Nitrate Photochemistry and Interrelated Chemical Phenomena in Ice

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Abstract

The detailed photochemistry of nitrate ions trapped within polycrystalline ice has been investigated. Using a variety of experimental techniques, the photolysis of NO_3^- within ice is shown to produce NO, HONO, NO_2^- and NO_2 as stable and metastable products. The gaseous products are released to the overlying gas phase. Implications of these results for chemical transformations in polar regions are discussed.

The isotopic composition of nitrate in polar ice cores exhibits mass-independent fractionation ($\Delta^{17}O \sim 25$ ‰). However, in this study it is shown that nitrate photolysis is a mass-dependent process and that nitrate can be a conservative tracer for past atmospheric conditions.

Photolysis of NO_3^- produces nitrite ions within ice and the rate of photolysis increases with increasing temperature. A linear Arrhenius temperature dependence for the measured quantum yield, $\phi_{NO_2^-}$, was found both above and below the normal melting point of water ice. These results indicate that nitrate photochemistry occurs primarily in the quasi-liquid layer (QLL), which is a disordered layer of ice that has chemical properties closer to water than solid crystalline ice.

The photochemical production of gas-phase NO and NO_2 from ice-phase nitrate was determined in real-time using laser-induced fluorescence, two-photon laser-induced fluorescence, and chemiluminescence. These results showed that NO and NO_2, which was produced at lower temperatures is released in much larger quantities at -7 ± 2 ^{o}C from subsurface regions of the QLL or at the ice/vapor interface. These results highlight the importance of the QLL and sub-eutectic sub-surface solutions at grain boundaries in polycrystalline ice. In addition, it was shown that the total amount of NO_2 that is photodesorbed scales nonlinearly with $[NO_3^-]_o$ or the heating rate. Evidence for extensive chemical and photochemical losses of NO_2 before release into the gas-phase is presented. In the case of NO, photo-induced desportion occured at ~ −20 °C, which suggests a preferential retention of NO_2 over NO in the nanoporous water channels of the QLL domains.

The impact of the specific nature of the chemical solutes in water on the nominal pH of the QLL was explored using the temperature dependence of ^{19}F-NMR chemical shifts of 3-fluorobenzoic acid. The ^{19}F-NMR measurements during the freezing of NaCl, $NaNO_2$ and KNO_3 solutions indicated that the QLL domains within the polycrystalline ice were shifted to higher pH values, while the freezing of NH_4OH or Na_2SO_4 solutions produced QLL domains that showed a drop in pH (i.e., protons were released from the ice-phase to the QLL). These results help explain the release of HONO which is formed by protonation of NO_2^- within the QLL domains and are relevant to the observed release of nitrous acid to the atmospheric boundary layer in the Arctic and Antarctic.

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