Chapter 1

Introduction

Faraday was the first to propose that water ice was not an absolutely rigid solid as assumed by most scientists of his era.[1-4] However, over the last 150 years a much greater understanding of the chemical, physical, and structural nature of ice has evolved. Furthermore, ice phases are now known to be a viable chemical reaction medium that is relevant to both interstellar[5-10] and terrestrial environments.[11-29] For example, there are many investigations underway that explore ice chemistry relevant to outerspace (e.g., several studies have argued strongly for possible links between interstellar chemistry on ice matrices and the origin of life on earth[30-36]).

In 1985, the discovery of the Antarctic "Ozone Hole" during the polar springtime, spawned a renewed interest in the role of ice and other solid phases as potential catalytic sites for ozone depletion.[37] The formation of the ozone hole was partially attributed to variations in the solar cycle or to atmospheric dynamics. However, these forcing factors were insufficient to account for the dramatic and rapid loss of ozone in a very short timeframe. In addition, homogeneous, free radical catalytic cycles involving oxygen alone were also insufficient to explain the substantial ozone depletion, due to the negligible degree of photodissociation of O_2 in the polar stratosphere. As well, CFC photochemistry and the subsequent catalytic cycles involving various halogen species could not account for ozone reduction due to the height at which halogen radicals become substantial enough (~ 40 km). Even at an altitude of 40 km, concentrations of the gas-phase radicals would account for only 5 to 10% of the total observed depletion. However, a catalytic cycle involving the ClO radical and its dimer, Cl_2O_2, was proposed, that could lead to more significant ozone loss; however, this reaction mechanism alone was also shown to be insufficient.[38] Eventually, it was shown that heterogeneous chemical reactions on polar stratospheric clouds (PSCs) plays an essential role in polar ozone destruction.[39-41] This discovery renewed an interest in the chemical properties of ice phases and the role that they play in mediating chemical reactions in the atmosphere.

In the case of tropospheric chemistry, there is a growing interest in the photochemical conversion of nitrate, NO_3^-, in ice and in ice/snowpack environments. This ‘interest’ spawned from investigations showing that inorganic as well as organic compounds can undergo efficient light-induced chemical transformations in ice and the snowpack.[21,42,43] For example, field studies have shown that snowpacks are active environments for nitrate photolysis with the formation of NO_x (= NO + NO_2), which is then released to the overlying boundary layer.[18-20,23,27,44-48] Laboratory studies have also exemplified that NO_x is readily released during the irradiation of nitrate-doped snow/ice matrices.[49-52] These series of investigations strongly suggest the that postdepositional chemical and photochemical processes could alter ice core records of trace gases (i.e., CO, CO_2, HCHO, H_2O_2, CH_4, NO, NO_2, and HONO), which in turn could alter the interpretation of the chemical composition of past atmospheres.[53,54] In addition, nitrate photolysis provides a source of $^{\cdot}OH$ to interstitial air within a snowpack and the overlying boundary layer.[14,21,44,55] Hydroxyl radicals derived from nitrate photolysis could lead to the oxidation of organic matter contained in snowpacks producing aldehydes, such as HCHO and CH_3CHO.[14,21] Furthermore, nitrate photodecomposition produces NO_2^-, which in acidic snowpacks would allow for the release of HONO[56] to the boundary layer. Nitrous acid photolyzes readily in the gas phase to produce HO and NO.

In order to further our general understanding of photochemical reactions within water ice, the following experimental tasks were undertaken and are addressed in this thesis:

1. The quantum yields for nitrite formation, $\phi_{NO_2^-}$, over the range of 238 to 298 K for the photolysis of $NaNO_3$ in ice were determined in order to clarify whether low temperature values in a water ice medium were comparable to reported quantum yields of nitrite formation during the irradiation of nitrate in liquid water. The goal was to explore the role in a disordered phase of ice known as the quasi liquid layer (QLL), which was first identified by Faraday (*vide supra*).
2. The temperature-programmed photodesorption (TPP) of NO and NO_2 at a fixed heating ramp rate of 0.70 $^{o}C\ min^{-1}$ in real-time during the irradiation of $[NO_3^-]_o = 2\ \mu M$, 10 and 50 mM KNO_3 over the temperature range $-35 \leq T/^{o}C \leq 5$ was examined. This series of experiments were designed to provide new insight into the effect of the temperature of the ice undergoing photolysis with respect to the release of NO and NO_2 to the gas phase. Furthermore, these results provided qualitative information on the relative thickness of the QLL as a function of solute concentration and temperature and on the rate of NO and NO_2 release as a function of the change in the spatial dimensions of the QLL.
3. An additional aspect of the above experimental design was to investigate the temperature-programmed photodesorption (TPP) of NO_2 at variable heating ramp rates of 0.70, 0.30, and 0.10 $^{o}C\ min^{-1}$ in real-time during the irradiation of μM and mM $NaNO_3$ over the temperature range of $-40 \leq T/^{o}C \leq 5$. These experiments were designed to study the effect of solute concentration on surface premelting

and the related thickness of the QLL and the extent to which these temperature-dependent changes affect the flux of NO and NO_2 to the gas phase.

4. Additional temperature-programmed photodesorption (TPP) fluxes of NO and NO_2 were determined at heating ramp rates of 0.70 and 0.10 $^{o}C\ min^{-1}$ during the irradiation of μM and mM $NaNO_3$ over the temperature range of $-40 \leq T/^{o}C \leq 5$ in order to obtain a qualitative assessment of the variation in diffusivity of NO and NO_2 within a polycrystalline ice matrices.
5. The isotopic fractionation of ^{17}O- and ^{18}O during photolysis of nitrate in water and within ice at 313 nm was measured in order to assess the relative role of post-depositional photolysis and volatilization, which may alter the isotopic signatures of nitrate within snowpacks.
6. The nominal pH or equilibrium acidity of frozen dilute solutions of various electrolytes (> 98% ice) over the temperature range of $200 \leq T/K \leq 298$ was determined indirectly by probing the temperature dependence of the ^{19}F chemical shifts of 3-fluorobenzoic as an *in situ* chemical indicator. These measurements are used to determine the relative shifts in the nominal pH or acidity of the QLL due to relative partitioning and exclusion of various solutes from pure crystalline ice into the QLL domains during freezing. The relative shift in pH has a significant impact on the release of HONO to the gas phase during nitrate photolysis since the pK_a (25 ^{o}C at an ionic strength of 0.0) of HONO is ~ 3.2.

In the following chapters the research tasks identified above are addressed in order. In Chapter 3 we discuss the determination of the quantum yields for nitrite formation during nitrate photolysis and establish that nitrate photolysis occurs primarily in the QLL. In Chapters 4, 5, and 6, we give a detailed analysis of the effects of variable heating ramp rates and initial nitrate concentrations on the release of NO and NO_2 from the ice matrix during the photolysis of nitrate-doped ice. From these experiments we determine the following: 1) that nitrate photolysis is not only occurring in the QLL but in subeutectic solutions deeper within the ice matrix; 2) that NO_2 fluxes can be hindered by secondary photolysis and rapid hydrolysis; 3) that temperature transitions around -10 ^{o}C have a profounding effect on the relative fluxes of NO and NO_2 off of the ice surface; and 4) that NO and NO_2 flux profiles are substantially different indicating their relative degrees of interaction within the polycrystalline ice matrices. In Chapter 7, we show that the potential post-depositional photolysis of nitrate in ice does not alter the overall isotopic signature of ice or snowpacks. Lastly, the relative changes in the nominal pH of the QLL as a function of the nature and concentration of electrolytes are reported in Chapter 8. This is followed by a summary of observations and conclusions in Chapter 9.

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