

Rate coefficient for the OH radical reaction with HONO₂ under UT/LS conditions

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Abstract:

Nitric acid (HONO₂) is one of the most reactive nitrogen-containing species in our atmosphere and its oxidation chemistry plays an important role in controlling the O₃ budget in the upper troposphere/lower stratosphere (UT/LS). The O₃ budget in the UT/LS is largely controlled by the cycling of HO_x (OH + HO₂) and NO_x (NO + NO₂). The HONO₂ reaction with OH is a net HO_x radical sink and drives NO_{x/y} partitioning chemistry by yielding NO₃ radicals; therefore, understanding the rate coefficient of the OH + HONO₂ reaction is critical for accurate prediction of the O₃, HO_x, and NO_x budgets in the UT/LS. Previous studies have observed both negative temperature-dependent and pressure-dependent kinetics below, which results from the formation of a pre-reactive complex between OH and HONO₂ (~6 kcal mol⁻¹). Currently, the JPL recommended uncertainty in $k_{\text{OH}+\text{HONO}_2}$ is 20% ($\pm 1\sigma$) at STP, but under UT/LS conditions (low T and p), the uncertainty could increase to as much as $\pm 50\%$, which translates to 10 - 20% in model predictions of NO_x/NO_y partitioning. Previous groups have measured the concentration of HONO₂ after or before the reaction cell but never *in-situ*, which could lead to greater uncertainties in the overall determination of the rate coefficient from heterogeneous uptake of the low volatility HONO₂. Here, we present experimental results into the matrix of the temperature and pressure dependence of the OH + HONO₂ rate coefficient. Specifically, our results represent the first determination of $k_{\text{OH}+\text{HONO}_2}$ using *in-situ* [HONO₂] measurements coupled to a Light Induced Fluorescence (LIF) technique to probe OH radicals. Results and importance to UT/LS chemistry are discussed.