Production of gas-phase nitrogen dioxide and nitrous, peroxynitrous and peroxynitric acid from photolysis of nitrate in ice

Otman Abida[1,2] and Hans D. Osthoff [1,*]

[1] University of Calgary, Calgary, AB, Canada
[2] Now at: State University of New York, Albany, NY, USA
* Corresponding author: hosthoff@ucalgary.ca

Photochemically induced emissions from the surfaces of snow and ice crystals are known to alter the composition of the troposphere. In particular, photolysis of the nitrate anion (NO_3^-) in snow and ice has been shown to yield NO_x (= NO+NO_2) and nitrous acid (HONO) in the gas-phase. Subsequent photolysis reactions involving HONO and NO_x can alter the oxidative balance of the atmosphere and increase the rate of formation of the greenhouse gas ozone, significantly affecting the composition of the polar boundary layer.

In this work, we examined the nitrogen oxides evolved from irradiated frozen solutions containing nitrate as a function of acidity[1,2] and in the presence of selected organic compounds.[3] Gas-phase products were monitored by cavity ring-down spectroscopy, NO-O_3 chemiluminescence, and chemical ionization mass spectrometry. The photochemical release of NO_2 from irradiated frozen solutions containing NO_3^- was promoted by acidic conditions similar to those found in moderately polluted environments. In unbuffered ice or under basic conditions, the main gas-phase nitrogen oxide observed was NO_2 (>95% relative to odd nitrogen, or NO_y). The yield of gas-phase NO_2 increased with decreasing pH (measured prior to freezing) in the range from 9.5 to 4.5. Acid-promoted production of NO_2 is rationalized by formation of peroxynitrous (HOONO), which was observed alongside peroxynitric acid (HO_2NO_2) in the gas-phase. Under very acidic conditions (pH < 4.5), production of additional nitrogen oxides was in the form of species belonging to NO_z, i.e., nitrous (HONO) and nitric acid ($HONO_2$). The presence of formate, methanesulfonate, toluene or phenol suppressed production of gas-phase nitrogen oxides. In contrast, para-halogenated phenols (in the order of Cl>Br>F) promoted the conversion of NO_3^- to gas-phase nitrogen oxides, rationalized by acidification of the ice surface. Acid-promoted conversion of condensed-phase NO_3^- to gas-phase NO_2 is currently not considered in atmospheric chemistry and aerosol models but may be a significant but overlooked aerosol nitrate volatilization pathway and source of OH radicals in the troposphere.

References

(1) Abida, O.; Mielke, L.H.; Osthoff, H.D. *Chem. Phys. Lett*. **2011**, 511, 187-192.
(2) Abida, O.; Osthoff, H.D. *Geophys. Res. Lett*. **2011**, 38, L16808.
(3) Abida, O.; Osthoff, H.D. *J. Phys. Chem. A* **2012**, article ASAP, doi: 10.1021/jp210249t.