

with these and other concepts is clearly needed. Nevertheless, it has been demonstrated in measured or calculated atomic stopping powers that the hierarchy double bond > ring structure > single bond holds for C, O, and S with maximum differences $\approx 28\%$, 17% , and 5% , respectively. It is proposed that stopping power measurements may serve as a useful supplement to existing spectroscopic techniques currently used by chemists to determine bond order. For example, stopping powers can be used³⁴ to assign a resonance hybrid structure³⁹ consisting of one S-O double bond and one S-O single bond for SO₂ and a single coordinate covalent bond for the third oxygen atom in dimethyl sulfite, in contradistinction to double-bonded structures

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predicted by Gillespie's VSEPR model⁴⁰ which requires d-orbital participation.

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Supplementary Material Available: Table of three stopping power parameters E_{peak} , ϵ_{peak} , and δ used to characterize the stopping power curve for 72 substances (2 pages). Photocopies of this material or microfiche (105 × 148 mm, 24× reduction negatives) may be obtained from Business Operations, Books and Journal Division, American Chemical Society, 1155 16th St., NW, Washington, DC 20036. Full bibliographic citation (journal, title of article, author) and prepayment (check or money order) for \$5.50 for photocopy or \$3.00 for microfiche (include \$1.00 additional postage for foreign mail) are required.

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Variational Transition-State Theory

DONALD G. TRUHLAR* and BRUCE C. GARRETT

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

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The two most accurate practical methods for calculating the rate constants for thermally activated bimolecular reactions in the gas phase are trajectory calculations¹⁻³ and transition-state theory. In conventional formulations the transition state is a surface in configuration space that divides reactants from products and passes through the saddle point of the potential-energy surface.⁴⁻¹⁰ In order to improve on this treatment, we have been studying the effects on the computed rate constants of using generalized transition states. Generalized transition states are surfaces in phase space dividing reactants from products but not necessarily passing through a saddle point. Instead we determine the position of the dividing surface using a variational criterion.¹¹⁻¹⁷ This general procedure is called variational transition-state theory. We have recently completed several applications¹⁷⁻²⁴ and a preliminary review² for collinear reactions and several applications^{21,22,25-30} to three-dimensional reactions. In this Account we provide a general introduction to this work and survey some of the results.

It is customary to derive transition-state theory by postulating a quasiequilibrium between transition-state

species and reactants.⁴⁻¹⁰ Although this is valid, the conditions for validity of transition-state theory become

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Donald G. Truhlar is Professor of Chemistry and Chemical Physics at the University of Minnesota. He was born in Chicago in 1944 and obtained a B.A. in chemistry from St. Mary's College in Winona, MN, and his Ph.D. from Caltech. He has been on the faculty at the University of Minnesota since 1969. His research interests include the theory of molecular energy transfer, molecular quantum mechanics, and electron impact spectroscopy as well as the theory of chemical reactions.

Bruce C. Garrett is a member of the scientific staff at Battelle Columbus Laboratories. He was born in Fort Knox, KY, in 1951 and obtained a B.S. from the University of California at Irvine and his Ph.D. from the University of California at Berkeley. From 1977 to 1979, during which time most of the work reviewed here was performed, he was a Postdoctoral Research Specialist at the University of Minnesota. His research interests include the theory of molecular energy levels and molecular energy transfer as well as the theory of chemical reactions.

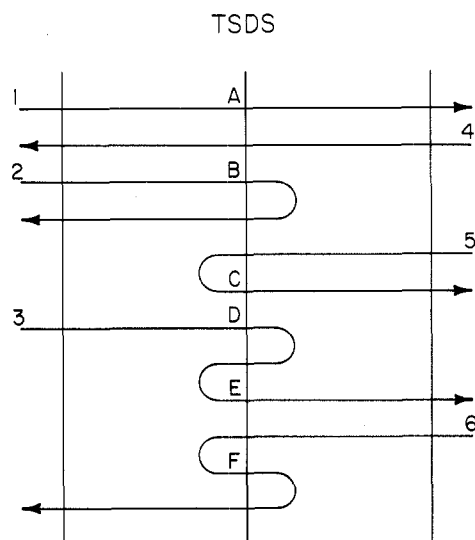


Figure 1. Strings across a Ping-Pong table or trajectories across a phase-space dividing surface. The trajectories are numbered, and the forward crossings of the dividing surface are lettered.

clearer when it is formulated dynamically. In this language and stated classically, the fundamental assumption of transition-state theory is that the net rate of forward reaction at equilibrium equals the equilibrium flux in the product direction through the transition state, where the transition state is a surface in phase space dividing reactants from products.³¹ A consequence of the fundamental assumption is that classical transition-state theory with unit transmission coefficient agrees with exact classical dynamics if and only if all trajectories through the transition-state dividing surface cross it only once.³² This may be illustrated by a strings-across-the-Ping-Pong-table diagram,^{33,34} such as Figure 1. The strings represent trajectories in a system at equilibrium. The left side, middle, and right side of the table represent the reactants, the transition-state dividing surface, and products. In Figure 1 there are six forward-crossing trajectories at equilibrium at the dividing surface, and transition-state theory counts all of them as contributing to the net one-way reactive flux. Notice, however, that the net one-way flux is only two trajectories in the example shown. Using this analogy it is easy to see that the errors in classical transition-state theory may be classified as (i) nonreactive trajectories which cross the dividing surface toward products and then recross toward reactants, e.g., trajectory 2, (ii) trajectories which originate in the product region, cross the dividing surface, but are ultimately nonreactive, e.g., trajectory 5, and (iii) reactive trajectories which cross the dividing surface more than once, e.g., trajectories 3 and 6 (tra-

jectory 3 contributes two forward-crossing trajectories at the dividing surface but only one net forward-reactive one; trajectory 6 contributes one forward-crossing trajectory at the dividing surface but contributes nothing to the forward reaction). This example clearly illustrates that the breakdown of transition-state theory is due entirely to recrossing effects. If the transition state were truly located at a bottleneck to which trajectories, having left, never returned, transition-state theory would give exact equilibrium rate constants in a classical world. The illustration also makes clear an important corollary of the fundamental theorem: If trajectories do recross the transition-state dividing surface, classical transition-state theory with unit transmission coefficient overestimates the classical equilibrium rate.

Conventionally one locates the transition-state dividing surface so that it passes through the saddle point, which is the highest energy point on the minimum energy path (MEP) from reactants to products. It is clear that one can define generalized transition states at other locations and calculate the one-way equilibrium flux in the product direction through any of them. If one allows unconstrained variations of the dividing surface in phase space, one can calculate the exact classical equilibrium rate constant this way. If, however, one constrains the dividing surface to be a function of at most the coordinates and the total energy (and for three-dimensional reactions perhaps also the total angular momentum), one obtains an upper bound, which may sometimes be exact. This procedure is called classical variational transition-state theory.

Thermal equilibrium at a given temperature T corresponds to a canonical ensemble. It is useful to consider a canonical ensemble as a Boltzmann distribution of microcanonical ensembles, each of which corresponds to a given total energy E . Similarly the equilibrium rate constant $k(T)$ may be written as an average over microcanonical rate constants $k(E)$:

$$k(T) = [\Phi^R(T)]^{-1} \int_0^\infty dE \exp(-E/kT) \phi^R(E) k(E) \quad (1)$$

where $\Phi^R(T)$ and $\phi^R(E)$ are the reactants' partition function per unit volume and density of states per unit energy and volume, respectively. Notice that

$$\Phi^R(T) = \int_0^\infty dE \exp(-E/kT) \phi^R(E) \quad (2)$$

Equations 1 and 2 illustrate that the thermal rate constant is a properly weighted average of the microcanonical one. The conventional transition state theory results for $k(T)$ and $k(E)$ are

$$k^*(T) = \frac{kT Q^*(T)}{h \Phi^R(T)} e^{-\Delta V^*/kT} \quad (3)$$

and

$$k^*(E) = \frac{N^*(E)}{h \phi^R(E)} \quad (4)$$

where $Q^*(T)$ is the transition-state partition function, ΔV^* is the potential energy at the saddle point, and $N^*(E)$ is the number of energetically available internal states of the transition state. Classically the number of states is a volume in phase space in units of one power of h for each degree of freedom, and classical

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partition functions are phase space integrals. We have taken the zeroes of energy for $Q^*(T)$ and for $\Phi^R(T)$ and E as the saddle point energy and the bottom of the reactant potential well, respectively.

We define the reaction coordinate s as the distance along the MEP from the saddle point. Thus $s = -\infty$ for reactants and $s = +\infty$ for products. For each s we define a generalized transition state perpendicular to the MEP and intersecting it at that s . Then generalized transition-state theory (GT) rate constants are given as

$$k^{\text{GT}}(T,s) = \frac{kT}{h} \frac{Q^{\text{GT}}(T,s)}{\Phi^R(T)} e^{-\Delta V(s)/kT} \quad (5)$$

and

$$k^{\text{GT}}(E,s) = \frac{N^{\text{GT}}(E,s)}{h\phi^R(E)} \quad (6)$$

where the phase-space integrals $Q^{\text{GT}}(T,s)$ and $N^{\text{GT}}(E,s)$ are defined analogously to $Q^*(T)$ and $N^*(E)$ but for the dividing surface at s , and $\Delta V(s)$ is the classical potential energy along the minimum energy reaction path. $\Delta V(s)$ is called the classical potential-energy barrier because zero-point effects are not included in it.

We distinguish three levels of variational transition-state theory (VTST): canonical variational theory (CVT),¹⁷ improved canonical variational theory (ICVT),¹⁸ and microcanonical variational theory (μ VT).¹⁷ In μ VT we find a best dividing surface for each E to minimize $N^{\text{GT}}(E,s)$ and hence $k^{\text{GT}}(E,s)$. The resulting microcanonical rate constant $k^{\mu\text{VT}}(E)$ is substituted into (1), which is integrated numerically to yield a thermal rate constant that is called $k^{\mu\text{VT}}(T)$. In ICVT we choose the dividing surface location to be at the microcanonical variational transition state for energies below the μ VT threshold; this makes $k^{\text{ICVT}}(E)$ zero at these energies. Then for each T we choose a single best compromise dividing surface to minimize the contribution of all higher energies to the thermal rate constant at that temperature. The result is called $k^{\text{ICVT}}(T)$. In CVT we do not separate out the contributions from below threshold, but rather for each T we choose one single best compromise dividing surface which directly minimizes $k^{\text{GT}}(T,s)$ for that temperature. The result is called $k^{\text{CVT}}(T)$.

The CVT may be given another interpretation by using the quasithermodynamic representation of transition-state theory. For the conventional theory this involves rewriting (3) as

$$k^*(T) = \frac{kT}{h} K^0 e^{-\Delta G^{*,0}(T)/RT} \quad (7)$$

where K^0 is the reciprocal of the standard-state concentration and $\Delta G^{*,0}$ is the free energy of activation in the standard state. The generalization is

$$k^{\text{GT}}(T,s) = \frac{kT}{h} K^0 e^{-\Delta G^{\text{GT},0}(T,s)/RT} \quad (8)$$

where (5) and (8) together define a generalized free energy of activation curve $\Delta G^{\text{GT},0}(T,s)$. This formulation shows that minimization of $k^{\text{GT}}(T,s)$ is equivalent to maximization of $\Delta G^{\text{GT},0}(T,s)$; thus the CVT may also be called the method of free-energy curves. For discussion purposes we may associate $Q^{\text{GT}}(T,s)/\Phi^R(T)$ in (5) with "entropic" effects and $\exp[-\Delta V(s)/RT]$ with "energetic" effects.^{26,27} Then we see that conventional

Table I
Ratios of Generalized Transition-State Theory
Rate Constants to Exact Classical Dynamical Ones
at 300 K (Upper Entry) and 2400 K (Lower Entry)
for Several Collinear Reactions

reaction ^a	†	CVT	ICVT	μ VT
H + H ₂	1.0	1.0	1.0	1.0
	1.5	1.5	1.3	1.2
Cl + HD	1.1	1.1	1.1	1.0
	5.0	2.8	2.7	2.5
F + H ₂	1.0	1.0	1.0	1.0
	2.0	1.8	1.8	1.8
Br + H ₂	1.1	1.1	1.1	1.1
	4.2	3.9	3.9	3.7
I + H ₂	1.7	1.0	1.0	1.0
	2.1	1.0	1.0	1.0
H + Cl ₂	1.0	1.0	1.0	1.0
	1.3	1.3	1.3	1.1
⁵⁷ C + H ⁵⁷ C ^b	4.3	2.0	1.4	1.3
	11.4	2.0	1.9	1.7

^a For information about potential-energy surfaces, see ref 17 and 18. ^b Three-body model of C₂H₆ + H-C₂H₅ → C₂H₆-H + C₂H₅.

transition-state theory chooses the dividing surface solely on the basis of energetic considerations while the CVT uses a free-energy criterion which involves a compromise of energetic and entropic effects.

So far we have not given the exact definition of the minimum-energy path. The minimum-energy path may be defined by joining the path of steepest descent from the saddle point to reactants to that from the saddle point to products. This definition yields a different path through configuration space for different choices of coordinate system. It has been suggested by several workers^{20,35-37} that the way to resolve this ambiguity is to use a coordinate system that diagonalizes the internal kinetic energy as a quadratic form in momenta with the same reduced mass for every direction. This reduces the motion to that of a frictionless mass point governed by the potential energy as a function of these coordinates. The path of steepest descents in this coordinate system corresponds to the trajectory of a damped system whose motion is continuously stopped and allowed to restart under the influence of the potential-energy hypersurface, i.e., to a locally zero-kinetic-energy trajectory. This is the definition we use.

Classical Collinear Reactions

To test the power of the variational methods and to study the quantitative importance of classical recrossing effects we compared^{17,18} classical generalized-transition-state-theory calculations for nine collinear systems to classical trajectory calculations. Ratios of the approximate rate constants to the exact classical dynamical ones for several of these systems are shown in Table I. At energies just sufficient for a trajectory to cross the saddle point, conventional classical transition-state theory is exact. In fact it is usually accurate enough at low energy that the error is the 300-K classical rate constant is usually 10% or less. As the temperature is increased, the error in conventional transition-state theory becomes large, typically a factor of 1.5 at 1000 K and a factor of 2 at 2400 K. In some cases the error

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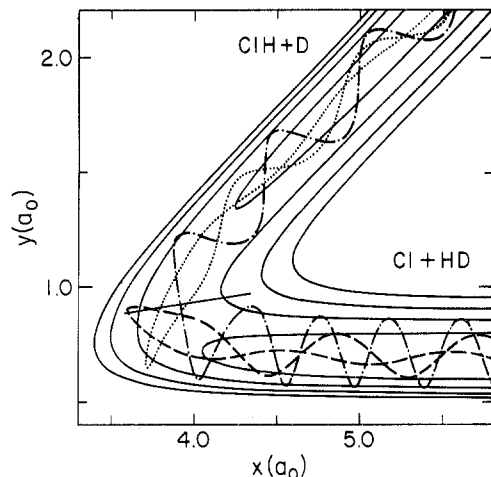


Figure 2. Trajectories and potential-energy contours (solid curves) for Cl + HD. The abscissa is the distance from Cl to the center of mass of HD and the ordinate is the HD internuclear distance scaled to the same reduced mass. The straight line in the corner region is the conventional transition-state dividing surface for a total energy of 12.67 kcal/mol (5.00 kcal/mol above the saddle point). The dashed trajectory is a nonreactive Cl + HD collision, the dotted trajectory is a nonreactive ClH + D collision, and the dash-dot trajectory is reactive.

is much larger; e.g., a hydrogen atom being transferred between two similar, heavy radicals may hop back and forth several times, causing a severe breakdown of the no-recrossing assumption for a symmetric dividing surface. Table I shows that considerable improvement can be obtained by optimizing the location of the dividing surface using the variational bound property.

Figure 2 is an illustration of some simple trajectories that recross the conventional transition-state dividing surface. Three collinear trajectories for Cl + HD are shown, two of which recross the conventional transition state. These trajectories, and the results for this system in Table I, were computed by using the realistic (GSW) potential-energy surface of Stern et al.,³⁸ and the trajectories are shown superposed on a contour map of that surface. For Cl + HD conventional transition-state theory overestimates the exact classical dynamical result by a factor of 1.99 at 1000 K. At this temperature the classical canonical variational transition state is located $0.15a_0$ past the saddle point (in coordinates scaled to the reduced mass for Cl + HD), and the CVT reduces the error to a factor of 1.71. The ICVT and μ VT further reduce the error at this temperature to factors of 1.51 and 1.35, respectively. In general the differences between CVT, ICVT, and μ VT are much smaller for quantized systems because of zero-point energy.

Some earlier studies^{39,40} suggested that the high-energy breakdown of conventional classical transition-state theory might be less severe in three dimensions than in one. Thus Chapman et al.³⁹ found such a result for H + H₂. Comparison of the three-dimensional results of Koepl and Karplus⁴⁰ for a model system to our collinear ones¹⁷ for the same system shows about the same deviation at 4.5 kcal/mol above the classical barrier but less deviation in three dimensions than in

one dimension at 10 kcal/mol above the barrier. However we have found several other systems for which conventional transition-state theory appears to break down more severely at high temperature in three dimensions than in one dimension. Typically, as in H + Cl₂,²² this occurs where the chief variational effect is to tighten the bending vibration that is created when the generalized activated complex is formed.

Quantal Collinear Reactions

Quantum mechanical effects cannot be ignored for real chemical reactions. The most important effects are quantized energy levels and barrier penetration. If one attempts to translate the fundamental assumption of transition-state theory into quantum mechanics, the result is ambiguous because the fundamental assumption of transition-state theory involves simultaneous specification of momentum and position along the reaction coordinate.⁴¹ The usual method of quantizing classical transition-state theory is to replace all classical partition functions for bound degrees of freedom of reactants and transition states by quantum mechanical partition functions computed from quantized energy levels;⁴⁻¹⁰ we adopt this same scheme for generalized transition-state theory. Quantizing the partition functions still leaves the reaction-coordinate motion classical, and thus it neglects tunneling. We attempt to include such barrier penetration effects in a multiplicative transmission coefficient. A difficulty with these methods of including quantal effects on bound degrees of freedom and the reaction coordinate is that they do not adequately account for the nonseparability of the reaction coordinate from the other degrees of freedom.⁴²

To calculate $Q^{GT}(T,s)$ for (5) we must calculate energy levels $\epsilon_{\text{int}}(\alpha,s)$ for the bound degrees of freedom with quantum numbers α as functions of the reaction coordinate s . We obtain $\epsilon_{\text{int}}(\alpha,s)$ by fixing s and applying standard techniques to the bound degrees of freedom: we calculate stretching energies using Morse approximations, and for three-dimensional reactions we calculate rotational energies by the rigid-rotator approximation and bending energies by a harmonic-plus-quartic⁴³ approximation. Since s is fixed, the other degrees of freedom are being treated adiabatically with respect to reaction-coordinate motion. The resulting $\epsilon_{\text{int}}(\alpha,s)$ may also be used to calculate rotationally and vibrationally adiabatic potential curves

$$V_a(\alpha,s) = \Delta V(s) + \epsilon_{\text{int}}(\alpha,s) \quad (9)$$

which may be plotted as adiabatic rotational-vibrational correlation diagrams. These potential curves are the effective potentials for reaction-coordinate motion under the assumption that not only the electronic degrees of freedom adjust adiabatically to motion along s [this is the Born-Oppenheimer approximation leading to the appearance of the adiabatic electronic energy in $\Delta V(s)$] but also all other degrees of freedom adjust adiabatically, i.e., preserve their quantum numbers.

Adiabatic potential curves may also be used to calculate rate constants by the adiabatic theory of reactions.⁴⁴ In this theory one calculates state-selected rate

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constants for each set α of quantum numbers by making the adiabatic approximation. With this approximation, for classical reaction-coordinate motion, if a system initially in state α has enough total energy to surmount the maximum of $V_a(\alpha, s)$ as a function of s , it reacts; if not, it does not. The thermal rate constant is the appropriate thermal average of the state-selected rate constants. Even in the classical limit for all degrees of freedom, this does not involve specification of a unique dividing surface in phase space; thus the adiabatic theory of reactions is not strictly a generalized transition-state theory. However, we have shown that, as long as the reaction-coordinate motion is treated classically, the adiabatic theory of reactions is 100% equivalent to microcanonical variational transition-state theory.¹⁷ Thus we call it adiabatic transition-state theory (ATST or simply A).

The adiabatic derivation of μ VT is very useful for consistently incorporating quantum mechanical effects on the reaction coordinate in generalized transition-state theory. Thermal rate constants are usually dominated by low-energy threshold regions where the adiabatic approximation is most valid and quantal effects are largest. The calculation of quantal reaction probabilities requires a state-to-state language, and the equivalence of μ VT and ATST shows that the adiabatic approximation provides the consistent conversion of transition-state theory to state-to-state language. Since quantum effects are most important at low temperature where the ground state (denoted $\alpha = G$) eventually becomes the dominant one, we have improved the treatment of the threshold region by including an adiabatic ground-state transmission coefficient in our calculations.²¹ We have developed consistent procedures for doing this for all three versions of variational transition-state theory and for conventional transition-state theory. We use quantized internal energies for the whole calculation (here and in all that follows), but first we perform calculations in which the reaction-coordinate motion is still being treated classically. The resulting thermal rate constants are called $k^*(T)$, $k^{\text{CVT}}(T)$, $k^{\text{ICVT}}(T)$, and $k^{\mu\text{VT}}(T)$. The ground-state rate constant computed with ATST and this same mixture of quantized and classical parts is called $k^A(\alpha = G, T)$. If however, the one-dimensional motion governed by the ground-state adiabatic barrier $V_a(\alpha = s, T)$ is computed quantum mechanically we call the ATST ground-state rate constant $k^{\text{VA}}(\alpha = G, T)$. We define the adiabatic ground-state transmission coefficient as

$$\kappa^{\text{VAG}}(T) = \frac{k^{\text{VA}}(\alpha = G, T)}{k^A(\alpha = G, T)} \quad (10)$$

At low enough temperature, both $k^{\mu\text{VT}}(T)$ and $k^{\text{ICVT}}(T)$ tend to $k^A(\alpha = G, T)$. Thus $\kappa^{\text{VAG}}(T)$ also becomes an appropriate quantal correction for $k^{\mu\text{VT}}(T)$ and $k^{\text{ICVT}}(T)$. We define corrected rate constants by

$$k^{\mu\text{VT/VAG}}(T) = k^{\mu\text{VT}}(T)\kappa^{\text{VAG}}(T) \quad (11)$$

and

$$k^{\text{ICVT/VAG}}(T) = k^{\text{ICVT}}(T)\kappa^{\text{VAG}}(T) \quad (12)$$

At low temperature, $k^{\mu\text{VT/VAG}}(T)$ and $k^{\text{ICVT/VAG}}(T)$ both tend to $k^{\text{VA}}(\alpha = G, T)$. If more than one rotational-

vibrational state makes an important contribution to the rate at temperatures where tunneling is still important, then this method of including quantal effects on reaction-coordinate motion assumes that the important rotational-vibrational states all have similar transmission coefficients. As the temperature is raised and more states contribute, tunneling becomes less important, $\kappa^{\text{VAG}}(T) \rightarrow 1$, and it no longer matters that the transmission coefficient is based on the ground state. Unlike $k^{\mu\text{VT}}(T)$ and $k^{\text{ICVT}}(T)$, both $k^{\text{CVT}}(T)$ and $k^*(T)$ may have contributions from energies below the ATST threshold. Thus the consistent formulation of transmission coefficients for CVT and conventional transition-state theory is more complicated.^{21,29}

There are two more considerations involved in $k^{\text{VA}}(\alpha = G, T)$. First of all, the transmission probabilities for scattering by the vibrationally adiabatic barrier should be calculated quantum mechanically. Although straightforward methods exist, it is more convenient to use semiclassical methods, such as a uniform WKB method. We have systematically tested such semiclassical calculations against fully quantum mechanical calculations.^{21-24,45} Although quantitative differences exist, the semiclassical methods are usually adequate. When tunneling is calculated semiclassically, we replace the acronym VAG by SAG. The next consideration is the choice of tunneling path. The adiabatic approximation reduces the problem of motion in many dimensions on a potential-energy hypersurface to motion in one dimension on an effective potential $V_a(\alpha, \xi)$. The coordinate ξ is determined by specifying a particular path through the multidimensional space. For instance, if the system follows the MEP, then ξ is just the reaction coordinate s . Streamlines of the accurate quantum mechanical wavefunction for collinear $\text{H} + \text{H}_2$ at tunneling energies show that the tunneling flux does not follow the MEP; rather the hydrogen-atom transfer occurs when the end atoms are farther apart than at the saddle point.⁴⁶ This corresponds to "cutting the corner" in a plot like Figure 2. This is the opposite of a bobsled effect, but Marcus has shown by analytical mechanics that when the kinetic energy is negative (as it is for tunneling), the bobsled effect is also negative⁴⁷ (i.e., the motion is directed to the concave rather than the convex side of the MEP). In fact, according to classical S matrix theory tunneling can be described by classical mechanics with imaginary or complex-valued time increments, coordinates, and momenta.⁴⁸ Therefore the best tunneling path is obtained by analytic continuation of the classical mechanical principle of least action. By examining a sequence of constrained and parameterized paths for collinear $\text{H} + \text{H}_2$ with this variational principle, Marcus and Coltrin found that the path of outer classical turning points is a better tunneling path than the MEP.⁴⁹ (The path of outer classical turning points roughly parallels the MEP in a plot like Figure 2, but it is displaced to the concave side.) We have calculated transmission coefficients for the collinear path of outer classical turning points (which we call the Marcus-Coltrin path or MCP) as well

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(49) R. A. Marcus and M. E. Coltrin, *J. Chem. Phys.*, **67**, 2609 (1977).

(44) D. G. Truhlar, *J. Chem. Phys.* **53**, 2041 (1970).

as the MEP for several reactions, and we find that the MCP is much superior.^{19-24,29} The resulting transmission coefficients are called $\kappa^{\text{MCPVAG}}(T)$ for quantal calculations and $\kappa^{\text{MCPSAG}}(T)$ for semiclassical calculations.

The transmission coefficients defined here account for quantal effects on reaction-coordinate motion. They are greater than unity when the effect of tunneling is important. Sometimes they are less than unity because of nonclassical reflection in collisions with enough energy to surmount the barrier classically.

An important consequence of the ad hoc nature of the classical-to-quantal correspondence in transition-state theory is that the rigorous bound on the classical equilibrium rate constant is lost in the real quantum mechanical world. Thus one of our first questions is: can one still obtain better results for real quantum mechanical systems by variationally locating the transition-state dividing surface to minimize the calculated rate constant? One way to study this question is by comparing variational transition-state theory calculations for collinear reactions on realistic potential-energy surfaces to rate constants calculated for these same collinear reactions with the same potential-energy surfaces by accurate quantal scattering theory.¹⁹⁻²⁴ The restriction to collinear reactions at this stage is necessitated by the fact that accurate quantum scattering calculations are generally unavailable for three-dimensional reactions. The reason one wishes to study the validity of transition-state theory by comparing its predictions to the results of accurate quantal scattering theory rather than to experiment is that this provides a direct test of the dynamical assumptions for a given potential-energy surface. On the other hand, comparison to experiment is complicated by the uncertainties in the potential-energy surface, which may either compound or partially cancel the inaccuracies in the dynamical treatment. Of course, if we succeed in obtaining a treatment which produces trustworthy results for theoretical systems with known potential-energy surfaces, then we hope we can ultimately use that treatment to interpret experiments and thereby extract reliable information from them about unknown potential-energy surfaces.

In testing the approximate theories against accurate quantal dynamics we are interested in knowing not just their relative accuracy but also their absolute accuracy. The classical tests of conventional and variational transition-state theory do not provide quantitative guides here because the typical contributions to classical reaction rates at temperature T come from energies up to a few kT above the barrier height. For most of the cases in Table I the accurate quantum mechanical rate is very small at such energies because of zero-point effects at the dividing surface.

In Table II we tabulate some ratios of approximate collinear rate constants^{20,21,23,24} to accurate quantal ones^{20,23,24,50,51} for given potential-energy surfaces.^{38,50,52,53}

(50) D. G. Truhlar and A. Kuppermann, *J. Chem. Phys.*, **56**, 2232 (1972).

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Table II
Ratios of Approximate Calculated Rate Constants to Accurate Quantum Mechanical Ones for Several Collinear Reactions

method	300 K	600 K	1500 K
H + H ₂			
*	0.30	0.70	1.06
*/W	0.92	1.06	1.15
ICVT	0.30	0.69	0.93
ICVT/MEPVAG	0.31	0.64	0.88
ICVT/MCPSAG	0.84	0.86	0.96
ICVT/MCPVAG	0.88	0.85	0.95
Cl + T ₂			
*	0.49	0.85	1.51
*/W	0.85	1.01	1.55
ICVT	0.48	0.76	1.07
ICVT/MEPVAG	0.69	0.87	1.12
ICVT/MCPSAG	0.80	0.86	1.09
ICVT/MCPVAG	0.99	1.00	1.18
T + HD			
*	0.37	0.72	1.36
*/W	1.01	1.03	1.45
ICVT	0.22	0.53	0.94
ICVT/MEPVAG	0.32	0.60	0.97
ICVT/MCPSAG	0.46	0.64	0.95
ICVT/MCPVAG	0.50	0.71	1.02
I + H ₂			
*	12.1	3.66	2.12
*/W	13.4	3.76	2.13
ICVT	1.09	1.05	1.03
ICVT/MEPVAG	1.01	0.99	1.00
ICVT/MCPSAG	1.09	1.05	1.03
ICVT/MCPVAG	1.01	0.99	1.00
F + H ₂			
*	2.88	2.98	3.01
*/W	3.24	3.07	3.03
ICVT	1.74	2.31	2.70
ICVT/MCPSAG	1.81	2.34	2.73
ICVT/MCPVAG	1.73	2.28	2.67
D + F ₂			
*	0.84	0.97	1.04 ^a
*/W	1.00	1.02	1.05 ^a
ICVT	0.82	0.95	1.01 ^a
ICVT/MCPSAG	0.98	0.99	1.02 ^a

^a 1260 K.

We have found that the ICVT, which is better justified than CVT, is easy enough to apply to have wide practical use and it is often just as accurate as μ VT. Thus ICVT is the only version of VTST included in Table II. (Anyway the μ VT results agree with the ICVT ones to the number of figures shown in every case in Table II.) The symbols * and */W are used to denote conventional transition-state theory with classical reaction-coordinate motion⁴⁻¹⁰ and with the leading quantal correction (of order \hbar^2) on the reaction coordinate as determined by the method of Wigner.^{5,7,10} Another popular procedure is to base a transmission coefficient on quantal tunneling through the classical potential-energy barrier $\Delta V(s)$. Comparison of this barrier to the adiabatic ground-state curve $V_a^G(s) [= \Delta V(s) + \epsilon_{\text{int}}(\alpha = G, s)]$ shows that use of $\Delta V(s)$ as the effective barrier is equivalent to assuming conservation of rotational-vibrational energy as the system proceeds along the reaction coordinate. This is inconsistent with transition-state theory,³⁵ and so we do not present our tests^{19,20,29,50,54} of this prescription here. We note that

(53) J. W. Duff and D. G. Truhlar, *J. Chem. Phys.*, **62**, 2477 (1975); J. T. Muckerman, *Theor. Chem. Adv. Perspect.*, **6**, in press; N. Jonathan, S. Okuda, and D. Timlin, *Mol. Phys.*, **24**, 1143 (1975); **25**, 496E (1973).

Table III
Kinetic Isotope Effect $k(\text{Cl} + \text{HD})/k(\text{Cl} + \text{DH})$ for
Collinear Reaction with the Potential Surface of Ref 38

	300 K	450 K
accurate	0.68	0.69
‡	1.59	1.38
‡/W	1.93	1.58
ICVT	0.53	0.65
ICVT/MEPVAG	0.77	0.85
ICVT/MCPSAG	0.52	0.65
ICVT/MCPVAG	0.60	0.74

the derivation of the Wigner transmission coefficient assumes that quantal effects are well localized to the quadratic region around the saddle point; this is seldom satisfied in practice,^{15,19} but the method is consistent through order \hbar^2 and is sometimes fortuitously accurate even when the higher order terms are important.

The results of Table II are largely self-explanatory. We see that conventional transition-state theory is sometimes accurate, but in other cases it makes large underestimates or overestimates. The Wigner quantal correction is sometimes successful at correcting the low-temperature results but usually increases the error at high temperature. The high-temperature errors can be attributed to recrossing effects as seen in the purely classical systems, and variational transition-state theory generally provides considerable improvement for this aspect. When the low-temperature results are two small, the Marcus-Coltrin-path vibrationally adiabatic transmission coefficients usually provide considerable improvement, although in the worst case the underestimate at 300 K is still a factor of 2 even for the best theory. In several cases, the best theory is accurate within 20% or better over a range of a factor of 5 in temperature. Notice the excellent agreement for $\text{D} + \text{F}_2$; results for $\text{H} + \text{F}_2$ ²³ and $\text{H} + \text{Cl}_2$ ²² are very similar.

For the $\text{Cl} + \text{HD}$ reaction we can compare several methods for calculating the intramolecular isotope effect. Such a comparison is shown in Table III. Conventional transition-state theory predicts the wrong direction for this isotope effect because at low temperature the calculated rate for reaction with the H end of HD becomes much smaller when the generalized transition state is located variationally rather than at the saddle point, but this variational improvement does not occur for reaction with the D end. Thus the ‡/W rate for $\text{Cl} + \text{HD}$ is a factor of 2.6 larger than the accurate rate at 300 K.

Overall the results in Tables 2 and 3 and ref. 19–24 show that variational transition-state theory with Marcus-Coltrin-path vibrationally adiabatic transmission coefficients is usually quite accurate over a wide temperature range. We conclude that these procedures provide systematic, general improvement as compared to conventional transition-state theory.

Survey of Three-Dimensional Reactions

In general we cannot compare our three-dimensional calculations to accurate quantal results for three-dimensional reactions because the latter are not available. The one exception is $\text{H} + \text{H}_2$, for which Schatz and Kuppermann⁵⁵ have calculated accurate rate constants

(54) D. G. Truhlar, A. Kuppermann, and J. T. Adams, *J. Chem. Phys.*, **59**, 395 (1973).

(55) G. C. Schatz and A. Kuppermann, *J. Chem. Phys.*, **65**, 4668 (1976).

Table IV
 $k^\ddagger(T)/k^{\text{ICVT}}(T)$ for Three-Dimensional Reactions for
Extended, Modified BEBO Potential-Energy Surfaces

	300 K	600 K	1500 K
¹² C + H ¹² C	24.7	6.12	3.63
¹⁴ C + H ¹⁴ C	28.0	6.60	3.83
¹² C + D ¹² C	3.79	2.34	2.16
C + H ₂	7.94	2.84	1.76
C + D ₂	2.98	1.80	1.54
I + HBr	1.99	2.45	3.45
I + TBr	1.94	2.42	3.42
I + ID	1.36	1.56	1.91

for $T \leq 600$ K for a potential-energy surface of Porter and Karplus.⁵⁶ Although these results have larger uncertainties than the accurate collinear calculations do (about 25% error in the rate constants for the assumed potential-energy surface vs. about 2% or less for collinear systems), we can still use them to test our theory. For 300–600 K, our ICVT/MCPVAG calculations reproduce the Schatz-Kuppermann calculations within 23% or better.²⁸ This made us confident enough to carry out calculations^{28,29} for $\text{H} + \text{H}_2$, $\text{D} + \text{D}_2$, $\text{H} + \text{D}_2$, and $\text{D} + \text{H}_2$ with an accurate potential-energy surface based on the ab initio calculations of Liu and Siegbahn.⁵² In general the results are in good agreement (within about 30%) with experiment^{57,58} and in fact might even be just as reliable as experiment or even more reliable. The use of the ICVT/MCPVAG theory allows a better understanding of the dynamics than does conventional transition-state theory. In particular, because the variational transition state is farther from the saddle point for $\text{D} + \text{H}_2$ than $\text{H} + \text{D}_2$, variational optimization of the generalized transition state allows one to explain the observed trends without invoking “anomalous” tunneling corrections, as was previously⁵⁸ necessary.

Unfortunately, $\text{H} + \text{H}_2$ and isotopic analogues are the only reactions for which the potential-energy surface is known accurately enough for testing the theory against experiment. For all other systems, we believe that the uncertainties caused by the potential-energy surface would exceed the errors in the dynamical treatment. Thus, at this time one would like to use generalized transition-state theory (i) to estimate plausible potential-energy surfaces by adjusting their features so that dynamical predictions agree with experiment and (ii) to provide a guide for future electronic structure calculations as to which regions of plausible potential-energy surfaces are most important and should be studied more carefully. To begin working on these tasks, we considered a sequence of model potential-energy surfaces and made a survey of the differences between the predictions of conventional transition-state theory and those of variational transition-state theory. To construct the model potential-energy surfaces, we modified and extended the bond-energy, bond-order (BEBO) method^{5,59} so that it provides a consistent model for all the quantities needed for var-

(56) R. N. Porter and M. Karplus, *J. Chem. Phys.*, **40**, 1105 (1964).

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(58) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **47**, 1393 (1967).

(59) H. S. Johnston and C. A. Parr, *J. Am. Chem. Soc.*, **85**, 2544 (1963).

ational transition state calculations.^{25,26}

Table IV shows some examples of the ratio $k^*(T)/k^{\text{CVT}}(T)$ where reaction-coordinate motion is treated classically but other degrees of freedom are quantized. This ratio must be greater than or equal to unity, and when it is large it indicates that recrossing effects are probably large at the conventional transition state. The C + HC reaction, a three-body model of a hydrogen-atom transfer between methyl groups, has a symmetric saddle point and the primary factor responsible for relocating the transition state is the small symmetric stretch frequency at the saddle point. We may understand the smallness of this frequency from the fact that the hydrogen does not move in the symmetric stretch; thus the reduced mass is determined by the carbons. As we vary the generalized transition state, we increase the contribution of H motion and thus raise the frequency and local zero-point energy. (An alternative but equivalent viewpoint is to scale all motions to the same reduced mass and visualize the system motion as a point mass governed by a potential-energy surface; in this picture, the small symmetric stretch frequency is a consequence of the small "skew Angle" when a light particle is transferred between two heavier ones.^{20,26}) It turns out that, if the dividing surface is moved $0.06a_0$ or less (in a coordinate system^{17,25} scaled to the initial reduced mass), the zero-point energy increases more rapidly than the classical potential-energy decreases. Thus the variational dividing surface is located about $0.06a_0$ from the saddle point. (Since the system is symmetric, there are actually equivalent variational dividing surface locations at this distance to either side of the saddle point.) Since the location of the variational dividing surface is determined by a zero-point effect, the error in conventional transition-state theory decreases with increasing temperature. Notice that although the predicted error in conventional transition-state theory is very large, it corresponds to an energy error of only 1.9 kcal/mol, i.e., $\exp(\Delta E/kT) = 24.7$ at 300 K for $\Delta E = 1.9$ kcal/mol. In interpreting experiments with conventional transition-state theory, this kind of error could be compensated by misestimating the barrier height by about 2 kcal/mol. In this way conventional transition-state theory can lead to systematic misinterpretations of experimental data. For example, if one interprets the free energy of activation as due to a symmetric bottleneck with 2 kcal/mol fictitious extra potential energy rather than an asymmetric bottleneck with 2 kcal/mol more zero point and potential energy than the symmetric geometry, one will make erroneous predictions about isotope effects, substituent effects, solvent effects, the role of electron correlation, etc.

A similar, but less dramatic, effect is operative for the C + H₂ reaction and is illustrated in Table V. This table shows that the stretching frequency is 1344 cm⁻¹ higher at the canonical variational dividing surface than at the saddle point. This corresponds to a zero-point increase of 1.9 kcal/mol, which easily overcomes a potential-energy decrease of 0.7 kcal/mol. At the variational transition state the CH bond is 0.08 Å longer and the HH bond is 0.08 Å shorter than at the saddle point.

The last three rows of Table IV show cases with very asymmetric saddle points. One of these, I + ID, is also included in Table V. The dominant variational effect

Table V
Properties of CHH and IID Configurations for A + BC
Reactions on Extended, Modified BEBO Surfaces

configuration	n_{AB}^a	r_{AB}, a_0^b	r_{BC}, a_0^b	$V, \text{kcal/mol}^c$	$\omega_{\text{str}}, \text{cm}^{-1d}$	$\omega_b, \text{cm}^{-1e}$
C + H ₂						
H ₂	0.00	∞	1.40	0.0	4390	0
CVT DS ^f	0.40	2.51	1.65	13.93	3103	673
saddle point	0.55	2.36	1.79	14.60	1759	662
CH	1.00	2.06	∞	3.90	2912	0
I + ID						
ID	0.000	∞	3.04	0.00	1641	0
CVT DS ^f	0.989	5.05	5.25	37.93	215	41
saddle point	0.998	5.05	6.04	38.25	216	27
I ₂	1.000	5.05	∞	37.90	216	0

^a Bond order of new bond. ^b Bond distances. ^c Classical potential energy. ^d Frequency of bond stretching motion. ^e Frequency of bending motion. ^f Canonical variational dividing surface for 600 K.

for I + ID is that the variational dividing surface is more symmetric than the saddle point because this leads to a higher bending frequency. I + HBr shows a similar effect: the bending frequency is only 83 cm⁻¹ at the saddle point but the bend tightens to 163 cm⁻¹ at the variational dividing surface for 600 K. This is a classical example of entropy vs. energy; the dynamical bottleneck is located at a location where the angle of release of Br is very constrained. Since the bending degree of freedom is a low-frequency mode, this kind of effect does not lead to errors in conventional transition-state theory as large as those that occur when the stretching degree of freedom dominates. However, when the bend dominates, the effect increases with temperature.

We have also found many cases where conventional and variational transition-state theory agree better than the cases shown in Tables IV and V. For example, for 36 H-atom transfers the median value of $k^*(T)/k^{\text{CVT}}(T)$ at 600 K was found to be 1.75.²⁵ Examination of a large number of cases^{21,22,25-29} has given useful indications of when the predicted rate is greatly minimized by moving the dividing surface away from the saddle point and when it is not.

The tests of conventional transition-state theory for kinetic isotope effects^{19-24,27-29} are very important since this theory "forms the basis of almost all our discussions of isotope effects in chemical reaction".⁶⁰ Table IV shows that the error in conventional transition-state theory is sometimes significantly different for one isotope than another. We have also found large differences using extended LEPS potential-energy surfaces.³⁰ The consequences for the theoretical interpretation of kinetic isotope effects are very serious: one cannot always assume that the isotope effect is the result of changing the masses but not changing the force field of the activated complex.

Conclusion

We believe that variational transition-state theory provides useful insight into the successes and failures of the conventional theory. It also provides useful quantitative estimates of possible errors in the predictions of conventional transition-state theory. Finally it provides a means for removing or reducing these errors so that it is the most accurate theory now

available for the practical calculations of chemical reaction rates and thermochemical and structural interpretations of rate processes.

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Stereospecific Reactions of Nitrilium Ions and Analogous 1,3-Dipoles

ANTHONY F. HEGARTY

Chemistry Department, University College, Belfield, Dublin 4, Ireland

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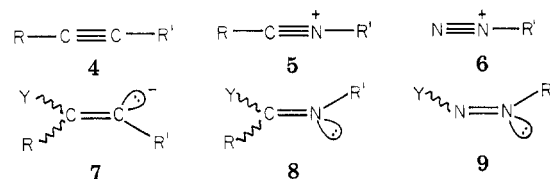
The quest for reaction pathways which are stereospecific and not merely stereoselective continues to intrigue the synthetic chemist. This is an area which is particularly susceptible to the tools of physical organic chemistry, since it is the structure of the transition state of the reaction (probed by means of kinetics, isotope effects, modeling, etc) which is important in determining the initial product formed. A rational approach to synthesis then depends to a large extent on an understanding of the factors which control transition-state structure.

The concept of stereoelectronic control of organic reactions has received a new impetus from the work of Deslongchamps.¹ These ideas are particularly useful when applied to the problem of which way a short-lived intermediate is likely to break down to products. It appears that the preferred mode of cleavage is determined by the necessity of having one (or more) electron pairs on an adjacent heteroatom arranged *antiperiplanar* to the leaving group to "assist" its departure. This important factor must now be routinely taken into account when determining the course of organic reactions (or in devising a successful synthetic scheme). The driving force for reaction in the stereoelectronically controlled direction may outweigh other factors (e.g., steric) in the transition state, leading to products with less stable (but desirable) geometries.

The question arises as to whether the same factors apply to the addition of nucleophiles to unsaturated systems and whether this can be reflected in the preferred geometries of the product(s). Thus addition to a protonated ketone (1, XZ = OH) could, in theory, lead

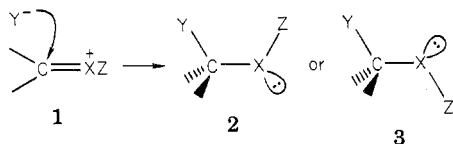
initially to **2** or **3** (or indeed any intermediate geometry). However, because of rapid C-O bond rotation, one can only surmise the stereochemistry of the initial addition from the way in which the adduct (**2** or **3**) further reacts.¹ The same problem arises in additions to the carbon-carbon double bond (1, XZ = CR₂) and the carbon-nitrogen double bond (1, XZ = NR₂); in each case the bond order of the C-X bond is decreased from two to one.

This problem is less severe in the addition of nucleophiles to alkynes **4**, nitrilium ions **5**, and diazonium ions **6**. Here just two geometries can arise when a



nucleophile is added, but again inversion of the carbanion (from addition to the alkyne **4**) or of the imino (in **8**) or azo (in **9**) nitrogen may be so rapid as to obscure stereospecificity. There are indications in the case of diazonium ion adducts² and nucleophilic addition to alkynes³ that the formation of one isomer may be preferred and, indeed, certain conditions (dependent on the nucleophile Y⁻ and the substituents) only one isomer of **7** and **9** is actually formed.

Our interest in this area stemmed from a study of displacement reactions at the carbon-nitrogen double bond. We were struck by the ease with which nitrilium ion intermediates (**5**) are formed in these reactions (see below). The step which determines the product is essentially the trapping of this nitrilium ion by a nucleophile. The marked stereospecificity noted in these trapping reactions has wide implications not only for our understanding of the factors which control transition-state geometry but also in the selective formation of reactive synthons of known stereochemistry.



Frank Hegarty was born in Ireland in 1942. Following completion of a Ph.D. at Cork in 1967, he worked with J. E. Dubois (Université de Paris) and T. C. Bruice (University of California at Santa Barbara). He was appointed to Cork as Lecturer in Chemistry (in 1970) and was subsequently on sabbatical leave at Brandeis (W. P. Jencks). He has recently moved to University College, Dublin, as Professor of Organic Chemistry. His research interests are in the area of mechanistic studies on organic and biological reactions, including catalysis, reactive intermediates, and new reagents for synthesis.

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