

Cavity Ringdown Spectroscopic Studies of Nitric Acid and Peroxynitrous Acid Yields in the HO₂ + NO Reaction

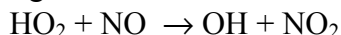
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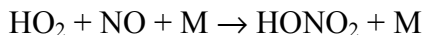
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One of the key reactions influencing HO_x and NO_x chemistry throughout the atmosphere is



which converts the hydroperoxyl radical HO₂ to the more reactive hydroxyl radical OH, as well as converting NO to photolabile NO₂. This reaction influences ozone concentrations in the stratosphere and troposphere, as well as the oxidation of volatile organic compounds in the troposphere. HO_x and NO_x radicals cycle through this reaction many times in the atmosphere; thus, even a small yield of a chain termination channel could have significant effects on trace free radical composition. In a series of important papers, Butkovskaya, LeBras and co-workers have found that this reaction can produce nitric acid[1-3]



with small but atmospherically significant yields (on the order of 1%). Their experiment employed a turbulent flow reactor coupled with sensitive Chem-Ionization Mass Spectrometer (CIMS) detection. The reported yields are sufficient to have significant effects on model predictions of ozone, nitric acid and NO_x throughout the atmosphere.[4]

We have re-examined this reaction in a flow-cell Pulsed Laser Photolysis experiment using Mid-Infrared Cavity Ringdown Spectroscopy (CRDS) to detect the ν_1 spectra of possible HONO₂ and HOONO products formed on short (< 1ms timescales). As in the Butkovskaya experiments [2,3], detectable concentrations of products are generated using chemical amplification with added CO, which also suppresses secondary OH. Wall reactions and diffusion effects are minimal due to the short interrogation times following pulsed initiation. Amplification is measured through detection of CO₂ products, and other secondary reactions, in particular formation of nitric acid from the reaction of OH + NO₂, are determined by detection of secondary products. Absolute product yields are determined from known band intensities with high sensitivity.

References

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3. Butkovskaya, N.; Rayez, M. T.; Rayez, J. C.; Kukui, A.; Le Bras, G. *J. Phys. Chem. A* **2009**, 113, 11327-11342.
4. Cariolle, D.; Evans, M. J.; Chipperfield, M. P.; Butkovskaya, N.; Kukui, A.; Le Bras, G., *Atmos. Chem. Phys.* **2008**, 8, 4061-4068.