ass}}(T)}{RT}\right) \tag{2}$$

where $\alpha$ is the mass accommodation coefficient of chlorine nitrate on ice (assumed to be one under stratospheric conditions), $\sigma_0$ is the area of one adsorption site on the surface (approximated to be $10^{-19}$ $\mathrm{m}^{-2}$), $M$ is the weight of a molecule of chlorine nitrate ($1.618 \times 10^{-25}$ kg), $k_B$ is the Boltzmann constant ($1.381 \times 10^{-23}$ J $\mathrm{K}^{-1}$), $T$ the temperature (in K), $R$ is the gas constant (8.315 J $\mathrm{K}^{-1}$ $\mathrm{mol}^{-1}$), and $\Delta G^{\ddagger}_{\mathrm{ass}}(T)$ represents the temperature-dependent Gibbs free energy barrier to association (in J $\mathrm{mol}^{-1}$), which is assumed to be zero as long as the Gibbs free energy barrier to desorption (dissociation) $\Delta G^{\ddagger}_{\mathrm{des}}(T)$ has a positive sign. The latter is used to calculate the desorption rate constant $k_{\mathrm{des}}(T)$ (in $\mathrm{s}^{-1}$) [*Pilling*, 1995; *Billing*, 2000]:

$$k_{\mathrm{des}}(T) = \frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}_{\mathrm{des}}(T)}{RT}\right) \tag{3}$$

where $h$ is the Planck constant ($6.626 \times 10^{-34}$ J s). The desorption rate constant $k_{\mathrm{des}}(T)$ is calculated from the simplified reaction scheme:

$$\mathrm{ClONO_2} \cdot (\mathrm{H_2O})_n \xrightarrow{k_{\mathrm{des}}^{\mathrm{ClONO_2}}} \mathrm{ClONO_2} + (\mathrm{H_2O})_n \tag{4}$$

where $n$ is the number of water molecules representing the ice surface. Ideally, one would like to use a hexagonal crystal for $(H_2O)_n$. However, as we are solving the time-independent Schrödinger equation using post-Hartree Fock methods and large basis sets in order to achieve the best possible description for the hydrogen bond interaction and dynamics, this task cannot be achieved because of limitations in computer time. These high-accuracy methods scale unfavorably with system size, so that incorporating $n = 4$ water molecules instead of $n = 3$ water molecules means an approximate 100fold increase of computer time for calculating a single-point energy (at 0 K) and a 1000-fold increase for calculating thermal corrections (including entropy contributions) to the single point energies. Thermal corrections are obtained at stationary points of the potential energy surface (PES), where the first-derivative with respect to nuclear coordinates (gradient) equals zero by calculating the Hessian matrix (second derivative). We estimate that a calculation at this level of theory using a state-of-the art high-speed computer would take several years for $n > 10$. We are using a chain of four water molecules representing the ice surface to which chlorine nitrate is bound via dangling OH bonds therefore and calculate the desorption barrier by removing chlorine nitrate from the surface at G2MP2 level of theory [*Curtiss et al.*, 1993]. Thermal corrections to the electronic energy are obtained at the hybrid density functional level of theory (B3LYP/6-31+G(d)) [*Becke*, 1993, 1997].

[7] The reaction rate constant $k_{rxn}(T)$ for the conversion of adsorbed chlorine nitrate to adsorbed HOCl and nitric acid is also calculated under the cluster assumption:

$$\mathrm{ClONO_2} \cdot (\mathrm{H_2O})_{\mathrm{n}} \overset{\mathrm{k_{rxn}}}{\rightleftharpoons} \mathrm{HOCl} \cdot \mathrm{HNO_3} \cdot (\mathrm{H_2O})_{\mathrm{n-1}} \tag{5}$$

using high-accuracy quantum-mechanical methods. In particular G2(MP2) is employed to calculate the reaction barrier, and B3LYP/6-31+G(d) energies along the minimum energy path are interpolated to the G2(MP2) barrier. The details for the calculation on the full-dimensional PES (45 vibrational degrees of freedom for the $n = 4$ system) can be found elsewhere [*Loerting and Liedl*, 2001]. In brief, $k_{rxn}(T)$ (in $\mathrm{s}^{-1}$) is calculated from quantum mechanical variational transition state theory [*Chuang et al.*, 1999; *Corchado et al.*, 1999; *Frisch et al.*, 1998]:

$$k_{rxn}(T) = \kappa(T)\frac{k_B T}{h} \exp\left(-\frac{\Delta G^{\ddagger}_{rxn}(T)}{RT}\right) \tag{6}$$

where $\kappa(T)$ is the enhancement factor of the reaction due to quantum mechanical tunnelling along all possible directions of the PES (of course dominated by contributions corresponding to proton motion) and $\Delta G^{\ddagger}_{rxn}(T)$ is the free energy barrier approximated by the zero-point corrected energy barrier along the minimum energy path (MEP) on the PES [*Truhlar and Garrett*, 1984; *Truhlar et al.*, 1985;

*Truhlar and Gordon*, 1990; *Truhlar*, 1995]. The rate for the backward reaction is also calculated with the same approach, and is found to be slower by several orders of magnitude at any given temperature. As in all common derivations, the influence of the back reaction on the uptake probability $\gamma$ is neglected, therefore.

[8] Using such a data set of $k_{rxn}(T)$, $k_{\mathrm{des}}(T)$, and $k_{\mathrm{ass}}(T)$, i.e., without the use of experimental data, $\gamma$ can be estimated from [*Tabazadeh and Turco*, 1993]

$$\gamma\left(T, p^{\mathrm{ClONO_2}}\right) = \frac{4k_B T K k_{rxn}}{\sigma_0 \bar{c}\left(1 + K p^{\mathrm{ClONO_2}}\right)} \tag{7}$$

where $\bar{c}$ is the average thermal velocity,

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi M}} \tag{8}$$

$p^{\mathrm{ClONO2}}$ is the partial pressure of chlorine nitrate (in Pa) and $K$ (in $\mathrm{Pa}^{-1}$) is calculated from rate constants only:

$$K = \frac{k_{\mathrm{ass}}}{k_{rxn} + k_{\mathrm{des}}} \tag{9}$$

$K$ can be employed to calculate the surface coverage $\theta$ of ice according to the (surface reactive) Langmuir adsorption isotherm [*Langmuir*, 1922]:

$$\theta\left(p^{\mathrm{ClONO_2}}\right) = \frac{K p^{\mathrm{ClONO_2}}}{1 + K p^{\mathrm{ClONO_2}}} \tag{10}$$

We base this model on the simple Langmuir isotherm on a similar basis as a previous model simulating the effect of competitive adsorption on PSC material [*Mozurkewich*, 1993]. Note that for $k_{rxn} \gg k_{\mathrm{des}}$, equation (7) simplifies to

$$\gamma = \frac{4k_B T k_{\mathrm{ass}}}{\sigma_0 \bar{c}} = \alpha \exp\left(-\frac{\Delta G^{\ddagger}_{\mathrm{ass}}(T)}{RT}\right) \tag{11}$$

and is no longer temperature-dependent (as long as there is no association barrier and $\alpha$ is constant with temperature), and equals to 1 under the assumptions made for the stratosphere. On the other hand, for $k_{\mathrm{des}} \gg k_{rxn}$, equation (7) simplifies to

$$\gamma(T) = \frac{4k_B T k_{\mathrm{ass}} k_{rxn}}{\sigma_0 \bar{c} k_{\mathrm{des}}} \tag{12}$$

and the temperature dependence of $\gamma$ originates from the temperature dependence of $\frac{k_{rxn}}{k_{\mathrm{des}}}$. Note that equation (7) can alternatively be written as

$$\gamma(T) = \alpha \frac{k_{rxn}}{k_{rxn} + k_{\mathrm{des}}} \exp\left(-\frac{\Delta G^{\ddagger}_{\mathrm{ass}}(T)}{RT}\right) \tag{13}$$

which reduces to

$$\gamma(T) = \frac{k_{rxn}}{k_{rxn} + k_{\mathrm{des}}} \tag{14}$$

under the assumptions of $\alpha = 1$ and no association barrier.

[9] We set $p^{\mathrm{ClONO2}}$ to $10^{-8}$ Pa, which is very close to the polar stratospheric partial pressure, and use equation (7) to estimate $\gamma$ and equation (10) to estimate $\theta$. We note that a wide range of partial pressures of chlorine nitrate has been employed in different experimental studies. However, the estimate of $\gamma$ does not depend much on the partial pressure of chlorine nitrate. In fact, under the assumptions of equation (14), $\gamma$ does not depend on the partial pressure of chlorine nitrate. Therefore our data can be compared with experimental data, even though some flow tube studies employed higher partial pressures.

[10] The experimental results are influenced from differences in ice surface area, porosity and tortuosity [*Keyser et al.*, 1991; *Grassian*, 2001] and surface poisoning by $HNO_3$ [*Hanson and Ravishankara*, 1991], which decreases $\gamma$ by approximately a factor of 50 when the surface saturates with the product $HNO_3$. Surface porosity might play a role in the magnitude of the uptake probability [*Chu et al.*, 1993; *Hanson and Ravishankara*, 1993]. The recommendations given by International Union of Pure and Applied Chemistry/Jet Propulsion Laboratory (IUPAC/JPL) are based on a critical evaluation of the available experimental studies. In particular they have evaluated, to which degree the experimental studies suffer from $HNO_3$ contamination. Therefore the IUPAC/JPL recommendations provide the benchmark for our theoretical estimates of $\gamma$ on a fresh ice surface.

## 3. Results and Discussion

### 3.1. Reaction Mechanism

[11] Figure 1 shows the chemical reaction mechanism, denoted by $n = 4$, that was found on minimizing the electronic energy as a function of the positions of the nuclei for a system containing four water molecules and one molecule of chlorine nitrate (as implemented by *Frisch et al.* [1998]). In comparison to the molecular systems studied previously by two of us (see Figure 1, $n = 1$ to $n = 3$) [*Loerting and Liedl*, 2001], there is one crucial difference: The reaction barrier is considerably lower, and amounts to 5.61 kcal $\mathrm{mol}^{-1}$ (G2MP2 level of theory), which is a reduction of the barrier by 14.34 kcal $\mathrm{mol}^{-1}$ as compared to the system with just one molecule of water less ($n = 3$). This reaction barrier agrees well with the best estimate given in the literature of 3–7 kcal $\mathrm{mol}^{-1}$ [*Tabazadeh et al.*, 1994]. Also the fact that on ice films kept between 90 and 120 K no reaction product was observed is indicative of a barrier for the surface reaction [*Donsig et al.*, 1999]. We believe that the drastic reduction of the reaction barrier for the surface reaction is caused by the change of the angle of water molecules with respect to each other. Whereas for $n = 3$ the O-O-O angle amounts to 102.5°, it amounts to 120.0° for any combination of three $H_2O$ oxygen atoms in the $n = 4$ model system for the ice surface-$ClONO_2$ interaction. All of these angles are reasonably close to the ideal tetrahedral angle of 109.5° observed in X-ray studies of hexagonal ice [*Hobbs*, 1974]. However, in the reaction product, and according to the Hammond postulate [*Hammond*, 1955] also to a certain degree in the transition state, the angle between three oxygen atoms adopts unfavorable values far away from 109.5° for the $n = 3$ model, but still reasonably close values for the $n = 4$ model. This situation allows shuttling of hydrogen atoms between oxygen atoms in a favorable near-linear configuration. Whereas in a true hexagonal crystal the angular flexibility would be significantly reduced, the cluster employed here shows flexibility in the optimized structures.

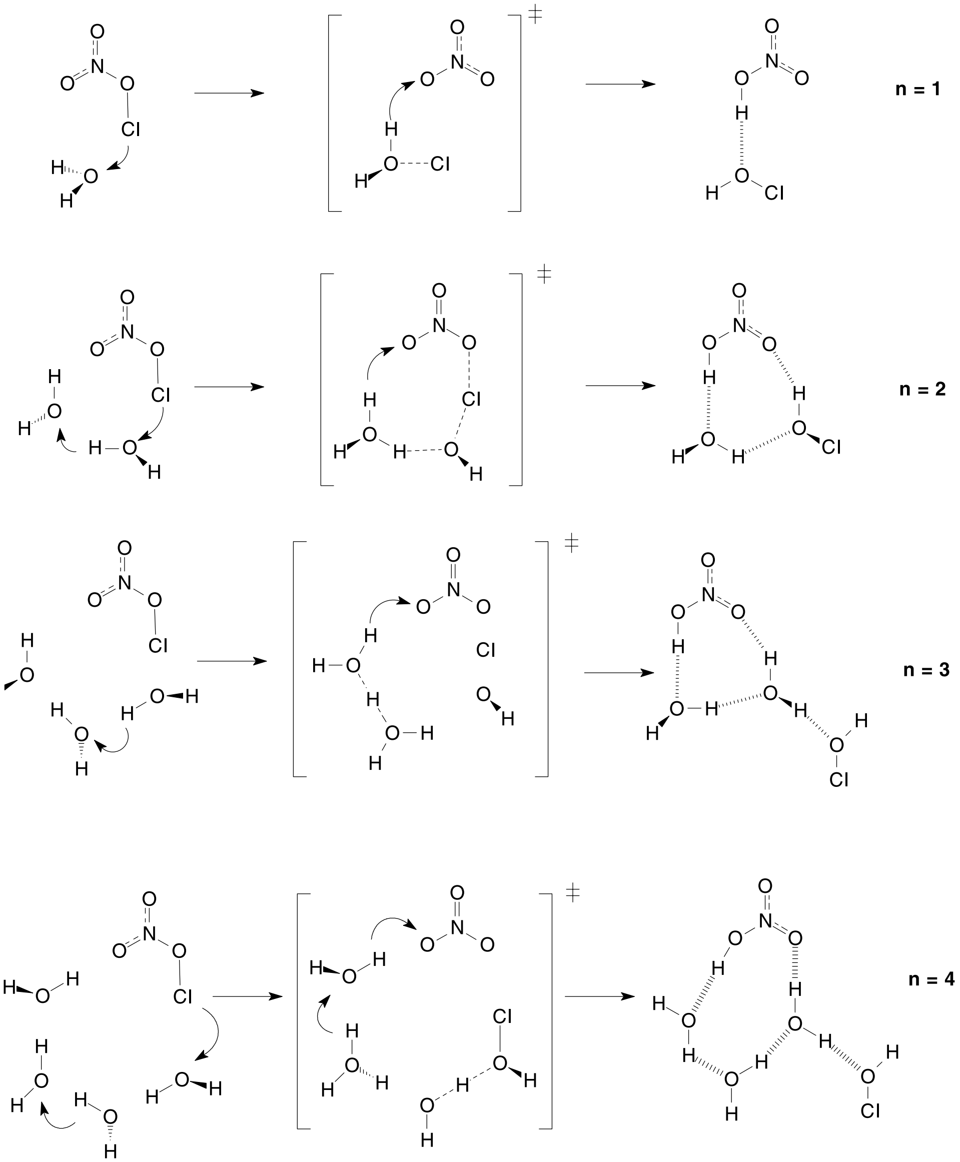

**Figure 1.** Chemical reaction mechanism for heterogeneous chlorine nitrate hydrolysis in clusters containing $n = 1$ to $n = 4$ water molecules, including $ClONO_2$-water surface adsorbate, transition state to hydrolysis, and hydrogen-bonded reaction product of $HOCl \cdot HNO_3$ adsorbed to the surface. Note that for $n = 4$ the ice surface is represented by a water tetramer for the educts and reduced to a water trimer for the hydrolysis products. The angles between the water molecules resemble very much the crystallographic angles between water molecules in hexagonal ice, and the gas-phase cluster simplification of the reaction system results in the molecular flexibility that is presumably encountered at polar stratospheric conditions.

The combination of this flexibility and the near-hexagonal structure, to our opinion, results in the low-barrier situation that is also found in the stratosphere, and represented by both a JPL as well as a IUPAC-recommended estimate for the reaction probability at 200 K of $0.3^{+0.7}_{-0.1}$ [*Hanson and Ravishankara*, 1991; *DeMore et al.*, 1997; *Sander et al.*, 2000]. Of course, also microsolvation effects, which are not studied here, can contribute significantly to this flexibility [*Bianco and Hynes*, 1998]. It may seem awkward to think of oxygen atoms at the crystal surface as flexible. However, on type II polar stratospheric water-ice clouds such a flexibility could possibly be caused by a thin quasi-liquid layer, which may be induced by atmospheric species present in rather low mixing ratios at temperatures of 185–210 K [*Molina*, 1994; *McNeill et al.*, 2006].

### 3.2. Surface Reaction and Desorption

[12] In Figure 2 the rate constants for the hydrolysis $k_{rxn}(T)$ on the model surface and the rate constant for chlorine nitrate desorption $k_{\mathrm{des}}(T)$ from the model surface employed for estimating the reaction probability $\gamma$ are depicted. The $k_{rxn}(T)$ has been calculated from variational transition state theory as discussed in section 2. The $k_{\mathrm{des}}(T)$ has been calculated by employing equation (3) and the free energy barriers for desorption as depicted in Figure 3.

[13] Because of a tunnelling enhancement of $k_{rxn}(T)$ by a factor of 2–4 at temperatures from 250 to 100 K (see Figure 4)

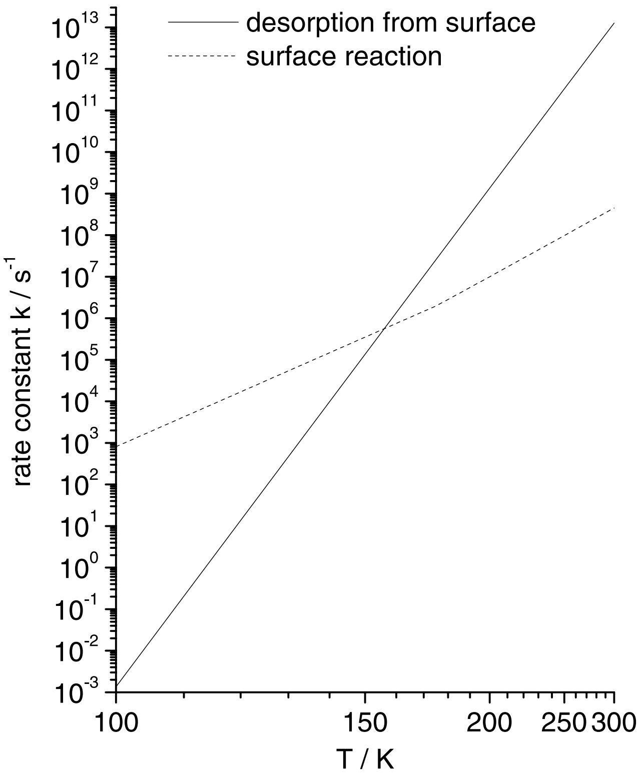

**Figure 2.** Rate constants of desorption from the model ice surface as compared to the rate constants of reaction on the model ice surface. Reaction rate constants $k$ for the decomposition of chlorine nitrate in an (unimolecular) supermolecule containing four water molecules are calculated at a B3LYP/6-31+G(d) potential energy surface and interpolated to G2MP2 barriers as well as corrected for quantum effects. Rate constants for desorption were calculated according to equation (3) by employing the free energy barrier depicted in Figure 3.

the Arrhenius plot in Figure 2 is nonlinear. As compared to the model systems employing two or three water molecules, which show tunnelling enhancement factors reaching several orders of magnitude at 100 K (see Figure 4), the contribution of tunnelling is much smaller in the case of four water molecules. This can be attributed to enhanced movement of O atoms, which results in a higher reduced mass for proton transfer. At stratospheric temperatures the tunnelling effect is weak and comparable to the effect calculated for the homogeneous gas-phase reaction ($n = 1$) [*Atkinson et al.*, 1986]. So-called direct corner cutting, which causes a strong tunnelling effect, is important only at T < 150 K. It therefore does not play a significant role under tropospheric or stratospheric conditions.

[14] The rate constants calculated here compare to the estimate of $10^4$ s$^{-1}$ (200 K) to $10^6$ s$^{-1}$ (300 K) [*Robinson et al.*, 1997; *Shi et al.*, 2001]. This literature estimate is based on an extrapolation to pure water on the basis of experimentally measured values on sulfuric acid solutions. It is surprising that gas-phase clusters and an experimental extrapolation to pure water shows only a difference of about two orders of magnitude. We therefore conjecture that the hydrolysis in the gas-phase cluster and the hydrolysis in liquid water take place via a similar molecular mechanism.

[15] The rate constant of surface desorption $k_{\mathrm{des}}(T)$ of chlorine nitrate on the other hand follows a near-linear Arrhenius behavior in the temperature region between 100 and 300 K, although the Gibbs free energy barrier to desorption $\Delta G^{\ddagger}_{\mathrm{des}}(T)$ (compare Figure 3) significantly drops on increasing the temperature due to an increasing contribution of the translational entropy. Note that the barrier is neither sensitive to the cluster size nor sensitive to the quantum mechanical method employed, as judged from the near equality of the two approaches to the desorption barrier of chlorine nitrate.

[16] At all temperatures the barrier to desorption for HOCl is lowest, and becomes even negative at T > 170 K, which implies immediate desorption from the surface at, e.g., 200 K. The fact that HOCl is released to the gas phase on a timescale of minutes [*Molina et al.*, 1987] in some experiments may be related to the fact that before desorbing from the ice surface the hydrogen bond between HOCl and $HNO_3$ adsorbed on the surface has to be broken first. This retarding function of $HNO_3$ has also been mentioned lately from second harmonic generation studies on the basal ice surface of hexagonal ice [*Geiger et al.*, 2001], which showed also that HOCl desorbs immediately as long as the ice surface is relatively fresh and free of $HNO_3$. Nitric acid by itself sticks to the surface at stratospheric temperatures, as shown in all experiments as well as by our calculations [*Hanson and Ravishankara*, 1992]. This sticky behavior is represented by the very high $\Delta G^{\ddagger}_{\mathrm{des}}(HNO_3)$,

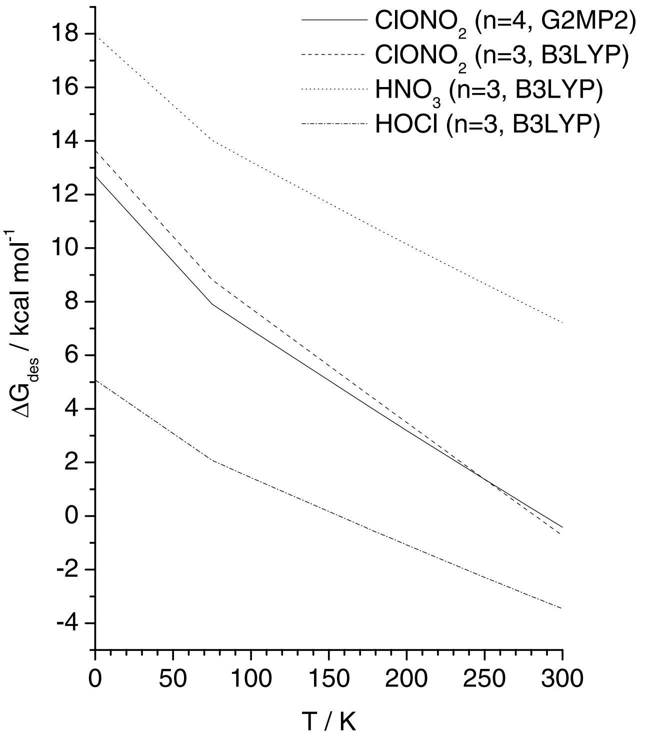

**Figure 3.** Gibbs free energy barriers of desorption from a model ice surface represented by either a linear water trimer or water tetramer as calculated at either G2MP2 or B3LYP/6-31+G(d) level of theory and thermally corrected by calculating second derivatives of the electronic energy with respect to nuclear coordinates, i.e., the Hessian matrix, at B3LYP/6-31+G(d) level of theory.

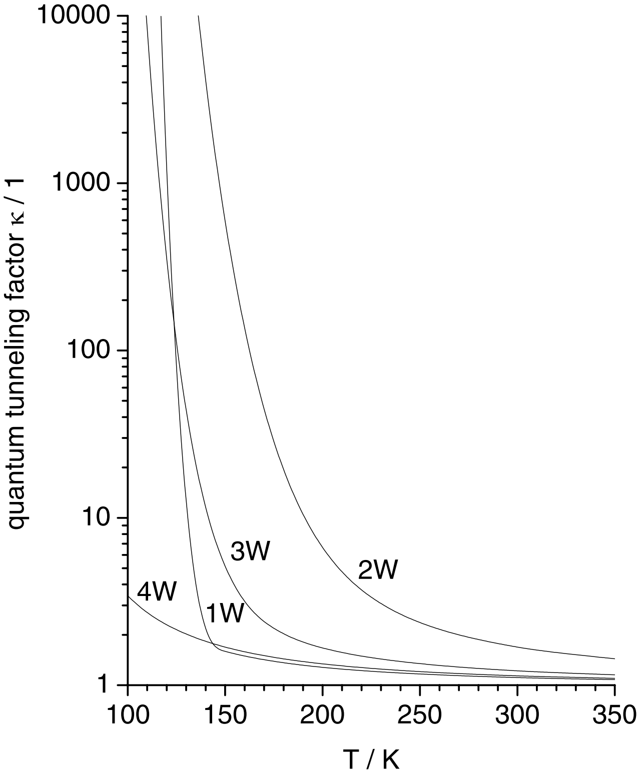

**Figure 4.** Tunnelling correction factors κ for the decomposition of chlorine nitrate in an unimolecular complex containing one (1W), two (2W), three (3W), or four (4W) water molecules as calculated at a B3LYP/6-31+G(d) potential energy surface under the microcanonical optimized multidimensional tunnelling approximation.

leading to desorption on a timescale much longer than hours. The desorption barrier of chlorine nitrate from the ice surface is intermediate between $HNO_3$ and HOCl. Similarly, *Bianco and Hynes* [2006] have found an activation barrier for desorption of $ClONO_2$ of 7 kcal $mol^{-1}$.

### 3.3. Ab Initio Estimate of the Reaction Probability

[17] As a result of the strong temperature dependence of the desorption rate constant and the much weaker dependence of the surface reaction rate constant these two curves cross each other at approximately 150 K. According to equation (14) this implies a reaction probability of 0.5 at the intersection point, which can also be seen in Figure 5. In Figure 5 the reaction probability γ (left ordinate, obtained from equation (7)) is shown together with the surface coverage θ (right ordinate, obtained from equation (10), $p^{ClONO2} = 10^{-8}$ Pa). The surface coverage is far below monolayer coverage for all investigated temperatures, which justifies the use of the Langmuir isotherm and also allows us to use equation (13) instead of equation (7). These low coverages are in qualitative agreement with findings by *Hanson and Ravishankara* [1992], who detect a surface coverage clearly lower than $10^{-3}$ at 191 K.

[18] The estimate of γ drops from approximately 0.1 to 0.01 in the temperature range 180–210 K. At temperatures lower than 100 K γ is estimated to be unity, whereas it becomes lower than 0.0001 near the melting point of ice. A similar negative temperature dependence has been found in recent experiments, in which a temperature increase from ca. 120 K to 140 K was accompanied by a drop in γ of a factor of 6 [*Berland et al.*, 1997]. They have also found that below 105 K γ is independent of temperature and reaches the maximum value provided by the mass accommodation coefficient α of chlorine nitrate on an ice surface. Their curve displayed in

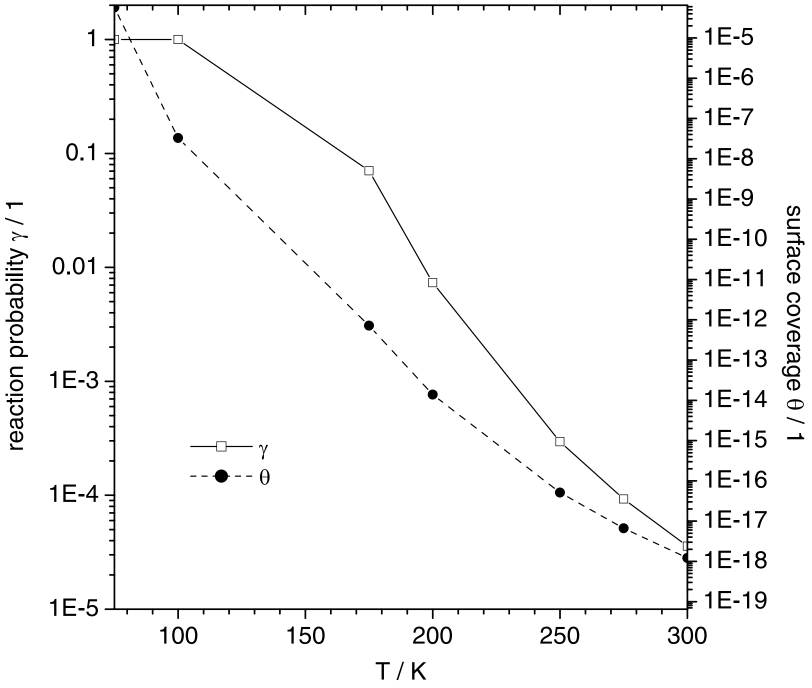

**Figure 5.** Prediction of the reaction probability γ and surface coverages θ obtained from $k_{ass}(T)$, the data in Figure 2 and by using equations (7) and (10), respectively, and employing a partial pressure of $10^{-8}$ Pa $ClONO_2$.

*Berland et al.*'s [1997] Figure 11 obtained from a combination of laser-induced thermal desorption and a precursor-mediated adsorption model shows the same S shape as our calculated curve. Even the temperature of 105 K at which $\gamma$ starts to drop is in agreement. The only apparent discrepancy to this study seems to be the very low trapping coefficient $\alpha$. From classical trajectory simulations the trapping coefficient $\alpha$ was found on the other hand to be unity [*Bolton et al.*, 1999].

[19] Another experiment has shown no significant temperature dependence between 180 and 200 K, though, where $\gamma$ was reported to be 0.20 ± 0.05 [*Oppliger et al.*, 1997]. For $BrONO_2$ hydrolysis a drop of $\gamma$ from 0.3 (180 K) to 0.025 (210 K) has been found in the same Lausanne laboratory for single-crystal ice surfaces. Similar, but less pronounced negative temperature dependencies for both bulk and condensed ice were also noticed in the same study [*Aguzzi*, 2001]. The reason why $ClONO_2$ and $BrONO_2$ behave differently as a function of temperature is unclear to us and remains subject to further investigation.

[20] In a static secondary ion mass spectrometry study in an ultrahigh vacuum chamber only polarization of chlorine nitrate was observed on ice films held at temperatures as low as 90–120 K but no chemical reaction [*Donsig et al.*, 1999]. According to our rate constant data this interesting finding can be interpreted to arise from the fact that equilibrium was not reached because of the very long equilibration times of the system at these low temperatures. For instance, the rate constant for desorption amounts to less than $10^{-3}$ $s^{-1}$ at 100 K implying equilibration times of many hours. On the other hand from infrared spectra evidence for the formation of nitric acid, i.e., chemical reaction, was found at temperatures of 140 K [*Horn et al.*, 1998], where the rate constants seen in Figure 2 are of the order of $10^4$ $s^{-1}$, implying equilibration times of seconds.

### 3.4. Error Estimates

[21] The inherent error for calculating reaction barriers and desorption barriers at G2(MP2) level is estimated to be 1.5 kcal $mol^{-1}$ [*Curtiss et al.*, 1993]. The reaction barrier increases from 5.61 kcal $mol^{-1}$ (4:1) to 19.95 kcal $mol^{-1}$ (3:1) to 26.63 kcal $mol^{-1}$ (2:1) and to 58.61 kcal $mol^{-1}$ (1:1) at G2(MP2) level on decreasing the number of water molecules. That is, the uncertainty inherent to the method is much smaller than the difference between different assumed reaction mechanisms. The error in the reaction barrier causes an error in the rate constant because of the proportionality $k \propto \exp(-\Delta G/RT)$. A large fraction of the error in the rate constants cancels out on calculating $\gamma$ as a ratio of rate constants, especially because of the systematic error in the binding energy inherent to the G2(MP2) calculation. The error in $\gamma$ is likely to be a few percent, when either $k_{rxn} \gg k_{\mathrm{des}}$ or $k_{\mathrm{des}} \gg k_{rxn}$. At temperatures where both $k_{rxn}$ and $k_{\mathrm{des}}$ are comparable, the errors in k add up in the denominator and result in the worst error, which we presume to be around a factor of 3 around 200 K. That is, the prediction of $\gamma = 0.03$ implies an error range from 0.01 to 0.10. This error is comparable to the experimental uncertainty in the reaction probability determination [*Molina et al.*, 1987; *Hanson and Ravishankara*, 1991].

[22] Our estimate for $\gamma$ is slightly lower than the recommended value and the latest determination of $\gamma$ for chlorine nitrate hydrolysis on ice [*Oppliger et al.*, 1997], but within the estimated error. It is slightly higher compared to early pioneering studies [*Molina et al.*, 1987; *Tolbert et al.*, 1987; *Leu*, 1988], which fall in the range 0.007–0.09 at 185–200 K. By using $n = 3$ instead of $n = 4$ for calculating $k_{rxn}$ the estimate is $\gamma \approx 10^{-7}$ at stratospheric conditions, which is clearly lower than all of the experimental results, even those on NAT or sulfuric acid tetrahydrate (SAT) surfaces. Using $n = 1$, thereby calculating the homogeneous reaction, leads to slow reaction and $\gamma = 0$, as also evidenced in the laboratory [*Rowland et al.*, 1986]. By using $n = 5$, $n = 6$ or microsolvated clusters, for which surface reaction becomes barrierless and $k_{rxn}$ much higher, $\gamma = 1$ in the whole temperature range.

## 4. Conclusions

[23] We have attempted to model the reaction probabilities for chlorine nitrate hydrolysis on an ice surface for the first time a priori without the aid of widely available experimental data. This has been done by performing high-level ab initio calculations on a system composed of one molecule of chlorine nitrate ($ClONO_2$) and a linear water tetramer (as opposed to the cyclic tetramer [*Loerting et al.*, 1998]). The rate constants of association, surface reaction (including multidimensional tunnelling corrections) and surface desorption have been calculated and used to estimate the heterogeneous reaction probability. Quantum mechanical tunnelling does not play a significant role at tropospheric/stratospheric temperatures in the case of the 4:1 cluster by contrast to the 3:1 and 2:1 clusters. Our prediction for the 4:1 cluster is within the range of the recommended values by IUPAC/JPL, which are based on the available laboratory measurements and chosen so that the effect of the reduction of $\gamma$ by $HNO_3$ poisoning is minimized.

[24] The reaction barrier of 5.61 kcal $mol^{-1}$ obtained at G2(MP2) level of theory agrees with the literature estimate of 3–7 kcal $mol^{-1}$ [*Tabazadeh et al.*, 1994]. On increasing the cluster size and/or including microsolvation effects of the ice lattice the reaction barrier disappears [*McNamara et al.*, 1999; *Bianco and Hynes*, 2006], and on decreasing the cluster size the reaction barrier becomes higher by a factor of 3–10. The former is inconsistent with no detectable chemical reaction on surfaces kept at 90–120 K [*Donsig et al.*, 1999] as well as with a remaining reaction barrier in supersonic molecular beam studies on water clusters containing up to 450 water molecules [*Akhmatskaya et al.*, 1997; *Apps et al.*, 1997]. The latter would imply a negligible reaction probability, which is also inconsistent with experimental data.

[25] Since the experimental observations on an ice surface can be reproduced reasonably with a 4:1 water:chlorine nitrate gas-phase cluster, which shows highly flexible O-O-O angles, we conjecture that for type II PSCs the surface layers are disordered even at 190 K in the presence of $ClONO_2$. The idea of a liquid-like ice surface at stratospheric temperatures was first postulated in 1994 by Molina to explain HCl adsorption [*Molina*, 1994]. Evidence for this postulate was provided later by a zeroth-order dependence of the reaction rate constant on HCl partial pressure [*Lee et al.*, 1999] as well as a study of the heterogeneous and photochemistry of $ClONO_2$ on HCl-doped ice at 181 and 190 K [*Faraudo and Weibel*, 2001]. Recently it was found that the premelting of ice, i.e., surface disorder, can be strongly enhanced by hydrocarbon contamination [*Bluhm et al.*,

2002] or induced by HCl traces [*McNeill et al.*, 2006]. The evidence for the migration of acetone into the bulk of an ice film additionally corroborates the possibility of a liquid-like layer under stratospheric conditions in the presence of a variety of impurities [*Schaff and Roberts*, 1994, 1998]. Further support comes from molecular dynamics simulations showing that the dynamics of the top 2–3 bilayers of water molecules in hexagonal ice at 180–210 K is substantially faster than in the bulk [*Bolton and Pettersson*, 2000] leading to partial disorder in the uppermost bilayer [*Mantz et al.*, 2000]. This disorder even increases when HCl doses up to the monolayer are deposited on ultrathin (5 bilayers thick) hexagonal ice films supported on MgO(001) as seen from a combined quasi-elastic neutron scattering and molecular dynamics study [*Girardet and Toubin*, 2001]. Finally, it is hard to imagine how a crystal, with well defined positions of oxygen atoms, would rearrange after a molecule of water is consumed for the reaction. Thus the observations can be reconciled by regarding the ice crystal as being surface-disordered and highly dynamic [*Haynes et al.*, 1992; *George and Livingston*, 1997]. We want to emphasize that we do not want to imply that a 4:1 mechanism is what happens on polar stratospheric clouds since the microsolvating ice lattice is known to have a strong influence on the reaction barrier, and hence $\gamma$ [*Bianco and Hynes*, 2006].

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