INFRARED ACTION SPECTROSCOPY AND STABILITY OF THE OH-HONO$_2$ REACTION INTERMEDIATE

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The reaction of nitric acid (HONO$_2$) with the hydroxyl radical (OH) is of significant atmospheric interest. Kinetic studies have revealed unusual behavior including a negative temperature dependence, pressure dependence, and an overall reaction rate strongly affected by isotopic substitution.[a] This suggests that the reaction occurs through an intermediate, theoretically predicted to be a hydrogen-bonded OH-HONO$_2$ complex in a six-membered ring-like configuration.[b] In this study, OH-HONO$_2$ is produced in the gas phase by the association of photolytically generated OH radicals with HONO$_2$ in the collisional region of a supersonic expansion. Infrared action spectroscopy is used to identify the fundamental OH radical stretch (ν_1) and OH nitric acid stretch (ν_2) of the complex. The rotationally structured ν_1 band[c] is centered at 3216 cm^{-1}, while the extensively broadened ν_2 band is centered at 3260 cm^{-1}, both shifted from their respective monomer. Following infrared excitation, the OH fragments resulting from vibrational predissociation are detected by laser-induced fluorescence on the OH $A\,^2\Sigma^+$-$X\,^2\Pi$ (1,0) transition. The highest observed OH (v=0) product channels, J=17/2, Ω=1/2 for the OH radical stretch and J=15/2, Ω=1/2 for the OH nitric acid stretch, lead to determination of an upper limit for the binding energy of OH-HONO$_2$, $D_0 \leq 6.2$ kcal mol^{-1}, which is consistent with *ab initio* predictions.[b]

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[a] S. S. Brown, R. K. Talukdar, and A. R. Ravishankara, J. Phys. Chem. A 105, 9 (2001).

[b] S. Aloisio and J. S. Francisco, J. Phys. Chem. A 103, 30 (1999).

[c] Open-shell theoretical analysis by Mark D. Marshall.