

Interaction of HONO with mineral oxides: uptake and products

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HONO is an important atmospheric species representing a significant daytime source (via photolysis) of OH radical, the major atmospheric oxidant. The mechanisms of HONO formation in the atmosphere are still not completely understood. One current issue in the chemistry of HONO is that the models fail to reproduce unexpectedly high daytime concentrations of HONO observed in field studies, indicating the existence of new, yet unknown, daytime sources of HONO. Heterogeneous processes, including those on humid surfaces, being thought to be the major source of HONO in the atmosphere, have been intensively studied in the laboratory and several mechanisms of HONO formation on aerosol and ground surface have been proposed. Conversely, the atmospheric aerosol can also act as a sink for gaseous HONO, probably, hardly competitive with HONO photolysis during the day, but potentially important during nighttime. The information on the nature, rate and products of HONO interaction with solid surfaces of atmospheric interest is very scarce and seems to be limited to a few studies carried out with ice and soot surface.

The present work reports the results of an experimental study of the kinetics and products of the heterogeneous reaction of HONO with different constituents of mineral aerosol (TiO_2 , Al_2O_3 , Fe_2O_3) and Arizona Test Dust (ATD). The interaction of HONO with solid films of the mineral oxides was studied for the first time under dark and UV irradiation conditions using a low pressure flow reactor (1 – 10 Torr) combined with a modulated molecular beam mass spectrometer for monitoring of the gaseous species involved. The reactive uptake of HONO was studied as a function of HONO concentration, relative humidity ($\text{RH} = 3 \times 10^{-4} - 60\%$), temperature ($T = 275 - 320\text{ K}$) and irradiance intensity ($J_{\text{NO}_2} = 0.002 - 0.012\text{ s}^{-1}$). A deactivation of mineral oxide surface upon exposure to HONO was observed. The measured initial uptake coefficients of HONO were found to be independent of the HONO concentration and temperature. The effect of UV irradiation on the reactivity of HONO (increase of uptake) was observed for TiO_2 and Al_2O_3 surfaces only and was negligible for ATD and Fe_2O_3 . The relative humidity (RH) was found to have a strong impact on the uptake coefficient: $\gamma_0 \sim (\text{RH})^{-\alpha}$, with $\alpha \approx 0.65$, for all samples under dark conditions and $\alpha \approx 0.3$ and 0.45 on irradiated TiO_2 and Al_2O_3 films, respectively.

NO_2 and NO were observed as products of the HONO reaction with all mineral oxides studied with the sum of their yields corresponding to nearly 100% of the nitrogen mass balance. The yields of NO and NO_2 were found to be around 40 and 60 %, respectively, independent of relative humidity, temperature, concentration of HONO and irradiance intensity on all surfaces except TiO_2 under irradiation where similar (~ 50%) yields of NO and NO_2 were observed.