THEORETICAL INVESTIGATION OF A NONADIABATIC MECHANISM FOR ALKYLPERNITRITE DECOMPOSITION

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We investigate a nonadiabatic two-state mechanism for reaction of alkylperoxyl radicals (ROO) with nitric oxide, an important step in the tropospheric ozone cycle. In our proposal, which is supported by high-level *ab initio* electronic structure calculations for $\mathrm{R} = \mathrm{CH_3}$, the pernitrite adduct ROONO propagates initially on a diabatic potential surface that correlates asymptotically with the $\tilde{A}\ ^2B_2$ state of $\mathrm{NO_2}$. This potential intersects a second diabatic potential corresponding to the stable nitrate species $\mathrm{RNO_2}$, which correlates with ground-state ($\tilde{X}\ ^2A_1$) $\mathrm{NO_2}$. Near the intersection of these two surfaces, ROONO exhibits substantial diradical character. Diabatic potentials for the model system FONO have been developed based on CCSD(T)/cc-pVTZ electronic structure calculations. Here we report the results of classical and quantum dynamics simulations for $\mathrm{FO} + \mathrm{NO} \rightarrow \mathrm{FONO} \rightarrow \mathrm{FNO_2}$.