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Photoenhanced nitrous acid formation upon NO2 uptake on tannic and gentisic acid films

Yulia Sosedova (1,2), Aurélie Rouvière (1), and Markus Ammann (1)

(1) Paul Scherrer Institute, 5232 Villigen PSI, Switzerland (yulia.sosedova@psi.ch / +4156 310 4435), (2) University of Bern, Freistrasse 3, 3012 Bern, Switzerland

The heterogeneous chemistry of nitrogen dioxide (NO2) is a potential source of nitrous acid (HONO). Hydroxy and methoxy substituted phenols may play a significant role in the aqueous-phase chemistry occurring on the ground or within aerosol particles in air masses affected by biomass burning. It is well established that electron transfer between phenols and NO2 in alkaline aqueous solutions is fast and could be a source of nitrite in the aqueous phase and HONO in the gas phase. However its kinetics is very slow under atmospheric conditions. The role of phenolic species as electron donors has also been suspected to be responsible for the photoenhanced transformation of NO2 to HONO over humic acids [1]. In this study we used tannic (TA) and gentisic (GA) as another proxy for atmospheric phenolic compounds. TA was shown to easily decompose under near UV light irradiation [2] resulting in oxidized products that might change the hygroscopic properties of the original material or have some potential photosensitizing effect. It was interesting to check the hypothesis that the presence of such products could lead to photoenhanced HONO formation upon NO2 uptake to aqueous surfaces containing TA.

Experiments were performed in a horizontal coated wall flow tube (40 cm × 5.9 cm i.d.) circularly surrounded by 7 fluorescence lamps (UV: 300-420 nm, or visible: 400-750 nm), in an air cooled lamp housing. The inner surface coating was containing ∼0.5 mg/cm-2 of either TA or GA, and was operated under RH 20-80%, 21-23 °C and ambient pressure. Concentration of HONO in the gas phase at the flow tube exit was measured with a LOPAP (Long Path Absorption Spectrometer).

The uptake coefficient () leading to NO2 to HONO conversion above aqueous films containing GA or TA in the dark was in the range 4×10-7 – 2×10-6. The photochemically enhanced HONO production was demonstrated by UV irradiation of the GA or TA coatings being in contact with gaseous NO2. In this case was 3-10 times higher depending on the light intensity. HONO formation under illuminated conditions increased linearly with increasing gas-phase NO2 concentration, [NO2]g, from 0 to 30 ppb and approached saturation for [NO2]g above 100 ppb. This behavior could be explained by adsorption saturation preceding the photochemical reaction or by a limiting production of a photochemical intermediate.

As GA does not absorb light at wavelengths above 400 nm, no enhancement of HONO formation was monitored under irradiation of GA coatings with visible light. In the presence of 1% of a photosensitizer (methylene blue), HONO production was 25 - 75 % higher than in the dark. On the contrary, films containing TA converted NO2 to HONO under visible light irradiation twice more efficiently than in the dark even without photosensitizer addition. It will be discussed if a TA or GA films aging could lead to the enhancement of NO2 to HONO transformation under the light.

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[2] Cowen, S.; Al-Abadleh, H. A. Physical Chemistry Chemical Physics 2009, 11, 7838.