Geophysical Research Abstracts
Vol. 16, EGU2014-2174, 2014
EGU General Assembly 2014

Photo-induced formation of nitrous acid (HONO) on protein surfaces

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The study of nitrous acid (HONO) is of great interest, as the photolysis of HONO leads to the OH radical, which is the most important oxidant in the troposphere. HONO is directly emitted by combustion of fossil fuel and from soil biogenic nitrite (Su et al., 2011), and can also be formed by gas phase reactions of NO and OH and heterogeneous reactions of NO_2. Previous atmospheric measurements have shown unexpectedly high HONO concentrations during daytime. Measured mixing ratios were about one order of magnitude higher than model simulations (Kleffmann et al. 2005, Vogel et al. 2003). The additional daytime source of HONO might be attributed to the photolysis of adsorbed nitric acid or heterogeneous photochemistry of NO_2 on organic substrates, such as humic acids or polyphenolic compounds (Stemmler et al., 2006), or indirectly through nitration of phenols and subsequent photolysis of nitrophenols (Sosedova et al., 2011, Bejan et al., 2006).

An important reactive surface for the heterogeneous formation of HONO could involve proteins, which are ubiquitous in the environment. They are part of coarse biological aerosol particles like pollen grains, fine particles (fragments of pollen, microorganism, plant debris) and dissolved in rainwater, soil and road dust (Miguel et al. 1999).

In this project a thin film of bovine serum albumin (BSA), a model protein with 67 kDa and 21 tyrosine residues per molecule, is irradiated and exposed to nitrogen dioxide in humidified nitrogen. The formation of HONO is measured with long path absorption photometry (LOPAP). The generated HONO is in the range of 100 to 1100 ppt depending on light intensity, NO_2 concentration and film thickness. Light induced HONO formation on protein surfaces is stable over the 20-hours experiment of irradiation and exposure. On the other hand, light activated proteins reacting with NO_2 form nitrated proteins, as detected by liquid chromatography (LC-DAD). Our experiments on tetranitromethane (TNM) nitrated ovalbumin (OVA) also show a clear light induced decomposition of nitrated proteins with HONO identified as one of the major products. This suggests a shortening of the lifetime of nitrated proteins during daytime. Our results indicate an important role of light to the fate of proteins, and through HONO, important OH precursors. Proteins and nitrated proteins on aerosol and ground surfaces may therefore influence the atmospheric chemistry and contribute to the oxidation capacity.

References

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