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Atmospheric Pollution: The Role of Heterogeneous Chemical Reactions

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Abstract. The chemical kinetics of heterogeneous chemical reactions of importance in the atmosphere are discussed using six examples: *1*) water vapor and *2*) HCl interacting with ice, *3*) $ClONO_2$ + HCl on ice, *4*) HONO + HCl on H_2SO_4 and ice, *5*) HNO_3 reacting on dry $CaCO_3$ powder and *6*) reactions of HNO_3, N_2O_5, $ClONO_2$, $ClNO_2$ on salts such as NaCl and KBr. Quantitative results of uptake coefficients are presented and the importance of ionic displacement reactions at the interface is stressed.

1. Introduction

The discovery of the 'ozone hole' atop the Antarctic Continent by *Farman* and coworkers in 1985 was a shock to the scientific community not only because of the observation of the dramatic depletion of stratospheric ozone but rather because it came as a total surprise which no one had foreseen [1]. The recurrent event may be of rather limited importance with respect to the global stratospheric ozone balance as it is localized in space and time. It is occurring over an uninhabited area for a period of several weeks and does not do any harm to human or animal beings. Its significance lies in the demonstration that even the most inclusive and sophisticated computer models running at that time were unable to 'understand' the newly discovered phenomenon because the chemistry involved was qualitatively incorrect since the models were completely lacking in heterogeneous chemical processes. Up to 1985 significant advances of our understanding of homogeneous gas-phase chemistry had been made such that the scientific community was lulled into the thought that most if not all of stratospheric chemistry was well understood and under control [2]. The occurrence of the ozone hole drew attention to a hitherto neglected area of atmospheric chemistry, namely heterogeneous atmospheric chemistry taking place at the interface of the gas and the condensed phase. Even in the three volume assessment of our knowledge of stratospheric ozone, which appeared in 1985, heterogeneous processes received only cursory attention and were deemed to be unimportant in the atmosphere [3].

These heterogeneous processes convert inactive chlorine in the form of reservoir molecules such as HCl and $ClONO_2$ during the polar night into an active photolyzable form such as HOCl and Cl_2 on the surfaces of tiny frozen atmospheric particulates called polar stratospheric clouds (PSC's) according to the following reactions [4]:

$$ClONO_2 + HCl \rightarrow Cl_2 + HNO_3 \quad (1)$$

$$ClONO_2 + H_2O \rightarrow HOCl + HNO_3 \quad (2)$$

After the polar sunrise the active chlorine-containing molecules Cl_2 and HOCl release atomic Cl through photodissociation and initiate the chain destruction of ozone according to the fast reaction

$$Cl + O_3 \rightarrow ClO + O_2 \quad (3)$$

which is responsible for the fast ozone depletion event taking place in a matter of several days to tens of days. It has become clear that rather unique chemistry is taking place due to the low temperatures of 180–200 K encountered in the lower stratosphere at altitudes between 15 and 25 km atop Antarctica, a fact that is also responsible for the formation of condensed atmospheric particulate on which these interfacial processes can occur. In addition, another unusual chain-propagation step, reaction according to *Eqn. 4*, is taking place under polar stratospheric conditions. It replaces the 'classical' chain-propagation reaction converting the inactive ClO back to Cl in the global background stratosphere, *Eqn. 5* [5]:

$$ClO + ClO \rightarrow (ClO)_2 \quad (4a)$$

$$(ClO)_2 + h\nu \text{ (or thermal for } T \geq 190 \text{ K)} \rightarrow 2Cl + O_2 \quad (4b)$$

$$ClO + O \rightarrow Cl + O_2 \quad (5)$$

In a nutshell, both the heterogeneous chemistry as well as the chain propagation based on the dimer mechanism of ClO conversion to Cl, *Eqn. 4*, explain the rapid springtime ozone decrease in the polar regions. This explanation has withstood the test of time and is essentially valid today albeit with some important additions such as the participation of bromine-based chemistry [6]. Moreover, some of the heterogeneous atmospheric processes are also occurring elsewhere in the stratosphere and are responsible *e.g.* for the ozone depletion in the background stratosphere, typically resulting in a 6% decrease of the ozone column per decade in the northern hemisphere, or the occurrence of the spring-time ozone hole above the Arctic, which however is not nearly as pronounced as above Antarctica, both in duration and geographical extent of ozone depletion. *Fig. 1* presents two observations as a case in point, one of global ozone decrease (*Fig. 1a*) and the other of polar ozone decrease (*Fig. 1b*).

What have we learned from a chemical point of view of these dramatic observations that led us to draw attention to heterogeneous chemical processes? One of the important lessons is that *ionic chemistry* renders these heterogeneous reactions at the interface between the gas and the condensed phase so fast and efficient. Most of the homogeneous chemical reactions taking place as bimolecular or termolecular reactions have small energy barriers resulting in negligible rates at those low temperatures of interest. However, the condensed phase offers the important possibility of ionic reaction mechanisms which are characterized by fast rates down to very low temperatures and which were overlooked by the scientific community in the context of atmospheric chemistry because of lack of precedent. The ozone-hole episode conclusively showed that sophisticated models of atmospheric processes must include the correct chemistry

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CHIMIA 50 (1996) Nr. 5 (Mai)

in order to yield useable and reliable projections of the state of the atmosphere into the future. The global atmosphere is a very complex system of interacting radiative, transport and chemical processes so that the only reliable tool for projections into the future are sophisticated computer models. The question whether or not a measured heterogeneous chemical reaction may or may not be important under atmospheric conditions must be left to the modelers as it is next to impossible to duplicate atmospheric conditions in the laboratory. Most atmospherically relevant densities (10^8–10^{10} molecules cm^{-3}) and the associated time scales (days to weeks) are difficult to achieve under laboratory conditions. Therefore, we adopted the strategy to first *study the chemical mechanism* in order to enable reliable extrapolation of the kinetics to atmospheric conditions, assuming that the mechanism does not change within a factor of 100 or so in variation of reactant density.

Today the polar and background ozone decrease is understood as one possible manifestation of the *increase of atmospheric trace gases* due to human activities. The observed ozone decrease is directly linked to the increasing chlorine load of the atmosphere, primarily in the form of chlorofluorocarbon (CFC's) source gases transforming into reservoir (= inactive) gases such as HCl and $ClONO_2$ [7]. Some of the other consequences of the change in atmospheric trace-gas composition are the greenhouse effect which has to do with the increase of IR-absorbing gases in the lower atmosphere (troposphere) such as CO_2, CH_4, CFC's and related compounds (hydrofluorocarbons (HFC's), hydrofluorochlorocarbons (HCFC's)), N_2O and tropospheric (surface) ozone. The latter gas is especially difficult to treat as its increase depends on global emission scenarios of NO_x and hydrocarbons which are both linked to the future production and use of energy and projected industrial activity.

Atmospheric 'anomalies' such as acid rain and photochemical smog are well known nuisances to humans adversely affecting the air quality [8]. In the case of acid rain SO_2 is known to be the source gas, and with successful abatement strategies to control the emission of SO_2 in place the acid-rain problem has been significantly reduced in many parts of the industrialized world in the last ten years. The photochemical smog problem is intimately connected to the presence of NO_x and hydrocarbons, in part of natural, and in part of anthropogenic (= manmade) origin. To date many urban areas are plagued by smog, especially under stagnant meteorological conditions in summer, and significant efforts are undertaken in order to control the emission of the primary source gases. The formation of smog is controlled by four factors: NO_x, hydrocarbons, the availability of sunlight and temperatures in excess of 18° thus sustaining a dark flame wherein the hydrocarbon fuel is burnt in the presence of NO_x as the catalyst and where the chain carriers, mainly OH and HO_2, are generated through photolysis. In this case the abatement strategy is more difficult to design because it depends on a combination of measures. In Switzerland the most promising strategy seems to limit the NO_x emissions which may be obtained by equipping all motor vehicles with catalytic converters as 75% of the NO_x emissions seem to originate from this source [9].

In a similar manner the emission of jet aircraft and its effects on the atmosphere are presently an intense field of study [10]. It seems that the injection of NO_x and other combustion products such as H_2O which is responsible for the formation of the visible contrails at temperatures ≤ –40°, SO_2, soot and other species into the atmospheric layer around the tropopause of 8–15 km of altitude may cause important changes in the protective stratospheric ozone layer. The quantitative change of stratospheric ozone depends very sensitively on flight altitude and on the chemistry model used for assessment. The corollary is that for all the atmospheric effects presented in the last paragraphs heterogeneous processes are suspected to be important, and ongoing research is centered on the discovery of important new interfacial processes. In this presentation we will place the emphasis on work that has been performed in our laboratories at the Laboratoire de Pollution Atmosphérique et Sol (LPAS) of the EPFL in the last four years.

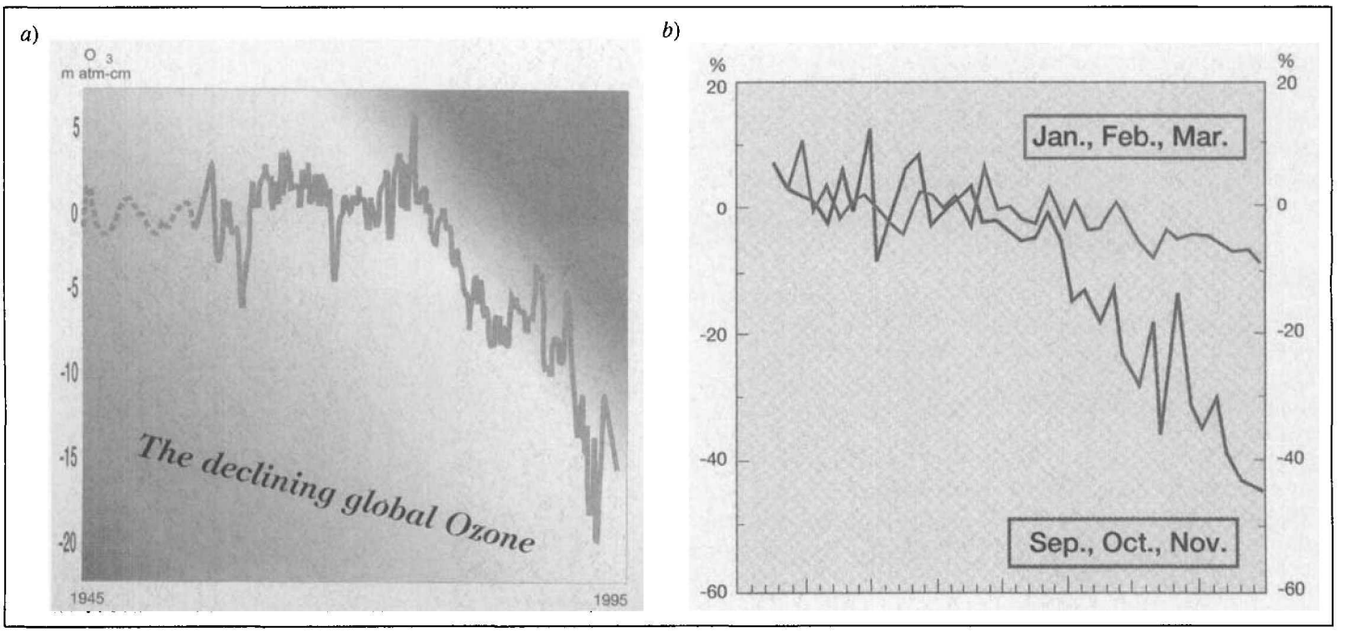

Fig. 1. a) *Time series of the decrease of the global total ozone column in milliatm·cm* (= 1 *Dobson* unit) *from 1945 to 1995.* The variations superimposed on the general decline are regular oscillations in total ozone such as the quasibiennial (~two year) oscillation and the 11 year solar-cycle variation. b) *Ozone seasonal deviations averaged over 1985–1994 from pre-ozone hole* (1957–1978) *averages in the Antarctic.* Summary for stations Faraday, Syowa, Halley Bay, South Pole.

CHIMIA 50 (1996) Nr. 5 (Mai)

2. Experimental Apparatus

The majority of the experimental investigations were performed in a low-pressure reactor or *Knudsen* cell which was part of a flowing gas experiment. The low pressure of typically 1 mTorr, give or take an order of magnitude (1 mTorr corresponds to a density of 3.21×10^{13} molecules cm^{-3} at 300 K), affords molecular flow conditions such that each molecule preferentially undergoes wall collisions rather than collisions with other molecules in the gas phase. The molecular flow regime, therefore, enables the molecules to diffuse to the surface of interest at their molecular velocity thus making surface processes the rate-limiting step rather than diffusion which may become rate-limiting at higher total pressures [11].

The molecules enter the *Knudsen* cell and effuse out of an escape orifice after they have spent a certain amount of time, the lifetime τ, inside the reactor during which they underwent several thousand collisions with the wall. The inverse of τ is k_e, the escape rate constant, and depends only on the molecular velocity as well as on the geometry of the reactor:

$$1/\tau = k_e = (\{c\}/4\,V)\cdot A_h \qquad (6)$$

where $\{c\}$ is the average molecular velocity with which the molecules actually move inside the cell in the molecular flow regime, V and A_h are the volume and the area of the escape orifice, respectively. Values for k_e are on the order of one second, give or take an order of magnitude for the reactor geometries used. At a constant flow of molecules into the reactor giving rise to a steady-state partial pressure, the average molecule is lost through physical pumping across the escape orifice. The molecules effusing out of the orifice are forming an effusive (thermal) molecular beam which is monitored using electron-impact mass spectrometry. The goal of the measurement is to determine a rate constant for chemical loss of a given molecule on a surface of interest. To this end a part of the reactor wall is replaced by the surface of interest which is often placed in a second (sample) chamber which can be isolated from the *Knudsen* reactor (reference) by a gas-tight plunger or isolation stopcock. Upon opening of the isolation plunger the steady-state pressure drops to a lower value if the molecule interacts with the surface. It is thus irreversibly removed from the gas phase. This 'chemical' loss of interest is a competitive pathway to ordinary 'physical' loss by effusion across the escape aperture and is measured relative to the escape rate. The rate constant k_e is, therefore, the 'yardstick' for the measurement of the rate constant of interest, k_h. Simple steady-state considerations lead to the following expression for k_h assuming that the rate law for heterogeneous interaction is first order in the molecular density or pressure:

$$k_h = ((S_0 - S)\,/\,S)k_e \qquad (7)$$

where S_0 and S correspond to the mass-spectrometric signal with the sample isolated (no heterogeneous interaction) and exposed to the gas flow, respectively. *Eqn. 7* demonstrates that the relative measurement of S_0 and S corresponding to active surface 'off' and 'on' is put on an absolute basis using k_e thus leading to an absolute measurement of k_h [12].

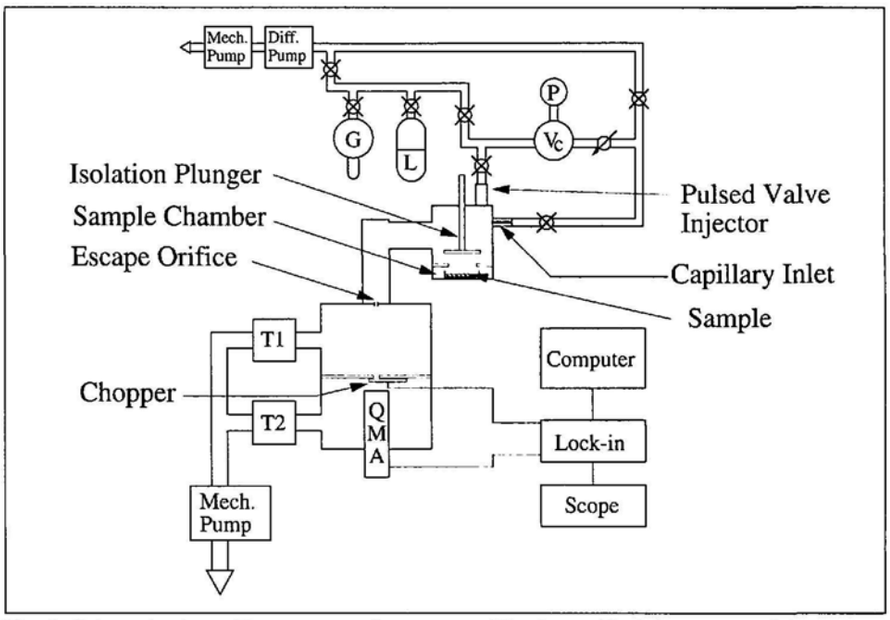

Fig. 2. *Schematic view of low-pressure flow reactor (Knudsen cell) sitting on top of the vacuum chambers the lower of which houses the molecular-beam-modulated electron-impact mass spectrometer (QMA)*

The values of k_h obtained from experiment may be expressed on a per collision basis leading to uptake coefficients γ which correspond to the probability that a molecule interacting with a surface stays adsorbed on it and is, therefore, removed from the gas phase. The uptake coefficient is calculated according to:

$$\gamma = k_h / \omega = 4Vk_h / \{c\}A_s \qquad (8)$$

where ω is the gas-surface collision frequency of the molecule with the surface of interest of area A_s. The uptake coefficient describes the net uptake corresponding to the difference between adsorption and desorption rate. The range of uptake coefficients that are accessible to measurement using our *Knudsen* cell approach lies in the range $10^{-6} \leq \gamma \leq 1.0$. This large dynamic range in the measurement of γ is made possible by changing A_h by two orders of magnitude thus changing the yardstick or meter against which k_h is measured.

It is also important to note that we are exposing the gas to *model* surfaces whose overall bulk chemical composition is identical to or at least comes very close to the one of atmospheric particulates such as combustion aerosols (soot), ice crystals and H_2SO_4 aerosol of various composition. For studies where the substrate has to be kept at low temperatures such as for kinetic studies involving ice and other frozen surfaces a special low-temperature sample holder has been constructed. The sample is placed into a copper dish that is in contact with a heat exchanger which is alternatively cooled by circulating cold air and resistively heated using a double-loop temperature controller. A design has been chosen which maximizes the gradient between the cold temperature-controlled surface and the rest of the *Knudsen* reactor remaining at ambient temperature. A similar design has been chosen for a high-temperature sample support which enables the heating of samples up to temperatures of 500 K.

Fig. 2 displays an overview of the two-chamber *Knudsen* reactor with which we have performed most of the measurements described below. In addition to molecular-beam-modulated mass spectrometry we have used real-time *in situ* optical diagnostics based on pulsed laser excitation such as laser-induced fluorescence (LIF) and Resonance-Enhanced Multiphoton Ionization (REMPI). To this end the *Knudsen* cell displayed in *Fig. 2* was equipped with a set of optical windows to allow pulsed laser excitation and photon detection. This dual diagostic capability enables us to calibrate the optical signals in terms of absolute density using the mass spectrometer. We believe it to be necessary to know the absolute concentrations of the reactants when studying heterogeneous kinetics because most mechanisms turn out to be complex [11].

We have recently developed an additional real-time kinetic technique based on the *Knudsen* cell which involves pulsed admission of molecules interacting with easily saturable surfaces such as soot, salt and ices. A known number of gas molecules are admitted by a pulsed solenoid valve into the reactor and interact with the active surface. The decay of the gas burst is followed in real time using time-dependent mass spectrometry. In the case of a measurable heterogeneous interaction the lifetime of the molecule will be shortened as the time-dependent signal will decay faster in the presence of the active surface according to the relation:

$$S = S_0 \exp(-(k_e + k_h)t) \qquad (9)$$

This technique has two important advantages over the traditional steady-state technique: *a*) it affords the separation between the kinetics of the adsorption and desorption step because there are no molecules on the surface at $t = 0$ which are able to desorb, and *b*) it keeps the dose to a minimum thereby avoiding surface saturation and contamination phenomena. A typical lower limit for a gas burst is in the range of 2% of a formal monolayer, depending somewhat on the identity of the molecule. In any case, we do not expect any measurable saturation effect at surface coverages

CHIMIA 50 (1996) Nr. 5 (Mai)

of a few percent of a formal monolayer. Finally, it has to be pointed out as well that the experimental effort also includes a fair amount of preparative work as compounds such as N_2O_5, $ClONO_2$, $BrONO_2$, $ClNO_2$, HONO, NOBr and others have to be synthesized and purified shortly before their use in view of their limited thermal stability.

3. Representative Results and Discussion

In what follows we will briefly present some representative examples of studies of heterogeneous reactions performed at EPFL over the last four years emphasizing both the fundamental aspects of the chemical kinetic studies as well as their atmospheric implications.

3.1. *The Interaction of Water Vapor with Ice*

The condensation and evaporation of H_2O vapor on its own solid (ice, snow) and fluid condensed phase is one of the most important processes in the atmosphere. Although the vapor pressure of H_2O over liquid water and ice is well known from experiments down to 170 K the kinetics of condensation and evaporation was the subject of many studies over the years [13]. The measurement of the vapor pressure, which is a thermodynamic quantity and corresponds to an equilibrium constant, says nothing about the kinetics of the individual condensation and evaporation process for which experimental results cast in the form of evaporation and condensation coefficients vary up to a factor of 200 depending on the experimental technique and the temperature [14]. We embarked on a program to experimentally determine this simplest of systems in order to measure a reference reaction against which all others may be compared to.

The simplest experiment consisted of measuring the H_2O vapor effusing out of the *Knudsen* cell in the presence of ice in the temperature range 160–220 K according to the following simple kinetic scheme involving H_2O vapor and bulk ice, B:

$H_2O \rightarrow B$	vapor condensation (k_{cond})	(10)
$B \rightarrow H_2O$	water evaporation (k_{ev} [B]= R_{ev})	(11)
$H_2O \rightarrow$	gas effusion out of the *Knudsen* reactor (k_e)	(12)

where k_{cond} and k_e correspond to the condensation and escape rate constant, respectively, and R_{ev} equals the *rate* of evaporation in molecules s^{-1}. The experimentally observed vapor pressure is a steady-state vapor pressure and is not equal to its equilibrium value because it is perturbed by the reaction according to *Eqn. 12*. However, it is possible to calculate the equilibrium vapor pressure by separately determining k_c and R_{ev}. By obtaining two independent data sets corresponding to *Knudsen* reactors with two different escape orifices we may obtain the desired parameters. *Fig. 3* presents an *Arrhenius* plot of k_{cond} as a function of inverse temperature in the range 160–220 K. By dividing the values of k_{cond} by $\omega = 150\ s^{-1}$ one obtains the condensation coefficient as a function of temperature which varies between 0.05 and 0.5.

The measured negative activation energy for k_{cond} of -3.0 ± 1.5 kcal/mol suggests kinetic complications and points towards a complex mechanism, a fact that is surprising for such a simple physical system. The numerical values of the evaporation rates of H_2O from an ice surface are impressive even at low temperatures: R_{ev} corresponds to the evaporation of 10 monolayers of H_2O per s at 180 K and to 80 monolayers at 200 K. These high values for R_{ev} reveal the dynamic nature of an ice surface even at low temperatures which has important consequences for the condensation of less volatile molecules on ice surfaces. A short time after a heavy molecule has 'landed' on an ice surface it is 'buried' and incorporated into the bulk of the ice by the rapid evaporation and condensation of H_2O.

In view of the suspected complexities of this simple reaction we performed additional kinetic experiments in real time admitting bursts of water vapor into the *Knudsen* reactor and observing the subsequent decay of the H_2O pulse. Surprisingly, k_h (*Eqn. 9*) was found to be a function of the dose. The measured values for k_h are displayed in *Fig. 4* for an ice surface at 180 K. This dependence of k_h on the dose of H_2O is a subtle effect and corresponds to an increase of k_h by at most a factor of six over almost a three order of magnitude variation in dose. The dose corresponding to a nominal monolayer of H_2O on ice is on the order of 10^{16} molecules. *Fig. 4* displays thus a dose dependence ranging from less than 10% of a nominal monolayer per pulse to more than 400 monolayers. This dose dependence is more pronounced at 200 K whereas it is not observed at 160 K. The interpretation of these results necessitates chemical kinetic modeling because of the incidence of a pressure-dependent mechanism.

The simplest mechanism which explains both our steady-state as well as the pulsed valve experiments involves the competition between a *Langmuir-Hinshelwood*-type condensation process and an autocatalytic process whose rate is depending upon the H_2O pressure [15]. It is given by the following reversible equations:

$H_2O + S \rightleftharpoons I + B$	(k_1, k_2)	(13)
$I + B \rightleftharpoons P + S$	(k_3, k_4)	(14)
$H_2O + P \rightleftharpoons B + P$	(k_5, k_6)	(15)

where S is a nominal surface site for H_2O condensation and I and P are two intermediate states which correspond to adsorbed H_2O molecules. Each H_2O molecule is surrounded by four others in bulk ice whose lattice corresponds to a distorted diamond structure, thus forming four H-bonds with neighboring H_2O molecules. The various species in the model differ in the number of 'free valences', that is the ability to engage in H-bond formation up to the maximum coordination number of four. H_2O has four free valences, each following species has one valence less (I = 3, P = 2 , S = 1 and B = 0). When H_2O is forming one H-bond to S it itself becomes an I molecule with one H-bond and three free valences thereby converting the original S state to a B state (*Eqn. 13*). The reverse process of breaking a H-bond is also possible and is embodied in the reaction according to *Eqn. 14* where B is split into two S states, one of which forms a H-bond with I thus becoming a P state. Finally, H_2O may directly form two H-bonds at once in a concerted fashion thereby transforming a P state into a B state and at the same time becoming a P state (*Eqn. 15*).The reaction corresponding to *Eqn. 15* seems to be essential and is in fact *autocatalytic* in P thus preserving the density of catalytic P states which are necessary for the increase of the rate of H_2O adsorption at increasing pressure.

The increase of the condensation coefficient with increasing pressure essentially results from the increased coverage of P at increasing pressure and may help explain the fact of the large range of experimental values obtained to date [14]. The model reproduces both the observed negative temperature dependence of k_{cond} (*Fig. 3*) as well as the dose dependence (*Fig. 4*). The significance of the kinetic work, how-

ever, lies in the fact that they require a mechanism dealing with at least *two additional kinetically distinguishable species* in going from the simple mechanism, *Eqns. 10* and *11*, to the more complex one given by *Eqns. 13–15*.

3.2. *The Interaction of HCl with Ice*

HCl is a stable chlorine-containing reservoir molecule which plays a pivotal role in the chemistry of the polar stratosphere. Together with the slightly more reactive $ClONO_2$ whose heterogeneous reactivity will be discussed below, it constitutes the main chlorine-containing species throughout the stratosphere, and the sum of both HCl and $ClONO_2$ attains values on the order of 2–3 ppb. In view of the strong bond of 103 kcal/mol and the UV absorption spectrum of HCl it was believed that once chlorine was transformed into HCl, mainly by abstraction of an H-atom from CH_4 by HCl, it would be removed from the catalytic ozone-destruction cycle. However, it was shown that chlorine in HCl could be activated efficiently in a heterogeneous reaction following *Eqn. 1* meaning it could be transformed into another chlorine-containing molecule which would readily release atomic chlorine upon photolysis. The reaction given by *Eqn. 1* is very popular amongst atmospheric modelers because it kills two birds with one stone by converting the chlorine of *two* reservoirs into the active form Cl_2 releasing two active Cl-atoms upon photolysis.

It is well known from general chemistry that HCl is very soluble in liquid H_2O but scarcely so in ice. The known phase diagram of HCl/H_2O reveals a coexistence line between fairly concentrated HCl solutions and 'ice' in the temperature range between 220 and 180 K which is of interest in the context of stratospheric chemistry (*Fig. 5*) [16]. However, in the pertinent pressure range of 10^{-7} Torr HCl does not form a stable fluid phase atop the ice and the system is better described as bulk ice contaminated by small amounts of adsorbed HCl.

In order to study the uptake kinetics of HCl on ice we performed pulsed valve experiments of HCl on ice and were able to conclude that at doses corresponding to even less than a nominal monolayer HCl is rapidly forming a fluid layer on the ice thus facilitating further dissolution of gas phase HCl into the fluid condensed phase [17]. Such a pulse of HCl results in a rapid decay of the gas-phase HCl density corresponding to k_h values of 30 s^{-1} at 170 K and 5 s^{-1} at 210 K reflecting the high solubility of HCl in the liquid layer created by its own pulse. After the decay of the pulse a steady-state HCl partial pressure is maintained in the *Knudsen* cell which agrees with the equilibrium vapor pressure of *Molina* and coworkers at the liquid-solid coexistence line [18] (*Fig. 5*). This steady-state signal persists for a certain time depending on the dose and drops to zero after the supply of HCl from the surface is exhausted.

The mass balance reveals that most of the HCl is retained by the ice sample. In view of the dynamic nature of the interface this can be expected as many of the molecules are 'buried' in the bulk of the pure ice never again to desorb. The fact that even doses corresponding to less than a nominal HCl monolayer lead to a well defined HCl equilibrium vapor pressure predicted by the HCl/H_2O phase diagram can be interpreted that localized 'patches' or 'potholes' of HCl/H_2O fluid form on the ice surface. Apparently, the formation of a macroscopic fluid layer is not necessary to maintain an equilibrium HCl vapor pressure.

If, on the other hand, the dose or the flow rate falls below a certain limit in pulsed and steady-state experiments, re-

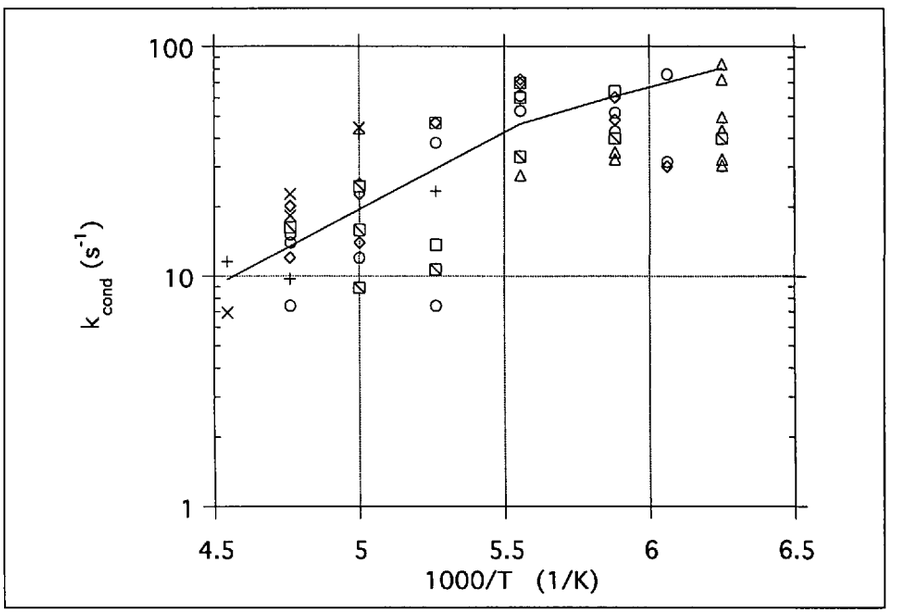

Fig. 3. Arrhenius *plot of the rate constant* k_{cond} *for the condensation of* H_2O *on ice under near-equilibrium conditions in the temperature range 160–220 K.* The *Knudsen* reactor had the following characteristics: V = 1.18 dm^3, area of the active surface = 11.3 cm^2, k_e (H_2O) = 1.0 (small aperture) and 7.5 (large aperture) s^{-1}, ω = 150 s^{-1}.

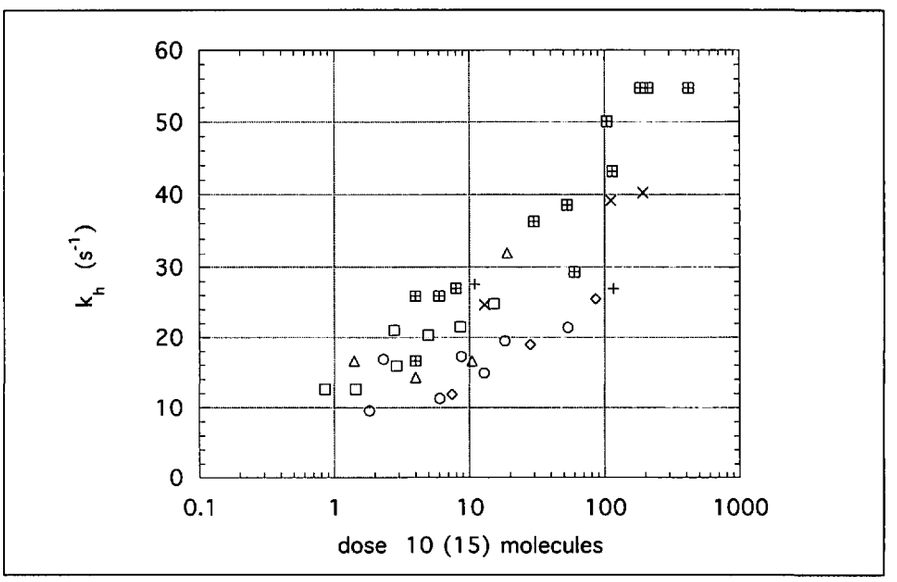

Fig. 4. *Dependence of the decay time constant* k_h *of a* H_2O *pulse admitted to the* Knudsen *cell in the presence of ice at 180 K as a function of the dose* (number of H_2O molecules in the pulse). The different symbols pertain to different experiments, and the *Knudsen* reactor parameters are the ones from *Fig. 3*.

CHIMIA 50 (1996) Nr. 5 (Mai)

spectively, k_h drops to values comparable to k_c in pulsed valve experiments and the steady-state uptake drops to unmeasurably low values. This threshhold may be interpreted that the formation of the liquid HCl/H_2O layer on the ice surface is enabled by a minimum-required impact rate which probably must exceed the evaporation rate of H_2O of the ice surface. It thus follows that this threshhold value for the impact rate expressed as the number of HCl molecules striking 1 cm^2 of the ice surface in unit time largely depends on the temperature and is in fact equivalent to a pressure barrier for dissolution of HCl in ice.

We may conclude that HCl only scarcely dissolves in pure ice at stratospheric conditions in view of the HCl partial pressures on the order of 10^{-7}–10^{-6} at temperatures between 180 and 220 K. The physical state of HCl under those conditions corresponds to an impurity adsorbed along grain boundaries or hairline cracks within the ice sample. On the other hand no change in physical behavior of the HCl/H_2O system has been observed in going from an ice sample deposited from the vapor phase at 160 K to one generated from freezing a sample of distilled H_2O after several freeze-pump-thaw cycles. This may well mean that the natural surface roughness of the ice adsorbs and retains a certain quantitiy of HCl.

3.3. *The Interaction of $ClONO_2$ with HCl and Ice*

The discovery in the early seventies of $ClONO_2$ in the atmosphere and its mechanism of formation by recombination from $ClO + NO_2$ caused a false sense of security amongst the atmospheric science community. The reasoning followed the hypothesis that the formation of an inactive reservoir such as $ClONO_2$ which has a small actinic absorption cross section and which is generated from two free radicals participating in catalytic ozone-destruction cycles, removed the immediate threat of massive ozone destruction. However, it later turned out that this expectation was a fallacy because heterogeneous pathways of activation of $ClONO_2$ had not been taken into account. In view of the importance of the reactions corresponding to *Eqns. 1* and *2* for the chlorine activation scenario we will briefly present some of the fundamental processes of heterogeneous chemistry.

Fig. 6 displays a typical steady-state experiment, wherein a bulk ice sample at 180 K is exposed to a steady flow of $ClONO_2$ of 10^{14} molecules s^{-1} monitored at $m/e = 46$ (NO_2^+). Upon exposing the ice sample the signal *m/e* at 46 rapidly drops corresponding to an initial value of $\gamma = 0.3$ for $ClONO_2$ uptake by ice. Subsequently, the signal gradually rises again due to a rapid saturation process on ice and eventually reaches a steady-state level. The rate of formation of HOCl monitored at $m/e = 52$ ($HOCl^+$) is slowly rising after an initial burst and reaches also a steady-state level similar to the $ClONO_2$ signal. At higher flow rates of $ClONO_2$, Cl_2O is accompanying the formation of HOCl. It is the formal anhydride of HOCl and is thermodynamically favored by 1 kcal/mol in equilibrium (*Eqn. 16*) [19]:

$$2HOCl \rightleftharpoons Cl_2O + H_2O \qquad \Delta H^0_r = -1.0 \text{ kcal/mol} \qquad (16)$$

In separate reference experiments we established that the HOCl interaction with water ice and HNO_3-exposed water ice is negligible at our used flow rates. Moreover, no Cl_2O formation could be observed using HOCl as the precursor so that we conclude that it is a secondary product formed at higher flow rates of $ClONO_2$.

From the difference in the rate of $ClONO_2$ uptake and the rate of appearance of the primary product HOCl, which is especially apparent at higher $ClONO_2$ flow rates, it is clear that an intermediate which is slowly releasing HOCl is generated at the interface. *Sodeau* and coworkers identified an unusual intermediate resulting from $ClONO_2$ exposure to their ultrathin ice samples and attributed it to $H_2OCl^+\cdots NO_3^-$ based on its IR-absorption spectrum [20]. This species corresponds to protonated hypochloric acid stabilized by nitrate ion and represents an HOCl precursor. We assume that the intermediate in our case is identical to that found by *Sodeau* even though our experimental conditions differ significantly from theirs. When we 'interrogate' our ice sample that was previously exposed to $ClONO_2$ by exposing it to an excess flow of HCl we observe to our surprise only spurious amounts of Cl_2 [21]. We expected quantitative conversion of HOCl or its precursor, protonated hypochloric acid, H_2OCl^+, with HCl according to the fast reactions of *Eqns. 17a* and *17b*:

$$HOCl + Cl^- \rightarrow Cl_2 + OH^- \qquad (17a)$$

$$H_2OCl^+ + Cl^- \rightarrow Cl_2 + H_2O \qquad (17b)$$

Apparently, the HOCl precursor is completely unreactive towards displacement of OH^- by Cl^- (*Eqn. 17b*), perhaps because of the limited kinetic activity of H_2O as a leaving group in nucleophilic displacements.

Pulsed valve experiments of $ClONO_2$ interacting with ice indicate an extreme sensitivity of the reaction corresponding to *Eqn. 2* to surface saturation, presumably due to the accumulation of stable HNO_3 hydrates that form when HOCl is liberated according to *Eqn. 2* [21]. A pertinent observation is the fact that no saturation of $ClONO_2$ uptake is observed when a simultaneous flow of $ClONO_2$ and NH_3 is brought to interact with the ice sample suggesting a rapid destruction of the HOCl precursor by NH_3. A large sustained uptake of $ClONO_2$ is observed whereas HOCl is not because it is neutralized by NH_3 to result in NH_4OCl. On the other hand, a high rate of Cl_2O formation is also observed indicating that it results from a facile secondary nucleophilic displacement, *Eqn. 18*:

$$ClO^- + HOCl \rightarrow Cl_2O + OH^- \qquad (18)$$

where ClO^- represents the reactive part of gas-phase $ClONO_2$ interacting with HOCl. In addition, gas-phase HOCl also reacts with the same precursor according to *Eqn. 18*.

If on the other hand the ice sample is exposed first to HCl and subsequently to $ClONO_2$, Cl_2 is seen to rise promptly and quantitatively as a result of the reaction given by *Eqn. 17*. *Figs. 7a* and *7b* present a good example for the determination of k_h for the decay of a pulse of $ClONO_2$ in the presence of ice and the correlated rise of Cl_2 on the same time scale, thus emphasizing the prompt mode of Cl_2 compared to HOCl formation (in the absence of HCl).

From a mechanistic point of view both HCl and H_2O are competing for reaction with $ClONO_2$ according to *Eqns. 19* and *1*:

$$ClONO_2 + H_2O \rightarrow [H_2OCl^+\cdots NO_3^-] \rightarrow HOCl + H^+ + NO_3^- \qquad (19)$$

$$ClONO_2 + HCl \rightarrow Cl_2 + H^+ + NO_3^- \qquad (1)$$

where the spontaneous decomposition of the HOCl precursor in the reaction according to *Eqn. 19* may be accelerated by a base such as NH_3. As an important corollary we note that Cl(+1) in the HOCl precursor is not titratable by Cl(−1) whereas formation of the secondary product Cl_2O by nucleophilic displacement with ClO^- seems facile (*Eqn. 18*).

These few kinetic facts may have ramifications for atmospheric chemistry. For one, the sequence of interaction of ClO-

NO_2 and HCl with ice certainly matters as our sequential exposure experiments have shown. For instance the conclusion reached by some authors that the reaction following *Eqn. 1* occurs first through the reaction according to *Eqn. 2* with subsequent fast titration by HCl according to *Eqn. 17b* needs careful reexamination for the case of an ice substrate [19][22]. The reactivity of $ClONO_2$ has to be seen in terms of two competitive reactions, one slow through the HOCl precursor (*Eqn. 19*), the other one rapid by way of a direct reaction (*Eqn. 1*) involving Cl^- in a mobile phase. Our results point towards the importance of nucleophilic displacement reactions and ionic mechanisms.

3.4. *The Heterogeneous Interaction of HONO and HCl*

Burley and *Johnston* recently presented an interesting hypothesis according to which HCl may be activated by HONO using H_2SO_4 as a catalyst following *Eqns. 20* and *21* [23]:

$$HONO + H_2SO_4 \rightarrow NO^+HSO_4^- + H_2O \quad (20)$$

$$NO^+HSO_4^- + HCl \rightarrow NOCl + H_2SO_4 \quad (21)$$

The N(+3) species is effectively dissolved in H_2SO_4 as nitrosylsulfuric acid (NSA) which is stable at H_2SO_4 concentrations exceeding 72% by weight at ambient temperature. Below this concentration HONO is dissolved in molecular (undissociated) form although the stability range of NSA may be extended to more dilute solutions with decreasing temperature. The reason for the interest in this reaction is the hypothesis that the exhaust from commercial and military jet aircraft flying at heights corresponding to both just above and below the tropopause may affect the stratospheric ozone layer by activating HCl into readily photolyzable NOCl. Aircraft exhaust with its emission of H_2O, NO, SO_2, soot particles and many other reactive species represents a very reactive environment for heterogeneous reactions in which background gases such as HCl may also actively participate [10].

We devised a two-pronged approach to consider this atmospheric question [24]: First, we intended to study the uptake of gas-phase HONO on H_2SO_4 in order to see if NSA was indeed generated at all. The second step consisted of investigating the activation reaction according to *Eqn. 21* of HCl on NSA. *Fig. 8* displays the results of the uptake coefficients γ of HONO on aqueous solutions of H_2SO_4 of variable concentration. It is in marked contrast to most reactants such as HCl whose solubility in H_2SO_4 dramatically decreases with inceasing H_2SO_4 concentration. Our resulting γ values are significantly lower than the ones recently obtained by *Leu* and coworkers, the reason for which is unclear [25]. When we bring HCl to interact with a HONO-saturated H_2SO_4/H_2O solution we measure low uptake coefficients γ on the order of 10^{-3} or less, also in distinct contrast to results recently published which are in the range between 10^{-2} and 10^{-1}. However, if we measure the heterogeneous interaction of concurrent flows of HONO and HCl on ice we observe large γ values ranging from 0.07 at 180 K to 0.03 at 200 K thus showing a slight negative temperature dependence. The heterogeneous reaction is driven by the dissolution of HCl in ice and the formation of a liquid layer on the ice surface. HONO is taken up in a reversible process in less than a monolayer quantity on pure ice in the absence of HCl, whereas it interacts quite efficiently on a fluid layer containing HCl. Experimental data show conclusively that the uptake of HONO is strongly, and that of HCl somewhat enhanced in each other's presence.

This result may have far-reaching consequences as far as atmospheric implica-

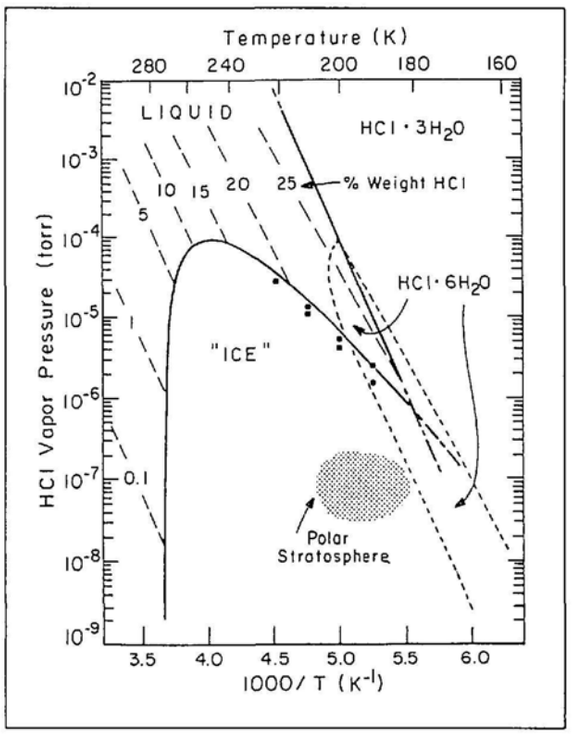

Fig. 5. *Phase diagram for the HCl/H_2O system.* The equilibrium vapor pressure of HCl determined from pulsed HCl dosing experiments in several different *Knudsen* reactors follow the line established in equilibrium experiments by *Molina* and coworkers [18]. Two independent data sets were used to calculate the equilibrium vapor pressure (● combination of 8- and 15-mm-diameter, ■ combination of 4- and 8-mm-diameter-aperture *Knudsen* reactor).

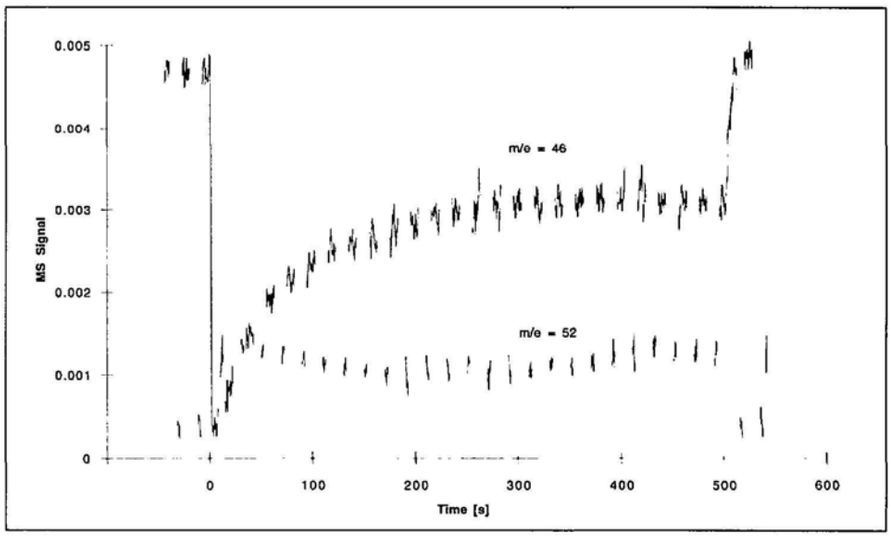

Fig. 6. *Typical continuous flow experiment of $ClONO_2$ on ice at 180 K using a 4-mm-diameter-aperture* Knudsen *reactor at a flow rate of $1.0 \cdot 10^{15}$ molecules s^{-1}*

tions in relation to air traffic are concerned, but it also seems to weaken the importance of this chlorine activation scheme on H_2SO_4 aerosols of the global background atmosphere contrary to the conclusions spelled out in [25]. However, only model calculations approaching atmospheric conditions in their degree of realism may be able to assess the real significance of these experimental results including the weak interaction of NOCl with H_2SO_4 solutions displayed in *Fig. 8*. Once again, the operating mechanism may be described as a nucleophilic substitution reaction involving the displacement of OH^- by Cl^-:

$$Cl^- + HONO \rightarrow NOCl + OH^- \quad (22)$$

Apparently, this S_N2-type displacement reaction is a much more facile process than the corresponding S_N1-type reaction (*Eqn. 23*) which may even point to an inhibiting effect of H_2SO_4 rather than a catalytic one:

$$NO^+ + Cl^- \rightarrow NOCl \quad (23)$$

We, therefore, conclude that the chlorine activation scheme proposed by *Burley* and *Johnston* may not occur on catalytic surfaces such as H_2SO_4 aerosols but rather in a direct way on ice particles.

3.5. *The Reaction of HNO_3 with $CaCO_3$*

Due to the corrosive nature of the polluted atmosphere, many monuments containing $CaCO_3$, including marble, sandstone and calcareous stone, are badly damaged. This fact has been summarily attributed to exposure to acid rain. However, even parts of monuments and statues that were never directly exposed to precipitation sometimes show roughly the same degree of damage. The incidence of episodes where acid fog or acidified aerosols are in contact with those monuments is highly variable and does not represent a coherent explanation for the damages incurred. Therefore, gas-phase pollutants have been searched for which model calculations predict to be ten times as efficient as acid precipitation because of longer contact/exposure times. We assumed that HNO_3 may play the role of the gas-phase corroding agent because it is a reservoir compound for NO_x that is in steady increase in polluted urban atmospheres in view of the increasing emission strength of NO_x-releasing sources such as fossil fuel combustion. Gas-phase HNO_3 does not possess acidic character and is characterized by a weak HO–NO_2 bond of 50 kcal/mol.

The experiments show the rapid uptake of HNO_3 and an equally as rapid formation of H_2O and CO_2 when a HNO_3 flow is exposed to powdered $CaCO_3$. It demonstrates conclusively that an acid-base reaction is occurring between HNO_3 and the ionic calcite surface [26]:

$$2\,HNO_3 + CaCO_3 \rightarrow Ca(NO_3)_2 + CO_2 + H_2O \quad (24)$$

However, the generation of H_2O and CO_2 desorbing from the powdered sample hints at a complex mechanism possibly involving a precursor because of their delayed formation. Once steady state has been reached we observe complete mass balance between HNO_3 consumed and CO_2 generated. In separate reference experiments it was established that H_2O interacted with the calcite powder so that the incomplete mass balance for H_2O can be explained by incomplete desorption of the H_2O primary product. The surprise lies in the fact that the reaction according to *Eqn. 24* seems to be quite an efficient hydrolysis reaction despite the 'dry' nature of the reaction system and is characterized by a reactive uptake coefficient for HNO_3 on the order of $\gamma = 0.10$. Part of the explanation for such a large value of γ certainly lies in the 'sticky' nature of HNO_3 whose tendency for adsorption on a variety of surfaces is well known. The pertinent description for the surface reactivity of HNO_3 follows the *Langmuir-Hinshelwood* model of heterogeneous catalysis, wherein adsorbed HNO_3 moves to active surface sites

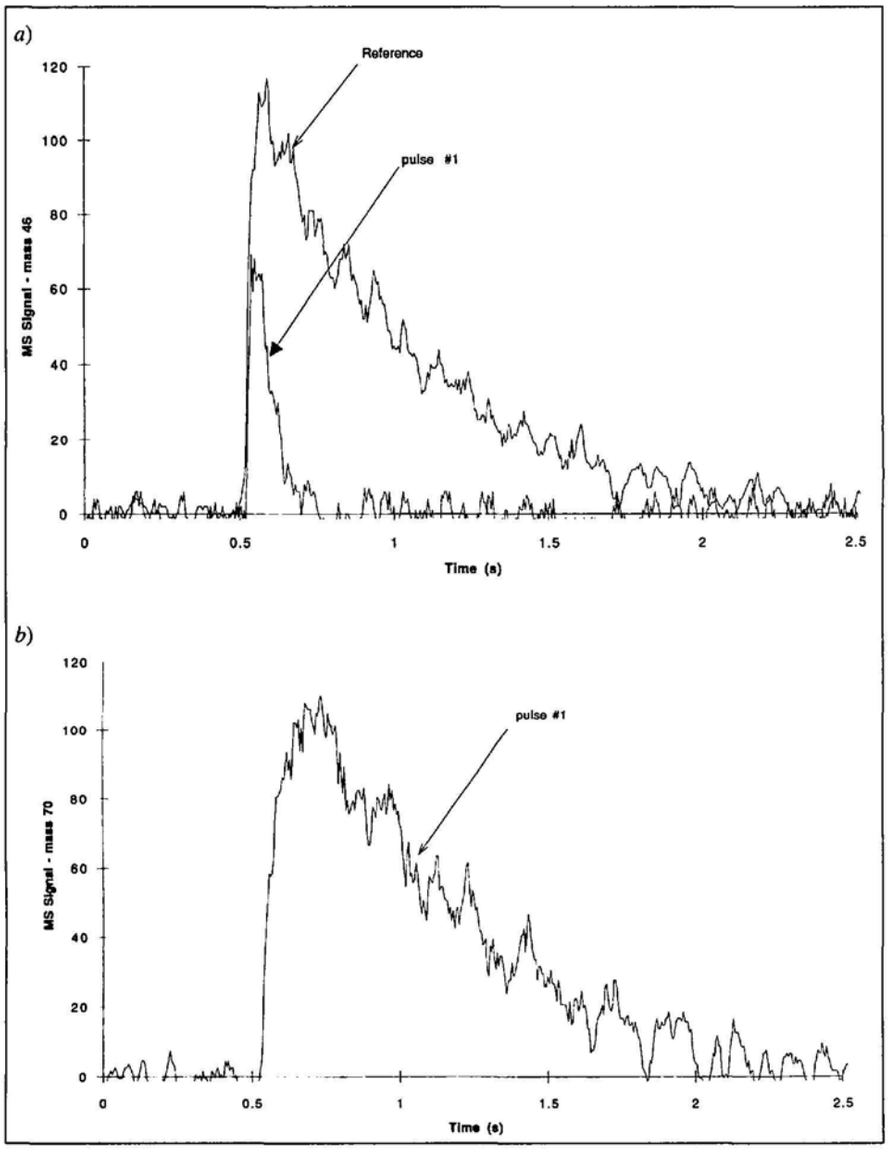

Fig. 7 a) *Pulsed dosing experiment of $ClONO_2$ on ice previously exposed to HCl at 200 K at a dose of $ClONO_2$ of $1.0 \cdot 10^{14}$ molecules corresponding to 10% of a formal monolayer.* The mass-spectrometric trace displays *m/e* = 46 (NO_2^+) as a marker for the time dependent density of $ClONO_2$ effusing out of the reactor. b) *Same experiment as in* Fig. 7a *except that Cl_2 is recorded as a function of time*

CHIMIA 50 (1996) Nr. 5 (Mai)

by surface diffusion without ever desorbing [11].

3.6. *The Reaction of N-Containing Oxides, Acids and Anhydrides with Salt Surfaces*

90% of the world population lives in coastal areas which include a strip of land along the ocean's coastlines 100 km wide. These population centers generate massive amounts of air pollution which forms acids and oxidants such as tropospheric (surface) ozone in photochemical smog episodes which deteriorate the air quality to a significant extent. The OH free radical, mainly generated from photolysis of ozone and subsequent reaction with H_2O vapor plays a central role in ozone formation which is just a by-product of NO_x-catalyzed slow hydrocarbon oxidation (combustion) processes supported by photochemistry. This dark flame atmospheric process is comparable to internal combustion of fossil fuels with the main difference being that in combustion the free radicals necessary for maintaining the flame are generated in thermal dissociation processes, whereas they are generated mostly from photolytic processes in the atmosphere. When such heavily polluted urban air masses interact with the marine aerosol hovering above the coastline qualitatively new chemistry is occurring. Of prime interest is the question to what extent the normal chain carrier OH may be replaced by atomic chlorine whose reactivity is a factor of 20 larger than that of OH as far as chain-initiating H-abstraction reactions are concerned [27]. In addition, salt aerosol may also be found in the stratosphere after major volcanic eruptions which propel their ejecta up into the lower stratosphere to heights of just under 20 km.

We recently embarked on a program to systematically study the heterogeneous reactivity of NO_x, HNO_3, N_2O_5, $ClONO_2$, and $ClNO_2$ on NaCl and KBr which are two important constituents of sea salt [28–30]. Some of the reactions and their products are the following:

$$HNO_3 + NaCl \rightarrow HCl + NaNO_3 \quad (25)$$

$$N_2O_5 + NaCl \rightarrow ClNO_2 + NaNO_3 \quad (26)$$

$$N_2O_5 + KBr \rightarrow BrNO_2 + KNO_3 \quad (27)$$

$$BrNO_2 + KBr \rightarrow Br_2 + KNO_2 \quad (28)$$

$$ClONO_2 + KBr \rightarrow BrCl + KNO_3 \quad (29)$$

$$ClNO_2 + KBr \rightarrow BrNO_2 + KCl \quad (30)$$

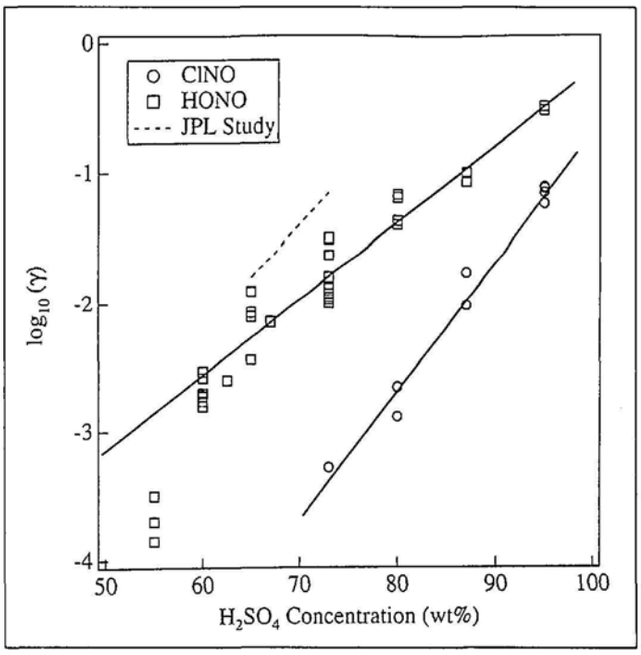

Fig. 8. *A semi-logarithmic plot of the determined uptake probabilities for HONO and ClNO as a function of H_2SO_4 concentration in the temperature range 215–273 K.* The vapor pressure was balanced by an external flow of H_2O.

Eqn. 25 corresponds to a simple exchange reaction in which volatile HNO_3 is exchanged for HCl. The *Table* displays the results for the measured uptake coefficients when gas-phase HNO_3 interacts with a salt sample that is presented either as a finely ground powder, as salt grains or as a thin film of several mg of mass and several μm of thickness. The *Table* shows that the uptake coefficient for HNO_3 on salt is invariant of the sample presentation: identical values of γ are obtained for exposure on a single crystal flat and on finely ground powder, two sample presentations which differ greatly with respect to their internal surface. The reason for this behavior lies in the fact that HNO_3 is known to be a 'sticky' compound which mainly stays on the external surface and thereby 'ignores' deeper layers of the sample as it never diffuses into the powder. This behavior is in marked contrast to the heterogeneous interaction of N_2O_5 with salts, *Eqns. 26* and *27*, which is immeasurably small for a polished single crystal flat. The *Table* displays the results which are of the same magnitude as in the case of HNO_3 when the sample is presented in a form which gives the N_2O_5 an opportunity to explore the internal surface of the sample. In this case the gas penetrates into the bulk and the measured uptake coefficient becomes dependent on the sample mass, thus of the number of grain layers. N_2O_5 behaves like an ideal gas which does not stick to the sample surface and interacts with the chemical conversion sites on the salt sample from the gas phase by multiple adsorption-desorption steps. The corrected results for γ displayed in the *Table* reduce the observed uptake coefficient to a per collision basis on a single layer of salt following a pore diffusion model proposed by *Keyser* and coworkers [31].

The primary reaction product $BrNO_2$ in *Eqn. 27* was not directly monitored in view of its fast secondary reaction according to *Eqn. 28*. However, we observed its hydrolysis product HONO which forms with traces of moisture in the salt sample, whereas NO_2Cl generated according to *Eqn. 26* is kinetically stable under our conditions. An important switch in chemical reactivity takes place in going from $ClNO_2$ to $BrNO_2$. The first corresponds to the formal anhydride of HNO_3 (N(+5)) and HCl (Cl(−1)), whereas the latter represents the formal anhydride of HONO (N(+3)) and HOBr (Br(+1)). The fast secondary reaction given by *Eqn. 28* is, therefore, due to the change of oxidation state of the bromine in $BrNO_2$ compared to the chlorine in $ClNO_2$.

In summary, we learned two important things from this systematic study: *a*) reactions according to *Eqns. 26–30* all generate active halogen that is readily photolyzable in the daylight atmosphere thus supplying free radical-chain carriers for atmospheric oxidation processes, and *b*) we are able to distinguish 'sticky' from 'non-sticky', that is ideal gas, compounds in their heterogeneous interaction on salt. This is an important contribution to the ongoing discussion whether or not sample porosity has an effect on the determination of kinetic parameters of the heterogeneous interaction on frozen surfaces such as ices. The main result from the data presented in the *Table* can be summarized

Table. *Synopsis of Uptake Coefficients* γ [%] *of Atmospherically Relevant Gases on Salt.* The corrections to the observed uptake coefficients were performed according to [31].

Gas	Salt	Powder	Corr.	Grain	Corr.	Spray
$ClNO_2$	KBr	1.9 ± 0.5	0.03 ± 0.02	0.08–0.7	0.015	0.007 ± 0.004
$ClONO_2$	NaCl	24 ± 5	–	18 ± 4	–	28 ± 6
$ClONO_2$	KBr	33 ± 5	–	36 ± 10	–	36 ± 10
HNO_3	NaCl	2.8 ± 0.5	–	–	–	1.3 ± 0.8
HNO_3	KBr	2.8 ± 0.5	–	4.7 ± 0.6	–	1.7 ± 0.8
N_2O_5	NaCl	3.0 ± 0.5	0.17	5–27	0.2	0.5 ± 0.2
N_2O_5	KBr	5.5 ± 0.1	0.35	25–58	0.4	0.3 ± 0.2

that γnot only depends on the properties of the substrate but also on the gas. In our case N_2O_5 and $ClNO_2$ behave as ideal (non-sticky) gases whose heterogeneous interaction depends on the porosity of the substrate, whereas $ClONO_2$ and HNO_3 are sticky gases that do not penetrate into the bulk and are stopped at the external surface. In these latter two cases porosity is not an issue with respect to their interaction with salt which presents an ideal training ground for exploring aspects of sample porosity because their presentation is easily controlled at ambient temperature.

4. Concluding Remarks

We have seen that many different areas of physical chemistry contribute to the study of heterogenoeus chemistry such as chemical reaction kinetics, the theory of gas kinetics, thermochemistry, material properties (phase diagrams), vacuum technology and inorganic/organic synthesis, to name just a few. It is our opinion that this field is quickly moving across traditional scientific disciplines as it already includes aspects of atmospheric physics and meteorology, which makes this field so fascinating. The interaction with biology and the biosphere, oceanography and other fields of the earth sciences may loom just around the corner.

We set out to elucidate the *mechanistic* implications of heterogeneous reactions in order to provide the correct chemistry that goes into a model which may be fit for reliable projections into the future behavior of the atmosphere. It is impossible to reproduce realistic atmospheric conditions in the laboratory because the concentrations are often too low, the particle growth rates and the associated time scales too long. However, with an understanding of the *mechanism* we may be able to extrapolate from laboratory conditions to the atmosphere in order to reconcile and interprete field observations which may then be used to validate atmospheric chemistry models.

I would like to express my sincere gratitude to Prof. *H. van den Bergh* for having given me the opportunity to conduct these studies in his laboratory and for his continuing support of the tasks still lying ahead of us. I have also benefitted from his insights as well as from his lively interest in the progress of the scientific enterprise. My thanks go also to the sponsors of this research at *Fonds National Suisse de la Recherche Scientifique*, the *Office Fédéral de l'Education et de la Science* (OFES) and the *Office Fédéral de l'Environnement, Forêt et Paysage* (OFEFP) for their generous financial support. I would like to thank my many collaborators who contributed to the undisputable success of the Laboratoire de Pollution Atmosphérique et Sol since its inception in 1991 and without whom none of these experimental investigations would have been possible. My thanks go to *Arnaud Allanic*, *Talis Bauer*, *François Caloz*, *Agostino Clericetti*, *Fred F. Fenter*, *Lukas Gutzwiller*, *Raoul Oppliger*, *Marçal Pires*, *Kevin D. Tabor*, *Axel Thielmann*, *Wang Wei*, and *Matthias Wolf*. I also would like to acknowledge the efforts of our Italian mastercraftsman *Flavio Comino* for whom no task as daunting as it may seem was and is impossible.

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