

FINAL REPORT: DE-FG02-98ER14902**Theoretical Modeling of the Kinetics of Barrierless Reactions**

Stephen J. Klippenstein
 Chemistry Department
 Case Western Reserve University
 Cleveland, OH, 44106-7078

Program Scope

This research program aimed to develop and apply sophisticated transition state theory based models for the kinetics of barrierless reaction of importance in combustion. Various applications involving the coupling of the variable reaction coordinate (VRC) transition state theory (TST) methodology with ab initio quantum chemical evaluations and/or master equation simulations were provided.¹⁻⁸

Recent Progress*VariFlex*

The first version of a general purpose computer code (VariFlex) for modeling the temperature and pressure dependence of the kinetics of barrierless reactions was made available [1]. Recently, procedures for treating multiple well chemical reactions have also been incorporated [2].

Variable Reaction Coordinate Transition State Theory

Studies of the $C_3H_3 + H$ and $C_3H_5 + H$ addition reactions, have been performed in collaboration with Larry Harding (Argonne).⁴ Grid-based fits of wide-ranging ab initio simulations at the CAS+1+2/cc-pvdz level provided analytic representations of the transitional mode potentials in the transition state region. Estimates for the high pressure limiting recombination rate constants were then obtained on the basis of VRC-TST calculations employing these potentials. Both predictions were in good agreement with experimental measurements at room temperature. The theoretical predictions for higher temperature provide valuable results for combustion modeling.

For these and related H + radical reactions the optimized transition state dividing surfaces were found to be closely correlated with the contours of the molecular orbitals. The optimized pivot points in the VRC-TST evaluations were generally found to lie somewhere along the radical orbital. Recent experimental studies of kinetic isotope effects for CH addition reactions provide a reasonably direct verification of such pivot point locations. In particular, in joint work with Craig Taatjes (Sandia) we have examined the dependence of VRC-TST predictions for the kinetic isotope effect on the location of the pivot point.⁶ Quantitative agreement with experiment is found for pivot points located about 2 bohr away from the C atom. In contrast, pivot points located at the center-of-mass yielded kinetic isotope effects that are in the wrong direction.

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M P Dvorscak

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Date

Mark P. Dvorscak

(630) 252-2393

E-mail mark.dvorscak@ch.doe.gov

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Master Equation Studies of Pressure Dependent Reactions

In collaborative studies with Jim Miller and Struan Robertson we have examined the pressure dependence of the $C_2H_3 + C_2H_2$ and $C_2H_5 + O_2$ reactions on the basis of time dependent master equation simulations employing *ab initio* properties for the transition states.^{2,3} For both reactions the transition state energetics were evaluated with both Gaussian-2 like calculations and with B3LYP density functional theory.

For the $C_2H_5 + O_2$ reaction, the theoretical results suggest three separate temperature regimes for the kinetics.³ At low temperatures, below about 600 K, the time evolution is exponential and the rate coefficient and branching fraction are functions of temperature and pressure. Above 700 K, the reaction can be written as an elementary step $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ with a pressure independent rate coefficient, even though the reaction goes through an intermediate complex which may suffer numerous collisions. At intermediate temperatures the time behaviour is decidedly non-exponential and it is impossible to rigorously extract a rate coefficient from the calculations. In this temperature regime, the redissociation of the $C_2H_5O_2$ complex begins to compete with the stabilization process and the $C_2H_4 + HO_2$ branching fraction rapidly rises towards unity as the temperature increases.

The reaction of vinyl radicals with acetylene is somewhat more complicated due to the presence of multiple energetically accessible low-lying wells for the complex.² The inclusion of up to three separate wells in a multi-well master equation yields valid predictions for the time-dependence of the reactants and products. One novel result of this analysis is an indication of the significance of the cyclic- C_4H_5 complex. Interestingly, there are again three separate temperature regimes.

In an extension of our ethyl plus O_2 work, we also considered the reactions of propyl and butyl with O_2 .^{7,8} These studies were performed in conjunction with experimental studies in Craig Taatjes laboratory. The theoretical work involved a collaboration between my group (including my postdoc David Hahn) and Jim Miller. For the propyl and butyl radical oxidation reactions, we again generated *ab initio* based mechanisms for each of the isomers of the two radicals. The detailed experimental results for the time dependent HO_2 and OH yields provided important tests for the master equation simulations.

One interesting finding from the *ab initio* studies is that the hydroperoxy species (generally labeled $QOOH$ and formed via the internal transfer of an H atom) have high barriers to bimolecular product formation when they are formed via transition states with 6-membered rings or smaller. Only one of the $QOOH$ species in n-butyl, formed via a 7-membered ring transition state, is expected to yield a significant increase in the OH yield. Apparently, the product cyclic ethers must have a ring size of 5 or greater in order to minimize the ring strain in the transition state for the OH producing channel.

A separate analysis of the $C_3H_3 + O_2$ reaction, again in collaboration with Jim Miller and my postdoc David Hahn, began with a density functional theory based exploration of the potential energy surface. A combination of QCISD(T)/6-311++G(*d,p*) and MP2/6-311++G(3*df*,2*pd*) evaluations at the B3LYP/6-311+G(*d,p*) geometries provided higher level energy estimates. In many respects, the potential energy surface is at least qualitatively analogous to those for $C_2H_3 + O_2$ and for $HCC + O_2$. However,

among other things, the resonance stabilization of the radical leads to important quantitative differences.

At low temperatures the reaction is dominated by addition to the CH_2 side of the propargyl radical followed by stabilization. Addition to the CH side, which is followed by one of various possible internal rearrangements, becomes the dominant process at higher temperatures. These internal rearrangements involve a splitting of the O-O bond via the formation of 3-, 4-, or 5-membered rings, with the apparent products being $\text{CH}_2\text{CO} + \text{HCO}$. Rearrangement via the 3-membered ring is predicted to dominate the kinetics, but the saddlepoints for the 4- and 5-membered rings lie only a few kcal/mol higher. Rearrangement from the CH_2 addition product, via a 4-membered ring, would yield $\text{H}_2\text{CO} + \text{HCCO}$, but the barrier to this rearrangement is too high to be kinetically significant. Other possible products require H transfers and as result appear to be kinetically irrelevant.

The small values for the master equation predictions of the $\text{C}_3\text{H}_3 + \text{O}_2$ rate coefficient ($<10^{-13} \text{ cm}^3 \text{ s}^{-1}$ for temperatures of 2000 K or lower) provide an explanation for the enhanced concentrations of resonantly stabilized free radicals in the combustion environment. The smallness of the rate coefficients is the direct result of various effects arising from the resonance stabilization of the propargyl radical. Firstly, the addition to either side is predicted to have a significant saddlepoint arising from the need to break the resonance during the addition process. In contrast, related calculations for a variety of other alkyl radicals provide no indication of a saddlepoint along the addition path. The resonance stabilization also results in a sharp reduction in the well depth for the addition products, from 30-50 kcal/mol for related radicals to <20 kcal/mol for propargyl and allyl radicals. This reduction in the well depths correlates with increased barrier heights (relative to reactants) for the internal rearrangements required for bimolecular product formation. These internal rearrangement barriers provide the dominant bottleneck to reaction at higher temperatures.

Direct Dynamics

We have performed *ab initio* molecular dynamics simulations of the unimolecular dissociation of ketene.⁵ Here we were interested in the deviations of the product rotational distributions from phase space theory (PST) predictions. The average rotational energy in both the CO and the $^1\text{CH}_2$ fragments were found to decrease during the propagation from the inner (variational) transition state onto the separated fragments. Asymptotically, the propagated CO distribution remains slightly hotter than PST, whereas that for $^1\text{CH}_2$ ends up significantly colder than PST, with both results being in good agreement with experiment. Our calculations did not, however, reproduce the experimentally observed correlations between $^1\text{CH}_2$ and CO rotational states, in which the simultaneous formation of low rotational levels of each fragment is suppressed relative to PST.

References

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DOE Supported Publications

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Supported Students

1. Brian J. Serve (Ph. D. student)
2. David K. Hahn (postdoctoral student)