Measurements of Nitrous Acid (HONO), Hydroxyl (OH), Nitric Oxide (NO), Hydroperoxyl (HO_2), and Nitrogen Dioxide (NO_2) in the upper Troposphere: is Peroyxnitrous Acid (HOONO) a missing source of HONO?

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Abstract

Discrepancies between expected and observed NO-NO_2 ratios in the upper troposphere suggest the presence of an unknown NO_X reservoir. We report on airborne remote sensing limb observations from the mini-DOAS instrument on board the HALO (High Altitude Long Range) aircraft during the CAFÉ-Africa (Chemistry of the Atmosphere Field Experiment) campaign in 2018. Nitrous acid (HONO) slant column densities in limb scattered sunlight in the ultraviolet wavelength range retrieved by DOAS (Differential Optical Absorption Spectroscopy) are converted to volume mixing ratios using the O_3 / O_4 scaling method. Over the tropical Atlantic Ocean, in the cold upper troposphere, HONO is found in excess of what may be expected from known gas phase formation mechanisms or is predicted by the ECHAM/MESSy Atmospheric Chemistry (EMAC) model. At these altitudes (10-15 km), heterogeneous sources of the excess HONO are inefficient and thus unlikely. Therefore, we investigate the possibility of a gas phase HONO source, namely the oxidation of peroxynitrous acid (HOONO) formed in the reactions NO + HO_2 and OH + NO_2. Since there are no reported atmospheric measurements of HOONO, we use complementary, simultaneous in situ measurements of OH, NO, HO_2, NO_2, O_3 and photolysis frequencies from onboard HALO to make steady state arguments and quantify reaction rate coefficients for both formation pathways and destruction of HOONO by O_3, OH, and NO. According to DFT calculations, the reaction between HOONO and NO to produce HONO and NO_2 is barrierless. The associated reaction rate constants are currently under investigation.

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