

263g Constraining the Mechanism and Kinetics of $\text{OH} + \text{NO}_2$ Using the Multiple-Well Master Equation

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The $\text{OH} + \text{NO}_2$ reaction, forming nitric acid (HONO_2), is critically important to radical chain termination in tropospheric chemistry. However, it has now been confirmed that a minor channel leading to peroxyxynitrous acid (HOONO) formation has a branching ratio approaching 15% at STP. This minor channel reveals itself in several ways: through biexponential OH kinetics (HOONO can decompose on the timescale of some kinetics experiments); through ^{18}O isotopic scrambling experiments (H atom migration is possible in HONO_2 but not HOONO); and through direct observation of HOONO products (there are two conformers, cis- and trans- HO-ONO). Our objective is to model both biexponential and isotopic scrambling kinetics data with a multiple-well master equation simulation.

Recent experiments for biexponential decay of OH in the reaction $\text{OH} + \text{NO}_2$ were modeled using a multiple-well master equation. Based on the analysis of three-well system (HONO_2 , HOONO , and $\text{HO} + \text{NO}_2$) and four-well system (HONO_2 , trans- HOONO , cis- HOONO , and $\text{HO} + \text{NO}_2$), we have considered different critical energies and isomerization rate constants among various wells and thus constrained the reaction mechanism for the $\text{OH} + \text{NO}_2$ reaction system. The model results agree well with the data.

H scrambling in HONO_2 was then studied by running a nine-well master equation for ^{18}OH , ^{16}OH , and NO_2 reaction system. A scrambling transition state was located using density function theory (B3lyp/6-31G+(d,p)). The model shows that H-atom scrambling is rapid and the rapid scrambling can explain the experimental results by D'Ottone et al. The sensitivity analysis for the critical energy and microcanonical rate constant for the isotopic scrambling transition state shows that the scrambling is complete.