Protonated Nitrosamide and its Potential Role in the Release of HONO from Snow and Ice in the Dark

The effects of photolysis on frozen, thin films of water-ice containing nitrogen dioxide (as its dimer dinitrogen tetroxide) have been investigated using a combination of FT-Reflection Absorption IR spectroscopy (RAIRS) and a Hiden mass spectrometer. The observed release of HONO observed using the crucial combination of these techniques was ascribed to a mechanism in which nitrosonium nitrate ($NO^+NO_3^-$) is formed. Subsequent solvation of the cation leads to the nitroacidium ion, H_2ONO^+, *i.e.* protonated nitrous acid. How are such results relevant to studies of chemistry that take place in Earth's Cryosphere (Polar Stratospheric Clouds or PSCs, cirrus clouds, frost flowers, freezing fogs, snowflakes, permafrost and hailstones)?

The global impact of chemistry and physics that occurs in the polar troposphere is only just being raised due to recent advances in satellite observation, field measurement and climate change concerns. Two phenomena of chemical origin noted for both the Arctic and Antarctic regions, have been identified as being of particular importance: (i) halogen-promoted, ozone and mercury depletion events accelerated by the effects of cooling and freezing; (ii) photochemical release mechanisms of NOx and oxygenated volatile organic compounds (OVOC) from snow/ice surfaces.

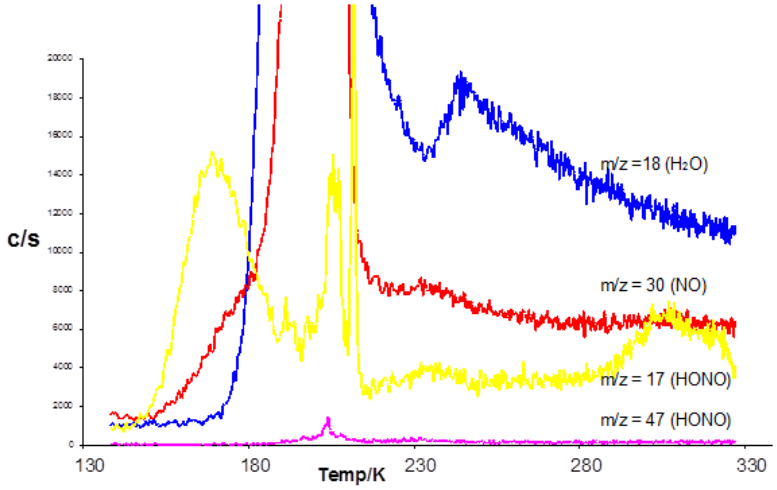
The possibility that a range of "cryo-reactions" (chemistry in/on ice) could play important roles in atmospheric chemistry began to be explored in the 1980s. Subsequently a variety of cold/frozen materials dispersed throughout the "Earth System" such as snowpack, have been put forward as potential surfaces for heterogeneous chemistry to take place on. Perhaps the most famous example is provided by the so-called Antarctic ozone "hole" driven by PSCs.

Monitoring studies at Summit, Greenland, performed in the late 1990s have shown significant enhancement in the concentrations of several trace gases in the snowpack pore (also known as firn) air relative to the atmosphere. Analytical measurements have been reported for organic compounds such as formaldehyde, alkenes, halocarbons, and alkyl nitrates that are typically a factor of 2-10 higher in concentration within the firn air than in the ambient air 1-10 m above the snow. Firn air also contains elevated levels of nitrogen dioxide and mechanisms involving nitrate ion photolysis are thought likely to be important. And that is where the study described at the start of this article is relevant. In the overall process, NO^+ produced on the ice surface by photolysis of the nitrogen dioxide dimer was shown to become solvated with water and is then hydrolysed to HONO, which is efficiently released to the gas-phase. In contrast the nitrate component is retained on the surface as Nitric Acid Trihydrate.

The mechanism proposed in the paper goes some way to explain why the field measurement of HONO at different snow-pack polar sites is often contradictory…..at some locations nothing at all is detected. But if organic compounds (like humic acids or formaldehyde) are present, the solvated NO^+ may, in preference to becoming solvated, act as a nitrosating agent leading to little or no HONO release.

HIDEN ANALYTICAL LTD
420 Europa Boulevard, Warrington, WA5 7UN, England
t: +44 (0) 1925 445225 f: +44 (0) 1925 416518
e: info@hiden.co.uk **w: www.HidenAnalytical.com**

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Thermal Desorption Profiles obtained on the Hiden Mass Spectrometer of NO_y and H_2O subsequent to photolysis of D_{2h}-N_2O_4 in water ice. The mass spectral signal m/z=17 has been corrected for the contribution from water using the water fragmentation pattern 74% m/z=18, 17% m/z=17.

Project Summary by:
John Sodeau
Department of Chemistry
University College Cork
College Road
Cork, Ireland

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For more information on Cryochemistry, a recent review has been published:
"The effect of freezing on reactions with environmental impact". R. O'Concubhair and JR Sodeau. Accounts of Chemical Research. DOI 10.1021/ar400114e. (2013)

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