Thermochemistry and Kinetic Modeling for OH Addition to Propene and O$_2$ Association to the Activated CH$_2$(OH)C•HCH$_3$ Adduct

Suarwee Snitsiriwat and Joseph W Bozelli*
Department of Chemistry and Environmental Science, New Jersey Institute of Technology
University Heights, Newark, NJ 07102

Abstract
Regeneration of OH radicals has recently been considered as an important process in atmospheric chemistry of unsaturated hydrocarbons, where current atmospheric modeling does not correctly predict levels during regeneration periods. The reaction of OH with propene and the subsequent reactions of the energized and stabilized hydroxyl-propyl radical adducts with O$_2$ are studied using density functional theory and CBS-QB3 ab initio theoretical methods. Enthalpies of formation ($\Delta_f H^{\circ} _{298}$) Entropies ($S^{\circ} _{298}$) and heat capacities ($C_p(T)$) are determined. Internal rotor contributions are included in $S$ and $C_p(T)$ values. Detailed potential energy surfaces for these reactions are presented with rate parameters calculated for each reaction step from transition state theory. The chemically activated hydroxyl-propyl radical + O$_2$ adducts are modeled using quantum Rice-Ramsperger-Kassel (qRRK) theory, with master equation analysis for falloff. The reaction system is modeled using the CHEMKIN modeling program (v3.2) under conditions of atmospheric chemistry for varied NO$_x$ concentration using an elementary reaction mechanism with all reactions reversible. Hydroxyl radical addition to propene forms an energized hydroxyl-propyl adduct with 26.2 kcal mol$^{-1}$ of chemical activation energy from the new bond formation. The energized hydroxyl-propyl radical is treated as having up to 60 energized adducts spaced evenly between the ground state of the hydroxyl-propyl adduct. Each of these adducts can be stabilized, re-energized via collisions, or react further with O$_2$ (association) to form a second, new, energized adduct, which is a hydroxyl-propyl-peroxy adduct with an additional 38.2 kcal mol$^{-1}$ before stabilization. The further chemical activation reactions of the distributed energized hydroxyl-propyl adduct and the stabilized hydroxyl-propyl adduct, with O$_2$ can lead to OH regeneration via two parallel paths: cyclic ether + OH and CH$_2$O + CH$_3$CHO + OH formation paths. Data is presented for different $\Delta E^{\circ} _{\text{down}}$ step sizes and for presence of varied NO concentrations.