Uptake of Nitrosyl Chloride (NOCl) by Aqueous Solutions

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The uptake kinetics of nitrosyl chloride (NOCl) by aqueous solutions has been measured as a function of temperature, using two different techniques, i.e., the wetted-wall at atmospheric and reduced pressure and the droplet train flow tubes, both techniques being combined with FTIR and HPLC detection. Uptake coefficients, which were shown to be slightly temperature dependent, range from 0.012 to 0.0058 for temperatures between 273 and 293 K. The production of HONO was observed from the hydrolysis of NOCl, and its yield in the gas phase is in agreement with the Henry's law constant of nitrous acid. The uptake of NOCl was also studied on solutions containing HCl, NaCl, and NaOH. Only the latter affected the uptake kinetics, probably through a nucleophilic reaction with OH^-. The observed kinetics are shown to be consistent with a lower limit of 0.03 for the mass accommodation coefficient. These results suggest that heterogeneous removal of NOCl is very efficient, meaning that this compound is not expected to be a significant precursor of atomic Cl in the atmosphere. The Henry's law constant for NOCl was observed to be greater than 0.05 mol L^{-1} atm^{-1}.

Introduction

Sea salt particles are mostly generated by breaking waves at the ocean's surface and should therefore have a chemical composition close to that of seawater. It is known[1] that marine aerosol particles and droplets exhibit a deficiency in chloride and a change in bromide compared to the original composition of seawater. This change is generally attributed to the release of acid halides (HCl and HBr) when the aerosol becomes acidic due to the uptake or heterogeneous formation (in or on the aerosols) of strong acids (HNO_3, H_2SO_4) that may displace HCl and HBr.[2,3] Recent observations by Keene et al.[4] showed that marine aerosol particles are even more depleted than simply expected from acid displacement. They postulated that this large depletion of Cl^- is coupled with chemical processes transforming these rather stable ions into gas-phase active halogens. Accordingly, measurements of gas-phase inorganic chlorine compounds in polluted marine surface air were undertaken.[5] Total HCl* (comprising mainly HCl, but with possible interference from $ClNO_x$) was observed at concentrations of up to 250 ppt. Similar concentrations of Cl_2* (Cl_2 + HOCl) were also observed. The diurnal variation of Cl_2* was suggestive of nonradical nonphotochemical source reactions. In fact, Chameides and Stelson[6] were unable to reproduce the observed chloride deficits in their model of aqueous-phase chemical processes in deliquescent sea salt aerosols and found that free radical mechanisms were not responsible for these deficits. They emphasized that a lack of data resulted in uncertainties in their model that render their conclusions rather speculative.

A photochemical model[5] including these results yields daytime concentrations of atomic chlorine between 10^4 and 10^5 atoms cm^{-3}, considerably higher than the 10^3 atoms cm^{-3} predicted by Singh and Kasting[7] for the remote marine troposphere where the reaction

$$HCl + OH \rightarrow H_2O + Cl \qquad (1)$$

was considered to be the only source of atomic Cl and where HCl was assumed to be formed by acid displacement from sea salt aerosol. Cl atom concentrations of this magnitude indicate a new pathway for the oxidation of tropospheric trace gases, especially for lighter NMHC, for which the rate constant of reaction with Cl is considerably greater than that for reaction with OH.

Heterogeneous activation of halogens, X, via reactions of nitrogen oxides, that might be able to explain the observed increase of gas-phase inorganic halogens during the dark period has been postulated[8−13] according to

$$2NO_2(g) + NaX(s) \rightarrow NOX(g) + NaNO_3(s) \qquad (2)$$

$$N_2O_5(g) + NaX(s) \rightarrow XNO_2(g) + NaNO_3(s) \qquad (3)$$

where (s) and (g) denote the solid (or surface adsorbed) and gaseous states, respectively. In contrast to acid displacement, these reactions lead to the formation of chemically reactive products, which are photolyzed in the troposphere to produce atomic halogens.[14−16]

To assess the extent of this halogen activation, it is crucial to understand the fate of the products, i.e., nitryl chloride ($ClNO_2$) and nitrosyl chloride (NOCl), during the night in the presence of aerosols. In fact, photolysis of NOCl and $ClNO_2$ will be important only if it is the main loss process and if other loss pathways, such as heterogeneous removal, are minor. The heterogeneous chemistry of $ClNO_2$ has already been investigated by Behnke et al.,[17] who presented an extensive study of the N_2O_5/NaCl system. For NOCl, there exists an earlier study by Behnke et al.,[13] performed in a smog chamber with NaCl aerosol in the presence of NO_2 at 76% relative humidity. No production of atomic Cl from NOCl was observed, but instead, OH was

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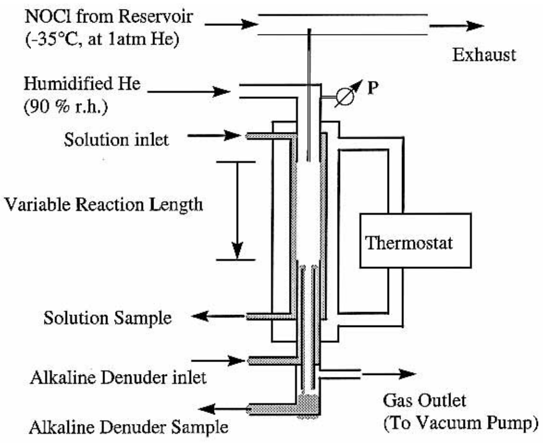

Figure 1. Experimental setup of the wetted-wall flow tube for experiments at reduced pressure (90 hPa)

formed from the photolysis of HONO, the hydrolysis product of NOCl. In addition, the heterogeneous hydrolysis of NOCl has been subject to a recent determination and has been shown to be fairly rapid[18] (compared to $ClNO_2$), while its gas-phase reaction with water is rather slow.

It is the purpose of this article to investigate the heterogeneous chemistry of NOCl on aqueous solutions to verify whether this component can act as a potential source of atomic Cl. This study has been conducted with the help of two complementary methods: the wetted-wall flow tube and the droplet train technique.

Experimental Section

The rate of mass transfer of trace gases into a liquid phase can be limited by several processes (gas-phase diffusion, surface saturation, and reaction in the liquid phase) in addition to the interfacial resistance (represented by the mass accommodation coefficient α). This means that (under our experimental conditions, where we are subject to these limitations) it will usually be impossible to measure the mass accommodation coefficient directly. Instead, we measure an uptake coefficient γ (with $\gamma \leq \alpha$) which represents the measured flux of molecules through the interface. This uptake coefficient is a convolution of all processes that may influence the rate of heterogeneous mass transfer. To determine this coefficient for NOCl, we used two different techniques (the wetted-wall and droplet train flow tubes) which are briefly described below.

The Wetted-Wall Flow Tube. The wetted-wall flow tube technique has already been described by Behnke et al.,[17] and here we give only a brief description of the modified setup, which is drawn in Figure 1. This technique allows us to measure the heterogeneous loss of a compound from the gas phase onto a constantly renewed macroscopic liquid surface. A gas stream is flowing down in a vertically mounted flow tube, the walls of which are covered by a thin liquid film continuously flowing down. The reaction time between the gas and liquid phases is varied by changing the reaction length. In test experiments, the FTIR detection was placed downstream of the flow tube, and in this case we observed nonexponential decays attributed to the back formation of NOCl, arising probably from the wall reaction of HONO at the flow tube outlet. HONO itself was most probably the result of the hydrolysis of NOCl. The wall reactivity was probably introduced by a very acidic deposit on the Teflon tubings, originating from the humidity (the gas stream was saturated with water vapor) and the presence of NOCl over long times (i.e., from several minutes up to hours). To overcome these problems, we later detected NOCl and its hydrolysis product (i.e., HONO) by a continuous wet denuder mounted directly inside the flow tube to avoid contact of the outflowing gas with any other walls before detection. Some first experiments were carried out at atmospheric pressure, where the uptake was observed to be near the gas-phase diffusion limit. Therefore, further experiments were performed under low-pressure conditions (~90 hPa).

Investigations at atmospheric pressure were conducted with a gas stream (500 mL min^{-1}) of 500 ppmv (parts per million by volume) NOCl in He, and the inlet concentration was measured by FTIR. Then the gas passed through the wetted-wall flow tube (6 mm inner diameter), where a fraction of the NOCl reacted at the wall surface with the solution flowing down at 5 mL min^{-1}. NOCl surviving the flow tube was then scavenged by the wet denuder, together with the gaseous hydrolysis product HONO. The wet denuder was operated with a 5 mL min^{-1} alkaline solution (1.1 mM Na_2CO_3/2.57mM $NaHCO_3$), and all the gas injected in the flow tube was allowed to flow through the denuder. Both the flow tube solution and the wet denuder solution were collected at their respective outlets and analyzed by ion chromatography. NOCl taken up by the liquid in the flow reactor was analyzed as chloride ions and HONO escaping from the flow tube was obtained by the difference between chloride and nitrite ions. These concentrations could not be measured in experiments where chloride solutions were used. NOCl surviving the flow tube was represented by chloride in the denuder solution, whereas nitrite in this solution was considered to be the sum of NOCl and of the escaping HONO.

Figure 1 shows the setup of the flow tube (inner diameter 10 mm) for the experiments at reduced pressure (89−90 hPa). NOCl was introduced at the inlet of the flow tube through a capillary, from a source gas stream into a stream of He, which was humidified (90% r.h.) to avoid large temperature changes at the surface of the liquid. The gas flow rate was about 700−900 mL min^{-1} STP, and the flow rate of the solutions was between 5 and 9 mL min^{-1}. The continuous wet denuder was operating with alkaline solution (0.02 M Na_2CO_3) at a flow rate between 5 and 8 mL min^{-1}. All solutions were degassed by filtering through a 0.45 mm nylon filter into water jet vacuum and storing the reservoir at experimental pressure. The solutions at the outlet of the flow tube and of the wet denuder were collected under low-pressure conditions and analyzed by ion chromatography. The pressure was measured by a capacitance manometer (MKS Baratron) before the inlet of the flow tube and checked behind the wet denuder. The pressure drop observed was less than 1 hPa and was therefore neglected in further evaluation.

The determination of the uptake coefficient was based on the wet denuder chloride signal. Figure 2 shows the linear dependence of ln(n) as a function of reaction time. The concentration n of a trace species that undergoes a first-order wall reaction in a flow reactor with diffusion resistance in the gas phase can be described by the solution of the differential equations for transport and diffusion in the gas phase given by Cooney et al.[19] (further on called the CKD equation):

$$n/n_0 = B_1 \exp(-\Lambda_1^{\ 2} z^*) + B_2 \exp(-\Lambda_2^{\ 2} z^*) + ... \qquad (4)$$

where n_0 is the initial concentration and z^* a dimensionless reaction length. The eigenvalues Λ_n are available from Murphy and Fahey;[20] they depend upon the uptake coefficient γ and upon the gas-phase diffusion coefficient D_g. The uptake coefficients were evaluated by fitting the CKD solution to the experimental data, with γ as an adjustable parameter. At high uptake coefficients ($\gamma \geq 5 \times 10^{-4}$) the fitted values for γ are

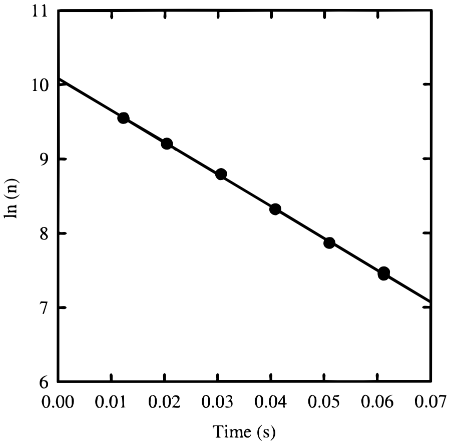

Figure 2. Typical plot of $\ln(n)$ versus t at 293 K for the low-pressure wetted-wall flow tube experiments, showing the first-order uptake behavior on pure water.

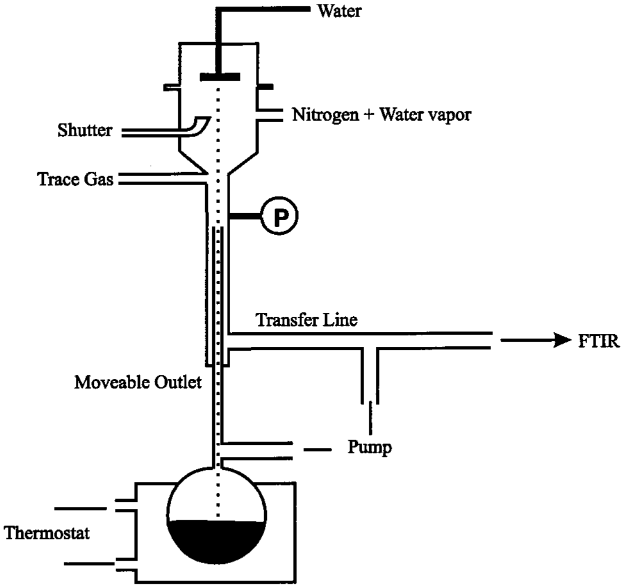

Figure 3. Experimental setup of the droplet train flow tube.

highly dependent on the gas-phase diffusion coefficient D_g used in the calculation. This dependency will be discussed below.

The Droplet Train Flow Tube. The droplet train technique, which is depicted in Figure 3, has already been described in detail elsewhere,[21] and we will only briefly summarize its principle of operation. The uptake rate of NOCl was measured by monitoring the relative concentration of a gas before and after its interaction with the liquid phase, which consists of a train of micrometric droplets.

One of the major difficulties in studying gas/liquid interactions is to obtain a well-defined liquid surface that can be rapidly renewed. To overcome this difficulty, we used a train of high-speed droplets generated by the vibrating orifice method, based on forcing water through a calibrated orifice that is excited by a piezoelectric ceramic. Its vibration controls the disintegration of the jet emerging from the orifice. The water was forced through a calibrated orifice (68 μm diameter) by a typical back pressure of 2−4 bar, leading to droplet diameters in the range 90−150 μm. The diameters d were calculated from the vibrational frequency of the orifice, f (in the range 4−60 kHz), and the liquid volume flow rate F_1 (in the range 1.5−5 mL min^{-1}) using

$$d = \sqrt[3]{6F_1/\pi f} \tag{5}$$

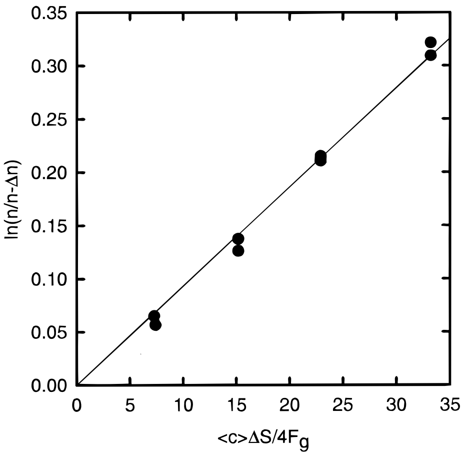

Figure 4. Typical plot of $\ln(n/n-\Delta n)$ versus $\langle c\rangle\Delta s/(4F_g)$ for the droplet train experiments at 276 K on pure water. The linearity is a proof of the constancy of the uptake coefficient with time.

Since the jet passes through the orifice and disintegrates with negligible energy losses, the speed of the droplets can be calculated from the liquid flow rate and the orifice's surface as experimentally verified by Ponche et al.[23] In this study, these velocities were in the range 680−2300 cm s^{-1}, leading to short transit times of the droplets in the interaction chamber (i.e., 2−20 ms). The quality of the droplet train was monitored in the flow tube using a light-emitting diode.

This train of droplets passed through a vertically aligned flow tube made of glass (inner diameter 1.8 cm). Its length could be changed from 2 to 20 cm, to vary the gas/liquid interaction time or the surface exposed by the droplet train. This surface could also be changed by switching, during an experiment, the frequency of production of the droplets, affecting more the droplets' number than their size (eq 5). Since the uptake process is directly related to the surface exposed by the droplets, any changes in this surface result in different trace gas concentrations n at the exit ports of the flow tube. Applying kinetic theory of gases, it is possible to calculate the instantaneous uptake rate dn/dt as

$$\frac{dn}{dt} = -\frac{S}{4V}\langle c\rangle\gamma_{obs}n \tag{6}$$

where S is the total surface exposed by the droplet train, γ_{obs} is the measured uptake coefficient, $\langle c\rangle$ is the average thermal velocity of the trace gas, and V is the volume of the interaction chamber. Since we are measuring the signal due to changes in the exposed surface, averaged during the transit time of the droplets through the flow tube, we have to integrate this relation, leading to[22]

$$\gamma_{obs} = \frac{4F_g}{\langle c\rangle\Delta S}\ln\left(\frac{n}{n-\Delta n}\right) \tag{7}$$

where F_g is the carrier gas volume flow rate, n is the trace gas density before frequency or length switching, and Δn is the difference in signal due to the change in exposed surface ΔS.

Figure 4 shows a typical plot of $\ln(n/n-\Delta n)$ versus $\langle c\rangle\Delta S/4F_g$ for an experiment where the surface exposed by the droplet train was changed stepwise by modifying the length of the interaction zone. During such an experiment, changing the contact length will affect both the number of droplets and their transit time. It has been shown[22,23] that for poorly soluble gases which do not undergo chemical reactions, the uptake coefficient is a decreasing function of the square root of the droplets transit time t. As shown in Figure 4, the relationship between ln(n/

$n-\Delta n$) and $\langle c\rangle \Delta S/4F_g$ is linear over the complete range of surface changes, i.e., for contact times between 2 and 20 ms. From this observation, we conclude that the measured uptake rates are at steady state and that the slope of plots similar to Figure 4 yield uptake coefficients that are independent of the contact time. Therefore, all uptake coefficients described below were determined using this procedure.

The droplet train technique enables us to measure mass transfer rates, even for quite large uptake coefficients such as those measured for NOCl (see below). In such a situation, the uptake may be limited by gas-phase diffusion because of the buildup of a concentration gradient nearby the droplet train; that is, the unknown gas-phase concentration at the droplet's surface may be significantly lower than the known bulk concentration in the gas phase. To overcome this difficulty, the measured uptake coefficients are corrected according to[22]

$$\frac{1}{\gamma} = \frac{1}{\gamma_{\mathrm{obs}}} - \frac{1}{\gamma_{\mathrm{diff}}} = \frac{1}{\gamma_{\mathrm{obs}}} - \frac{\langle c\rangle d_{\mathrm{eff}}}{8D_g} + \frac{1}{2} \qquad (8)$$

where D_g is the gas-phase diffusion coefficient, and $d_{\mathrm{eff}} = 1.8d_{\mathrm{orif}}$, where d_{orif} is the diameter of the orifice used to produce the droplets. The term 1/2 corrects this formula for a non-Maxwellian behavior that may occur for large uptake rates.[22]

An important aspect of this technique is the careful control of the partial pressure of water in the flow tube since it controls the surface temperature of the droplets. Therefore, the carrier gas (nitrogen) was always saturated, at the desired temperature, with water vapor in order to prevent water evaporation from the droplets. The water vapor partial pressure was in the range 4.7−11.8 Torr, leading to droplet's surface temperature in the range 273−287 K, while the flow tube's walls were at room temperature. As shown by Worsnop et al.,[22] the measured uptake rate is therefore an average over a range up to 2 K around the desired temperature (including an uncertainty of 10% on the water partial pressure and the temperature gradient between the droplet's surface and the flow tube's wall). The temperature was not increased to higher values because at 288 K and above we observed strong wall reactions leading to a highly nonlinear behavior between $\ln(n/n-\Delta n)$ and $\langle c\rangle \Delta S/4F_g$. This results from the fact that during length switching experiments, we modified the surface exposed by the walls of the flow tube up to a factor 2 (due to the moveable outlet). This affects the contribution of potential wall reactions, and the relationship between gas-phase concentration and surface exposed by the droplets as described in eq 7 is not longer valid. The occurrence of wall reactions was also indicated by the formation of a visible deposit on the glass walls. However, at lower temperature, no deposit was observable and eq 7 was always verified. Therefore we are confident that our results are not affected by wall reactions.

Chemicals and Analytical Methods. A continuous flow of NOCl was produced by passing dry helium over pure liquid NOCl (Merck, purity > 97%) thermostated at 238 K. In the atmospheric pressure experiments, this gas (1 mL min^{-1}) was diluted with dry He (500 mL min^{-1}) and then used directly. In the low-pressure experiments, a portion (5 mL min^{-1}) of an at 238 K saturated excess gas stream (10 mL min^{-1}) was fed into the wetted wall flow tube, or the droplet train apparatus respectively, by an inert quartz capillary (90 cm length, 150 mm inner diameter), controlled by the pressure difference. This resulted in a stable and continuous source of NOCl.

Solutions were prepared from freshly bidistilled water and reagent grade chemicals: NaOH (Fixanal, Riedel de Haen), HCl (Fixanal, Riedel de Haen), NaCl (>99.8%, Riedel de Haen), Na_2CO_3 (>99.5%, Merck), $NaHCO_3$ (>99.5%, Merck).

Gas-phase NOCl was detected by FTIR spectrometry (Bruker, IFS 113v) equipped with a gas cell (20 cm length, 4 cm diameter, PTFE walls, AgCl windows). This was done at the outlet of the droplet train flow tube or, for experiments conducted at atmospheric pressure, at the inlet of the wetted wall flow tube. Spectra were taken in the range 4000−400 cm^{-1} with a 1 cm^{-1} resolution, and 32 scans were coadded.

Ion chromatographic analysis of chloride and nitrite from the denuder solutions and other liquids was done with a DIONEX AS4 column and 1.1 mM Na_2CO_3/2.57 mM $NaHCO_3$ eluent at a flow rate of 1.3 mL min^{-1} with continuous ion suppression (regenerated by 25 mM H_2SO_4 solution) and conductivity detection.

Results

Table 1 presents the results, as a function of temperature, of the uptake coefficients of NOCl over pure water, obtained by the three methods, i.e., low-pressure and atmospheric pressure flow tube experiments and droplet train measurements (see also Figure 5). The wetted-wall flow tube was operated in the temperature range 283−293 K, while for the droplet train technique, the temperature was varied between 273 and 287 K. The uptake coefficients measured by the wetted-wall flow tube are implicitly corrected for gas-phase diffusion limitation by the CKD equation (eq 4), whereas the droplet train results given here have been corrected for gas-phase diffusion limitations according to eq 8, in which D_g refers to the diffusion coefficient of NOCl in a background of helium or nitrogen and water vapor. D_g has been calculated from the following relationship:

$$\frac{1}{D_g} = \frac{P_{\mathrm{H_2O}}}{D_{\mathrm{NOCl-H_2O}}} + \frac{P_G}{D_{\mathrm{NOCl-G}}} \qquad (9)$$

where G represents the carrier gas (helium or nitrogen) and where P_{H2O} and P_G are the water vapor or carrier gas partial pressures. $D(\mathrm{NOCl-H_2O})$ and $D(\mathrm{NOCl-G})$ are unknown and had to be estimated using the semiempirical method of Fuller et al. as taken from the review of Reid et al.[24] At 1 atm and 273 K, the estimated diffusion coefficients of NOCl in helium, $D(\mathrm{NOCl-He})$, in nitrogen, $D(\mathrm{NOCl-N_2})$, and in water vapor, $D(\mathrm{NOCl-H_2O})$ are 0.456, 0.123, and 0.160 cm^2 s^{-1}, respectively. However, as will be explained later, the values of all these diffusion coefficients have been reduced by 10% for our calculations, which still remains within the uncertainties of the predictions. Diffusion coefficients at other temperatures were calculated assuming a $T^{1.75}$ dependency.

As shown in Table 1 and Figure 5, both techniques lead to uptake coefficients on pure water in very good agreement, if we exclude the coefficient obtained at atmospheric pressure by the wetted-wall flow tube, for which the uncertainty is very high. The values range between 5.8×10^{-3} and 1.24×10^{-2} and exhibit a slight negative temperature dependency.

As we just mentioned above, we reduced the estimated diffusion coefficients by 10%. This results from an analysis of the effect of diffusion on the three kinds of experiments. In Figure 6, we show how the experimental uptake coefficient γ is influenced by a variation of D_g for the droplet train technique at 287 K (horizontal line), for the wetted-wall flow tube at 291 K at atmospheric pressure on pure water (dotted lines) and on 1 M NaCl solution (solid line), and at 286 K and low pressure on pure water (broken lines). Note that the experiment with 1 M NaCl solution is also included, assuming that there is no significant effect of NaCl concentration on the uptake coef-

TABLE 1: Uptake Coefficient γ over Different Solutions for NOCl and HONO Release from Consumed NOCl. The Given Errors, $\Delta\gamma$, Are at the 2σ Level (As Determined by the Experimental First-Order Uptake Rate) and Are Increased in Order to Take into Account Possible Diffusion Limitations (Diffusion Corrections Are Dependent on the Experimental Technique Used, See Text). The Values Reported for the Product $Hk^{1/2}$ Should be Considered as Lower Limits

solution	temperature (K)	γ	$\Delta\gamma$	$Hk^{1/2}$ (mol L^{-1} atm^{-1} s$^{-1/2}$)	[HONO]$_{\text{released}}$/[NOCl]$_{\text{consummed}}$	
water	283	0.0092	+0.0035/−0.0021	906	0.46	*a*
water	286	0.0075	+0.0006/−0.0005	699	0.35	*a*
water	288	0.0086	+0.0072/−0.0030	802	0.53	*a*
water	291	0.0058	+0.0045/−0.0021	504	0.53	*a*
water	293	0.0060	+0.0007/−0.0006	498	0.65	*a*
water	291	0.0010	+0.0102/−0.0006	86	0.09	*b*
water	273	0.0080	+0.0017/−0.0016	966		*c*
water	275	0.0124	+0.0016/−0.0015	1439		*c*
water	276	0.0111	+0.0006/−0.0006	1262		*c*
water	279	0.0093	+0.0019/−0.0017	1003		*c*
water	282	0.0113	+0.0019/−0.0018	1147		*c*
water	285	0.0071	+0.0011/−0.0010	682		*c*
water	285	0.0061	+0.0016/−0.0015	590		*c*
water	287	0.0083	+0.0012/−0.0012	774		*c*
1 M NaCl	293	0.0134	+0.9866/−0.0107	1157	0.52	*a*
0.1 M HCl	293	0.0057	+0.0009/−0.0007	478	0.49	*a*
1 M HCl	293	0.0042	+0.0029/−0.0014	360	0.50	*a*
0.14 M NaOH	291	0.0037	+0.0996/−0.0027	323		*b*
1 M NaCl	291	0.0054	+0.0117/−0.0023	486	0.07	*b*
1 M HCl	291	0.0004	+0.0012/−0.0003	40	0.11	*b*
1 M NaOH	276	0.0294	+0.0017/−0.0016	3697		*c*
1 M NaCl	276	0.0063	+0.0004/−0.0005	736		*c*
1 M HCl	276	0.0021	+0.0003/−0.0002	245		*c*

[a] Low-pressure (90 hPa) flow tube experiments. [b] Atmospheric pressure flow tube experiments. [c] Droplet train experiments.

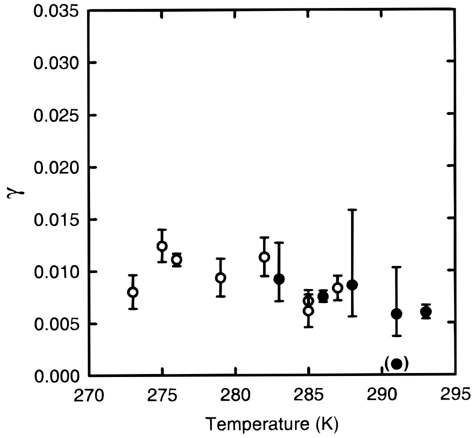

Figure 5. Uptake probability γ of NOCl over water at different temperatures. Hollow symbols, droplet train technique; filled, wetted-wall flow tube. The point in brackets was measured by the wetted-wall flow tube at atmospheric pressure (i.e., close to the diffusion limit) and must therefore be considered as a lower limit. The given errors are at the 2σ level (as determined by the experimental first-order uptake rate) and are increased in order to take into account possible diffusion limitations (diffusion corrections are dependent on the experimental technique used, see text).

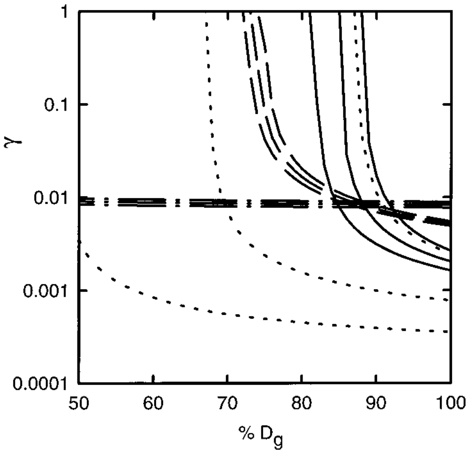

Figure 6. NOCl uptake evaluated by using different gas-phase diffusion coefficients for different experiments (each line represent the lower, measured, and upper values, respectively) (Solid line, FT on 1 M NaCl at 291 K; dotted line, FT on water at 291 K; broken line, FT at low pressure on water at 286 K; broken-dot line, DT on water at 287 K). 100% refers to the value estimated by the method of Fuller et al., as taken from the review of Reid et al.[24]

ficient. The droplet train technique, which is operated at the lowest pressures, shows nearly no influence of γ on D_g. For the wetted-wall technique, the influence is more pronounced and depends upon the pressure. For each experiment, three curves are depicted which respectively represent the lower, measured, and upper values based on a 95% confidence interval for the determination of the slope in Figure 2 or 4. The values measured by the wetted-wall flow tube at atmospheric pressure turned out to be very uncertain, indicating more or less a lower limit for γ. All the other values (droplet train and wetted wall) converge toward the same value of γ, if D_g is reduced by approximately 10%. Therefore the estimated diffusion coefficients reported above were lowered by 10% before they were used to correct the measured uptake rates. We recall again that a 10% difference is well within the accuracy of the method used to predict diffusion coefficients.

In addition to the measurements performed on pure water, we investigated the role of the liquids' nature on the uptake over NaOH, NaCl, and HCl solutions, measured at 291 and 293 K (flow tube at atmospheric and low pressure, respectively) and at 276 K (droplet train). The results are given in Table 1 and are also depicted in Figure 7. On the acidic solutions, it should be noted that there is a large systematic error for the droplet train experiment because the droplet production system was corroded by the HCl solutions, and to prevent any damage to the system, we did only one experiment with this solution. Therefore, γ on the 1 M HCl should only be considered as a rough estimate that did not differ significantly from the value on pure water. The wetted-wall method at atmospheric pressure leads to results that can be considered only as lower limits, while

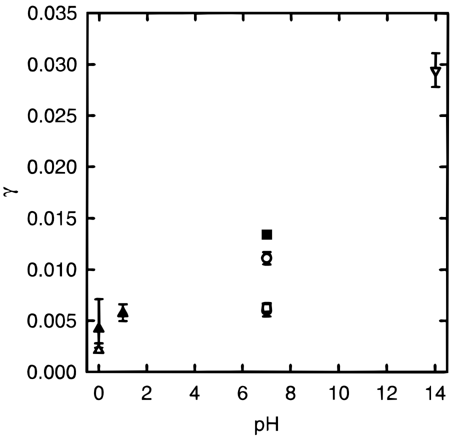

Figure 7. Uptake probability γ of NOCl over aqueous solutions at 276 K for the droplet train technique (hollow symbols) and 293 K for low-pressure wetted wall flow tube measurements (filled symbols). Circles, H_2O; squares, 1 M NaCl; triangles up, 0.1 and 1 M HCl; triangle down, 1 M NaOH. Measurements performed at atmospheric pressure with the wetted-wall flow tube have been omitted because they are close to the diffusion limit and must therefore be considered only as lower limits.

the low-pressure experiment leads again to results that are close to those obtained on pure water. The same conclusion can be drawn for solutions containing NaCl. On the contrary, the droplet train reveals that the presence of NaOH increases the rate of uptake.

From the difference between the nitrite and chloride ions found in the denuder solutions at the maximum reaction length, the release of HONO into the gas phase could be quantified. The results listed in Table 1 show that, in the low-pressure experiments, about 35−65% of the NOCl consumed on a water film are converted to HONO in the gas phase with a slightly positive temperature dependency. About 10% of NOCl consumed was found as gas-phase HONO in the atmospheric pressure experiment; certainly no HONO escaped from basic solution. From the data in the low-pressure experiment the points at reaction lengths between 7.5 and the maximum reaction length 15 cm (shorter distances exhibited a larger error due to the cross sensitivity of a large NOCl signal that had to be subtracted) were taken to calculate Henry's law constant of HONO, taking into account the acidification of the liquid film by the HCl formed in NOCl hydrolysis (the dissociation constant of HONO, $K_a = 5 \times 10^{-4}$ M was taken from Park and Lee,[25] and we assumed that $[H^+] = [Cl^-]$). The resulting values are compared with data published by Park and Lee [25] in Figure 8. The results agree well, within the given range of error except for one experiment. This indicates a good efficiency for HONO detection in the outlet denuder in most experiments.

Discussion

As shown in Figure 7, we measured an increase of γ on basic solutions. This effect is probably due to an augmentation of the hydrolysis rate in alkaline solutions as already identified for $ClNO_2$,[17] meaning that the uptake of NOCl is limited by the rate at which it is chemically transformed in the condensed phase. In such a situation, the uptake rate is a convolution of reactive uptake (described by γ_{rxn}) and mass accommodation, and the corresponding uptake coefficients are described according to[22]

$$\frac{1}{\gamma} = \frac{1}{\alpha} + \frac{1}{\gamma_{rxn}} = \frac{1}{\alpha} + \frac{\langle c \rangle}{4HRT\sqrt{kD_{aq}}} \qquad (10)$$

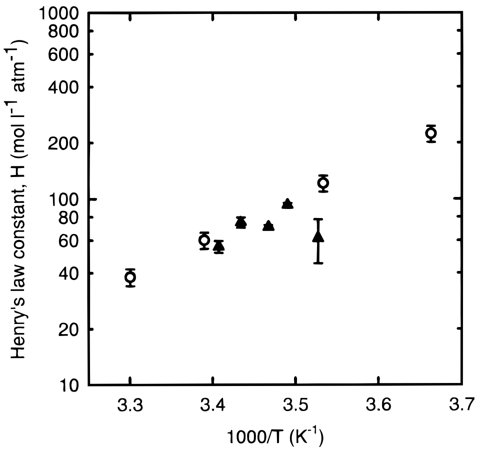

Figure 8. Observed Henry's law constants for HONO in dilute aqueous solution compared with literature values. Triangles, this work; circles, Park and Lee.[25] (Error bars are at the 1σ level.)

where D_{aq} is the aqueous phase diffusion coefficient, H is the Henry's law constant, k is the first-order rate constant, and α is the mass accommodation coefficient. When the uptake is mostly limited by the reactive uptake, we may simplify eq 10 to

$$\gamma \approx \frac{4HRT\sqrt{kD_{aq}}}{\langle c \rangle} \qquad (11)$$

where the uptake coefficient depends on the value of k or more exactly on $Hk^{1/2}$. The latter product may be deduced from eq 11 provided that D_{aq} is known. The values of D_{aq} were estimated by the method of Wilke and Chang as taken from the review of Reid et al.[24] The value estimated at 273 K is 7.5×10^{-6} cm^2 s^{-1} with a T/η temperature dependence, where η is the water viscosity. The values of $Hk^{1/2}$ are in the range 500−1440 M atm^{-1} s$^{-1/2}$ (see Table 1) and exhibit a negative temperature dependency. However, by applying eq 11, we neglected the possible influence of the mass accommodation step assuming that $\alpha \gg \gamma$. Identifying such a contribution is an experimentally difficult task; therefore, the values reported in Table 1 should be considered more realistically as lower limits for the product $Hk^{1/2}$.

We may, nevertheless, gain some insight into the system by a careful examination of the results given in Table 1. In fact, in droplet train experiments, we measured an enhancement of the uptake rate in alkaline solutions which was also observed in wetted-wall experiments at atmospheric pressure but to a smaller extent. The difference between these experiments may arise from the fact that studies at atmospheric pressure are measuring diffusion-limited uptake rates and experimental errors were high. Nevertheless an increased uptake coefficient was observed on 1 M NaOH solution which can be attributed to a higher reactivity of NOCl toward OH^- as compared to pure water (the observed increase in γ is beyond the experimental errors). If we assume that this increase is due to a change in the nucleophilic character of the reactant, then we can apply the Swain−Scott equation[26] i.e.,

$$\log\left(\frac{k^{II}_{OH^-}}{k^{II}_{H_2O}}\right) = sn \qquad (12)$$

where $k^{II}_{H_2O}$ and $k^{II}_{OH^-}$ are the second-order rate constants for the reaction between NOCl and water or OH^-, respectively, n is the nucleophilicity of OH^- (i.e., $n = 4.2$),[26] and s is the sensitivity of NOCl toward nucleophilic reactions. This latter being unknown, we used the value derived for $ClNO_2$, i.e., $s \approx$

1.[27] The ratio of the rate constants can be derived from the measured uptake coefficients by assuming that the presence of 1 M NaOH would affect the Henry's law constant by a factor of 0.7 (estimated roughly by the method of VanKrevelen and Hoftjizer as given by Danckwerts[28]) and has no effect on the rate constant. We measured a value of 2.9 for $\log(k^{II}_{OH-}/k^{II}_{H2O})$, which can be compared to the calculated value of 4.2. This difference may be due to a wrong sensitivity factor ($s \approx 0.7$ would fit our observations), to a first reaction step in the liquid phase that is not a nucleophilic reaction with water as discussed later, or to an uptake rate limited by interfacial mass transport for 1 M NaOH. In such a case, the chemical transformations must be fast enough so that they do not influence the uptake rate, meaning that $\gamma \approx \alpha$. In regard to the limited data set, we cannot definitively conclude but it appears safe to assume that NOCl is more reactive than $ClNO_2$ (see ref 17 for more information on this species); therefore an increase of 7 orders of magnitude in the OH^- concentration (from water to 1 M NaOH) should lead to a more pronounced increase of γ (as calculated by eq 12) than just a factor of ~3 (see Table 1). Therefore, we estimate from the measured uptake rate on alkaline solutions that $\alpha \geq 0.03$, the latter value being a rough estimate of α.

In a previous study,[17] we extensively studied the multiphase chemistry of $ClNO_2$ on different aqueous solutions. The results showed a very strong dependence of γ with the chloride concentration below 1 M which was attributed to a reversible hydrolysis of nitryl chloride. The situation appears to be completely different for NOCl. In fact, our experiments with chloride containing solutions (HCl and NaCl) showed no significant change in uptake probability up to 1 M concentrations despite the large difference in the applied experimental conditions. This may indicate that acid-catalyzed and chloride concentration dependent reactions do not significantly take place and are unimportant. This observation is different from the one made for nitryl chloride ($ClNO_2$), where the uptake rate was largely affected by the presence of chloride ions (Behnke et al.[17]). The chemistry of NOCl may not be described as that of $ClNO_2$ since NOCl is known[29] to be more an internal salt (nitrosonium chloride) in the solid phase, whereas solid-phase $ClNO_2$ has a covalent structure corresponding more to gas-phase $ClNO_2$. From this behavior one can speculate that a NOCl molecule in an aqueous solution is more in ionic form (with a corresponding low volatility) than in covalent form (with a higher volatility according to a liquid/gas-phase equilibrium described by physical Henry's law). From this observation, we propose the following steps for NOCl:

$$\mathrm{NOCl(g)} \leftrightarrow \mathrm{NOCl(aq,\ covalent)} \tag{13}$$

$$\mathrm{NOCl(aq,\ covalent)} \leftrightarrow \mathrm{NOCl(aq,\ ionic)} \tag{14}$$

$$\mathrm{NOCl(aq,\ ionic)} \leftrightarrow \mathrm{NO^+ + Cl^-} \tag{15}$$

$$\mathrm{NO^+ + H_2O} \rightarrow \mathrm{2H^+ + NO_2^-} \tag{16}$$

From our observations, we can conclude that the back transformation of ionic NOCl to covalent NOCl and/or the back reaction $NO^+ + Cl^-$ is not fast enough to lower the uptake probability of NOCl when introducing chloride in the solution. N_2O_5, which is known to be in the ionic form in the solid phase, also shows no significant effect of back reaction; that is, its uptake over water or NaCl solution[17,30] is not significantly different from the one observed over $NaNO_3$ solution.[31] This behavior is comparable to what we observed for NOCl; hence both uptakes might proceed via a first transformation step from a covalent to an ionic form. In contrast, $ClNO_2$, which is more likely to be in covalent form in the aqueous phase, shows a significant lowering of its uptake probability by back reaction in chloride solutions.[17] The proposed reaction step 14 is also in agreement with the observation over 1 M NaOH. In fact, if the uptake of NOCl first proceeds through a transformation to an ionic form (at a rate characterized by a first-order rate constant k_{14}), then it is highly probable that the application of the Swain–Scott relationship is no more justified explaining the discrepancy between calculations using eq 12 and experimental results. On the other hand, if we assume the upper limit of $k_{OH^-} < 10^{10}$ mol^{-1} L s^{-1}, then we may derive H > 0.05 mol L^{-1} atm^{-1} from the uptake rate measured at pH = 14, using the latter and the uptake coefficient on water, one may derive $k_{14} < 6 \times 10^8$ s^{-1} at 276 K.

Atmospheric Implications. The measured values of γ may be useful to estimate the lifetime τ of NOCl in the atmosphere. In fact, it is possible to estimate τ for NOCl in contact with liquid aerosols as

$$\tau_{\mathrm{aerosol}} = \frac{1}{(1/4)\langle c\rangle A_c \gamma} \tag{17}$$

where A_c is the condensed phase surface to gas volume ratio (cm^2/cm^3), taken as 5×10^{-7} for the marine boundary layer,[32] where NOCl may play a role in atmospheric chemistry. Using this equation, we calculated a lifetime ranging from 487 to 880 min for temperatures between 273 and 293 K, which can be compared with lifetimes of NOCl with respect to its reaction with OH and water vapor or to its photolysis, which are 36 days,[33] 0.5–7 h,[18] and 0.5 h,[33] respectively. The lifetime associated with photolysis was calculated at a solar zenith angle of 80°, i.e., representative of early morning conditions under clear sky. For cloudy periods, this lifetime can easily be increased by a factor of 2–5. The range of lifetime associated with gas-phase hydrolysis corresponds to summer (296 K) and winter (273 K) conditions. From this comparison, it appears evident that photolysis is the fastest removal process and that gas-phase and condensed-phase hydrolysis may be in competition during the night under winter conditions. It is interesting to note that these latter exhibit opposite temperature dependence, meaning that if a process slows down, the other one will be accelerated. Therefore, only a very small portion of NOCl will effectively act as a source of atomic Cl, as it was already shown experimentally by Behnke et al.,[34] who did not observe Cl atom production from the reaction between NO_2 and NaCl in a smog chamber simulation. Therefore, NOCl is potentially much less important than $ClNO_2$ for the production of Cl atoms since its production in the marine boundary layer will be very limited. This conclusion is in agreement with the study of Vogt et al.,[35] who showed that the production rate of NOCl is very small.

Conclusion

The NOCl uptake is fast and irreversible at moderate pH. This has implications for atmospheric chemistry where NOCl production was proposed to occur via NO_2 reaction with sea salt aerosol. NOCl is not likely to escape from sea salt droplets and will rapidly be consumed. This is in agreement with the observation of Behnke et al.,[13,34] where NO_2 reaction with NaCl aerosol led to the formation of HONO and not NOCl. So NOCl would not contribute as an important chlorine atom precursor. On the other hand NOCl hydrolysis produces quantitatively nitrite. HONO production and release depends more on acidification of the solution (i.e., sea spray). The calculated lifetime associated with the heterogeneous removal of NOCl is a few hours, i.e., much faster than the reaction with OH, slower than photolysis, but comparable to gas-phase hydrolysis.

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