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Rate Constants for the Reactions of OH with CO, NO and NO_2, and of HO_2 with NO_2 in the Presence of Water Vapour at Lower-Tropospheric Conditions

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Recent studies have shown that the chemistry of gaseous nitrous acid (HONO) in the lower troposphere is not fully understood. Aside from heterogenous reactions, the daytime HONO formation in the gas-phase is not well understood (Li et al., Science, 2014). For a better understanding of HONO in the gas-phase, we have reinvestigated the reaction rate constants of important tropospheric reactions of the HO_x radical family (OH and HO_2) with nitrogen oxides at realistic conditions of the lower troposphere (at ambient temperature/pressure and in humid air). In this study we apply a direct pump and probe technique with high accuracy, using small radical concentrations to avoid secondary chemistry.
Pulsed laser photolysis/laser-induced fluorescence (LP/LIF) was used to investigate the reaction rate constants of OH with CO, NO, NO_2, and HO_2 with NO_2 in synthetic air at different water vapor concentrations (up to 5×10^{17} molecules cm^{-3}). Photolysis of ozone in the presence of gaseous water was the source of OH. The reactions took place in a flow-tube at room temperature and atmospheric pressure. The chemical decay of the radicals was monitored by laser-induced fluorescence detection in a low-pressure cell, which sampled air continuously from the end of the flow-tube. Knowing the reactant concentrations subsequently allowed to calculate the bimolecular reaction rate constants at 1 atm from the pseudo-first-order decays. In order to observe HO_2 reactions, OH was converted into HO_2 with an excess of CO in the flow-tube. The newly measured rate constants for OH with CO, NO and NO_2 agree very well with current recommendations by NASA/JPL and IUPAC and have an improved accuracy (uncertainty < 5%). These rate coefficients are independent of the presence of water vapour. The measured rate constant of HO_2 with NO_2 was found to depend significantly on the water-vapour concentration (probably due to formation of HO_2*H_2O complexes) and to exceed current recommendations by NASA/JPL and IUPAC by up to a factor of 2.6. Our experiments confirm the existence of a water vapour influence similarly to the one reported previously by Sander and Peterson (1984) for a lower total pressure (470 hPa).