

An *Ab Initio* Study of the Kinetics and Thermodynamics of Prereactive Complexes in Gas-Phase Reactions of the OH Radical and Hydrocarbons

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The formation of a prereactive complex, in gas-phase reactions, can alter the shape of the potential energy hypersurface (PES), and thus affect the kinetics and thermodynamics of a reaction. Complexes result from the coulombic interactions of the reacting molecules as they move along the reaction coordinate towards the transition state. Prereactive complexes have been invoked by experimentalists to explain the observed negative temperature dependence of the rate constant in reactions involving unsaturated hydrocarbons with the OH radical. Prereactive complexes may also play a role in the rate of reactions where tunneling is statistically probable by shrinking the size of the classically forbidden region. Part of the hypothesis taken in this study is that prereactive complexes can affect reaction rates by shrinking the size of the classically forbidden region of the PES leading through the transition state. The other part of the hypothesis is that at 298K if the change in entropy from reactants to prereactive complex is less than zero, the effect of the temperature multiplied by the entropy in the equation for free energy: $\Delta G = \Delta H - T\Delta S$; the prereactive complex will not exist as a minimum on the PES for free energy.

In this study, optimizations and frequency calculations of the OH radical reacting with hydrocarbons have been run using the BHandHLYP density functional with triple-zeta basis sets for each proposed point along the potential energy surface from reactants to products. These complexes are minima on the PES that corresponds to electronic energy and enthalpy; however, when free energy is considered, the unfavorable change in entropy makes the complex no longer a minimum on the PES. If the change in entropy of the reaction is negative, the increase in temperature will decrease the rate of reaction because the free energy of activation barrier becomes higher and higher. These results were then used as input structures and energies for rate constant calculations using the program TheRate produced by the Truong group at the University of Utah. This data was compared with some experimental data to see the differences between the two approaches in calculating a rate constant. Preliminary results for transition state theory (TST) yield a rate constant for the reaction of OH• with methane of $k=3.388 \times 10^{-18}$ at 296K.

PES for Free Energy

