

The Tropospheric Chemistry of Sea Salt: A Molecular-Level View of the Chemistry of NaCl and NaBr

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B. J. Finlayson-Pitts was born and raised in Ottawa, Canada. She completed her B.Sc. (Hons.) at Trent University in Peterborough, Canada, in 1970, and her Ph.D. at the University of California, Riverside, with Professor James N. Pitts, Jr., in 1973. After one year of postdoctoral research at UC Riverside, she joined the faculty in the Department of Chemistry at California State University, Fullerton, in 1974. In 1994, she became Professor of Chemistry at the University of California, Irvine, where she is currently located. Her research interests are elucidating the kinetics and mechanisms of reactions of atmospheric interest, particularly those of sea salt and oxides of nitrogen on surfaces.

the interfaces with air of solid NaCl and NaBr, as well as of aqueous salt solutions.

As illustrated in sections 3 and 4 below, inorganic halogen chemistry is closely intertwined with the complex chemical cycles that form and remove ozone from the troposphere. As a result, a review of the atmospheric chemistry of organics (often designated VOCs = volatile organic compounds) and oxides of nitrogen (NO_x) that lead to ozone formation is first presented in order to provide the context in which tropospheric halogen chemistry should be considered. We then summarize the role that gas-phase chlorine and bromine atoms play in the VOC– NO_x cycles and present some of the evidence from field studies for the contributions of Cl_2 , Br_2 , and BrCl as well as BrO to tropospheric chemistry. We focus the remainder of the article on the molecular-level mechanisms for reactions of solid salts of NaCl and NaBr, with emphasis on the role of adsorbed water, as well as on evidence for unique reactions of chloride and bromide ions at the air–water interface. To place these in context, we also summarize aqueous-phase chemistry that can occur in the bulk of deliquesced NaCl, NaBr, and sea salt particles.

We do not treat tropospheric iodine in this article. Although I^- is also present in seawater, the concen-

1. Introduction

The chemistry of the troposphere entails a complex combination of gaseous, aqueous, and surface processes involving a wide variety of compounds, both organic and inorganic.¹ About three decades ago, it was suggested that gas-phase chlorine and bromine atoms could be generated from chloride and bromide ions in sea salt and play a role in tropospheric chemistry, particularly of the marine boundary layer.^{2,3} Since that time, increasing evidence has been generated from laboratory, field, and modeling studies regarding the importance of sea-salt-generated halogen atoms in the chemistry of the lower atmosphere.^{4–19} This chemistry is most interesting both from an atmospheric chemistry perspective and from a molecular-level view; the latter is particularly the case due to the recent recognition of unique reactions at

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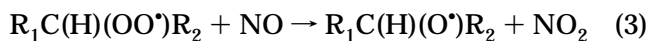
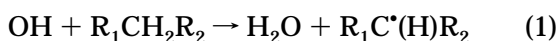
trations are much smaller than those of bromine and chlorine (molar ratio of I^- to Cl^- in seawater is $\sim 1:10^6$). The major iodine source in the troposphere is actually the photolysis of organoiodine compounds such as CH_3I and CH_2I_2 , and this is discussed in detail in the article in this issue by Carpenter. The reader is referred to this and several other recent articles^{12,17} for treatments of tropospheric iodine chemistry.

2. Tropospheric Chemistry of Oxides of Nitrogen and Organic Compounds

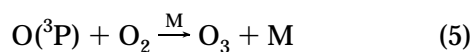
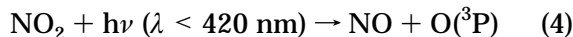
The tropospheric chemistry of VOCs and oxides of nitrogen and sulfur is well known to be driven by a few key oxidants, especially O_3 , OH, and NO_3 .¹ Chain reactions that oxidize organics and oxides of nitrogen and sulfur, as well as species such as CO, in air have been studied for more than five decades. Although the driving force initially was understanding the formation of photochemical air pollution, it has become clear that the same chemistry occurs in the remote troposphere, albeit with different relative importances of some processes. Ozone formation was identified in the earliest studies,^{20–22} and it was measured spectroscopically in 1957 as a major air pollutant in the Los Angeles area using long-path FTIR.²³ Ozone is present at measurable levels during both the day and night and contributes to the oxidation of alkenes and some inorganics such as NO_2 (see below).

In the 1960s, it became clear that in addition to O_3 , there must be some other highly reactive oxidizing species present in air that initiates organic oxidations starting at dawn. The hypothesis^{24–27} that the hydroxyl radical (OH) was the missing oxidant led to a large number of studies of the kinetics and mechanisms of oxidation of organics and inorganics by OH. Although OH can be generated at night via free radical reactions initiated by the decomposition of peroxyacetyl nitrate^{28,29} and by ozone–alkene reactions,^{30,31} its major sources are photolytic in nature, and hence its contributions to tropospheric chemistry peak during the day.

The hydroxyl radical oxidizes organics, forming alkyl peroxy (RO_2) or hydroperoxy (HO_2) radicals that convert NO to NO_2 in a cycle shown in Figure 1:



Nitrogen dioxide formed in reaction (3) photolyzes, generating ground-state oxygen atoms, $O(^3P)$, which then react with O_2 to form ozone:



$$(k_5 = 1.5 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{32}$$

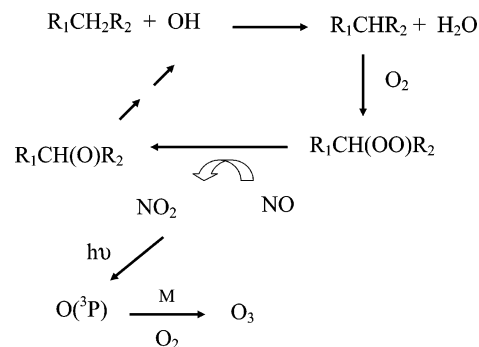
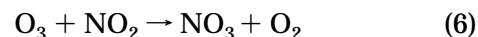


Figure 1. Schematic of VOC– NO_x chemistry in the troposphere.

(The M over the arrow represents a third body, usually N_2 or O_2 in air, that is required to stabilize the excited adduct formed as an intermediate in termolecular reactions. All rate constants for gas-phase reactions are given for 1 atm pressure and 298 K unless otherwise stated.) It is important to note that the photolysis of NO_2 is the sole known source of anthropogenic O_3 in the troposphere. Small amounts of tropospheric O_3 are also present due to stratospheric injection and VOC– NO_x chemistry from emissions of biogenic organics and small amounts of naturally occurring NO_x . These are responsible for only ~ 10 ppb O_3 (ppb = parts per billion (10^9) by volume or by molecules or moles) measured before the industrial revolution.^{33–39} This can be compared to the present-day global concentrations of ozone of ~ 30 – 40 ppb. The global increase in O_3 has been attributed to the increase in anthropogenic NO_x emissions from fossil fuel combustion.³⁴

About a decade after the recognition of the key role of OH, the importance of nighttime chemistry became evident.^{40–42} The nitrate radical (NO_3) drives this nighttime chemistry and is formed from the reaction of O_3 with NO_2 :



$$(k_6 = 3.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})^{32}$$

The nitrate radical photolyzes in the visible region, resulting in a rapid decrease in its concentration at dawn. (Wavelengths > 290 nm, the so-called “actinic region”, are available for photolysis in the troposphere.)

In summary, it is now known that tropospheric chemistry is largely driven by OH during the day, NO_3 at night, and O_3 both day and night.

3. Role of Gas-Phase Halogens in Tropospheric Chemistry

In 1974, Schroeder and Urone² reported that NO_2 at Torr pressures (1 Torr = 1.3×10^3 ppm at 298 K, 1 atm pressure; ppm = parts per million (10^6) by volume) reacted with solid NaCl to generate nitrosyl chloride (ClNO):

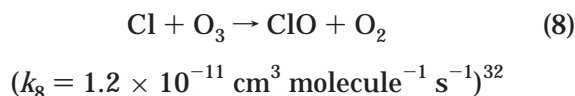


They proposed that because ClNO photodissociates in the visible region, it could be a source of highly

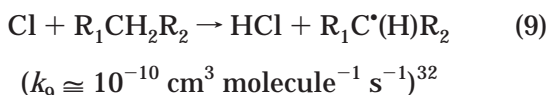
reactive chlorine atoms in marine areas where NaCl is the major component of airborne particles generated by wave action. In the troposphere, there are a number of different reactions that atomic chlorine can undergo, in contrast to the case in the stratosphere, where the major fate of chlorine atoms is reaction with ozone. Sea salt also contains bromide ions, and as discussed later, bromine plays a role in tropospheric chemistry that is disproportionate compared to its small concentration relative to chloride. The gas-phase tropospheric reactions of both chlorine and bromine are discussed in the following section.

3.1. Gas-Phase Chlorine Reactions in the Troposphere

Chlorine atoms react rapidly with O₃:



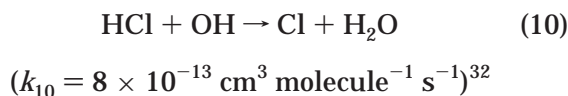
However, they are also highly reactive with organics, with rate constants greater than those for OH, approaching collision-controlled in many cases.^{32,43} This leads to the generation of alkyl, and subsequently alkylperoxy, radicals in reactions analogous to (1)–(5) for OH described earlier:



Ozone is then formed via reactions (2)–(5).

The total concentration of non-methane organic compounds varies with location, from a few ppb in remote regions to hundreds of ppb in polluted urban areas. Ozone concentrations fall approximately in the same range. Under conditions where the concentrations of VOC and O₃ are similar, the chlorine–organic reaction will dominate because of the very fast kinetics of these reactions.¹ This will lead to ozone formation, rather than destruction, in the troposphere. Depending on the structure of the organic, either HCl will be generated or characteristic chlorinated, oxygen-containing organics will be formed that can be used as unique “markers” of chlorine atom chemistry in the marine boundary layer.^{44–47}

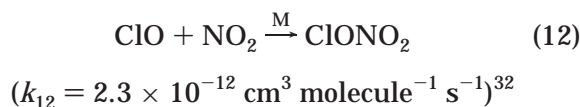
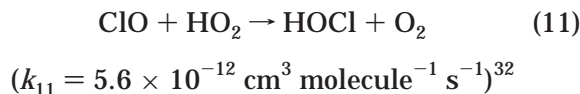
Although hydrochloric acid generated from the reaction of HNO₃ with sea salt aerosols does not photolyze at wavelengths above 290 nm that are available in the troposphere, it does react slowly with OH to generate chlorine atoms:



At an OH concentration of 5×10^6 radicals cm⁻³ that might be typical at mid-day,¹ the lifetime (τ , defined as the time for HCl to fall to 1/*e* of its initial concentration, $\tau = 1/k_{10}[\text{OH}]$) of HCl with respect to this reaction is approximately 3 days. However, HCl is highly soluble and is rapidly taken up into particles or undergoes deposition at the earth's surface. Due to this rapid removal of HCl, reaction (10) is not a

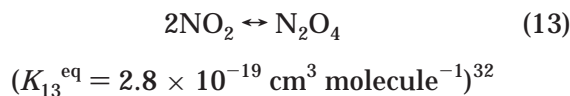
major source of chlorine atoms in most regions of the troposphere.

Under conditions where the concentration of organics is small, e.g., over the oceans, reaction (8) of chlorine atoms with O₃ dominates, generating ClO. Chlorine monoxide can further react with HO₂ and NO₂ to form hypochlorous acid and chlorine nitrate, respectively:



In remote marine regions where ClO can be generated, NO₂ levels are small (a few to tens of ppt) and of the same order as daytime HO₂ concentrations. Consequently, during much of the day, both HOCl and ClONO₂ will be formed. Similar to ClNO formed in reaction (7), HOCl and ClONO₂ can be photolyzed to chlorine atoms, as well as undergo further heterogeneous reactions described below to generate photochemically active halogen gases.

Schroeder and Urone's proposal² regarding the production of atomic chlorine that initiates the chlorine chemistry did not attract significant attention in the atmospheric chemistry community, in part because of the high NO₂ concentrations used (relative to the atmosphere). It was possible that the dimer, N₂O₄, whose equilibrium concentration varies with the square of the NO₂ concentration,



was the actual reactant in their experiments and that reaction (7) may not be important under atmospheric conditions. Subsequently, Finlayson-Pitts⁴⁸ showed that reaction (7) continued at measurable rates down to initial concentrations of NO₂ of 5 ppm. While this is still an order of magnitude or more above NO₂ concentrations found in polluted areas, it suggests that this chemistry should be at least considered in marine urban areas where both NO₂ and NaCl from sea salt particles are present. Consistent with these observations are smog chamber studies at 0.3 ppm NO_x, in which evidence for chlorine atom generation from reactions with NaCl aerosols was obtained by following the decay of organics in the mixture.⁴⁹

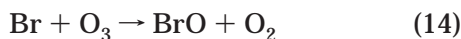
3.2. Gas-Phase Bromine Reactions in the Troposphere

Bromide ions are a minor component of seawater, and hence of sea salt particles, with a molar ratio of bromide to chloride of 1:650.⁵⁰ Despite such a small contribution to the composition of sea salt particles, bromine plays a disproportionately large role in tropospheric sea salt chemistry. The most startling example is its anticorrelation with the destruction of *surface*-level ozone in the Arctic at polar sunrise.^{51–53}

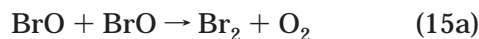
Since it was first recognized in the mid-1980s, this phenomenon of surface-level O₃ concentrations dropping rapidly at dawn in the spring has been observed consistently, with O₃ levels being very low (a few ppb or less) for periods of hours to weeks over a large horizontal and vertical domain.^{54–56} The anticorrelation between bromide in collected particles and O₃ in the first observations of this phenomenon suggested that a bromine species was responsible for the O₃ loss.^{53,57,58}

Several special issues of journals [*Tellus* **1997**, 49B, 450–601; *J. Atmos. Chem.* **1999**, 34, 1–170; and *Atmos. Environ.* **2002**, 36, 2467–2797] and a monograph⁵⁹ have been devoted to the study of polar tropospheric ozone depletion, and the reader is referred to those for further details.

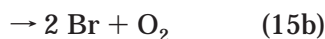
From years of research on bromine chemistry in the stratosphere,³² it is known that bromine atoms in the gas phase lead to O₃ destruction through a series of chain reactions such as (14)–(17):



$$(k_{14} = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$



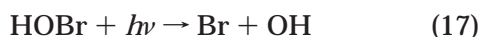
$$(k_{15a} = 0.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$



$$(k_{15b} = 2.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$

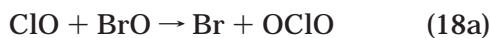


$$(k_{16} = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$



BrO also absorbs light in the 290–380 range,³² with an estimated lifetime of ~20 s at a solar zenith angle of 30° at the surface of the earth.⁶⁰

The cross-interactions of chlorine and bromine species have also been proposed to be important in the gas phase:^{61,62}



$$(k_{18a} = 6.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$



$$(k_{18b} = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$



$$(k_{18c} = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$$

However, in a study at polar sunrise, OClO, formed exclusively in this reaction, was not correlated with O₃ depletion, and the upper limits measured for its concentration suggested that this cross reaction is not important.⁶³

It is interesting that while bromine atoms lead to O₃ destruction in the troposphere, chlorine atoms are expected to lead to O₃ formation under most circumstances. The difference arises from the relative rates of reactions of these halogen atoms with organics.

While chlorine reactions with essentially all organics larger than one carbon are very fast, the corresponding bromine reactions are slow, with the exceptions of its reactions with aldehydes, alkenes, and acetylene.^{32,64–66} For example, the rate constant for the reaction of methane with atomic chlorine at 300 K is $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, while that with bromine atoms is very slow,⁶⁷ $6 \times 10^{-23} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. As a result, bromine does not contribute significantly to the VOC–NO_x cycle which leads to O₃ formation, reactions (1)–(5), as chlorine atoms do.

Before discussing the overall halogen chemistry that encompasses all three phases in the atmosphere (gas, liquid, solid), a brief review is presented of evidence that clearly establishes the importance of chlorine and bromine in the lower atmosphere.

4. Evidence for Sea Salt Halogen Chemistry in the Troposphere

4.1. Molecular Chlorine

There is now an increasing body of evidence from both laboratory and field studies for the generation of gaseous photochemically active inorganic chlorine compounds in the marine boundary layer. The most direct evidence is the detection and measurement of Cl₂ in a coastal region at concentrations up to 150 ppt (ppt = parts per trillion (10¹²) by volume) using atmospheric pressure ionization mass spectrometry.⁶⁸ These mass spectrometer measurements are in agreement with mist chamber observations by Keene, Pszenny, and co-workers of similar concentrations of inorganic chlorine gases (other than HCl), which were proposed to be Cl₂ and/or HOCl.^{69,70}

Molecular chlorine can be generated in the dark by the reaction of chlorine nitrate (ClONO₂) with NaCl,^{71–76}



with ClONO₂ originating from the three-body reaction (12) of ClO with NO₂. Since the ClO radical is a product of the reaction (8) of chlorine atoms with O₃, any chlorine atom precursor (e.g., ClNO) can, in principle, contribute ultimately to the formation of ClONO₂, and subsequently Cl₂. Molecular chlorine is also generated in the oxidation of Cl⁻ by OH via an acid-catalyzed mechanism in bulk solutions, and as discussed in more detail below, likely in a unique reaction at the air–water interface that does not require acid. Since the majority of OH sources in remote regions, particularly the marine boundary layer, are photolytic in nature however, the OH–Cl⁻ reaction is not expected to be a significant source of Cl₂ at night, when the Cl₂ concentrations have been observed to peak.

Modeling studies by Knipping and Dabdub⁷⁷ suggest that inclusion of chlorine chemistry from sea salt reactions may have a significant effect on ozone levels in a coastal urban area. For example, Figure 2 shows the increase in O₃ above a base case predicted for coastal regions of southern California when sea salt chemistry is included in the model. In this case,

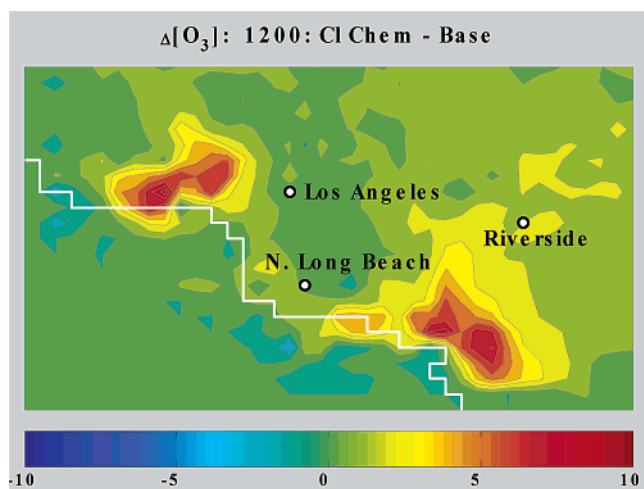


Figure 2. Predicted increases in surface-level ozone in southern California at noon due to reactions of NaCl in sea salt with N_2O_5 , ClONO_2 , and OH. This shows the increase in O_3 compared to a base case with VOC– NO_x chemistry that did not include chlorine chemistry. Reprinted with permission from ref 77. Copyright 2003 American Chemical Society.

reactions of NaCl with N_2O_5 and ClONO_2 as well as a reaction of OH with Cl^- at the solution interface (see below) were included. Knipping and Dabdub⁷⁷ predicted that in urban locations close to the ocean, the peak ozone level could be increased by as much as 12 ppb for short periods of time. Given a typical pre-industrial concentration of ozone of ~ 10 ppb^{33–39} and a current global concentration of ~ 30 – 40 ppb, this is quite substantial.

4.2. Molecular Bromine, Bromine Chloride, and Bromine Monoxide

As discussed above, rapid destruction of surface-level ozone, believed to be caused by bromine atom reactions, has been measured in the Arctic and Antarctic at polar sunrise. It was initially suggested⁵³ that the source of the bromine atoms was the photolysis of bromoform, generated by marine algae.^{78–81} However, although the quantum yield for bromine atom production is large,^{82,83} the absorption cross sections^{84,85} of CHBr_3 fall off rapidly with increasing wavelength, and in the actinic region above 290 nm, the photolysis is too slow to initiate the observed ozone loss.

Finlayson-Pitts and co-workers⁸⁶ subsequently proposed that sea salt particles could potentially be the source of bromine. The measured large and sustained loss of O_3 requires an autocatalytic release of bromine into the gas phase, dubbed a “bromine explosion”.^{17,87,88} It is believed that this involves reactions of bromide and chloride in sea salt with gaseous HOBr to generate Br_2 and BrCl, a cycle proposed by McConnell et al.⁸⁹ and Fan and Jacob.⁹⁰ Details of this chemistry are discussed below in section 6.

While there is insufficient bromide in suspended sea salt particles to cause the measured ozone losses, Tang and McConnell⁹¹ proposed that sea salt deposited on the ice snowpack provides the source of halogens. Even during winter, there are significant

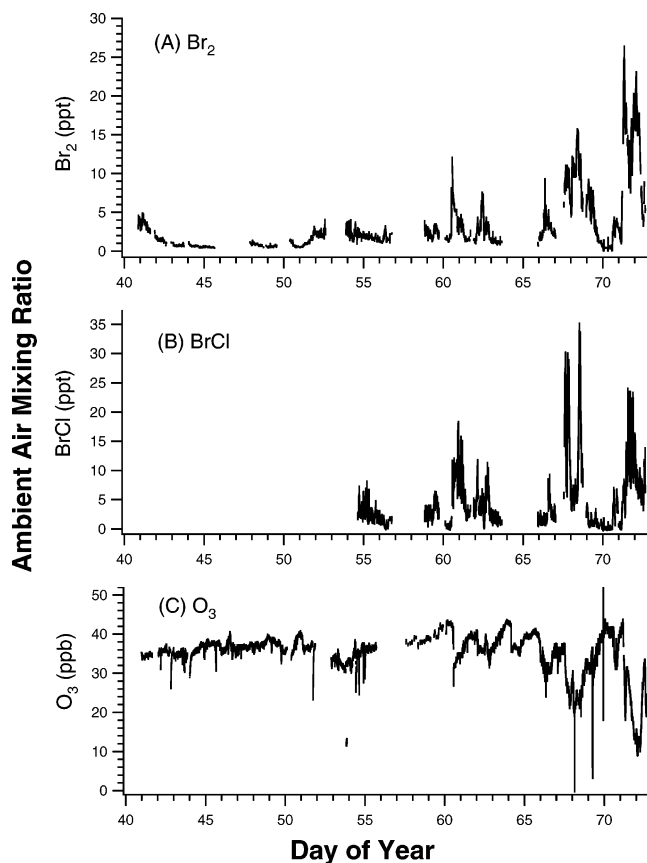


Figure 3. Measurements of Br_2 , BrCl, and O_3 at Alert (82° N) before and at polar sunrise. Reprinted with permission from *Science* (<http://www.aaas.org>), ref 93. Copyright 2002 American Association for the Advancement of Science.

areas of the Arctic Ocean that are open, providing a source of sea salt to the snowpack. In addition, very high salt content “frost flowers” are formed on the surface of ice as freezing takes place. The alkalinity and bromide ion content of these frost flowers are elevated by a factor of approximately 3 compared to seawater.^{92,113}

Consistent with these proposals, both gaseous Br_2 and BrCl have been measured directly using atmospheric pressure ionization mass spectrometry at the surface in the Arctic just prior to, and at the beginning of, polar sunrise.⁹³ As seen in Figure 3, Br_2 and BrCl are present at a few ppt, but their concentrations rise dramatically to the 25–35 ppt range during periods of ozone depletion. Molecular chlorine was not detected above its detection limit of 2 ppt.

The bromine measurements are consistent with the studies of Shepson and co-workers,^{94–96} who showed that there are gases present before and during Arctic sunrise which photolyze to generate atomic halogen atoms. They photolyzed air samples in the presence of added propene to trap halogen atoms as they were generated. The measured amounts of halogenated products indicated the initial concentrations of the halogen atom precursors. The concentrations of these precursors were measured to be up to 100 ppt expressed as Cl_2 and 38 ppt expressed as Br_2 , respectively. While the bromine concentrations are in agreement with the direct measurements, the chlorine is much larger than measured by Foster and co-

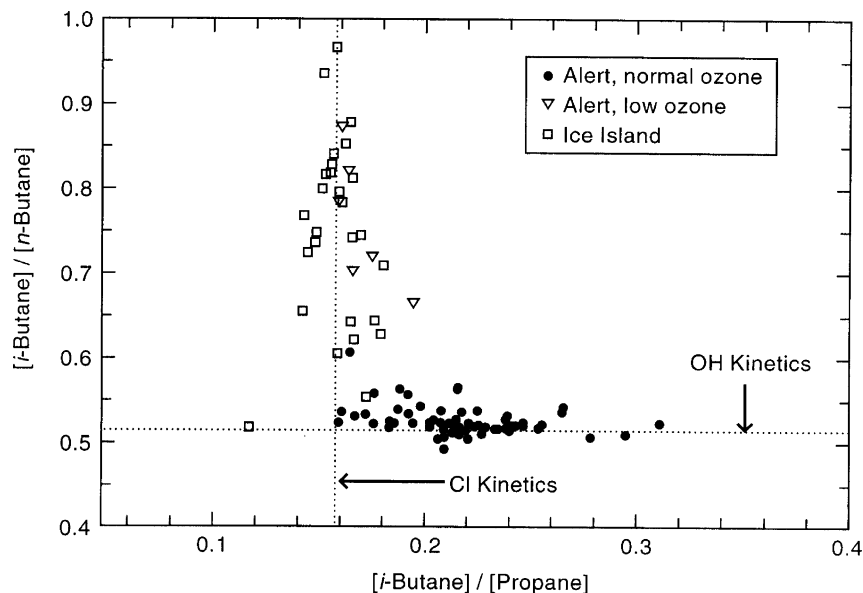


Figure 4. Relative rates of loss of some alkanes in the Arctic at polar sunrise. As discussed in the text, these particular pairs of compounds were chosen to differentiate loss due to reaction with OH from that due to reaction with Cl atoms. Reprinted with permission from ref 106. Copyright 1994 American Geophysical Union.

workers.⁹³ The reasons for the measurement of higher chlorine concentrations are not clear but may be related to different extents of reaction of the sea salt in the two field campaigns. As discussed in more detail below, the kinetics, thermochemistry, and molecular dynamics at interfaces all favor production of gas-phase bromine compounds if sufficient bromide is present. However, at larger extents of reaction, where bromide has been depleted from the sea salt, the formation of chlorine compounds becomes more important.

Bromine monoxide, a key intermediate in regenerating atomic and molecular bromine via reactions (14)–(17), has been detected in the Arctic spring at the surface by differential optical absorption spectrometry (DOAS). For example, Platt and co-workers^{62,97–100} have measured BrO at levels up to 30 ppt at polar sunrise. In addition, tropospheric column BrO concentrations in the Arctic have been extracted using satellite measurements (e.g., see refs 101–103) and high-altitude aircraft.¹⁰⁴ Tropospheric BrO is enhanced from February to May over large portions of the Arctic and is correlated with sunlight intensity increase and the retreat of sea ice.

Measurements of organics and their decay with time also provide evidence for the generation of chlorine and bromine atoms at polar sunrise in the Arctic. The relative rates of reactions for Cl and OH with selected organics are sufficiently different that removal of the organics by Cl can be differentiated from that by OH under some conditions.¹⁰⁵ Figure 4 shows measurements of the ratio of *i*-butane to *n*-butane in air at Alert as a function of the ratio of *i*-butane to propane.¹⁰⁶ The rate constants for the OH reactions with *i*-butane and *n*-butane are similar, so the ratio of these two compounds should remain constant with time if both are being removed only by OH. Similarly, the rate constants for chlorine atom reactions with *i*-butane and propane are similar, so the ratio of these two organics will be constant if

chlorine atom reactions dominate their removal. Under conditions of polar ozone depletion, the ratios of these pairs of organics are clearly consistent with chlorine atom reactions, while under normal conditions, OH predominates.

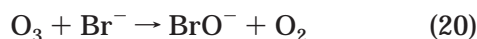
Bromine atom reactions with alkanes are too slow to be significant in the Arctic, but the reactions with some selected organics, such as acetylene and formaldehyde, are relatively fast and can be used to estimate bromine atom production rates. Thus, measurements of such organics, combined with knowledge of the rate constants for Cl and Br reactions, have been used to estimate the rate of production of halogen atoms at polar sunrise (e.g., see refs 106–111). The rate of bromine atom production has been measured using this approach to be of the order of 10^{12} – 10^{13} atoms $\text{cm}^{-3} \text{s}^{-1}$. The rate of generation of atomic chlorine is much smaller, by as much as 3–4 orders of magnitude. This is consistent with nonspecific measurements of ClO_x in the Arctic in the spring using a chemical amplifier technique, where the ClO_x was <2 ppt.¹¹²

In short, there is clear and convincing evidence that bromine atom precursors are generated in the gas phase and that their photolysis initiates chain reactions that lead to destruction of ozone via its reaction with atomic bromine. The source of bromine is sea salt, much of it deposited on the ice pack, perhaps in the form of frost flowers.^{92,113}

Halogen chemistry in the polar troposphere at sunrise affects not only O_3 but other species as well. For example, an interesting aspect is the simultaneous destruction of gas-phase mercury,^{114–117} which has also been observed in the Antarctic.¹¹⁸ This appears to be due to oxidation of Hg^0 by halogen species. Based on laboratory studies,¹¹⁹ bromine atoms again appear to be the most likely reactant.

While the overall chemistry leading to destruction of ozone at the surface at polar sunrise has been elucidated, the reactions that initiate these chain

processes are not as well established. The most likely source involves the oxidation of bromide ions by ozone,^{95,120} which occurs in solution to generate BrO^- and HOBr .^{121–126}



(Note that reaction (20) is proposed to proceed via the formation of BrOOO^- as an intermediate, which then forms HOBr via two routes, one of which is acid-catalyzed.¹²⁵) Differential scanning calorimetry¹²⁷ and NMR studies¹²⁸ show that as seawater or NaCl solutions are cooled below the NaCl eutectic temperature of 252 K, liquid not only remains on the surface of the precipitated solids but also is concentrated in halide ions. Hence, solution chemistry should be relevant to the chemistry occurring on the icepack.

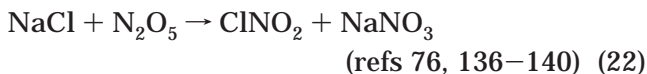
While the destruction of ozone at the surface by bromine is dramatic in the Arctic at polar sunrise due to the particular meteorology that isolates the boundary layer from the free troposphere above it,¹²⁹ similar chemistry is believed to occur at mid-latitudes as well. For example, Nagao and co-workers¹³⁰ observed a loss of ozone at sunrise at a coastal site in Japan and found it was correlated to the volume of airborne sea salt particles. This sunrise ozone destruction (SOD) has also been observed at Cape Grim, Tasmania.¹³¹ Similarly, the diurnal variation of ozone over the Indian Ocean was not in good agreement with model predictions of known ozone chemistry and photochemistry, but inclusion of bromine atom chemistry improved the agreement substantially.¹³²

Finally, many dry lakes, such as the Dead Sea in Israel and the Great Salt Lake in the U.S.A., are covered with alkaline salts that can participate in chemistry similar to that described above. Indeed, ozone destruction due to release of halogens from the salt flats of alkaline dry lakes has also been observed in such locations.^{12,133–135}

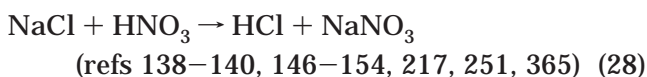
With this background in mind, we focus the remainder of this article on some particular aspects of the reactions of solid NaCl and NaBr and their aqueous solutions that may contribute to the tropospheric chemistry of sea salt particles. Since the kinetics of the solid salt reactions are treated in detail in this issue by Rossi, we focus primarily on the molecular-level mechanisms of these reactions, and in particular on the role of water that is strongly adsorbed to the salt surface. In addition, we briefly discuss aqueous-phase reactions of liquid salt solutions that exist above the deliquescence/effluorescence points of the salts, and in the liquid layers on sea salt ice. We focus particularly on reactions occurring at the air–water interface. As described in more detail in the following sections, there is increasing evidence that such interfacial processes play an important role in the chemistry of these salts and of trace gases such as SO_2 that interact with sea salt. Such interfacial reactions represent a relatively unexplored area of physical chemistry that is of fundamental scientific interest.

5. Mechanisms of Reactions of Solid NaCl and NaBr and the Role of Adsorbed Water

In addition to the reactions (7) and (19) of NaCl with NO_2 and ClONO_2 described above, there are a variety of additional potential reactions of solid NaCl in air, discussed in detail in the paper in this issue by Rossi:



An important reaction that competes with reactions (7), (19), and (22)–(27) is reaction (28) with HNO_3 :



As discussed earlier, HCl is not a significant source of chlorine atoms in the troposphere. Hence, a major factor determining the rate of generation of chlorine atoms is the rate and mechanism of reaction (28) compared to those that generate photochemically active gaseous chlorine compounds such as ClNO , ClNO_2 , and Cl_2 . This makes it imperative to understand these reactions on a molecular level, specifically what controls their kinetics and mechanisms. For example, one might expect that only the surface halide ions would be available for reaction and that once these have been reacted from the surface, the reactions would cease, i.e., the surface would “saturate” or “passivate”. While this has been observed for the reactions of single crystals, this is generally not observed to be the case for the reactions of powders. To gain some insight into the controlling factors for these reactions with solid salts, we focus here on the mechanistic details of the reaction of HNO_3 for which the most data are available. However, similar considerations will apply to other reactions that generate a product that remains on the surface of the reactant salt. The role of water is shown to be critical to understanding the mechanism and kinetics of such reactions.

5.1. Reactions with Oxides of Nitrogen

Reactions of the nitrogen oxide species with solid NaCl and NaBr generate a solid-phase product that is stoichiometrically NaNO_3 (see reactions (7), (19), (22), (23), and (28) above). Simple ion replacement, e.g., of chloride by nitrate ions in the HNO_3 reaction, would be expected to passivate the surface such that replacement of the top layer of chloride by nitrate shields the underlying NaCl, causing the reaction to cease. This has been observed in the reaction of

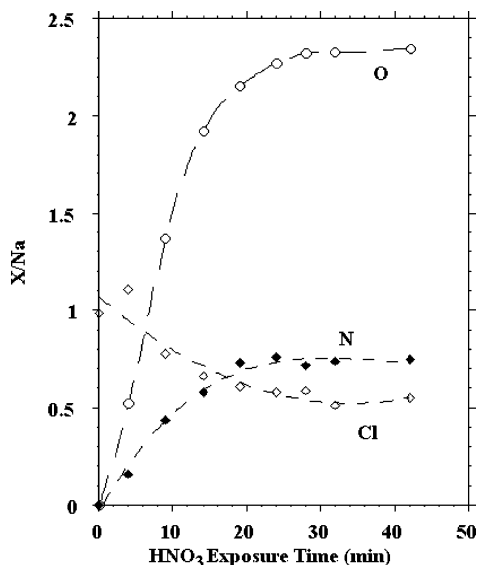


Figure 5. Loss of chlorine and increase in nitrogen and oxygen on the surface of NaCl(100) after exposure to increasing doses of gaseous HNO₃. Reprinted with permission from ref 146. Copyright 1994 American Geophysical Union.

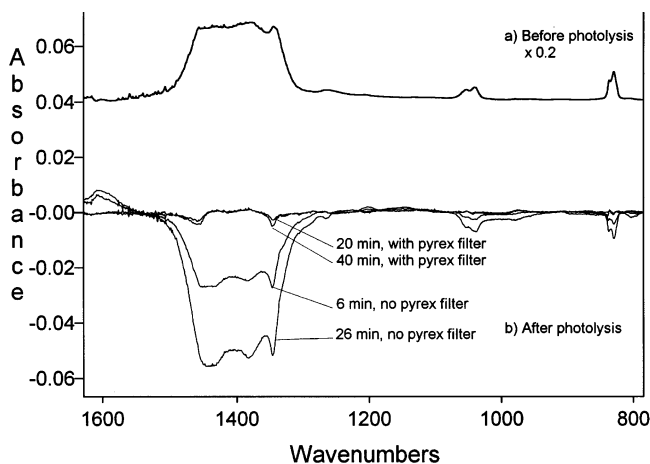
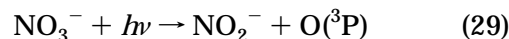


Figure 6. (a) DRIFTS spectrum of NaCl reacted with NO₂ (3.5×10^{15} molecules cm⁻³) for 5 min; spectrum has been multiplied by 0.2 for clarity. (b) Difference spectra after photolysis with a Pyrex filter and then with the filter removed. Reprinted with permission from ref 157. Copyright 1995 American Chemical Society.

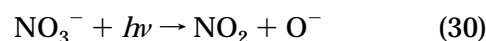
gaseous HNO₃ with single-crystal NaCl(100).^{146,155,156} Figure 5 shows the growth of oxygen and nitrogen on the face of NaCl(100) after sequential dosing of the surface with HNO₃, measured using X-ray photoelectron spectroscopy (XPS). As chlorine decreases, nitrogen and oxygen increase in a 1:3 ratio, consistent with replacement of surface Cl⁻ with NO₃⁻. The loss of chloride and increase in nitrogen and oxygen cease after approximately one or two monolayers of the surface have been reacted.^{146,155,156}

An interesting aspect of the surface nitrate film is that its photochemistry appears to differ from that of bulk crystalline NaNO₃. Figure 6a shows the diffuse reflectance infrared Fourier transform spectrum (DRIFTS) of NaCl that has been reacted with gaseous NO₂.¹⁵⁷ The formation of bands at ~1400, 1050, and 830 cm⁻¹, assigned to the ν_3 , ν_1 , and ν_2 bands, respectively, of NO₃⁻ is observed. Figure 6b

shows the difference spectrum after photolysis using a high-pressure xenon lamp ($\lambda > 200$ nm), first with a Pyrex filter to exclude wavelengths below 305 nm, and then with the filter removed. Peaks due to nitrate decrease, but no new peaks due to the formation of new surface products are observed. This is in contrast to the photolysis of bulk crystalline NaNO₃ under the same conditions in which nitrite ions, characterized by a peak at 1260 cm⁻¹, are clearly generated during the photolysis:¹⁵⁸⁻¹⁶⁰



The loss of surface nitrate without the accompanying increase in nitrite shows that for nitrate ions on the NaCl surface, photodissociation must occur predominantly through alternate paths, such as reaction (30):



(The gas-phase NO₂ product could not be measured in these experiments, as it was pumped away continuously during the experiment.) Although peroxy-nitrite (ONOO⁻) was not detected as an intermediate in these studies, as previously reported by Plumb and Edwards,¹⁶⁰ it may be an intermediate in reaction (30). Peroxynitrite is quite reactive, for example, reacting in solution with CO₂.¹⁶¹⁻¹⁶³ In the laboratory photolysis experiments, the fate of the O⁻ formed in reaction (30) is most likely to be reaction with trace amounts of water on the salt surface to generate OH + OH⁻. These studies clearly show that the thin film of nitrate formed on the NaCl is not bulk crystalline NaNO₃, but rather a metastable form of nitrate on the surface.

Once NaCl has reacted with gas-phase HNO₃, subsequent exposure of the reacted NaCl surface to water vapor pressures well below the deliquescence points of NaCl and NaNO₃ (75% and 74% respectively, at 298 K)¹⁶⁴⁻¹⁶⁶ leads to a very interesting phenomenon, the water-induced mobilization of surface ions and their recrystallization into microcrystallites of NaNO₃.¹⁵⁶ Figure 7, for example, shows transmission electron microscopy (TEM) images of NaCl that is unreacted (A), reacted with HNO₃ in the absence of water vapor (B), followed by exposure to water vapor pressures below the deliquescence points of NaCl and NaNO₃ (C). Although there is no apparent change in the particle morphology on reaction with HNO₃, it is known from the XPS experiments (Figure 5) that the salt surface is coated with nitrate ions. On exposure of the particle to water vapor followed by drying, microcrystallites can be seen attached to the particle surface. Energy-dispersive spectroscopy (EDS) of these microcrystallites showed that they are composed of NaNO₃, while the newly exposed surface of the salt particle is now NaCl. A second cycle of exposure to gaseous HNO₃ followed by water vapor forms more NaNO₃ microcrystallites (Figure 7D). It is clear from these experiments that water vapor substantially increases ion mobility on the surface, and that the subsequent removal of water results in recrystallization of microcrystallites of bulk NaNO₃. This process regenerates a fresh NaCl

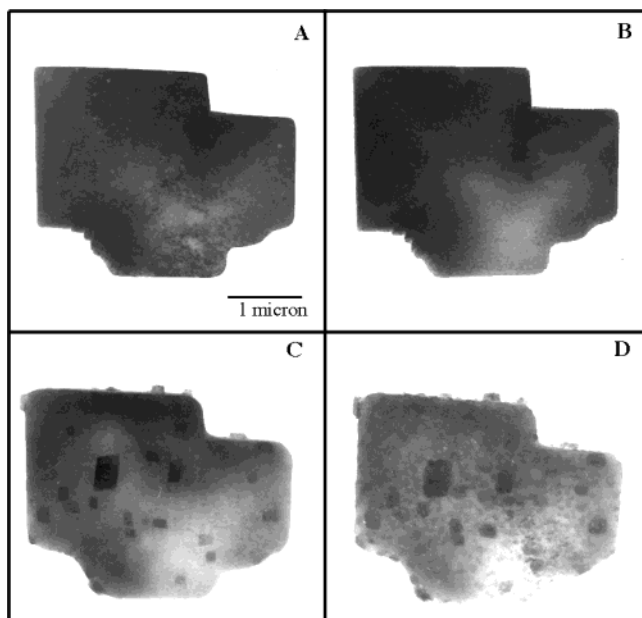


Figure 7. TEM micrographs of NaCl (A) before reaction, (B) after reaction with 1.2×10^{15} molecules cm^{-3} HNO_3 for 15 min, (C) after subsequent exposure of the crystal in (b) to water vapor (<15 Torr), and (D) after a second cycle of HNO_3 and then water vapor exposure. Adapted with permission from ref 156.

surface, allowing the reaction to continue well beyond one or two monolayers. A similar phenomenon has been observed in the NO_2 -NaCl reaction.^{167,168}

In many field studies of the composition of salt particles in marine urban regions, a deficit of chloride ions relative to sodium has been reported; in some cases, the particles are almost completely devoid of chlorine, particularly those in the smallest size range, and particles that appear to be almost pure NaNO_3 are observed.¹⁶⁹⁻¹⁷⁴ One mechanism consistent with these observations is the formation of nitrate on the surface of the NaCl, followed by the water-induced recrystallization into NaNO_3 . If the microcrystallites of NaNO_3 attached to the salt shatter on impact during collection, they will be devoid of chloride even though they originated in sea salt. This can occur during sample collection and analysis; that is, introduction of liquid salt particles into a vacuum will cause evaporation of the water and recrystallization into solid components.¹⁷⁵ If nitrate is present in the solution, separate NaNO_3 and NaCl particles may be observed, even though they were internally mixed in the original particle. Whether it occurs in ambient air itself is not clear, since as discussed in section 6.1, sea salt particles may not completely dry out to form solid crystals under atmospheric conditions.

A particularly important result is that experimental observations of the reactions of NaCl powders with nitrogen oxides are often in apparent conflict with the results from the dry, single-crystal NaCl-(100) experiments. For example, in contrast to the surface passivation observed for dry single crystals (Figure 5), the reaction of HNO_3 with NaCl powders has been observed in Knudsen cell^{139,147,148,154} and flow tube^{138,149} studies to continue long after complete reaction of the surface chloride ions should have occurred. The major difference between the powders

and the macroscopically large single crystals is the larger numbers of steps and edges in powder samples. These are well known from surface science studies to be much more reactive than the terraces of solids.¹⁷⁶

In addition, however, these steps and edges are known to hold water at room temperature under vacuum,^{148,152} in contrast to the (100) surface of NaCl from which water is readily removed by pumping. Given the effects of water on the mobility of surface ions, this increased water adsorption has the potential to alter the kinetics and mechanisms on the salt surface. For example, Yoshitake¹⁶⁸ reported that, with water on the salt surface, the NO_2 -NaCl reaction was first-order in NO_2 , but it was second-order if the NaCl was dry.

It is therefore of interest to first explore what is known about the uptake of water on NaCl, and then examine how this may affect the reactions of the salt surface with various gases.

5.2. Water on NaCl

The uptake of water on NaCl has been studied both experimentally and theoretically by a number of researchers (e.g., see refs 177-206). For example, Ewing and co-workers used FTIR to follow the water uptake on single-crystal NaCl(100) in real time as a function of relative humidity.^{191,196,197,203,206} The water coverage at room temperature increases slowly with relative humidity from zero coverage at 0% RH to ~ 0.5 layer at 35% RH. In this region, water binds to the salt surface, with the oxygen of water interacting with Na^+ on the surface.^{177,181,183,184,189,190,198,199,201} As the coverage increases, the water does not spread evenly over the surface. Thus, there is a blue-shift of the infrared peak for the adsorbed water to 3520 cm^{-1} , compared to 3420 cm^{-1} for bulk liquid water.^{196,197,203,206} This shift has been interpreted as being due to the formation of small islands in which there are interactions with the surface as well as between the adsorbed water molecules on the interior of the islands.

From 35% RH to 40% RH, there is an increase in the amount of adsorbed water from 0.5 layer to ~ 1 layer, followed by a very steep increase to about 2.5 layers at 45% RH. There is an accompanying shift in the band center from ~ 3520 to 3420 cm^{-1} . In this region, the adsorbed water is changing from strong interactions of the first layer of adsorbed water both with the salt surface and with adjacent adsorbed water molecules, to multilayer adsorption in which hydrogen bonding between water molecules predominates. (It should be noted that the quantification of water on the surface assumes that its infrared absorption cross section is not sensitive to the nature of its binding at the surface, i.e., that the absorption cross sections are the same when physisorbed to NaCl at low coverages as when in a three-dimensional water environment at higher coverages. Since the absorption cross section for water is dependent on the extent of hydrogen bonding,²⁰⁷ this assumption may lead to an underestimate of the amount of adsorbed water at low coverages.) Theoretical studies^{189,190,198} also support the view that the interaction of water with other water molecules becomes more

important than their interaction with the surface as the coverage increases. At RH above 50%, where three or more water layers are present, the water resembles bulk liquid water and the infrared peak remains constant at 3420 cm^{-1} ,^{196,197,203,206} indistinguishable from liquid water. At the deliquescence point (75% RH), the salt completely dissolves and forms a saturated solution of NaCl.

Hucher and co-workers¹⁷⁷ measured the conductance of the surface of salt crystals as a function of relative humidity. A linear increase in the conductance was measured from 32 to 40% RH, where there was an inflection point. They interpreted this first region as being due to adsorption of water on the salt, with the sodium ion responsible for the conductance. Electron microscopy images showed little mobility of material on the surface up to this RH. From 40 to 48% RH, there was a slower increase in the dependence of the conductance on RH than that observed at lower RH, followed by a sharply increasing and nonlinear conductance to the deliquescence point of 75% RH.

Williams and co-workers^{208,209} and Shindo and co-workers^{193,194} used AFM to follow the surface of NaCl as a function of RH. They observed movement of steps at 47% RH and above. From the previous discussion, the number of layers of water approaches three at this relative humidity, and the conductance is increasing significantly.

Salmeron and co-workers^{195,200} followed the evolution of the surface of NaCl with time using scanning polarization force microscopy (SPFM). This technique is a noncontact mode AFM in which the tip, biased relative to the sample, is kept at a distance of 10–100 nm from the surface. As a result, the tip does not drag material along the surface, as has been observed for NaCl and NaNO₃ using AFM in air where water is present.^{195,208,210} Thus, SPFM can be used to image liquids and liquid-like layers on surfaces. Using this approach, Salmeron and co-workers^{195,200} observed increasing movement of steps on the surface as the RH increased above 45%.

They also observed preferential solvation of surface Na⁺ at the lower RH (below 40%), with ~1% of the surface cations being solvated at 40% RH. Adsorption studies described earlier show that there is about one layer of water on the surface under these conditions. Slow step movement occurs here, since mobility of both cations and anions is needed to restructure the surface. At 46% RH, where the adsorption isotherms indicated ~2.5 layers of water, both Na⁺ and Cl⁻ are solvated, increasing the mobility of both ions and leading to rapid (on the order of minutes) restructuring of the surface. Subsequent drying gave a restructured surface that was closer to the equilibrium structure, with water concentrated at the step edges rather than on the terraces.

An important issue for reactivity of NaCl with atmospheric gases is whether water on the surface of the solid contains dissolved chloride ions, the reactive component of the salt. In their AFM studies, Shindo and co-workers¹⁹⁴ observed that step motion of NaCl was inhibited by voids in the natural rock salt crystals, and hypothesized that these voids are

filled with water that dissolves the salt, thus serving as reservoirs of concentrated salt solutions on the solid surface. The data presented above suggest that above ~46% RH, both Na⁺ and Cl⁻ dissolve in the surface film, leading to changes in the surface conductance and to rapid surface restructuring. In addition, water is preferentially trapped on the step edges as the RH decreases. The implications for the reactions of powders of NaCl are discussed in the following section.

5.3. Role of Water in NaCl and NaBr Reactions

Many laboratory studies of the reactions of NaCl and NaBr salts (reviewed in detail in the article by Rossi in this issue) have used powders rather than single crystals. As discussed above, a characteristic of the reactions of powders with various gases such as HNO₃ is that they do not saturate, i.e., the reaction continues well beyond the point that all of the chloride at the surface would have reacted. A major difference between single crystals and powders is the larger fraction of the surface ions located at steps, edges, and perhaps defects of the powders. As described above, AFM studies^{193–195,200,208,209} show that water is preferentially adsorbed at steps and edges. It is not clear whether the voids observed by Shindo and co-workers,¹⁹⁴ which they proposed to be filled with water at ~50% RH, continue to hold water when evacuated, but this is another potential source. Weis and Ewing²¹¹ observed anomalously large infrared liquid water peaks in NaCl aerosols at RH below 50% and attributed this to water trapped in small fissures in the individual crystals (perhaps analogous to the voids observed by Shindo et al.¹⁹⁴) and/or between crystals in clusters of particles. Barraclough and Hall¹⁸¹ reported that heating to 623 K under vacuum was required to remove the water from pressed disks of NaCl. It is not clear whether the water in this case was trapped between particles or in fissures on the individual NaCl crystals, as proposed by Weis and Ewing.²¹¹

It is known that surface-adsorbed water (SAW) on powders is not readily removed by pumping at room temperature. For example, when NaCl powders that had been pumped on in a Knudsen cell at $\sim 10^{-5}$ – 10^{-6} Torr were reacted with DNO₃, the major gas-phase product observed initially was HCl, rather than the expected DCl. The gaseous product HCl is gradually replaced by DCl as the reaction continues.¹⁴⁸ This clearly establishes that SAW remains on the surface of NaCl powders after pumping at room temperature. Tepper and co-workers¹⁸⁵ and Wassermann and co-workers¹⁸⁹ reported a detectable residual water signal on NaCl using second harmonic generation spectroscopy after exposure of the surface to water vapor followed by pumping at room temperature. Interestingly, the sample, which was a polished NaCl window rather than a powder, evidently had sufficient steps, edges, and defects to retain measurable amounts of SAW. Direct observation of water on particles in the 1–10 μm range, prepared by grinding NaCl(100), has been reported using XPS while heating to 200 °C; larger (500 μm) particles had significantly less SAW and water was not detectable on NaCl(100).¹⁵²

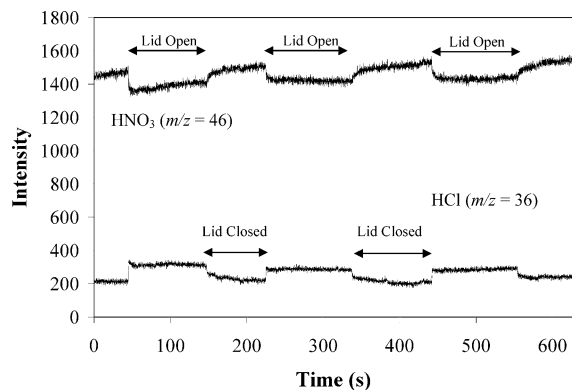


Figure 8. Typical data from Knudsen cell studies of the reaction of gaseous HNO_3 with NaCl powders at 298 K, using partial coverage of the sample holder to avoid corrections for diffusion into multiple salt layers. Reprinted with permission from ref 154. Copyright 2003 American Chemical Society.

If the steps, edges, and possibly voids are the sole sites for reaction, they would be expected to be consumed in the first stages of the reaction, causing the reaction to cease. Figure 8 shows the uptake of HNO_3 on NaCl powders in a Knudsen cell under conditions where the sample holder is only partially covered with NaCl .¹⁵⁴ In this case of small samples, the available reactive salt surface area is readily calculated without the uncertainty often introduced for Knudsen cell and flow tube studies^{212–215} from taking into account diffusion into multiple salt layers. With a reaction probability of $\gamma = 2 \times 10^{-3}$, the surface chloride should have been completely reacted in ~ 80 s. It is clear from Figure 8 that this is not the case. Such data establish that even though measurable amounts of water vapor are not present, there is sufficient SAW and mobility of the surface ions to continuously regenerate a fresh NaCl surface.

The mechanism of this surface ion mobility in the absence of significant amounts of water vapor is not well established. However, some insight can be gleaned from the knowledge that prior to the reaction, the SAW is likely bound to sodium cations on the steps and edges. For example, Ahlswede and Jug²⁰¹ calculated that the most stable configuration of water on a monatomic step is that shown schematically in Figure 9, where the oxygen atom of water interacts with two sodium cations, one at the step edge and one on the terrace below. This adsorption at a monatomic step is favored over that on the (100) terrace by about 10 kcal mol^{-1} .²⁰¹ During the HNO_3 reaction, a surface chloride ion is replaced by NO_3^- . Given the larger size of NO_3^- , it will not simply occupy the lattice site originally encompassing the Cl^- , but rather will be displaced somewhat above the plane of the (100) lattice. Theoretical calculations¹⁵³ suggest that NO_3^- lies parallel to the surface plane at low coverages but changes to a vertical orientation at higher coverages. In any case, as shown schematically in Figure 9, association of the NO_3^- with the hydrated cation at the adjacent step edge will allow the formation of NaNO_3 in its stable crystal structure. A new step on the NaCl surface is then generated, providing a template for the addition of more nitrate.

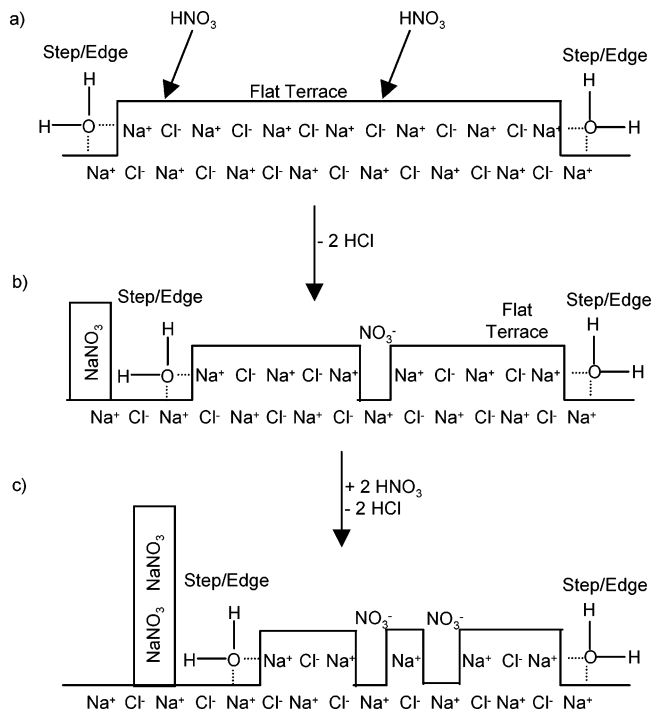


Figure 9. Schematic diagram of reaction of gaseous HNO_3 with NaCl at steps/edges and on the flat terrace. The presence of surface-adsorbed water at the steps and edges increases the mobility of the nitrate ion in these regions, allowing recrystallization of NaNO_3 at steps and edges. At terrace sites, the nitrate remains at the site of the chloride vacancy that is generated during the reaction. However, reaction of water vapor with this terrace-isolated nitrate ion to generate OH^- in the original chloride vacancy may be responsible for the XPS observations of OH^- formation after reaction with HNO_3 and exposure to water vapor.¹⁵⁵ Reprinted with permission from ref 154. Copyright 2003 American Chemical Society.

One might anticipate that water would congregate at the new NaCl steps as they are generated on the surface, and the process would continue. Such a mechanism would lead to continuous reaction at the steps, with increasing incorporation of the nitrate into microcrystallites of NaNO_3 . This mechanism would effectively move the step into the crystal layer by layer, incorporating nitrate ions formed on the terrace as they come into contact with a moving step edge.

Nitrate formed on a terrace site not associated with SAW would be immobilized, and hence lead to passivation of the terrace sites. This is supported by Knudsen cell studies of the time dependence of the uptake coefficient for HNO_3 , shown in Figure 10. The uptake coefficient decreases rapidly from $\sim 3 \times 10^{-3}$ to 1×10^{-3} over ~ 200 s reaction time, and then remains relatively constant for the duration of these experiments. The initial high uptake is attributed to reaction on a fresh, unreacted NaCl surface, at both the steps and the edges with which SAW is associated and on the terraces. As the terraces become covered with nitrate, the uptake decreases. At reaction times beyond ~ 200 s, all of the reaction is at the SAW-influenced steps and edges, where SAW assists in the recrystallization of NaNO_3 and the regeneration of fresh reaction sites.

This mechanism is consistent with the results of Gershenzon and co-workers on the reaction of NO_3

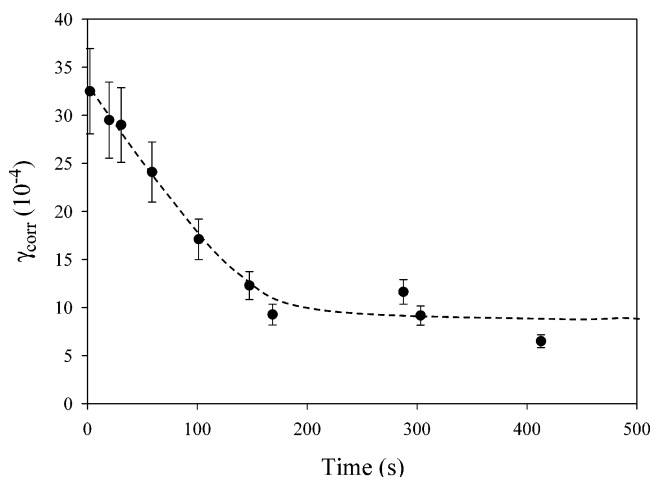


Figure 10. Uptake coefficients for HNO_3 on less than one (0.7) layer of $177\text{-}\mu\text{m}$ particles of NaCl as a function of time. Initial gas-phase HNO_3 concentration was 4.5×10^{11} molecules cm^{-3} . Reprinted with permission from ref 154. Copyright 2003 American Chemical Society.

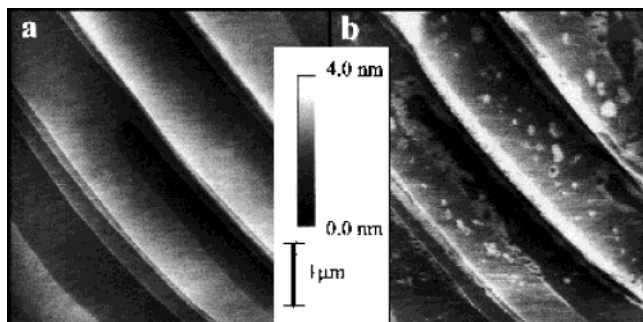


Figure 11. AFM images of (a) an unreacted NaCl(100) surface and (b) the same surface after reaction with gaseous HNO_3 . Adapted with permission from ref 216.

radicals with dry NaCl and NaBr.¹⁴¹ The measured initial uptake was more rapid than at longer times. Gershenzon et al.¹⁴¹ attributed this to an initial reaction with dislocations on the salt surface; however, it may be that in these studies, SAW on the dislocations, i.e., steps and edges, is the key determinant for this rapid initial uptake.

Such a mechanism is also consistent with the observation by AFM of NaNO_3 strings being formed initially along step edges during the HNO_3 –NaCl reaction.^{153,216} Figure 11 shows an AFM image of the surface of NaCl(100) before and after reaction with HNO_3 .²¹⁶ Steps are seen running diagonally on the surface of the unreacted NaCl (Figure 11a). Figure 11b shows the formation of NaNO_3 along the steps after exposure of the surface to HNO_3 ; smaller towers of NaNO_3 are also formed on the terraces under the high HNO_3 concentrations used in these experiments. Similarly, in infrared spectroscopic studies of the reactions of NaCl with HNO_3 ²¹⁷ and NO_2 ,¹⁶⁷ the absorption band around 1400 cm^{-1} due to the ν_3 asymmetric stretch of the product nitrate ion was observed as a doublet. This observation of two peaks was attributed to the formation of irregularly shaped microcrystallites of NaNO_3 in which longitudinal–transverse splitting of the degeneracy occurs due to the lowered symmetry.^{217,218}

Defects on the NaCl crystal surface can lead to dissociation of water to form OH^- . It is well known,

for example, from both experimental^{186,192} and theoretical^{199,201} studies that F-centers formed by electron bombardment of the NaCl surface, in which the chloride ion is replaced by a trapped electron, lead to water dissociation. In most studies carried out to probe atmospheric reactions, the samples are not exposed to such high-energy bombardment. Dai and co-workers¹⁹¹ observed, using infrared spectroscopy, that an NaCl surface consisting of aggregates of ~ 10 nm crystallites has about 20% surface site defects; however, only a small percentage of the surface sites ($< 1\%$) led to water dissociation and the formation of OH^- . Thus, it appears that relatively small amounts of OH^- are expected on unreacted NaCl surfaces under atmospheric conditions.

It is interesting that XPS studies¹⁵⁵ show that OH^- is generated on the NaCl surface upon reaction with HNO_3 followed by exposure to water vapor below the deliquescence point. One possible mechanism involves the immobilized nitrate formed on terraces (Figure 9). These metastable nitrate ions may react with water vapor to form gaseous HNO_3 and surface OH^- , the latter readily fitting into the void in the lattice created by the removal of Cl^- during the original $\text{HNO}_3 + \text{NaCl}$ reaction. Given the larger number of terrace chloride ions compared to the steps and edges, significant amounts of OH^- could be generated by such a process, consistent with the XPS experimental observations.¹⁵⁵ Desorption of HNO_3 into the gas phase and its removal at the end of each water exposure cycle would lead to a decrease in nitrate on the surface and an increase in OH^- , as is observed.¹⁵⁵

As described earlier in section 3.2, bromine from sea salt is responsible for the destruction of ozone in the boundary layer in the Arctic at polar sunrise and likely also in mid-latitudes at dawn. The relatively large contribution of bromine atoms compared to chlorine (considering the ratio of 1:650 Br:Cl in seawater) is due to a number of factors discussed above, including segregation mechanisms assisted by water. In mixtures of solid NaCl and NaBr, bromide segregates to the surface of the salt. For example, Ghosal and co-workers²¹⁹ used XPS and SEM–EDS to study changes in NaCl single crystals that were uniformly doped with small amounts of bromide ions in a ratio of $\sim 1:15$. On exposure to water vapor corresponding to 54% RH, below the deliquescence points of both NaCl (75% RH) and NaBr (58% RH), the ratio of bromine to chlorine on the surface increased by more than an order of magnitude. Zangmeister and co-workers²²⁰ applied similar techniques, along with AFM and SEM–EDS, to study the salt crystals precipitated from solutions of NaBr and NaCl of varying proportions. The Br/Cl ratio on the surface was typically 35 times larger than that in the bulk crystal for solutions of composition similar to seawater, and separate domains of NaBr were observed segregated on the surfaces of the NaCl crystals.

It is evident from such studies that bromide ions will be much more readily available at the surface of solid sea salts than their molar ratio in seawater would imply. Again, the role of water in ion mobility on the surface to allow surface reconstruction is

shown to be important in the chemistry of sea salt particles.

In summary, water plays a remarkable role in the surface chemistry of NaCl and NaBr. Despite this, the mechanism by which surface-adsorbed water participates in the segregation of surface compounds and in the chemistry is not well understood. This is an area that clearly warrants further investigation.

6. Reactions of Aqueous Solutions of Sea Salt and Its Components

6.1. Aqueous-Phase Chemistry

Under many tropospheric conditions, the relative humidity is sufficiently high that sea salt particles will be deliquesced. The effluorescence point of NaCl is 44% RH,^{127,221} and at lower relative humidities, crystallization occurs. However, sea salt is a mixture of salts, including some that form hydrates, e.g., MgCl₂. There is some indirect evidence from laboratory studies^{222–225} that these hydrates hold sufficient water, even under vacuum conditions, that their surfaces may be liquid-like in character.

Therefore, for sea salt particles that are deliquesced, and perhaps for particles even below the effluorescence point, understanding the uptake and reaction of gases into aqueous salt solutions is important. We treat here first the bulk aqueous-phase chemistry that is likely to occur in liquid sea salt particles. However, it is becoming increasingly clear that there is unique chemistry that occurs at the particle interfaces with air as well, and which likely plays an important role. We treat such interfacial chemistry in the final section.

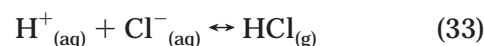
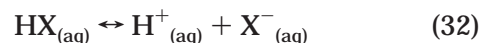
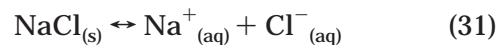
As discussed earlier with respect to the bromine-catalyzed loss of surface-level ozone in polar regions during sunrise, reactions of sea salt on the ice pack or in frost flowers appear to control this chemistry and the O₃ destruction. Laboratory studies have established that sea salt particles under these conditions maintain a liquid surface layer that is concentrated in chloride and bromide ions.^{127,128} While we focus here on solution chemistry, much of which has been studied only at room temperature, it is expected to be at least qualitatively similar to the chemistry of sea salt occurring on the surfaces of ice and frost flowers.

A number of models of the marine boundary layer that have extensive halogen chemistry have been developed (e.g., see refs 6, 14, 16, 18, and 226–237). Although chloride is the major anion in sea salt, its chemistry is intertwined with, and enhanced by, the smaller amounts of bromine present. Because the particles become depleted of bromide first, the chemistry changes from that of a chloride–bromide mixture to predominantly chloride chemistry as the particles age. A related complicating factor is that the chemistry is dependent on particle size, with the smaller particles becoming depleted of halogens more rapidly. This is at least in part due to the smaller available total mass in the smaller particles. In addition, as discussed below, many of the reactions that generate gas-phase halogen compounds from sea salt are acid-catalyzed, and the smaller particles tend

to be more acidic.^{15,238} The pH of sea salt particles is also sensitive to RH, decreasing as the relative humidity increases.^{239–242} As discussed in section 6.2 below, theoretical calculations indicate that bromide ions will reside to a significant extent at the air–water interface, with a greater preference for the interface compared to the bulk than is the case for chloride; the larger surface-to-volume ratio of small particles will therefore enhance interfacial Br[−] chemistry as well. Finally, the chemistry in small particles (~0.1 μm) can be impacted by the limitations on the absolute amount of material in each particle and the statistics involved in the distribution of trace components between particles, resulting in chemistry that differs significantly from that predicted on the basis of bulk-phase chemical reactions.^{243,244}

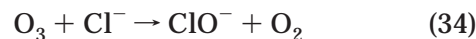
With these caveats in mind, we shall briefly summarize what are believed to be the most important reactions in the aqueous phase of sea salt particles that lead to depletion of halide ions and the formation of gas-phase halogen compounds. These include (1) acid displacement reactions, (2) reactions initiated by O₃, (3) reaction with OH, (4) reactions with sulfur compounds, and (5) reactions with NO₃ and N₂O₅. The rate constants cited are generally for bulk aqueous-phase reactions at room temperature.

Acid Displacement Reactions. Nitric and sulfuric acids are the major acids formed in the troposphere.¹ If sufficient acid is taken up and/or formed in sea salt particles, chloride and bromide will be displaced into the gas phase as HCl and HBr,^{245–249} e.g., for NaCl,

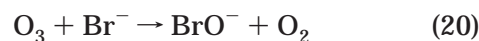


where X is typically nitrate, sulfate, or bisulfate.

Reactions Initiated by O₃. Chloride ions are oxidized slowly in solution by ozone,^{250–253} whereas bromide reacts at a higher rate:^{10,121,122,126}



$$(k_{34} < 3 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1})^{250}$$



$$(k_{20} = 258 \text{ M}^{-1} \text{ s}^{-1})^{122,125}$$

(Rate constants cited are generally those measured at room temperature.) The ClO[−] and BrO[−] are in equilibrium in solution with the corresponding hypohalous acids:^{122,254–257}



$$(K_{35} = 3.4 \times 10^{-8} \text{ M})^{256}$$



$$(K_{21} = 2.6 \times 10^{-9} \text{ M})^{257}$$

A second source of HOBr is hydrolysis of BrONO_2 :^{258,259}

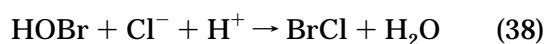


A third potential source of HOBr is the oxidation of bromide ions by Caro's acid:^{228,260}

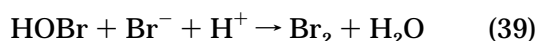


The reaction of BrO with HCHO was postulated as a potentially important source of HOBr ,²⁶¹ but it appears that the reaction is too slow²⁶² to be significant.

If the particle becomes sufficiently acidic, the hypobromous acids are degassed from solution. However, HOBr can also react with Cl^- to generate BrCl ,^{251,259,263-268} and with Br^- to generate Br_2 .^{251,259,263-265,267,269-272}



$$(k_{38} = 2.3 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1})^{273}$$



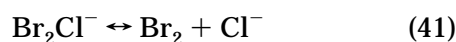
$$(k_{39} = 1.6 \times 10^{10} \text{ M}^{-2} \text{ s}^{-1})^{271}$$

Such chemistry can occur in solution, on solid salts, or on ice, although of course the kinetics differ for the different phases.

Vogt and co-workers²²⁸ proposed that, given the great excess of chloride in seawater, reaction (38) of HOBr with Cl^- would dominate over reaction (39) and generate BrCl as the product, consistent with the subsequent kinetics studies of Liu and Margerum.²⁷³ However, BrCl has the potential to react before it diffuses back to the interface with air and into the gas phase:



$$(k_{40} > 10^8 \text{ M}^{-1} \text{ s}^{-1}; K_{40}^{\text{eq}} = 1.8 \times 10^4 \text{ M}^{-1})^{274}$$



$$(k_{-41} = 2.6 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}; K_{41}^{\text{eq}} = 1.3 \text{ M})^{274,275}$$



$$(K_{42}^{\text{eq}} = 3.8 \text{ M}^{-1})^{273}$$



$$(K_{43}^{\text{eq}} = 3 \times 10^{-6} \text{ M}^3)^{274}$$

BrCl may also hydrolyze back to HOBr :



$$(k_{44a} = 3.0 \times 10^6 \text{ s}^{-1})^{273}$$



$$(k_{44b} = 2.4 \text{ s}^{-1})^{273}$$

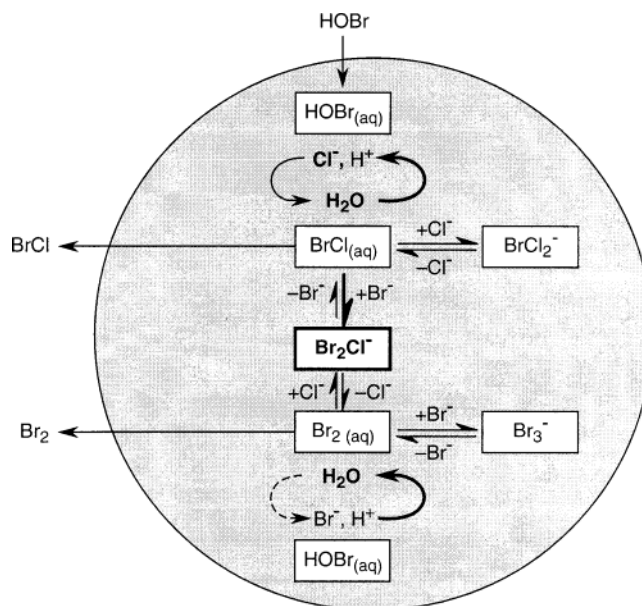


Figure 12. Schematic of chemistry of the uptake and reaction of HOBr with sea salt.³⁶⁴ The author is grateful to Professor T. Benter for permission to reproduce this figure.

Gaseous HOBr can also be taken up into NaCl and sea salt solutions. In this case, the uptake at the air–solution interface is characterized by the mass accommodation coefficient, which is defined as the fraction of collisions of gas with the surface that leads to uptake through adsorption and solvation followed by diffusion into the bulk.²⁷⁶ The mass accommodation coefficient for uptake of HOBr on deliquesced NaCl particles has been measured²⁵¹ to be between 0.2 and 1 for either highly acidic or buffered (to pH 7.2) NaCl aerosols at room temperature, with a lower limit of 0.01 measured at 274 K.²⁶⁷ In mixtures of chloride and bromide, the generation of Br_2 was undetectable for unbuffered and alkaline solutions, where the dissociation of HOBr is large.²⁶⁷

Uptake of HOBr onto ice or salts containing Cl^- and Br^- is also fast, particularly if the surface is acidic.^{259,263-266,277-279} As expected, the gas-phase products depend on the relative amounts of available Cl^- and Br^- . Initially, when there is sufficient bromide present, BrCl is converted to Br_2 via reactions (40) and (41). When the particle becomes depleted of bromide, the major product becomes BrCl . Figure 12 summarizes this chemistry. The transition from Br_2 to BrCl production has been observed in wetted wall flow tube studies,²⁶⁷ in sea-salt-doped ice,^{264,278} in bulk solutions,¹²⁴ and in solid salts and aerosols.^{265,280} The gas-phase products, Br_2 and BrCl , may also be taken up and react further on halide-containing ice and salt surfaces.^{278,281-284}

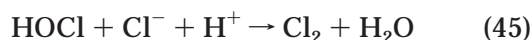
Direct mass spectrometric measurements of Br_2 and BrCl before and at the beginning of polar sunrise in the Arctic (Figure 3) show that they are present at similar concentrations.⁹³ In addition to the chemistry described above, there are a number of additional factors that determine the ratio of Br_2 to BrCl . The first is the solubility of BrCl compared to Br_2 . The Henry's law constant for BrCl at 245 K,

typical of the Arctic spring, is calculated to be 60 M atm⁻¹, compared to 13 M atm⁻¹ for Br₂,²⁸⁵ thus favoring gas-phase Br₂ relative to BrCl.

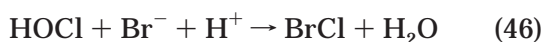
Selective ion segregation that occurs during phase transitions of salt solutions also favors Br₂ production over BrCl. Koop and co-workers¹²⁷ showed that chloride will be concentrated by a factor of ~11 and bromide by a factor of ~38 in the surface liquid layer of seawater deposited on the ice pack under conditions of polar sunrise. This would decrease the Cl⁻/Br⁻ ratio available for reaction in the surface film from 650:1 to 188:1. Indeed, the Cl⁻/Br⁻ ratio in snow at Alert has been found²⁸⁶ to be as low as 30:1. Enhancement of bromide ions in frost flowers formed on the ice has been reported by Rankin and co-workers.¹¹³ Also relevant to the enhancement of bromine are laboratory studies of bromine-doped NaCl crystals, where preferential surface segregation of bromide was observed on exposure to water vapor,²¹⁹ and studies of salts precipitated from NaCl/NaBr solutions.²²⁰

In addition to this chemistry in the bulk aqueous phase, reactions can also occur at the air–water interface, and these favor bromide over chloride. As discussed in more detail in the following section, while both chloride and bromide ions reside in part at the air–water interface, surface bromide is favored and hence readily available for reaction with gases such as HOBr.^{287,288}

Gaseous HOCl, formed for example by the reaction (11) of ClO with HO₂, can also be taken up into sea salt and react with Cl⁻ or Br⁻:



$$(k_{45} = 2.1 \times 10^4 \text{ M}^{-2} \text{ s}^{-1})^{269,273,289}$$



$$(k_{46} = 1.3 \times 10^6 \text{ M}^{-2} \text{ s}^{-1})^{290}$$

Reaction with OH. In contrast to the slow oxidation by O₃, chloride ions are well known to be oxidized by OH in solution. The mechanism has been attributed to reactions (47)–(53):



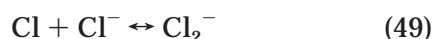
$$(k_{47} = 4.3 \times 10^9 \text{ M}^{-1} \text{ s}^{-1};$$

$$k_{-47} = 6.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{291}$$



$$(k_{48} = 3.2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1} \text{ at } I = 0;$$

$$k_{-48} = 3.6 \times 10^3 \text{ M}^{-1} \text{ s}^{-1})^{292}$$

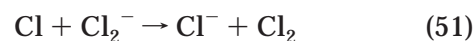


$$(k_{49} = 7.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1};$$

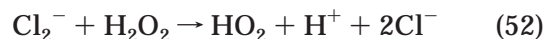
$$k_{-49} = 5.7 \times 10^4 \text{ M}^{-1} \text{ s}^{-1})^{291-293}$$



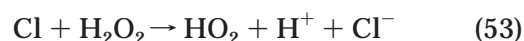
$$(k_{50} = 9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})^{292,294}$$



$$(k_{51} = 2.1 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{292}$$



$$(k_{52} = 1.4 \times 10^6 \text{ M}^{-1} \text{ s}^{-1})^{292}$$



$$(k_{53} = 2.0 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{292}$$

This mechanism is acid-catalyzed via step (48), so Cl₂ can be generated from sea salt particles that are at low pH (which appears often to be the case due to uptake of HNO₃ and H₂SO₄)^{234,238–241} and depleted of bromide ions. Note, however, that as discussed in the following section, there is good evidence for a reaction of OH with Cl⁻ at the interface that is not acid-catalyzed and, indeed, generates OH⁻ in the particles.

Bromide ions are even more readily oxidized by OH in solution, generating Br₂ as the gas-phase product:



$$(k_{54} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1};$$

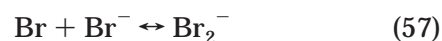
$$k_{-54} = 3.3 \times 10^7 \text{ s}^{-1})^{295}$$



$$(k_{55} = 4.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1})^{295}$$



$$(k_{56} = 1.9 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})^{295}$$



$$(k_{57} = 1.1 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1};$$

$$K_{57}^{\text{eq}} = 6 \times 10^5 \text{ M}^{-1})^{296}$$



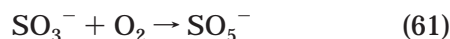
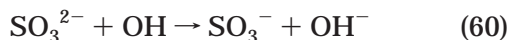
$$(k_{58} = 2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})^{297,366}$$



$$(K_{59}^{\text{eq}} = 6.2 \times 10^{-2} \text{ M})^{274,367}$$

Reactions with Sulfur Compounds. Sulfur dioxide is a ubiquitous component of polluted air masses because it is formed during combustion of fossil fuels¹ that contain sulfur. In addition, it is formed in the remote marine boundary layer by the oxidation of biogenically produced sulfur compounds, particularly dimethyl sulfide (DMS).^{298–303} Several

sulfur–halogen processes have been proposed that may lead to the oxidation of halide ions in sea salt and the generation of gas-phase halogen compounds. For example, Mozurkewich²⁶⁰ and Vogt and co-workers²²⁸ proposed that Caro's acid, HSO_5^- , oxidizes Br^- in sea salt to HOBr, reaction (37). Caro's acid (HSO_5^-) is an intermediate formed during the oxidation of dissolved SO_2 . When SO_2 is taken up into solution, it undergoes a series of equilibrium reactions similar to those of CO_2 , forming $\text{SO}_{2(\text{aq})}$, HSO_3^- , and SO_3^{2-} , commonly referred to as S(IV) [i.e., $\text{S(IV)} = \text{SO}_{2(\text{aq})} + \text{HSO}_3^- + \text{SO}_3^{2-}$]. Caro's acid and other reactive intermediates are formed by reactions such as the following:^{304–306}



Both HOCl and HOBr also oxidize S(IV) in solution.^{255,307}



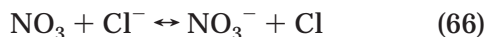
$$(k_{64} = 7.6 \times 10^8 \text{ M}^{-1} \text{ s}^{-1})$$



$$(k_{65} = 5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1})$$

Incorporating this chemistry into their model, Vogt and co-workers²²⁸ predicted complete loss of Br^- from the particles after ~ 12 h of reaction time, compared to less than a percent loss of Cl^- simultaneously. Ayers and co-workers³⁰⁸ reported measurements of chloride and bromide loss from sea salt particles in the remote Southern Ocean that were consistent with this mechanism, i.e., small chloride losses along with much larger bromide losses that were anticorrelated with non-sea-salt sulfate in the particles. (However, as discussed below, there are alternate mechanisms that are also consistent with this observation.)

Oxidation of Halide Ions by NO_3 and N_2O_5 . Halide ions are readily oxidized by NO_3 radicals in aqueous solution:^{309–317}

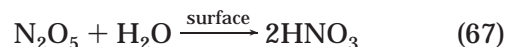


The kinetics of this reaction in the bulk aqueous phase have been studied by a number of researchers,^{309–311,316} and the rate constant k_{66} was reported to increase with ionic strength, from $\sim 10^7 \text{ M}^{-1} \text{ s}^{-1}$ to $\sim 10^8 \text{ M}^{-1} \text{ s}^{-1}$. However, a recent study of this reaction³¹⁷ found no dependence on the ionic strength between 0.1 and 2 M and measured a value of $k_{66} = (3.5 \pm 0.5) \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$. The equilibrium constant for the reaction is $K_{66}^{\text{eq}} = 3.5 \pm 0.5$.³¹⁷ The corresponding reaction with Br^- is faster.^{310,311}

Ravishankara and co-workers^{314,318,319} measured the uptake of gaseous NO_3 on water and aqueous

solutions of chloride, bromide, and iodide. The uptake increased in the presence of the halides, with that for iodide being faster than bromide, which was faster than chloride at comparable concentrations. From these studies, they report that the reaction of NO_3 radicals in solution with Br^- is a factor of 37 times faster than reaction (66) at a pH of ~ 6 and 273 K.³¹⁴

The nitrate radical reacts with NO_2 to generate N_2O_5 . Dinitrogen pentoxide is well known to hydrolyze readily on surfaces that hold water:¹



This reaction likely involves autoionization to $\text{NO}_2^+\text{NO}_3^-$ followed by reaction of this intermediate with water.^{320–327} However, if halide ions are available, a competition occurs for the NO_2^+ between water and the halide ion. For example, Behnke et al.³²³ measured the ratio of the rate constant for the reaction of NO_2^+ with Cl^- to that for reaction with H_2O to be 836 ± 32 , so that even in dilute solutions of NaCl, production of ClNO_2 will dominate:



The uptake coefficient for N_2O_5 on aqueous solutions of NaCl and on synthetic sea salt,⁷⁶ which holds substantial amounts of water,^{165,222,224,225,328} has been measured by a number of groups^{137,322,323,326,329} and is approximately 10^{-2} , with yields of ClNO_2 approaching 100%. The corresponding reactions with bromide solutions are also fast.³²⁶

As discussed in more detail in the following section, there is good reason to believe that chemistry at the air–water interface is a very important contributor to bromine chemistry as well and, indeed, may dominate over the aqueous-phase reactions under some conditions.

6.2. Chemistry at the Air–Water Interface

Figure 13a depicts the traditional view of the uptake of gases into solutions: diffusion (D_g) of the gas to the surface, collision of the gas with the surface, mass accommodation (α), and diffusion into the bulk (D) and reaction. Evidence from kinetics studies beginning some 15 years ago suggested that there may be unique chemistry that occurs at the interface itself for some inorganic species under conditions relevant to atmospheric processes. For example, Jayne and co-workers³³⁰ proposed that the uptake of SO_2 into aqueous solution involved the formation of a unique complex at the surface. This was supported in subsequent studies by Donaldson and co-workers,³³¹ Boniface and co-workers,³³² and Clegg and Abbatt,³³³ although a surface species was not detected by attenuated total reflectance FTIR.³³⁴ Hu and co-workers²⁷⁵ reported that the kinetics of Cl_2 uptake into droplets containing dissolved NaBr were not consistent with the mechanism shown in Figure 13a, and proposed that a reaction also occurred at the interface; similarly, an interfacial reaction of Br_2 with I^- was observed. Interface reactions have also been proposed for the reactions of ClONO_2 with HCl on ice³³⁵ and for ClNO_2 and BrCl

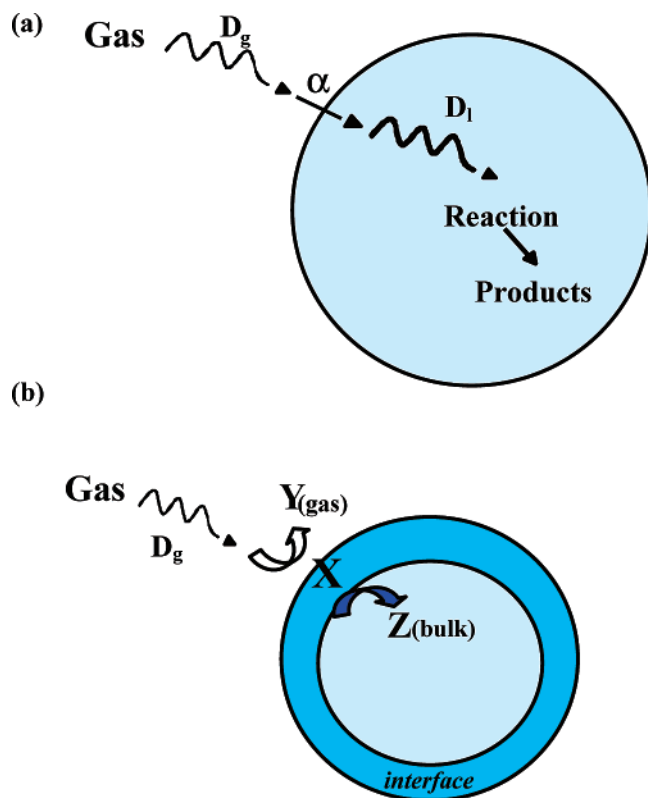


Figure 13. (a) “Conventional” view of uptake of gases into liquids and reaction and (b) interfacial mechanism. In the latter case, the reaction of the gas with species X at the interface leads to the generation of a gaseous product Y and a bulk-phase product Z.

with aqueous solutions containing I^- .^{336,337} This new aspect of the interaction of gases with liquids is represented schematically in Figure 13b.

There is increasing evidence that such interfacial processes are quite common for certain inorganic species such as the halides. For example, in studies of the reactions of deliquesced particles of NaCl with gas-phase OH, the formation of gas-phase Cl_2 was observed^{252,253} that was far in excess of that expected from the mechanism consisting of reactions (47)–(53) in the bulk aqueous phase. Molecular dynamics (MD) simulations showed that chloride ions were readily available at the interface, and based on this, a reaction of OH with Cl^- at the interface, shown schematically in Figure 14, was proposed.²⁵³ Further molecular dynamics simulations show that when OH from the gas phase impacts a concentrated solution of NaCl, there is sufficient contact time between OH and Cl^- on the surface for this reaction to occur.³³⁸

Additional evidence for this interface mechanism has been obtained by analysis of NaCl particles before and after reaction under similar conditions (i.e., RH between 80 and 85% in the presence of O_3 and 254 nm radiation).³³⁹ Loss of chloride and increase in oxygen were observed by SEM–EDS, and TOF–SIMS spectra showed peaks corresponding to O^- and OH^- on the surface of the reacted particles. These experimental observations are consistent with the formation of hydroxide ions expected for the interface mechanism shown in Figure 14.

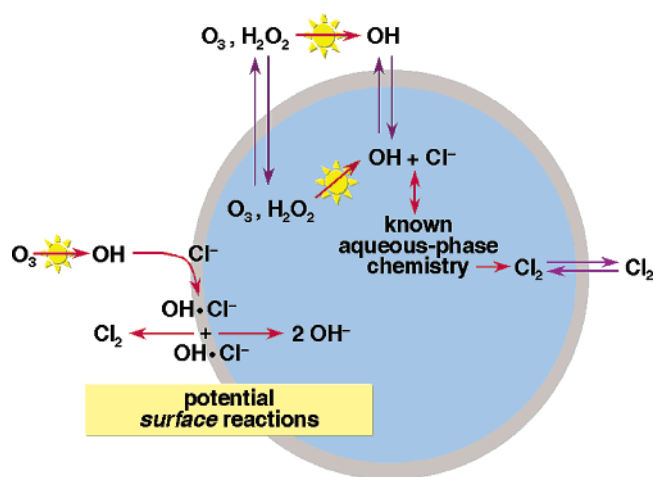


Figure 14. Schematic diagram of the mechanism of reaction of OH with Cl^- at the air–water interface. Reprinted with permission from *Science* (<http://www.aaas.org>), ref 253. Copyright 2000 American Association for the Advancement of Science.

The photochemical formation of OH^- in sea salt particles via the interface mechanism during the day may have significant implications for the uptake of SO_2 into these particles and its oxidation to sulfate. Oxidation of S(IV) by O_3 is fast under alkaline conditions,³⁴⁰ where the total amount of dissolved S(IV) is also enhanced.¹ Models predict that as the oxidation to sulfuric acid proceeds, the pH of the particles falls, decreasing both the O_3 reaction kinetics and the concentration of dissolved S(IV).^{226,239,341} This leads to a self-quenching of the reaction and limits the importance of sea salt particles as a vehicle for the oxidation of SO_2 to sulfate. However, during the day, the generation of OH^- by the interface oxidation of Cl^- by OH will contribute to modulating the effect of acid formation on the pH of the particles. By slowing the acidification, more SO_2 can be taken up into the particles and oxidized to sulfuric acid than would otherwise be expected.³³⁹

Recent theoretical studies show that inorganic anions, particularly the larger halide ions, tend to reside on the surface of clusters with water that contain more waters than the first solvation shell (and hence may provide insight into the behavior in bulk water).^{342–353} Although it is not intuitively obvious that halide ions would be readily available at the air–water interface, the physical basis for this appears to be the polarizability (see, for example, refs 287, 288, 346–348, 351, 352, 354–357). In bulk solution, the ions are surrounded by water molecules, and the average net dipole is zero. At the interface, the asymmetric arrangement of water molecules around the halide ion gives a net dipole that polarizes the ion, leading to an attraction that overcomes the partial loss of solvation energy compared to the bulk. In contrast, it is interesting that both experimental^{358–360} and theoretical studies³⁶¹ show that the doubly charged sulfate ion does not reside at the interface because the two charges require full solvation.

Figure 15 shows the results of molecular dynamics simulations for the series of halide ions from fluoride to iodide in aqueous solutions.^{287,288} There is a trend to increasing availability at the interface for larger,

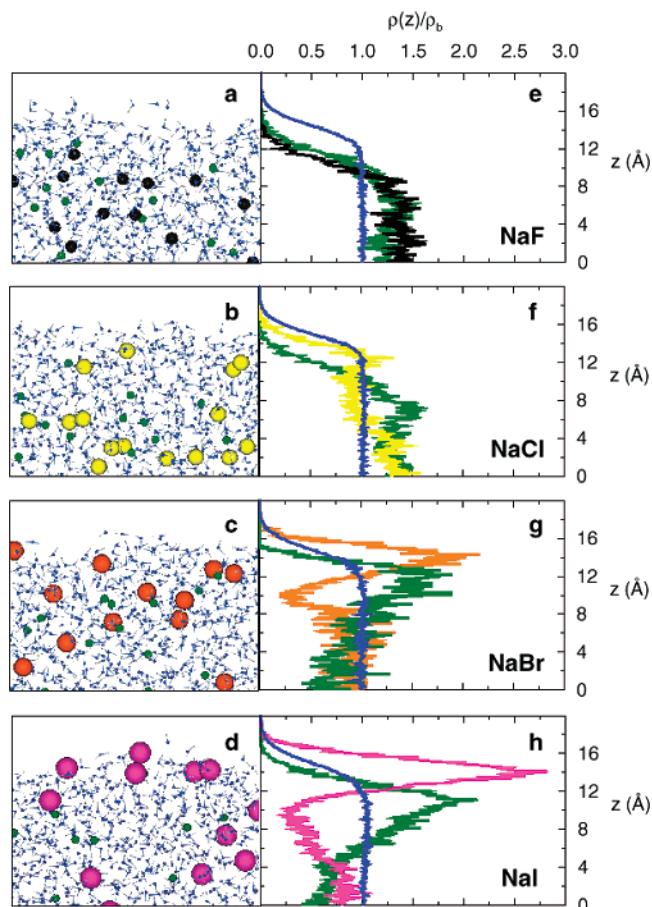


Figure 15. Molecular dynamics simulations of solution–air interfaces of solutions of sodium halides. (a–d) Snapshots of Na^+ (small green balls) and the halide ions (black = F^- ; yellow = Cl^- ; orange = Br^- ; pink = I^-). (e–h) Profiles for O, Na, and the halide ions from the center of the water slab ($z = 0$) to the air–water interface and beyond. Reprinted with permission from ref 287. Copyright 2001 American Chemical Society.

more polarizable ions. Fluoride is depleted at the surface relative to the bulk, while chloride is available in similar concentrations both at the interface and in the interior. However, bromide and iodide ions are enhanced at the interface relative to the bulk by factors of about 2 and 3, respectively. Such a trend is consistent with the increasing polarizabilities of the anions from F^- to I^- . In a similar vein, Dang³⁵³ carried out molecular dynamics simulations to calculate the potentials associated with transport of Cl^- , Br^- , and I^- (as well as Na^+) across the air–water interface. He showed that Cl^- was not as strongly bound to the interface as Br^- and I^- .

This surface enhancement of bromide relative to chloride is expected to contribute to the disproportionately large role of bromide ions in tropospheric halogen chemistry. For example, molecular dynamics simulations of equimolar mixtures of chloride and bromide ions show that there is more bromide at the interface, and indeed, in concentrated solutions (3 M), bromide displaces virtually all of the chloride from the interface.²⁸⁸ These theoretical calculations are consistent with the experimental observation of a reaction of gaseous Cl_2 with bromide ions at the interface of an aqueous droplet of NaBr, and of gaseous Br_2 with iodide ions.²⁷⁵

Given that polarization is the key for anions to reside at the interface, it is likely that anions other than the halides may also be preferentially located at the interface. Indeed, there is experimental evidence that Cl_2^- radical anions, intermediates in the $\text{OH}-\text{Cl}^-$ reaction (see reaction (49) above), are present at the air–water interface and react with ethanol, for example, much faster than in the bulk phase.³⁶² In addition, molecular dynamics simulations predict that the nitrate ion also has a propensity for the interface.³⁶³ It remains to be investigated what impact this has on the chemistry and photochemistry of such interfacial species.

7. Summary

It is becoming increasingly clear that halide ions, particularly chloride and bromide, play a major role in the chemistry of the troposphere. A variety of reactions of sea salt with gases lead to the formation of chlorine and bromine atom precursors that photolyze to generate reactive halogen atoms. Chlorine atoms generally lead to ozone formation in the troposphere, while bromine atoms destroy ozone. Studies of reactions of model solid salts such as NaCl and NaBr show that small amounts of water that remain adsorbed on the steps and edges of the solid surfaces even under vacuum play a major role in the reactivity and prevent surface passivation during such reactions. For aqueous salt solutions, reactions at the air–water interface play a major role in the reactions with gases and have the potential to alter other trace gases such as SO_2 and their associated tropospheric chemistry. Despite the demonstrated contributions of halogens to the chemistry of the lower atmosphere, a great deal more laboratory, field, and modeling work will be required to fully understand and quantify the contribution of halogens.

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9. References

- (1) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *Chemistry of the Upper and Lower Atmosphere—Theory, Experiments, and Applications*; Academic Press: San Diego, 2000.

- (2) Schroeder, W. H.; Urone, P. *Environ. Sci. Technol.* **1974**, *8*, 756.
- (3) Zafiriou, O. C. *J. Geophys. Res.* **1974**, *79*, 2730.
- (4) Cicerone, R. J. *Rev. Geophys. Space Phys.* **1981**, *19*, 123.
- (5) Finlayson-Pitts, B. J. *Res. Chem. Intermed.* **1993**, *19*, 235.
- (6) Sander, R.; Crutzen, P. J. *J. Geophys. Res.* **1996**, *101*, 9121.
- (7) Finlayson-Pitts, B. J.; Pitts, J. N., Jr. *J. Science* **1997**, *276*, 1045.
- (8) Andreae, M. O.; Crutzen, P. J. *Science* **1997**, *276*, 1052.
- (9) Ravishankara, A. R. *Science* **1997**, *276*, 1058.
- (10) DeHaan, D. O.; Brauers, T.; Oums, K.; Stutz, J.; Nordmeyer, T.; Finlayson-Pitts, B. J. *Int. Rev. Phys. Chem.* **1999**, *18*, 343.
- (11) Hemminger, J. C. *Int. Rev. Phys. Chem.* **1999**, *18*, 387.
- (12) Stutz, J.; Hebestreit, K.; Aliche, B.; Platt, U. *J. Atmos. Chem.* **1999**, *34*, 65.
- (13) Finlayson-Pitts, B. J.; Hemminger, J. C. *J. Phys. Chem. A* **2000**, *104*, 11463.
- (14) Moldanová, J.; Ljungström, E. *J. Geophys. Res.* **2001**, *106*, 1271.
- (15) Toyota, K.; Takahashi, M.; Akimoto, H. *Geophys. Res. Lett.* **2001**, *28*, 2899.
- (16) Knipping, E. M.; Dabdub, D. *J. Geophys. Res.* **2002**, *107*, 4360.
- (17) Platt, U.; Hönninger, G. *Chemosphere* **2003**, *52*, 325.
- (18) Herrmann, H.; Majdik, Z.; Ervens, B.; Weise, D. *Chemosphere* **2003**, *52*, 485.
- (19) Sander, R.; Keene, W. C.; Pszenny, A. A. P.; Arimoto, R.; Ayers, G. P.; Baboukas, E.; Caney, J. M.; Crutzen, P. J.; Duce, R. A.; Hönninger, G.; Huebert, B. J.; Maenhaut, W.; Mihalopoulos, N.; Turekian, V. C.; Dingenen, R. V. *Atmos. Chem. Phys. Discuss.* **2003**, *3*, 2963.
- (20) Middleton, J. T.; J. B. K., Jr.; Schwalm, H. W. *USDA Plant Dis. Rep.* **1950**, *34*, 245.
- (21) Haagen-Smit, A. J. *Ind. Eng. Chem.* **1952**, *44*, 1342.
- (22) Haagen-Smit, A. J.; Fox, M. M. *J. Air Pollut. Control Assoc.* **1954**, *4*, 105.
- (23) Scott, W. E.; Stephens, E. R.; Hanst, P. L.; Doerr, R. C. *Proc. Air Pollut. Inst.* **1957**, *III*, 171.
- (24) Hecklen, J.; Westberg, K.; Cohen, N. Center for Air Environmental Studies, 1969.
- (25) Weinstock, B. *Science* **1969**, *166*, 224.
- (26) Stedman, D. H.; E. D. M., Jr.; Daby, E. E.; Niki, H.; Weinstock, B. *Abstracts of Papers*, 160th National Meeting of the American Chemical Society, Chicago, IL, Fall 1970; American Chemical Society: Washington, DC, 1970.
- (27) Levy, H. *Science* **1971**, *173*, 141.
- (28) Gaffney, J. S.; Marley, N. A.; Prestbo, E. W. In *The Handbook of Environmental Chemistry*; Hutzinger, O., Ed.; Springer-Verlag: Berlin, 1989; Vol. 4.
- (29) Kleindienst, T. A. *Res. Chem. Intermed.* **1994**, *20*, 335.
- (30) Paulson, S. E.; Orlando, J. *J. Geophys. Res. Lett.* **1996**, *23*, 3727.
- (31) Bey, I.; Aumont, B.; Toupance, G. *Geophys. Res. Lett.* **1997**, *24*, 1067.
- (32) Sander, S. P.; Ravishankara, A. R.; Friedl, R. R.; Golden, D. M.; Kolb, C. E.; Kurylo, M. J.; Molina, M. J.; Huie, R. E.; Orkin, V. L.; Moortgat, G. K.; Finlayson-Pitts, B. J. Chemical Kinetics and Photochemical Data for Use in Atmospheric Studies, Evaluation No. 14; Jet Propulsion Laboratory, California Institute of Technology, 2003.
- (33) Bojkov, R. D. *J. Am. Meteorol. Soc.* **1986**, *25*, 343.
- (34) Volz, A.; Kley, D. *Nature* **1988**, *332*, 240.
- (35) McKeen, S.; Kley, D.; Volz, A. In *Ozone in the Atmosphere*; Bojkov, R. D., Fabian, P., Eds.; A Deepak Publishing: Hampton, VA, 1989.
- (36) Anfossi, D.; Sandroni, D.; Viarengo, S. *J. Geophys. Res.* **1991**, *96*, 17349.
- (37) Sandroni, S.; Anfossi, D.; Viarengo, S. *J. Geophys. Res.* **1992**, *97*, 2535.
- (38) Marenco, A.; Gouget, H.; Nedelec, P.; Pages, J.-P.; Karcher, F. *J. Geophys. Res.* **1994**, *99*, 16617.
- (39) Anfossi, D.; Sandroni, S. *Atmos. Environ.* **1997**, *31*, 3481.
- (40) Noxon, J. F.; Norton, R. B.; Henderson, W. R. *Geophys. Res. Lett.* **1978**, *5*, 675.
- (41) Noxon, J. F.; Norton, R. B.; Marovich, E. *Geophys. Res. Lett.* **1980**, *7*, 125.
- (42) Platt, U.; Perner, D.; Winer, A. M.; Harris, G. W.; Pitts, J. N., Jr. *Geophys. Res. Lett.* **1980**, *7*, 89.
- (43) Atkinson, R.; Baulch, D. L.; Cox, R. A.; R. F. H., Jr.; Kerr, J. A.; Rossi, M. J.; Troe, J. *J. Phys. Chem. Ref. Data* **2000**, *29*, 167.
- (44) Nordmeyer, T.; Wang, W.; Ragains, M. K.; Finlayson-Pitts, B. J.; Spicer, C. W.; Plastringe, R. A. *Geophys. Res. Lett.* **1997**, *24*, 1615.
- (45) Wang, W.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **2000**, *27*, 947.
- (46) Wang, W.; Finlayson-Pitts, B. J. *J. Geophys. Res.* **2001**, *106*, 4939.
- (47) Tanaka, P. L.; Riemer, D. D.; Chang, S. H.; Yarwood, G.; McDonald-Buller, E. C.; Apel, E. C.; Orlando, J. J.; Silva, P. J.; Jimenez, J. L.; Canagaratna, M. R.; Neece, J. D.; Mullins, C. B.; Allen, D. T. *Atmos. Environ.* **2003**, *37*, 1393.
- (48) Finlayson-Pitts, B. J. *Nature* **1983**, *306*, 676.
- (49) *Simulation of Atmospheric Photochemistry in the Presence of Solid Airborne Aerosols*; Zetzsch, C., Ed.; VCH Publishers: New York, 1987; Vol. 104.
- (50) Lide, D. R. *Handbook of Chemistry and Physics*, 74th ed.; CRC Press: Boca Raton, FL, 1994.
- (51) Bottenheim, J. W.; Gallant, A. G.; Brice, K. A. *Geophys. Res. Lett.* **1986**, *13*, 113.
- (52) Oltmans, S. J.; Komhyr, W. D. *J. Geophys. Res.* **1986**, *91*, 5229.
- (53) Barrie, L. A.; Bottenheim, J. W.; Schnell, R. C.; Crutzen, P. J.; Rasmussen, R. A. *Nature* **1988**, *334*, 138.
- (54) Solberg, S.; Schmidbauer, N.; Semb, A.; Stordal, F.; Hov, O. *J. Atmos. Chem.* **1996**, *23*, 301.
- (55) Hopper, J. F.; Barrie, L. A.; Silis, A.; Hart, W.; Gallant, A. J.; Dryfout, H. *J. Geophys. Res.* **1998**, *103*, 1481.
- (56) Bottenheim, J. W.; Fuentes, J. D.; Tarasick, D. W.; Anlauf, K. G. *Atmos. Environ.* **2002**, *36*, 2535.
- (57) Bottenheim, J. W.; Barrie, L. A.; Atlas, E.; Heidt, L. E.; Niki, H.; Rasmussen, R. A.; Shepson, P. B. *J. Geophys. Res.* **1990**, *95*, 18555.
- (58) Lehrer, E.; Wagenbach, D.; Platt, U. *Tellus* **1997**, *49B*, 486.
- (59) *The Tropospheric Chemistry of Ozone in the Polar Regions*; Niki, H., Becker, K. H., Eds.; Springer-Verlag: Berlin, 1993; Vol. 17.
- (60) Cox, R. A.; Sheppard, D. W.; Stevens, M. P. *J. Photochem.* **1982**, *19*, 189.
- (61) LeBras, G.; Platt, U. *Geophys. Res. Lett.* **1995**, *22*, 599.
- (62) Tuckermann, M.; Ackermann, R.; Golz, C.; Lorenzen-Schmidt, H.; Senne, T.; Stutz, J.; Trost, B.; Unold, W.; Platt, U. *Tellus* **1997**, *49B*, 533.
- (63) Miller, H. L.; Weaver, A.; Sanders, R. W.; Arpag, K.; Solomon, S. *Tellus B* **1997**, *49*, 496.
- (64) DeMore, W. B.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, M. J.; Howard, C. J.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation No. 12; Jet Propulsion Laboratory, California Institute of Technology, 1997.
- (65) Sander, S. P.; Friedl, R. R.; DeMore, W. B.; Golden, D. M.; Kurylo, M. J.; Hampson, R. F.; Huie, R. E.; Moortgat, G. K.; Ravishankara, A. R.; Kolb, C. E.; Molina, M. J. Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling, Evaluation No. 13; Jet Propulsion Laboratory, California Institute of Technology, 2000.
- (66) Barnes, I.; Bastian, V.; Becker, K. H.; Overath, R.; Tong, Z. *Int. J. Chem. Kinet.* **1989**, *21*, 499.
- (67) Russell, J. J.; Seetula, J. A.; Gutman, D. *J. Am. Chem. Soc.* **1988**, *110*, 3092.
- (68) Spicer, C. W.; Chapman, E. G.; Finlayson-Pitts, B. J.; Plastringe, R. A.; Hubbe, J. M.; Fast, J. D.; Berkowitz, C. M. *Nature* **1998**, *394*, 353.
- (69) Keene, W. C.; Maben, J. R.; Pszenny, A. A. P.; Galloway, J. N. *Environ. Sci. Technol.* **1993**, *27*, 866.
- (70) Pszenny, A. A. P.; Keene, W. C.; Jacob, D. J.; Fan, S.; Maben, J. R.; Zetwo, M. P.; Springer-Young, M.; Galloway, J. N. *Geophys. Res. Lett.* **1993**, *20*, 699.
- (71) Finlayson-Pitts, B. J.; Ezell, M. J.; Pitts, J. N., Jr. *Nature* **1989**, *337*, 241.
- (72) Timonen, R. S.; Chu, L. T.; Leu, M.-T.; Keyser, L. F. *J. Phys. Chem.* **1994**, *98*, 9509.
- (73) Caloz, F.; Fenter, F. F.; Rossi, M. J. *J. Phys. Chem.* **1996b**, *100*, 7494.
- (74) Aguzzi, A.; Rossi, M. J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 4337.
- (75) Gebel, M. E.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **2001**, *105*, 5178.
- (76) Hoffman, R. C.; Gebel, M. E.; Fox, B. S.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2003**, *5*, 1780.
- (77) Knipping, E. M.; Dabdub, D. *Environ. Sci. Technol.* **2003**, *37*, 275.
- (78) Sturges, W. T.; Cota, G. F.; Buckley, P. T. *Nature* **1992**, *358*, 660.
- (79) Cota, G. F.; Sturges, W. T. *Mar. Chem.* **1997**, *56*, 181.
- (80) Carpenter, L. J.; Sturges, W. T.; Penkett, S. A.; Liss, P. S.; Aliche, B.; Hebestreit, K.; Platt, U. *J. Geophys. Res.* **1999**, *104*, 1679.
- (81) Carpenter, L. J.; Liss, P. S. *J. Geophys. Res.* **2000**, *105*, 20539.
- (82) Xu, D.; Francisco, J. S.; Huang, J.; Jackson, W. M. *J. Chem. Phys.* **2002**, *117*, 2578.
- (83) Bayes, K. D.; Toohey, D. W.; Friedl, R. R.; Sander, S. P. *J. Geophys. Res.* **2003**, *108*, art. no. 4095.
- (84) Gillotay, D.; Jenouvrier, A.; Coquart, B.; Merienne, M. F.; Simon, P. C. *Planet. Space Sci.* **1989**, *37*, 1127.
- (85) Moortgat, G.; Meller, R.; Schneider, W. In *The Tropospheric Chemistry of Ozone in the Polar Regions*; Niki, H., Becker, K. H., Eds.; Springer-Verlag: Berlin, 1993.
- (86) Finlayson-Pitts, B. J.; Livingston, F. E.; Berko, H. N. *Nature* **1990**, *343*, 622.
- (87) Platt, U.; Lehrer, E. Final Report for Project CEV5V-CT93-0318, Arctic Tropospheric Ozone Chemistry; European Committee on Air Pollution Report, 1996.
- (88) Wennberg, P. *Nature* **1999**, *397*, 299.

- (89) McConnell, J. C.; Henderson, G. S.; Barrie, L.; Bottenheim, J.; Niki, H.; Langford, C. H.; Templeton, E. M. *J. Nature* **1992**, *355*, 150.
- (90) Fan, S.-M.; Jacob, D. J. *Nature* **1992**, *359*, 522.
- (91) Tang, T.; McConnell, J. C. *Geophys. Res. Lett.* **1996**, *23*, 2633.
- (92) Rankin, A. M.; Auld, V.; Wolff, E. W. *Geophys. Res. Lett.* **2000**, *27*, 3469.
- (93) Foster, K. L.; Plastringer, R. L.; Bottenheim, J. W.; Shepson, P. B.; Finlayson-Pitts, B. J.; Spicer, C. W. *Science* **2002**, *291*, 471.
- (94) Impey, G. A.; Shepson, P. B.; Hastie, D. R.; Barrie, L. A. *J. Geophys. Res.* **1997**, *102*, 15999.
- (95) Impey, G. A.; Shepson, P. B.; Hastie, D. R.; Barrie, L. A.; Anlauf, K. G. *J. Geophys. Res.* **1997b**, *102*, 16005.
- (96) Impey, G. A.; Mihele, C. M.; Anlauf, K. G.; Barrie, L. A.; Hastie, D. R.; Shepson, P. B. *J. Atmos. Chem.* **1999**, *34*, 21.
- (97) Platt, U.; Hausmann, M. *Res. Chem. Intermed.* **1994**, *20*, 557.
- (98) Hausmann, M.; Platt, U. *J. Geophys. Res.* **1994**, *99*, 25.
- (99) Kreher, K.; Johnston, P. V.; Wood, S. W.; Nardi, B.; Platt, U. *Geophys. Res. Lett.* **1997**, *24*, 3021.
- (100) Hönniger, G.; Platt, U. *Atmos. Environ.* **2002**, *36*, 2481.
- (101) Richter, A.; Wittrock, F.; Eisinger, M.; Burrows, J. P. *Geophys. Res. Lett.* **1998**, *25*, 2683.
- (102) Chance, K. *Geophys. Res. Lett.* **1998**, *25*, 3335.
- (103) Wagner, T.; Platt, U. *Nature* **1998**, *395*, 486.
- (104) McElroy, C. T.; McLinden, C. A.; McConnell, J. C. *Nature* **1999**, *397*, 338.
- (105) Parrish, D. D.; Hahn, C. J.; Williams, E. J.; Norton, R. B.; Fehsenfeld, F. C.; Singh, H. B.; Shetter, J. D.; Gandrud, B. W.; Ridley, B. A. *J. Geophys. Res.* **1993**, *98*, 14995.
- (106) Jobsen, B. T.; Niki, H.; Yokouchi, Y.; Bottenheim, J.; Hopper, F.; Leaitch, R. *J. Geophys. Res.* **1994**, *99*, 25355.
- (107) Yokouchi, Y.; Akimoto, H.; Barrie, L. A.; Bottenheim, J. W.; Anlauf, K.; Jobsen, B. T. *J. Geophys. Res.* **1994**, *99*, 25379.
- (108) Ariya, P. A.; Jobson, B. T.; Sander, R.; Niki, H.; Harris, G. W.; Hopper, J. F.; Anlauf, K. G. *J. Geophys. Res.* **1998**, *103*, 13.
- (109) Ariya, P. A.; Niki, H.; Harris, G. W.; Anlauf, K. G.; Worthy, D. E. *J. Atmos. Environ.* **1999**, *33*, 931.
- (110) Ramacher, B.; Rudolph, J.; Koppmann, R. *J. Geophys. Res.* **1999**, *104*, 3633.
- (111) Boudries, H.; Bottenheim, J. W. *Geophys. Res. Lett.* **2000**, *27*, 517.
- (112) Perner, D.; Arnold, T.; Crowley, J.; Klüpfel, T.; Martinez, M.; Seuwen, R. *J. Atmos. Chem.* **1999**, *34*, 9.
- (113) Rankin, A. M.; Wolff, E. W.; Martin, S. *J. Geophys. Res.* **2002**, *107*, art. no. 4683.
- (114) Schroeder, W. H.; Anlauf, K. G.; Barrie, L. A.; Lu, J. Y.; Steffen, A.; Schneeberger, D. R.; Berg, T. *Nature* **1998**, *394*, 331.
- (115) Lindberg, S. E.; Brooks, S.; Lin, C.-J.; Scott, K.; Meyers, T.; Chambers, L.; Landis, M.; Stevens, R. *Water Air Soil Pollut.: Focus* **2001**, *1*, 295.
- (116) Lu, J. Y.; Schroeder, W. H.; Barrie, L. A.; Steffen, A.; Welch, H. E.; Martin, K.; Lockhart, L.; Hunt, R. V.; Boila, G.; Richter, A. *Geophys. Res. Lett.* **2001**, *28*, 3219.
- (117) Lindberg, S. E.; Brooks, S.; Lin, C.-J.; Scott, K. J.; Landis, M. S.; Stevens, R. K.; Goodsite, M.; Richter, A. *Environ. Sci. Technol.* **2002**, *36*, 1245.
- (118) Ebinghaus, R.; Kock, H. H.; Temme, C.; Einax, J. W.; Löwe, A. G.; Richter, A.; Burrows, J. P.; Schroeder, W. H. *Environ. Sci. Technol.* **2002**, *36*, 1238.
- (119) Ariya, P. A.; Khalizov, A.; Gidas, A. *J. Phys. Chem. A* **2002**, *106*, 7310.
- (120) Oum, K. W.; Lakin, M. J.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **1998**, *25*, 3923.
- (121) Taube, H. *J. Am. Chem. Soc.* **1942**, *64*, 2468.
- (122) Haag, W. R.; Hoigné, J. *Environ. Sci. Technol.* **1983**, *17*, 261.
- (123) von Gunten, U.; Hoigné, J. *Environ. Sci. Technol.* **1994**, *28*, 1234.
- (124) Disselkamp, R. S.; Chapman, E. G.; Barchet, W. R.; Colson, S. D.; Howd, C. D. *Geophys. Res. Lett.* **1999**, *26*, 2183.
- (125) Liu, Q.; Schurter, L. M.; Muller, C. E.; Aloisio, S.; Francisco, J. S.; Margerum, D. W. *Inorg. Chem.* **2001**, *40*, 4436.
- (126) Anastasio, C.; Mozurkewich, M. *J. Atmos. Chem.* **2002**, *41*, 135.
- (127) Koop, T.; Kapilashrami, A.; Molina, L. T.; Molina, M. J. *J. Geophys. Res.* **2000**, *105*, 26393.
- (128) Cho, H.; Shepson, P. B.; Barrie, L. A.; Cowin, J. P.; Zaveri, R. J. *Phys. Chem. B* **2002**, *106*, 11226.
- (129) Bottenheim, J. W.; Dibb, J. E.; Honrath, R. E.; Shepson, P. B. *Atmos. Environ.* **2002**, *36*, 2467.
- (130) Nagao, I.; Matsumoto, K.; Tanaka, H. *Geophys. Res. Lett.* **1999**, *26*, 3377.
- (131) Galbally, I.; Bentley, S. T.; Meyer, C. P. *Geophys. Res. Lett.* **2000**, *27*, 3841.
- (132) Dickerson, R. R.; Rhoads, K. P.; Carsey, T. P.; Oltmans, S. J.; Burrows, J. P.; Crutzen, P. J. *J. Geophys. Res.* **1999**, *104*, 21.
- (133) Hebestreit, K.; Stutz, J.; Rozen, D.; Matveiv, V.; Peleg, M.; Luria, M.; Platt, U. *Science* **1999**, *283*, 55.
- (134) Matveev, V.; Peleg, M.; Rosen, D.; Tov-Alper, D. S.; Hebestreit, K.; Stutz, J.; Blake, D.; Luria, M. *J. Geophys. Res.* **2001**, *106*, 10375.
- (135) Stutz, J.; Ackermann, R.; Fast, J. D.; Barrie, L. *Geophys. Res. Lett.* **2002**, *29*, 1380.
- (136) Livingston, F. E.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **1991**, *18*, 17.
- (137) Msibi, I. M.; Li, Y.; Shi, J. P.; Harrison, R. M. *J. Atmos. Chem.* **1994**, *18*, 291.
- (138) Leu, M.-T.; Timonen, R. S.; Keyser, L. F.; Yung, Y. L. *J. Phys. Chem.* **1995**, *99*, 13203.
- (139) Fenter, F. F.; Caloz, F.; Rossi, M. J. *J. Phys. Chem.* **1996**, *100*, 1008.
- (140) Koch, T. G.; van den Bergh, H.; Rossi, M. J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 2687.
- (141) Gershenson, M. Y.; Il'in, S.; Fedotov, N. G.; Gershenson, Y. M.; Aparina, E. V.; Zelenov, V. V. *J. Atmos. Chem.* **1999**, *34*, 119.
- (142) Alebic-Juretic, A.; Cvitas, T.; Klasinc, L. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 493.
- (143) Ivanov, A. V.; Gershenson, Y. M.; Gratpanche, F.; Devolder, P.; Sawerysyn, J.-P. *Ann. Geophys.* **1996**, *14*, 659.
- (144) Gershenson, Y. M.; Grigorieva, V. M.; Ivanov, A. V.; Remorov, R. G. *Faraday Discuss.* **1995**, *100*, 83.
- (145) Remorov, R. G.; Gershenson, Y. M.; Molina, L. T.; Molina, M. J. *J. Phys. Chem. A* **2002**, *106*, 4558.
- (146) Laux, J. M.; Hemminger, J. C.; Finlayson-Pitts, B. J. *Geophys. Res. Lett.* **1994**, *21*, 1623.
- (147) Fenter, F. F.; Caloz, F.; Rossi, M. J. *J. Phys. Chem.* **1994**, *98*, 9801.
- (148) Beichert, P.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1996**, *100*, 15218.
- (149) Davies, J. A.; Cox, R. A. *J. Phys. Chem. A* **1998**, *102*, 7631.
- (150) ten Brink, H. M. *J. Aerosol Sci.* **1998**, *29*, 57.
- (151) Ghosal, S.; Hemminger, J. C. *J. Phys. Chem. A* **1999**, *103*, 4777.
- (152) Ghosal, S.; Hemminger, J. C., submitted to *J. Phys. Chem. A* **2003**.
- (153) Zangmeister, C. D.; Pemberton, J. E. *J. Phys. Chem. A* **2001**, *105*, 3788.
- (154) Hoffman, R. C.; Kaleuati, M.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **2003**, *107*, 7818.
- (155) Laux, J. M.; Fister, T. F.; Finlayson-Pitts, B. J.; Hemminger, J. C. *J. Phys. Chem.* **1996**, *100*, 19891.
- (156) Allen, H. C.; Laux, J. M.; Vogt, R.; Finlayson-Pitts, B. J.; Hemminger, J. C. *J. Phys. Chem.* **1996**, *100*, 6371.
- (157) Vogt, R.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1995**, *99*, 17269.
- (158) Narayanswamy, L. K. *Trans. Faraday Soc.* **1935**, 1411.
- (159) Johnson, E. R. *The Radiation-Induced Decomposition of Inorganic Molecular Ions*; Gordon and Breach: New York, 1970.
- (160) Plumb, R. C.; Edwards, J. O. *J. Phys. Chem.* **1992**, *96*, 3245.
- (161) Lyman, S. V.; Hurst, J. K. *J. Am. Chem. Soc.* **1995**, *117*, 8867.
- (162) Lyman, S. V.; Hurst, J. K. *Inorg. Chem.* **1998**, *37*, 294.
- (163) Coddington, J. W.; Wherland, S.; Hurst, J. K. *Inorg. Chem.* **2001**, *40*, 528.
- (164) Tang, I. N.; Munkelwitz, H. R. *Atmos. Environ.* **1993**, *27A*, 467.
- (165) Tang, I. N.; Munkelwitz, H. R. *J. Geophys. Res.* **1994**, *99*, 18801.
- (166) Tang, I. N.; Munkelwitz, H. R. *J. Appl. Meteorol.* **1994**, *33*.
- (167) Vogt, R.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1994**, *98*, 3747.
- (168) Yoshitake, H. *Atmos. Environ.* **2000**, *34*, 2571.
- (169) Mouri, H.; Okada, K. *Geophys. Res. Lett.* **1993**, *20*, 49.
- (170) Posfai, M.; Anderson, J. R.; Buseck, P. R.; Sievering, H. J. *Geophys. Res.* **1995**, *100*, 23063.
- (171) Gard, E. E.; Gross, D. S.; Hughes, L. S.; Allen, J. O.; Morrical, B. D.; Fergenson, D. P.; Diemers, T.; Galli, M. E.; Johnson, R. J.; Cass, G. R.; Prather, K. A. *Science* **1998**, *279*, 1184.
- (172) Kerminen, V.-M.; Teinilä, K.; Hillamo, R.; Pakkanen, T. *J. Aerosol Sci.* **1998**, *29*, 929.
- (173) Zhuang, H.; Chan, C. K.; Fang, M.; Wexler, A. S. *Atmos. Environ.* **1999**, *33*.
- (174) Laskin, A.; Iedema, M. J.; Cowin, J. P. *Environ. Sci. Technol.* **2002**, *36*, 4948.
- (175) Harvie, C. E.; Weare, J. H.; Hardie, L. E.; Eugster, H. P. *Science* **1971**, *208*, 498.
- (176) Somorjai, G. A. *Introduction to Surface Chemistry and Catalysis*; John Wiley: New York, 1994.
- (177) Hucher, M.; Oberlin, A.; Hocart, R. *Bull. Soc. Fr. Mineral. Cristallogr.* **1967**, *90*, 320.
- (178) Lad, R. A. *Surf. Sci.* **1968**, *12*, 37.
- (179) Walter, H. U. *Z. Phys. Chem.* **1971**, *75*, 287.
- (180) Kaiho, M.; Chikazawa, M.; Kanazawa, T. *Nippon Kagaku Kashi* **1972**, *8*, 1386.
- (181) Barraclough, P. B.; Hall, P. G. *Surf. Sci.* **1974**, *46*, 393.
- (182) Smart, R. S. C.; Sheppard, N. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 707.
- (183) Estel, J.; Hoinkes, H.; Kaarmann, H.; Nahr, H.; Wilsch, H. *Surf. Sci.* **1976**, *54*, 393.
- (184) Kantorovich, L. N.; Shlyuger, A. L. *Sov. J. Chem. Phys.* **1984**, *1*, 2277.
- (185) Tepper, P.; Zink, J. C.; Schmelz, H.; Wassermann, B.; Reif, J.; Matthias, E. *J. Vac. Sci. Technol. B* **1989**, *7*, 1212.
- (186) Fölsch, S.; Henzler, M. *Surf. Sci.* **1991**, *247*, 269.
- (187) Fölsch, S.; Stock, A.; Henzler, M. *Surf. Sci.* **1992**, *264*, 65.
- (188) Picaud, S.; Girardet, C. *Chem. Phys. Lett.* **1993**, *209*, 340.

- (189) Wassermann, B.; Mirbt, S.; Reif, J.; Zink, J. C.; Matthias, S. *J. Chem. Phys.* **1993**, *98*, 10049.
- (190) Bruch, L. W.; Glebov, A.; Toennies, J. P.; Weiss, H. *J. Chem. Phys.* **1995**, *103*, 5109.
- (191) Dai, D. J.; Peters, S. J.; Ewing, G. E. *J. Phys. Chem.* **1995**, *99*, 10299.
- (192) Malaske, U.; Pfnür, H.; Bässler, M.; Weiss, M.; Umbach, E. *Phys. Rev. B* **1996**, *53*, 13115.
- (193) Shindo, H.; Ohashi, M.; Baba, K.; Seo, A. *Surf. Sci.* **1996**, *357/358*, 111.
- (194) Shindo, H.; Ohashi, M.; Tateishi, O.; Seo, A. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 1169.
- (195) Dai, Q.; Hu, J.; Salmeron, M. *J. Phys. Chem. B* **1997**, *101*, 1994.
- (196) Peters, S. J.; Ewing, G. E. *Langmuir* **1997**, *13*, 6345.
- (197) Peters, S. J.; Ewing, G. E. *J. Phys. Chem. B* **1997**, *101*, 10880.
- (198) Taylor, D. P.; Hess, W. P.; McCarthy, M. I. *J. Phys. Chem. B* **1997**, *101*, 7455.
- (199) Allouche, A. *J. Phys. Chem. B* **1998**, *102*, 10223.
- (200) Luna, M.; Rieutord, F.; Melman, N. A.; Dai, Q.; Salmeron, M. *J. Phys. Chem. A* **1998**, *102*, 6793.
- (201) Ahlswede, B.; Jug, K. *Surf. Sci.* **1999**, *439*, 86.
- (202) Stöckelmann, E.; Hentschke, R. *J. Chem. Phys.* **1999**, *110*, 12097.
- (203) Foster, M.; Ewing, G. E. *Surf. Sci.* **1999**, *428*, 102.
- (204) Engkvist, O.; Stone, A. J. *J. Chem. Phys.* **1999**, *110*, 12089.
- (205) Engkvist, O.; Stone, A. J. *J. Chem. Phys.* **2000**, *112*, 6827.
- (206) Foster, M. C.; Ewing, G. E. *J. Chem. Phys.* **2000**, *112*, 6817.
- (207) Pimentel, G. C.; McClellan, A. L. *The Hydrogen Bond*; W. H. Freeman: San Francisco, 1960.
- (208) Williams, R. T.; Wilson, R. M.; Liu, H. *Nucl. Instrum. Methods Phys. Res. B* **1992**, *65*, 473.
- (209) Shluger, A. L.; Wilson, R. M.; Williams, R. T. *Phys. Rev. B* **1994**, *49*, 4915.
- (210) Nakahara, S.; Langford, S. C.; Dickinson, J. T. *Tribol. Lett.* **1995**, *1*, 277.
- (211) Weis, D. D.; Ewing, G. E. *J. Geophys. Res.* **1999**, *104*, 21.
- (212) Quinlan, M. A.; Reihls, C. M.; Golden, D. M.; Tolbert, M. A. *J. Phys. Chem.* **1990**, *94*, 3255.
- (213) Rogaski, C. A.; Golden, D. M.; Williams, L. R. *Geophys. Res. Lett.* **1997**, *24*, 381.
- (214) Underwood, G. M.; Li, P.; Usher, C. R.; Grassian, V. H. *J. Phys. Chem. A* **1999**, *104*, 819.
- (215) Li, P.; Al-Abadleh, H. A.; Grassian, V. H. *J. Phys. Chem. A* **2002**, *106*, 1210.
- (216) Zangmeister, C. D.; Pemberton, J. E. *J. Phys. Chem. B* **1998**, *102*, 8950.
- (217) Sporleder, D.; Ewing, G. E. *J. Phys. Chem. A* **2001**, *105*, 1838.
- (218) Rowland, B.; Kadagathur, N. S.; Devlin, J. P. *J. Chem. Phys.* **1995**, *102*, 13.
- (219) Ghosal, S.; Shbeeb, A.; Hemminger, J. C. *Geophys. Res. Lett.* **2000**, *27*, 1879.
- (220) Zangmeister, C. D.; Turner, J. A.; Pemberton, J. E. *Geophys. Res. Lett.* **2001**, *28*, 995.
- (221) Tang, I. N. *J. Geophys. Res.* **1996**, *101*, 19245.
- (222) Langer, S.; Pemberton, R. S.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **1997**, *101*, 1277.
- (223) Tang, I. N.; Tridico, A. C.; Fung, K. H. *J. Geophys. Res.* **1997**, *102*, 23.
- (224) Gebel, M. E.; Finlayson-Pitts, B. J.; Ganske, J. S. *Geophys. Res. Lett.* **2000**, *27*, 887.
- (225) Cziczko, D. J.; Abbatt, J. P. D. *J. Phys. Chem. A* **2000**, *104*, 2038.
- (226) Chameides, W. L.; Stelson, A. W. *J. Geophys. Res.* **1992**, *97*, 20565.
- (227) Chameides, W. L.; Stelson, A. W. *Ber. Bunsen.-Ges. Phys. Chem.* **1992**, *96*, 461.
- (228) Vogt, R.; Crutzen, P. J.; Sander, R. *Nature* **1996**, *383*, 327.
- (229) Sander, R.; Vogt, R.; Harris, G. W.; Crutzen, P. J. *Tellus Ser. B* **1997**, *49*, 522.
- (230) Rudich, Y.; Talukdar, R. K.; Ravishankara, A. R. *J. Geophys. Res.* **1998**, *103*, 16.
- (231) Vogt, R.; Sander, R.; Glasow, R. V.; Crutzen, P. J. *J. Atmos. Chem.* **1999**, *32*, 375.
- (232) Sander, R.; Rudich, Y.; von Glasow, R.; Crutzen, P. J. *Geophys. Res. Lett.* **1999**, *26*, 2857.
- (233) Sander, R. *Surv. Geophys.* **1999**, *20*, 1.
- (234) Keene, W. C.; Sander, R.; Pszenny, A. A. P.; Vogt, R.; Crutzen, P. J.; Galloway, J. N. *J. Aerosol Sci.* **1998**, *29*, 339.
- (235) Hermann, H.; Ervens, B.; Jacobi, H.-W.; Wolke, R.; Nowacki, P.; R. *Z. J. Atmos. Chem.* **2000**, *36*, 231.
- (236) von Glasow, R.; Sander, R.; Bott, A.; Crutzen, P. J. *J. Geophys. Res.* **2002**, *107*, art. no. 4341.
- (237) von Glasow, R.; Sander, R.; Bott, A.; Crutzen, P. L. *J. Geophys. Res.* **2002**, *107*, art. no. 4323.
- (238) Keene, W. C.; Pszenny, A. A. P.; Maben, J. R.; Sander, R. *Geophys. Res. Lett.* **2002**, *29*, art. no. 1101.
- (239) Keene, W. C.; Savoie, D. L. *Geophys. Res. Lett.* **1998**, *25*, 2181.
- (240) Keene, W. C.; Savoie, D. L. *Geophys. Res. Lett.* **1999**, *26*, 1315.
- (241) Fridlind, A. M.; Jacobson, M. Z. *J. Geophys. Res.* **2000**, *105*, 17325.
- (242) von Glasow, R.; Sander, R. *Geophys. Res. Lett.* **2001**, *28*, 247.
- (243) Mozurkewich, M. *Geophys. Res. Lett.* **1997**, *24*, 3209.
- (244) Lushnikov, A. A.; Bhatt, J. S.; Ford, I. J. *J. Aerosol Sci.* **2003**, *34*, 1117.
- (245) Tang, I. N.; Munkelwitz, H. R.; Wang, N. *J. Colloid Interface Sci.* **1986**, *14*, 409.
- (246) Brimblecombe, P.; Clegg, S. L. *J. Atmos. Chem.* **1988**, *7*, 1.
- (247) Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem.* **1990**, *94*, 5369.
- (248) Carslaw, K. S.; Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem.* **1995**, *99*, 11557.
- (249) Massucci, M.; Clegg, S. L.; Brimblecombe, P. *J. Phys. Chem. A* **1999**, *103*, 4209.
- (250) Hoigné, J.; Bader, H.; Haag, W. R.; Staehelin, J. *Water Res.* **1985**, *19*, 993.
- (251) Abbatt, J. P. D.; Waschewsky, G. C. G. *J. Phys. Chem. A* **1998**, *102*, 3719.
- (252) Oum, K. W.; Lakin, M. J.; DeHaan, D. O.; Brauers, T.; Finlayson-Pitts, B. J. *Science* **1998**, *279*, 74.
- (253) Knipping, E. M.; Lakin, M. J.; Foster, K. L.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B.; Dabdub, D.; Finlayson-Pitts, B. J. *Science* **2000**, *288*, 301.
- (254) Huthwelker, T.; Peter, T.; Luo, B. P.; Clegg, S. L.; Carslaw, K. S.; Brimblecombe, P. *J. Atmos. Chem.* **1995**, *21*, 81.
- (255) Troy, R. C.; Margerum, D. W. *Inorg. Chem.* **1991**, *30*, 3538.
- (256) Gerritsen, C. M.; Margerum, D. W. *Inorg. Chem.* **1990**, *29*, 2758.
- (257) Gerritsen, C. M.; Gazda, M.; Margerum, D. W. *Inorg. Chem.* **1993**, *32*, 5740.
- (258) Hanson, D. R.; Ravishankara, A. *J. Phys. Chem.* **1993**, *97*, 2802.
- (259) Allan, A.; Oppliger, R.; Rossi, M. J. *J. Geophys. Res.* **1997**, *102*, 23529.
- (260) Mozurkewich, M. *J. Geophys. Res.* **1995**, *100*, 14199.
- (261) Michalowski, B. A.; Francisco, J. S.; Li, S.-M.; Barrie, L. A.; Bottenheim, J. W.; Shepson, P. B. *J. Geophys. Res.* **2000**, *105*.
- (262) Orlando, J. J.; Ramacher, B.; Tyndall, G. S. *Geophys. Res. Lett.* **2000**, *27*, 2633.
- (263) Abbatt, J. P. D. *Geophys. Res. Lett.* **1994**, *21*, 665.
- (264) Kirchner, U.; Benter, T.; Schindler, R. N. *Ber. Bunsen-Ges. Phys. Chem.* **1997**, *101*, 975.
- (265) Mochida, M.; Akimoto, H.; van den Bergh, H.; Rossi, M. J. *J. Phys. Chem. A* **1998**, *102*, 4819.
- (266) Chu, L.; Chu, L. T. *J. Phys. Chem. A* **1999**, *103*, 8640.
- (267) Fickert, S.; Adams, J. W.; Crowley, J. N. *J. Geophys. Res.* **1999**, *104*, 23719.
- (268) Mössinger, J. C.; Hynes, R. G.; Cox, R. A. *J. Geophys. Res.* **2002**, *107*, art. no. 4740.
- (269) Eigen, M.; Kustin, K. *J. Am. Chem. Soc.* **1962**, *84*, 1355.
- (270) Hanson, D. R.; Ravishankara, A. R. *Geophys. Res. Lett.* **1995**, *22*, 385.
- (271) Beckwith, R. C.; Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1996**, *35*, 995.
- (272) Wachsmuth, M.; Gäggeler, H. W.; von Glasow, R.; Ammann, M. *Atmos. Chem. Phys.* **2002**, *2*, 121.
- (273) Liu, Q.; Margerum, D. W. *Environ. Sci. Technol.* **2001**, *35*, 1127.
- (274) Wang, T. X.; Kelley, M. D.; Cooper, J. N.; Beckwith, R. C.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 5872.
- (275) Hu, J. H.; Shi, Q.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1995**, *99*, 8768.
- (276) Ammann, M.; Pöschl, U.; Rudich, Y. *Phys. Chem. Chem. Phys.* **2003**, *5*, 351.
- (277) Chaix, L.; Allan, A.; Rossi, M. J. *J. Phys. Chem. A* **2000**, *104*, 7268.
- (278) Adams, J. W.; Holmes, N. S.; Crowley, J. N. *Atmos. Chem. Phys.* **2002**, *2*, 79.
- (279) Huff, A. K.; Abbatt, J. P. D. *J. Phys. Chem. A* **2002**, *106*, 5279.
- (280) Behnke, W.; Elend, M.; Kruger, U.; Zetzsch, C. *J. Atmos. Chem.* **1999**, *34*, 87.
- (281) Berko, H. N.; McCaslin, P. C.; Finlayson-Pitts, B. J. *J. Phys. Chem.* **1991**, *95*, 6951.
- (282) Mochida, M.; Hirokawa, J.; Kajii, Y.; Akimoto, H. *Geophys. Res. Lett.* **1998**, *25*, 3927.
- (283) Allan, A.; Oppliger, R.; van den Bergh, H.; Rossi, M. J. *J. Phys. Chem.* **2000**, *214*, 1479.
- (284) Huff, A. K.; Abbatt, J. P. D. *J. Phys. Chem. A* **2000**, *104*, 7284.
- (285) Bartlett, W. P.; Margerum, D. W. *Environ. Sci. Technol.* **1999**, *33*, 3410.
- (286) Toom-Sauntry, D.; Barrie, L. A. *Atmos. Environ.* **2002**, *36*, 2683.
- (287) Jungwirth, P.; Tobias, D. *J. Phys. Chem. B* **2001**, *105*, 10468.
- (288) Jungwirth, P.; Tobias, D. *J. Phys. Chem. B* **2002**, *106*, 6361.
- (289) Wang, T. X.; Margerum, D. W. *Inorg. Chem.* **1994**, *33*, 1050.
- (290) Kumar, K.; Margerum, D. W. *Inorg. Chem.* **1987**, *26*, 2706.
- (291) Jayson, G. G.; Parsons, B. J.; Swallow, A. J. *J. Chem. Soc., Faraday Trans. 1* **1973**, *69*, 1597.
- (292) Yu, X.-Y.; Barker, J. R. *J. Phys. Chem. A* **2003**, *107*, 1313.
- (293) Buxton, G. V.; Bydder, M.; Salmon, G. A. *J. Chem. Soc., Faraday Trans.* **1998**, *94*, 653.
- (294) Alegre, M. L.; Geronés, M.; Rosso, J. A.; Bertolotti, S. G.; Braun, A. M.; Martíre, D. O.; Gonzalez, M. C. *J. Phys. Chem. A* **2000**, *104*, 3117.
- (295) Zehavi, D.; Rabani, J. *J. Phys. Chem.* **1972**, *76*, 312.
- (296) Merényi, G.; Lind, J. *J. Am. Chem. Soc.* **1994**, *116*, 7872.

- (297) Sutton, H. C.; Adams, G. E.; Boag, J. W.; Michael, B. D. In *Pulse Radiolysis*; Ebert, M., Keene, J. P., Swallow, A. J., Baxendale, J. H., Eds.; Academic Press: London, 1965.
- (298) Berresheim, H.; Andreae, M. O.; Ayers, G. P.; Gillett, R. W.; Merrill, J. T.; Davis, V. J.; Chameides, W. L. *J. Atmos. Chem.* **1990**, *10*, 341.
- (299) Andreae, T. W.; Andreae, M. O.; Bingemer, H. G.; Leck, C. *J. Geophys. Res.* **1993**, *98*, 23389.
- (300) Thornton, D. C.; Bandy, A. R. *J. Atmos. Chem.* **1993**, *17*, 1.
- (301) Watanabe, S.; Yamamoto, H.; Tsunogai, S. *J. Atmos. Chem.* **1995**, *22*, 271.
- (302) Spicer, C. W.; Kenny, D. V.; Chapman, E.; Busness, K. M.; Berkowitz, C. M. *J. Geophys. Res.* **1996**, *101*, 29137.
- (303) DeBruyn, W. J.; Bates, T. S.; Cainey, J. M.; Saltzman, E. S. *J. Geophys. Res.* **1998**, *103*, 16703.
- (304) Huie, R. E.; Neta, P. *Atmos. Environ.* **1987**, *21*, 1743.
- (305) Buxton, G. V.; McGowan, S.; Salmon, G. A.; Williams, J. E.; Wood, N. D. *Atmos. Environ.* **1996**, *30*, 2483.
- (306) Sander, R.; Lelieveld, J.; Crutzen, P. J. *J. Atmos. Chem.* **1995**, *20*, 89.
- (307) Fogelman, K. D.; Walker, D. M.; Margerum, D. W. *Inorg. Chem.* **1989**, *28*, 986.
- (308) Ayers, G. P.; Gillett, R. W.; Cainey, J. M.; Dick, A. L. *J. Atmos. Chem.* **1999**, *33*, 299.
- (309) Kim, K. J.; Hamill, W. H. *J. Phys. Chem.* **1976**, *80*, 2320.
- (310) Neta, P.; Huie, R. E. *J. Phys. Chem.* **1986**, *90*, 4644.
- (311) Exner, M.; Herrmann, H.; Zellner, R. *Ber. Bunsen-Ges. Phys. Chem.* **1992**, *96*, 470.
- (312) Huie, R. E. In *Progress and Problems in Atmospheric Chemistry*; Barker, J. R., Ed.; World Scientific: Singapore, 1995.
- (313) Zellner, R.; Herrmann, H. In *Spectroscopy in Environmental Science*; Clark, R. J. H., Hester, R. E., Eds.; John Wiley & Sons Ltd.: Chichester, 1995; Vol. 24.
- (314) Rudich, Y.; Talukdar, R. K.; Ravishankara, A. R.; Fox, R. W. *J. Geophys. Res.* **1996**, *101*, 21023.
- (315) Herrmann, H.; Zellner, R. In *N-Centered Radicals*; Alfassi, Z. B., Ed.; John Wiley & Sons Ltd.: Chichester, 1998.
- (316) Buxton, G. V.; Salmon, G. A.; Wang, J. *Phys. Chem. Chem. Phys.* **1999**, *1*, 3589.
- (317) Poskrebyshev, G. A.; Huie, R. E.; Neta, P. *J. Phys. Chem. A* **2003**, *107*, 1964.
- (318) Imamura, T.; Rudich, Y.; Talukdar, R. K.; Fox, R. W.; Ravishankara, A. R. *J. Phys. Chem. A* **1997**, *101*, 2316.
- (319) Rudich, Y.; Talukdar, R. K.; Imamura, T.; Fox, R. W.; Ravishankara, A. R. *Chem. Phys. Lett.* **1996**, *261*, 467.
- (320) Mozurkewich, M.; Calvert, J. G. *J. Geophys. Res.* **1988**, *93*, 889.
- (321) Fried, A.; Henry, B. E.; Calvert, J. G.; Mozurkewich, M. *J. Geophys. Res.* **1994**, *99*, 3517.
- (322) George, C.; Ponche, J. L.; Mirabel, P. *J. Phys. Chem.* **1994**, *98*, 8780.
- (323) Behnke, W.; George, C.; Scheer, V.; Zetzsch, C. *J. Geophys. Res.* **1997**, *102*, 3795.
- (324) Robinson, G. N.; Worsnop, D. R.; Jayne, J. T.; Kolb, C. E.; Davidovits, P. *J. Geophys. Res.* **1997**, *102*, 3583.
- (325) Wahner, A.; Mentel, T. F.; Sohn, M.; Stier, J. *J. Geophys. Res.* **1998**, *103*, 31103.
- (326) Schweitzer, F.; Mirabel, P.; George, C. *J. Phys. Chem. A* **1998**, *102*, 3942.
- (327) Mentel, T. F.; Sohn, M.; Wahner, A. *Phys. Chem. Chem. Phys.* **1999**, *1*, 5451.
- (328) De Haan, D. O.; Finlayson-Pitts, B. J. *J. Phys. Chem. A* **1997**, *101*, 9993.
- (329) Behnke, W.; Scheer, V.; Zetzsch, C. *J. Aerosol Sci.* **1994**, *S25*, 277.
- (330) Jayne, J. T.; Davidovits, P.; Worsnop, D. R.; Zahniser, M. S.; Kolb, C. E. *J. Phys. Chem.* **1990**, *94*, 6041.
- (331) Donaldson, D. J.; Guest, J. A.; Goh, M. C. *J. Phys. Chem.* **1995**, *99*, 9313.
- (332) Boniface, J.; Shi, Q.; Li, Y. Q.; Cheung, J. L.; Rattigan, O. V.; Davidovits, P.; Worsnop, D. R.; Jayne, J. T.; Kolb, C. E. *J. Phys. Chem. A* **2000**, *104*, 7502.
- (333) Clegg, S. M.; Abbatt, J. P. D. *J. Phys. Chem. A* **2001**, *105*, 6630.
- (334) Yang, H.; Wright, N. J.; Gagnon, A. M.; Gerber, R. B.; Finlayson-Pitts, B. J. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1832.
- (335) Hanson, D. R.; Ravishankara, A. R. *J. Phys. Chem.* **1994**, *98*, 5728.
- (336) George, C.; Behnke, W.; Scheer, V.; Zetzsch, C.; Magi, L.; Ponche, J. L.; Mirabel, P. *Geophys. Res. Lett.* **1995**, *22*, 1505.
- (337) Katrib, Y.; Deiber, G.; Schweitzer, F.; Mirabel, P.; George, C. *J. Aerosol Sci.* **2001**, *32*, 893.
- (338) Roeselová, M.; Jungwirth, P.; Tobias, D. J.; Gerber, R. B. *J. Phys. Chem. B* **2003**, in press.
- (339) Laskin, A.; Gaspar, D. J.; Wang, W.; Hunt, S. W.; Cowin, J. P.; Colson, S. D.; Finlayson-Pitts, B. J. *Science* **2003**, *301*, 340.
- (340) Hoffmann, M. R. *Atmos. Environ.* **1986**, *20*, 1145.
- (341) van den Bergh, A.; Dentener, F.; Lelieveld, J. *J. Geophys. Res.* **2000**, *105*, 11671.
- (342) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1992**, *96*, 8288.
- (343) Dang, L. X.; Garrett, B. C. *J. Chem. Phys.* **1993**, *99*, 2972.
- (344) Perera, L.; Berkowitz, M. L. *J. Chem. Phys.* **1993**, *99*, 4222.
- (345) Sremaniak, L. S.; Perera, L.; Berkowitz, M. L. *Chem. Phys. Lett.* **1994**, *218*, 377.
- (346) Stuart, S. J.; Berne, B. J. *J. Phys. Chem.* **1996**, *100*, 11934.
- (347) Stuart, S. J.; Berne, B. J. *J. Phys. Chem. A* **1999**, *103*, 10300.
- (348) Dang, L. X. *J. Chem. Phys.* **1999**, *110*, 1526.
- (349) Peshherbe, G. H.; Ladanyi, B. M.; Hynes, J. T. *Chem. Phys. Lett.* **2000**, *258*, 201.
- (350) Tobias, D. J.; Jungwirth, P.; Parrinello, M. *J. Chem. Phys.* **2001**, *114*, 7036.
- (351) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. A* **2002**, *106*, 379.
- (352) Dang, L. X.; Chang, T.-M. *J. Phys. Chem. B* **2002**, *106*, 235.
- (353) Dang, L. X. *J. Phys. Chem. B* **2002**, *106*, 10338.
- (354) Benjamin, I. *J. Chem. Phys.* **1991**, *95*, 3698.
- (355) Wilson, M. A.; Pohorille, A. *J. Chem. Phys.* **1991**, *95*, 6005.
- (356) Dang, L. X.; Smith, D. E. *J. Chem. Phys.* **1993**, *99*, 6950.
- (357) Jungwirth, P.; Tobias, D. J. *J. Phys. Chem. B* **2000**, *104*, 7702.
- (358) Wang, X.-B.; Nicholas, J. B.; Wang, L.-S. *J. Chem. Phys.* **2000**, *113*, 10837.
- (359) Wang, X.-B.; Yang, X.; Nicholas, J. B.; Wang, L.-S. *Science* **2001**, *294*, 1322.
- (360) Yang, X.; Wang, X.-B.; Wang, L.-S. *J. Phys. Chem. A* **2002**, *106*, 7607.
- (361) Jungwirth, P.; Curtis, J. E.; Tobias, D. J. *Chem. Phys. Lett.* **2003**, *367*, 704.
- (362) Strekowski, R. S.; Remorov, R.; George, C. *J. Phys. Chem. A* **2003**, *107*, 2497.
- (363) Salvador, P.; Curtis, J. E.; Tobias, D. J.; Jungwirth, P. *Phys. Chem. Chem. Phys.* **2003**, *5*, 3752.
- (364) Benter, T., personal communication, 1999.
- (365) Guimbaud, C.; Arens, F.; Gutzwiller, L.; Gaggeler, H. W.; Ammann, M. *Atmos. Chem. Phys.* **2002**, *2*, 249.
- (366) Ferraudi, G. *J. Phys. Chem.* **1993**, *97*, 2793.
- (367) Ruasse, M.-F.; Aubard, J.; Galland, B.; Adenier, A. *J. Phys. Chem.* **1986**, *90*, 4382.

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