MASTER

VARIATIONAL TRANSITION STATE THEORY

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During the past year we carried out further development of the theory and made several applications.

We have made a test of bond-energy-bond-order (BEBO)-type potential energy surfaces for the Cl-H-H reaction system.¹ We considered two methods, the rotated-Morse BEBO (RMBEBO) method that we had developed previously and the Agmon-Levine-plus-anti-Morse-bend (AL/AB) method that we developed during the year in review. Each method was treated as a one-parameter semiempirical method. The parameter was adjusted to the energy of activation for $\text{Cl} + \text{H}_2$ and the test of the method was the comparison of predicted kinetic isotope effects (KIE's) to experiment. Dynamical calculations were carried out by the improved canonical variational transition state theory with Marcus-Coltrin-path semiclassical adiabatic ground-state transmission coefficients as well as with simpler methods. The RMBEBO surfaces are not successful, but the AL/AB method is as successful as previously employed two-parameter methods. I recommend the AL/AB method as a semiempirical method that can be used for other systems in the future. The anti-Morse-bend and exponential-bend approximations are general procedures, and they were tested successfully against ab initio calculations.

We derived a new expression for the effective mass along the reaction coordinate in a chemically reacting system.² This expression can be used in two convenient algorithms for including quantum mechanical effects on the reaction coordinate into transition-state theory or generalized transition state theory. One algorithm is based on a uniform semiclassical approximation; the other is based on a parabolic approximation to the effective potential. Examples have been presented to show that the theory accurately accounts for reaction-path curvature effects on the tunneling contributions

to the reactions $H + H_2$, $D + D_2$, and $D + H_2$. Although the derivation, and hence expected reliability, of the new methods is most valid for systems with small reaction-path curvature, the methods are generally applicable and should provide useful accuracy even for medium-curvature and some large-curvature systems. I believe that the new method, called the small-curvature-approximation semiclassical adiabatic ground-state (SCSAG) transmission coefficient, is the most accurate method now available for the incorporation of quantum tunneling effects for general reacting systems.

At the American Conference on Theoretical Chemistry, I presented a status report on practical aspects of the incorporation of quantum effects in generalized-transition-state theory.³ Attention was centered on methods for bound-mode quantization, including anharmonicity, and for estimating tunneling probabilities with account of the effects of reaction-path curvature. This review discussed methods that can be applied generally and tests of these methods against accurate quantal results that are available for a few relatively simple cases. The results presented at the Conference were for the reactions $H + H_2$, $D + D_2$, $Mu + H_2$, $Mu + D_2$, $Cl + T_2$, $Cl + HD$, $Cl + DH$, $I + H_2$, $Cl + HCl$, $OH + H_2$, $OH + HD$, and $OH + DH$.

A formalism for the application of variational transition-state theory and semiclassical vibrationally adiabatic transmission coefficients to bimolecular reactions involving an arbitrary number of atoms has been completed.⁴ This generalizes previous work of this program on atom-diatom reactions. We have made applications to the reactions $OH + H_2 \rightarrow H_2O + H$ and $OH + D_2 \rightarrow HDO + D$ using the Schatz-Elgersma fit to the Walch-Dunning ab initio potential energy surface. For both reactions we found large differences between conventional and variational transition-state theory and large effects

of anharmonicity on the calculated rate constants. The effect of reaction-path curvature on the calculated transmission coefficients and rate constants is also large. The final calculated values of the kinetic isotope effects are in good agreement with experiment at high temperature but too large at room temperature. The rate constants for the $\text{OH} + \text{H}_2$ reaction itself agree with experiment within a factor of 1.7 over the whole experimental temperature range 298-1000 K, and this is very encouraging. Now that the practical techniques have been carried through once, I look forward to applications to other reactions.

We have tested the applicability of variational transition state theory for muonium reactions, and we have made experimentally verifiable predictions of muonium kinetic isotope effects.⁵ These isotope effects provide a particularly stringent test of the methods we use to incorporate quantum effects in the theory because muonium has a mass only one ninth that of protium. We considered three reactions: $\text{H} + \text{H}_2 \rightarrow \text{H}_2 + \text{H}$; $\text{Mu} + \text{H}_2 \rightarrow \text{MuH} + \text{H}$; $\text{Mu} + \text{D}_2 \rightarrow \text{MuD} + \text{D}$. We calculated accurate quantum mechanical reaction probabilities and thermal rate coefficients for all three reactions in collinear geometry using the Liu-Siegbahn-Truhlar-Horowitz (LSTH) accurate potential energy surface. These rate coefficients were used to test conventional transition state theory (TST) and the improved canonical variational theory with Marcus-Coltrin-path semiclassical adiabatic ground-state transmission coefficients (ICVT/MCPSAG). The ICVT/MCPSAG theory was found to be greatly superior and reasonably reliable. (For example, a factor-of-23 error in TST is reduced to a factor of 2 in ICVT/MCPSAG, a factor-of-12 error is reduced to 38%, and factor-of-3 errors are reduced to 20-33%.) These conclusions were tested for sensitivity to variations in the potential energy

surface by repeating the calculations for the less accurate Porter-Karplus surface. The conclusions are unaltered by this. The ICVT/MCPSAG theory and LSTH surface were then employed to predict the rate coefficients for all three reactions in three dimensions.

We have computed the energy dependence of the activation energy for $D + H_2$ over the 300-2400 K temperature range.⁶ This study again employed the accurate LSTH potential energy surface. The calculated energy of activation increases from 6.8 to 14.0 kcal/mol over this temperature range, and it is in good agreement (0.2 kcal/mol) with available experiments. In contrast the conventional TST prediction is too high by 2 kcal/mol at 300 K.

We have developed a canonical-ensemble version of the unified statistical model, and we have applied it to calculate classical-mechanical thermal-rate constants for 11 collinear reactions of the type $A + BC \rightarrow AB + C$.⁷ The results were compared to accurate classical dynamics. The canonical unified statistical results are always more accurate than variational transition-state theory at high enough temperature, but in two cases they significantly overestimate the recrossing corrections at low and medium temperatures. This theory may be considered as a generalization of variational transition-state theory. I intend to test and apply a quantized version of this theory in the near future.

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