VARIATIONAL TRANSITION STATE THEORY

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MASTER

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During the past year we carried out several additional projects aimed at testing, extending, or applying the variational transition state theory of reaction rates.

We tested several approximate theories of thermal rate constants against accurate quantal equilibrium rate constants for collinear bimolecular reactions governed by given potential energy surfaces.¹ The systems considered were $F + H_2$ and $F + D_2$ for the Muckerman potential energy surface no. 5 at 200-1200 K and $H + F_2$, $D + F_2$, and $T + F_2$ for potential surface II of Jonathan, Okuda, and Timlin at 233-1260 K. For $F + H_2$, conventional transition state theory overestimates the accurate rate constant by factors of 2.9-3.4, with the largest errors at the lowest and highest temperatures. Vibrationally adiabatic transmission coefficients or variational transition state theory decrease the error to factors of 1.2-1.3 at the lowest temperature and to a factor of 3.2 at the highest temperature. The unified statistical model reduces the errors to a factor of 1.1 at the lowest temperature and a factor of 2.7 at the highest temperature. For $F + D_2$ the trends are similar but the errors in all the methods are smaller at all temperatures. For $H + F_2$ conventional transition state theory underestimates the rate constants by a factor of 0.56 at the lowest temperature, with the error decreasing to 2% at the highest temperature. Various formulations of vibrationally adiabatic transmission coefficients, in conjunction with either conventional or variational transition state theory, reduced the error to factors of 0.84-0.96 at the lowest temperature while not destroying the good agreement at the highest temperature. The unified statistical theory seems to overestimate the recrossing correction for this reaction, though only by about 10%. The results are similar for $D + F_2$ and $T + F_2$ except that the low-temperature underestimates of the calculations without tunneling are not as severe.

The best theory, improved canonical variational theory with the Marcus-Coltrin path semiclassical adiabatic ground-state transmission coefficient, reproduces the accurate quantal results for $H + F_2$, $D + F_2$, and $T + F_2$ within 5% or better in every case for the whole temperature range.

This study completed our series of tests of variational transition state theory (VTST) against all presently available accurate quantal rate constants for given potential energy surfaces. We have seen that VTST with Marcus-Coltrin-path vibrationally adiabatic ground-state transmission coefficients is overall the most successful theory now available. The study of $H + F_2$ and two isotopic analogs illustrates the power of this method: it is accurate within 5% for $H + F_2$ and within 3% for $D + F_2$ and $T + F_2$ over a temperature range of a factor of 5.4. The study of reference 1 also provides the worst case we have encountered, namely, $F + H_2$. The approximate theories are more accurate for $F + D_2$. For example, the unified statistical calculations with semiclassical adiabatic ground-state transmission coefficients are accurate within 39% over a temperature range of a factor of 6 for this reaction. For the same reaction, the variational transition-state-theory calculations with semiclassical adiabatic ground-state transmission coefficients are accurate within a factor of 1.59 over the same temperature range.

We have written a review² of the classical mechanical foundations for our work on variational transition state theory as well as selected results on collinear classical reactions and tests of the quantized theory against accurate quantum mechanical results for collinear and three-dimensional reactions. The review also provides a survey of effects for three-dimensional reactions.

Variational transition state theory and semiclassical adiabatic ground-state transmission coefficients have been applied to calculate the kinetic isotope effects for D- and T-substitution in the reaction $\text{Cl} + \text{H}_2$ at 245-445 K.³ The calculated isotope effects differ significantly from those calculated previously using conventional transition state theory and semiempirical potential energy surfaces. We used variational transition state theory and conventional transition state theory with the Wigner tunneling correction to adjust three new semiempirical surfaces to the experimental data. No one set of calculations is completely successful. The potential energy surfaces that are most successful at predicting the HD/DH intramolecular kinetic isotope effect have the earliest saddle points ($R_{\text{Cl-H}}^{\ddagger} = 2.64\text{--}2.78\text{ a}_0$, $R_{\text{H-H}}^{\ddagger} = 1.88\text{--}1.72\text{ a}_0$). For each surface studied except one, the canonical variational transition states are located past the saddle point for some of the isotopic reactions and earlier than the saddle point for others. The exceptional surface is the one of Valencich and coworkers; that surface has an early saddle point, but the variational transition states are always earlier than the saddle point. An important conclusion of these calculations is that the kinetic isotope effects predicted by variational transition state theory are quite different from those predicted by the conventional theory for all seven potential energy surfaces studied.

A new analytic approximation has been derived for thermally averaged transmission coefficients for tunneling through and reflection by truncated parabolic potential barriers.⁴ The main result of this paper is a continuous, divergence-free analytic expression that gives reasonable results for the Boltzmann-averaged transmission coefficient for a truncated parabolic barrier. The approximation has a wide range of validity and avoids the spurious singularities of the well known result for untruncated parabolic barriers. We

have applied the analytic result to effective parabolic fits to other barrier shapes. The results are quite encouraging and suggest that the approximation may be useful for a wide variety of chemical applications. In particular it should form the basis for estimating tunneling effects in a way that is both reliable and very easy to apply. In future work we shall show that the parabolic approximation discussed here can be combined with a simple but realistic treatment of reaction-path curvature to provide a nonempirical analytic formula for the transmission coefficient of atom-diatom reactions that rivals in accuracy the best state-of-the-art semiclassical treatments for simple cases. Since it is much easier to approximate a reaction barrier parabolically than to calculate it fully, the expression proposed in this paper may be very useful for practical work.

In work supported by this contract, we have used transition state theory and our accurate representation of the potential energy surface to predict the temperature dependence of the energy of activation (E_a) for the $H + H_2$ reaction at temperatures up to 2400 K.⁵ The calculations with our best vibrationally adiabatic ground-state transmission coefficient predict an increase in E_a from 5.4 kcal/mol at 200 K to 7.6 kcal/mol at 444 K and 14.5 kcal/mol at 2400 K. In other work, not supported by this contract, we have verified this prediction by extensive calculations of full quasi-classical trajectories. The trajectories predict an E_a of 7.9 kcal/mol at 444 K and 13.9 kcal/mol at 2400 K.

Accurate classical dynamical fixed-energy reaction probabilities and fixed-temperature rate constants have been calculated for the collinear reaction $H + FH$ on a low-barrier model potential energy surface.⁶ The potential energy surface has twin 1.75 kcal/mol saddle points. The

calculations cover energies from 0.1 to 100 kcal/mol above threshold and temperatures of 100-10000 K. The accurate results were used to test five approximate theories: conventional transition state theory, canonical variational theory, improved canonical variational theory, microcanonical variational theory, and the unified statistical model. The first four of these theories involve a single dividing surface in phase space, and the unified statistical theory involves three dividing surfaces. The tests are particularly interesting because of the two identical saddle points. At temperatures from 100 to 2000 K, the microcanonical variational theory is the most accurate theory, with errors in the range 11-14%; for temperatures from 2000 to 10000 K, the unified statistical theory is the most successful, with errors in the range 3-14%. Over the whole range, a factor of 100 in temperature, both theories have errors of 35% or less. Even conventional transition state theory has errors of 47% or less over the whole factor-of-100 temperature range. Although the unified-statistical model should become exact at threshold for this system, it already underestimates the reaction probability by a factor of 0.64 at 0.1 kcal/mol above threshold. Conventional transition state theory and microcanonical variational theory agree with each other within 12% up to an energy 13 kcal/mol above the saddle point energy.

We have studied the quantum mechanics of the collinear $H + FH \rightarrow HF + H$ and $D + FD \rightarrow DF + D$ reactions on the same potential energy surface.⁷ We calculated accurate quantal reaction probabilities over a wide energy range, including three resonance energies and three resonance widths for each isotopic case. From these we calculated accurate quantal rate constants at temperatures 75-7500 K for $H + FH$ and 75-2400 K for $D + FD$; and we separated out the contributions of the lowest-energy resonance to the

low-temperature rates. We presented plots of S matrix phases and eigenphases and Argand diagrams. The accurate quantal results were used to test a wide variety of approximate dynamics results: semiclassical and quantal resonance calculations based on the vibrationally adiabatic model; rate constants calculated by conventional transition state theory, three versions of variational transition state theory, and the unified statistical model; and vibrationally adiabatic transmission coefficients.

The $H + FH$ reaction with twin low-energy saddle points has three sharp resonances in the energy range studied, as does the $D + FD$ reaction. The minimum-energy-path vibrationally adiabatic model provides a reasonable explanation of all six resonances. The lowest-energy resonance for each case is particularly interesting because it occurs far below the nonresonant threshold. As a consequence it strongly dominates the very low-temperature rate constants. Microcanonical variational theory with the minimum-energy-path vibrationally adiabatic ground-state model for including quantal effects on reaction-coordinate motion reproduces the accurate quantal rates for $H + FH$ within 7% over the 200-2400 K temperature range. The unified statistical model, with the same transmission coefficient, gives the same 7% level of accuracy up to the highest temperature studied, 7000 K. Conventional transition state theory with unit transmission coefficient has a 132% error at 200 K and a 36% error at 7000 K. For both the resonance energy and the transmission coefficient, the quantum mechanical treatment of reaction-coordinate motion is significantly more accurate than the semiclassical treatment.

We have provided a general survey of the entropic effects that help determine bottleneck locations in atom-diatom reactions.⁸ For this study

we considered a large number of reactions, surface types, and mass combinations. We put a special emphasis on comparing results obtained with extended London-Eyring-Polanyi-Sato potential energy surfaces to those obtained with our own rotated-Morse bond-energy bond-order potential surface formalism.

We have made significant progress on a general computer program for applying variational transition state theory to polyatomic reactions.⁹ We are developing new methods for including anharmonicity in such calculations. We are applying the new program to the reaction $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ over the temperature range 200-4000 K. The preliminary results show significant differences from the predictions of conventional transition state theory.

Finally we have begun to develop new methods for including the curvature of the reaction coordinate in vibrationally adiabatic transmission coefficients.¹⁰ The goal of this work is to find accurate methods for including tunneling in rate calculations for polyatomic systems while keeping the methods simple enough for routine use.

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