

temperatures below its phase transition, only dilute mixed micelles form.^{11a,52}

With OPE-9, the monodispersity of the surfactant allows one to differentiate between surfactant polydispersity and temperature as the cause of poor micelle-forming properties with some phospholipids. Mixed micelles with dipalmitoylphosphatidylcholine form readily even at 20 °C (unlike Triton X-100, where mixed micelles form only at a very low mole fraction of phospholipid), but two populations of micelles result. The larger sized species are probably best described as very small bilayers with interspersed OPE-9 or very large mixed micelles although they are only about twice the diameter of pure OPE-9 micelles at comparable temperatures. The smallest known bilayer for pure phospholipid is the single bilayer spherical vesicle formed upon sonication of multibilayers,⁹ but with some detergent present, there would not be the need to vesiculate. For mixed-micelle formation with a lipid at low temperatures, lipid packing may be tighter laterally, leading to phase separation as is the case with pure lipid bilayers at temperatures below the thermotropic phase transition.⁵⁴

The overall structure of mixed micelles of phospholipid and nonionic detergents is probably similar to that of the pure detergent micelles as illustrated in Figure 3 but with a few phospholipid molecules intercalated in the structure.¹⁴ Much is known about the precise conformation of the phospholipid in the mixed micelle as derived from NMR studies on a large variety of

(54) Chapman, D.; Williams, R. M.; Ladbrooke, B. D. *Chem. Phys. Lipids* 1967, 1, 445-475.

phospholipids in Triton X-100 as well as in a number of other detergents.⁵⁵ In all cases, the phospholipid adopts a conformation in which the two fatty acyl chains are nonequivalent and are positioned at the interface with the carbonyl of the *sn*-2 chain more exposed and the carbonyl of the *sn*-1 chain more buried in the hydrophobic region.^{56c} The exposure of these carbonyl groups in the phospholipid to the aqueous solution is greater in mixed micelles than in sonicated vesicles but less than for monomers as demonstrated by the susceptibility of the phospholipid to alkaline hydrolysis.⁵⁶ Thus, the packing of phospholipid in mixed micelles with Triton X-100 is such that hydroxide can get to the phospholipid and it does so with an equal rate of hydrolysis at the carbonyl of the *sn*-1 and *sn*-2 fatty acyl chains. If it could be definitively shown whether the classical or nonclassical model is better for pure nonionic detergent micelles, it is likely that the mixed micelles would be found to form the same type of structure.

We wish to thank Anthony Ribeiro who, as a graduate student, contributed much to our understanding of Triton micelles. Mary Roberts and Jacqueline deBony as postdoctoral associates and Professors Askel A. Bothner-By and Karol Mysels provided us with many germane suggestions and much help. Critical reading of this manuscript by Dr. Dov Lichtenberg and Dr. Andreas Pluckthun is appreciated. This work was supported by the National Science Foundation through Grant PCM 82-16963.

(55) (a) Roberts, M. F.; Dennis, E. A. *J. Am. Chem. Soc.* 1977, 99, 6142-6143. (b) Roberts, M. F.; Bothner-By, A. A.; Dennis, E. A. *Biochemistry* 1978, 17, 935-942. (c) DeBony, J.; Dennis, E. A. *Ibid.* 1981, 20, 5256-5260.

(56) Kensil, C. R.; Dennis, E. A. *Biochemistry* 1981, 20, 6079-6085.

Variational Unimolecular Rate Theory

WILLIAM L. HASE

Department of Chemistry, Wayne State University, Detroit, Michigan 48202

Received June 14, 1982 (Revised Manuscript Received December 3, 1982)

The Rice-Ramsperger-Kassel-Marcus (RRKM) theory plays a very important role in the interpretation of unimolecular reaction kinetics.¹⁻⁴ Since it is a statistical theory, a unimolecular rate constant for a dissociating molecule can be calculated without acquiring information concerning the molecule's intramolecular dynamics. The assumptions of the theory are fundamental. During dissociation of the molecule, energy is assumed to be randomized amongst all internal degrees of freedom. The classical mechanical equivalent of this statement is that a microcanonical ensemble is postu-

lated for the phase space of the energized molecule. If the molecule is initially prepared with a nonrandom energy distribution, the theory further assumes that rapid intramolecular processes will render the distribution a random one on a time scale much shorter than the molecule's unimolecular lifetime.⁴

Another assumption of RRKM theory is a critical configuration⁵ that separates internal states of the energized molecule (reactant) from those of the products. In the language of classical mechanics the critical con-

(1) P. J. Robinson and K. A. Holbrook, "Unimolecular Reaction", Wiley, New York, 1972.

(2) W. Forst, "Theory of Unimolecular Reactions", Academic Press, New York, 1973.

(3) J. Troe in "Physical Chemistry, An Advanced Treatise", W. Jost, Ed., Academic Press, New York, 1975, Vol. 6B, p 835.

(4) W. L. Hase in "Modern Theoretical Chemistry", W. H. Miller, Ed., Plenum, New York, 1976, Vol. 2, p 121; D. L. Bunker and W. L. Hase, *J. Chem. Phys.*, 59, 4621 (1973).

(5) The critical configuration is often called an activated complex or transition state.

William L. Hase was born in Washington, MO, in 1945. Upon completing his undergraduate degree at the University of Missouri, Columbia, he went to New Mexico State University, where he received his Ph.D. degree in 1970. After spending 3 years as a postdoctoral research associate, 1 year at New Mexico State and 2 at the University of Columbia, Irvine, he joined the faculty at Wayne State University, where he is a Professor of Chemistry. Dr. Hase's research interests include the theory of gas-phase reaction kinetics (particularly unimolecular kinetics), derivation of potential energy surfaces for reactions involving polyatomic molecules, and computer simulation of both chemical reactions and intramolecular dynamics.

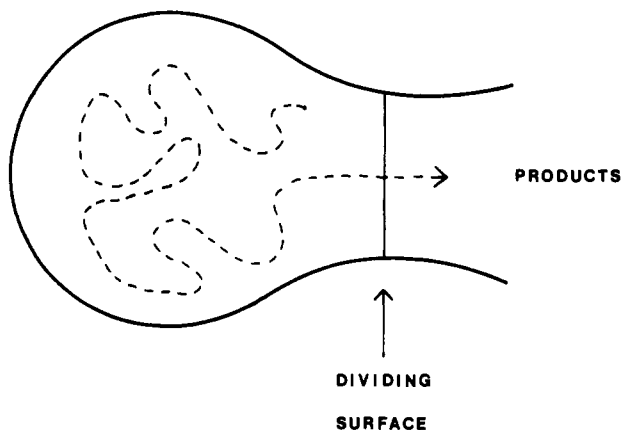


Figure 1. Depiction of a trajectory moving through the reactant phase space and crossing the dividing surface to dissociate to products.

figuration represents a dividing surface that separates the reactant and product regions of phase space. The crucial assumption is that, once a trajectory crosses this surface toward products, it never returns to the reactant region of phase space. Thus, the name critical configuration is a fitting description of the dividing surface. Figure 1 depicts a dissociating trajectory crossing the dividing surface. The figure also illustrates that the trajectory is free to move through all the reactant phase space as assumed by RRKM theory.

The postulates of the RRKM theory are readily apparent when the rate constant for a fixed internal energy and total angular momentum, $k(E, J)$, is derived in classical mechanical terms. This is accomplished by determining the flux of trajectories crossing the dividing surface for a microcanonical ensemble of reactant molecules.^{2,6,7} The resulting expression for the classical RRKM unimolecular rate constant is

$$k(E, J) = \int \dots \int_{0 < H < E^+} dp^+ dq^+ / \int \dots \int_{H=E} dp dq \quad (1)$$

For an energized molecule with s vibrational degrees of freedom, the numerator in eq 1 is the volume integral for the critical configuration's $s - 1$ degrees of freedom and the denominator is the surface integral for the reactant's s degrees of freedom. The critical configuration has one less vibrational degree of freedom than the reactant since one of its degrees of freedom is a translational motion perpendicular to the dividing surface. Dividing both the numerator and denominator by h^s gives

$$k(E, J) = G(E^+, J) / hN(E, J) \quad (2)$$

where $G(E^+, J)$ is the classical sum of states for the critical configuration and $N(E, J)$ is the classical density of states for the reactant.⁸ The quantum mechanical RRKM rate constant results from substituting quantal expressions for the sum and density, and including tunnelling corrections if necessary.⁹

(6) W. H. Miller, *Acc. Chem. Res.*, **9**, 306 (1976).

(7) P. Pechukas in "Modern Theoretical Chemistry", W. H. Miller, Ed., Plenum, New York, 1976, Vol. 2, p 269.

(8) N. Davidson, "Statistical Mechanics", McGraw Hill, New York, 1962.

(9) W. H. Miller, *J. Am. Chem. Soc.*, **101**, 6810 (1979); D. G. Truhlar, A. D. Isaacson, R. T. Skodje, and B. C. Garrett, *J. Phys. Chem.*, **86**, 2252 (1982).

Thus, RRKM theory is exact classically¹⁰ if the distribution of trajectories in the reactant phase space is given by a microcanonical ensemble, and if trajectories do not recross the dividing surface. The first assumption is currently under critical study, both theoretically¹¹⁻¹⁵ and experimentally,^{16,17} by many different research groups. The second assumption has been studied by Pechukas and co-workers¹⁸ from a dynamical perspective. They have investigated the properties of potential energy surfaces that give rise to recrossing of the dividing surface and discovered a dynamical procedure for choosing the dividing surface. In this Account, we focus on the second assumption and consider a statistical variational model for finding the dividing surface. Recently Truhler and Garrett¹⁹ have reviewed the variational approach as it applies to bimolecular reactions.

Historical Perspective

Unimolecular potential energy surfaces are usually classified as one of the following two types, though there are, of course, intermediate cases. Type 1 potential energy surfaces are for simple bond-dissociation reactions such as $\text{CH}_4 \rightarrow \text{H} + \text{CH}_3$ that do not have a potential maximum. In contrast, type 2 potential energy surfaces have a well-defined barrier as found in $\text{CH}_3\text{NC} \rightarrow \text{CH}_3\text{CN}$ isomerization. For a type 1 surface a potential maximum results from the centrifugal (rotational) barrier, while the potential maximum is only weakly affected by the centrifugal potential for a type 2 surface.

In the early applications of RRKM theory, it was assumed that the dividing surface is located at the potential maximum.^{1,2} Choosing the dividing surface in this manner is certainly an ad hoc procedure. A fundamental variational method for choosing the dividing surface had been given by Wigner,²⁰ Horiuti,²¹ and Keck,²² and as early as 1938 Horiuti pointed out that the best location for the dividing surface is not necessarily at the saddlepoint. However, this work was for the most part overlooked and not incorporated into unimolecular rate theory. Arguments were presented that, for a Boltzmann distribution of energized reactants, one should consider a surface of free energy instead of potential energy,²³ but the relationship of this

(10) One should recognize that there are inherent differences between the quantal and classical descriptions of statistical unimolecular dissociation. A difficulty in deriving a fully quantal RRKM theory similar to the classical one arises from the fact that specifying a localized entity like a critical configuration implies a fundamental uncertainty in momenta. E. E. Nikitin, "Theory of Elementary Atomic and Molecular Processes in Gases", Clarendon Press, Oxford, 1974.

(11) E. J. Heller, *J. Chem. Phys.*, **72**, 1337 (1980).

(12) K. G. Kay, *J. Chem. Phys.*, **72**, 3955 (1980); K. M. Cristoffel and J. M. Bowman, *ibid.*, **74**, 5057 (1981).

(13) W. L. Hase in "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhler, Ed., Plenum, New York, 1981, p 1; W. L. Hase, *J. Phys. Chem.*, **86**, 2873 (1982).

(14) D. W. Noid, M. L. Koszykowski, and R. A. Marcus, *Ann. Rev. Phys. Chem.*, **32**, 267 (1981).

(15) B. A. Waite and W. H. Miller, *J. Chem. Phys.*, **73**, 3713 (1980); **74**, 3910 (1981); **76**, 2412 (1982).

(16) K. V. Reddy and M. J. Berry, *Chem. Phys. Lett.*, **66**, 223 (1979).

(17) I. Oref and B. S. Rabinovitch, *Acc. Chem. Res.*, **12**, 166 (1979); J. D. McDonald, *Ann. Rev. Phys. Chem.*, **30**, 29 (1979).

(18) P. Pechukas and F. J. McLafferty, *J. Chem. Phys.*, **58**, 1622 (1973); P. Pechukas and E. Pollak, *ibid.*, **71**, 2062 (1979).

(19) D. G. Truhlar and B. C. Garrett, *Acc. Chem. Res.*, **13**, 440 (1980).

(20) E. Wigner, *J. Chem. Phys.*, **5**, 720 (1937).

(21) J. Horiuti, *Bull. Chem. Soc. Jpn.*, **13**, 210 (1938).

(22) J. C. Keck, *Adv. Chem. Phys.*, **13**, 85 (1967).

approach to the variational method was not well understood.

For a type 1 surface the rupturing bond is extended to about 4 times its normal length at the rotational barrier.^{1,2,24,25} At such extensions the dissociating fragments are thought to be freely rotating and have the same geometry and vibrational frequencies as the products, i.e., the Gorin model.²⁶ Some of the first tests of the Gorin model were alkane dissociations to alkyl radicals, and the model was found to be inapplicable. Tsang^{27,28} measured Arrhenius A factors for alkane dissociations much smaller than those calculated with activated complex theory, using the Gorin model. In chemical activation studies, Simons and co-workers²⁹⁻³³ measured $k(E)$ for a series of alkane dissociations. To fit the rate constants with RRKM theory, frequencies for alkyl radical rocking motions at the dividing surface are required that are only 4-5 times greater than their values for the molecule and much larger than the values expected for freely rotating radicals.

A dilemma soon arose in using activated complex theory to fit experimental thermal decomposition and recombination rate constants for the alkane-alkyl radical systems.³⁰⁻³³ Since barriers are not observed for alkyl radical recombination, it was thought that the unimolecular threshold should equal the 0 K C-C bond dissociation energy. With this assumption it is impossible to find an activated complex structure that fits both the decomposition and recombination rate constant. The wrong temperature dependence is also predicted for the recombination reaction rate.³⁴ Tsang²⁸ pointed out that both rates could be fit if a negative threshold was used for radical recombination, resulting in a unimolecular threshold less than the bond-dissociation energy.

Theoretical justification for Tsang's proposal came from Monte Carlo classical trajectory calculations by Bunker and Pattengill³⁵ for unimolecular bond dissociation of triatomics such as O_3 and NO_2 . They computed microcanonical unimolecular rate constants from their trajectories and located critical configurations by finding the smallest value of the reaction coordinate r^+ at which trajectories did not return to reactants (i.e., recross the dividing surface). They found nearly exact agreement between RRKM and trajectory microcanonical rate constants. The location of the critical configuration was found to be strongly dependent on both E and J , and only at low levels of excitation was it located at the rotational barrier. At higher excitation the critical configuration moves in from the rotational

barrier, which results in a unimolecular threshold E_0 for a fixed E and J less than the 0 K bond-dissociation energy and a "tighter" critical configuration than the structure at the rotational barrier.

Bunker and Pattengill proposed that the critical configuration represents a dynamical "bottleneck" in the molecular phase space.³⁵ They found that the critical configuration derived from the trajectory calculations could be fit by minimizing the convolution of the density of internal states and the translational density of states along the reaction coordinate. For $J = 0$ this criterion is

$$\partial \left[\int_0^{E^+} N(E^+ - E^+) N(E^+) dE^+ \right] / \partial r^+ = 0 \quad (3)$$

Bunker and Pattengill's idea was first applied to the $C_2H_6 \rightarrow 2CH_3$ system to see if the dilemma between activated complex theory and the experimental results could be eliminated.³⁶ A potential energy function for ethane dissociation was formulated with a Morse function and the bond-energy-bond-order (BEBO) method.³⁷ Instead of eq 3, the minimum in the quantal number of states along the reaction path

$$\partial G(E^+, J) / \partial r^+ = 0 \quad (4)$$

was used as the variational criterion. This criterion, that of Bunker and Pattengill, and the minimum density of states criterion

$$\partial N(E^+, J) / \partial r^+ = 0 \quad (5)$$

proposed by Wong and Marcus³⁸ were found to give identical unimolecular rate constants for C_2H_6 dissociation.³⁹ The unimolecular threshold for thermally excited C_2H_6 was predicted to be less than the 0 K bond-dissociation energy, and the dilemma between the forward and reverse rate constants for $C_2H_6 \rightleftharpoons 2CH_3$ was removed. In work nearly simultaneous to this, Gaedtke and Troe showed that the variational criterion was also important for NO_2 dissociation.⁴⁰ Later Quack and Troe considered the variational criterion for a series of unimolecular reactions.^{41,42}

Microcanonical Variational Criterion

Since classical RRKM theory equates the unimolecular rate constant to the one-way flux of a microcanonical ensemble across a dividing surface, it is obvious that, if trajectories recross the dividing surface, RRKM theory will overestimate the unimolecular rate constant. This point has been illustrated quite clearly by the work of Pechukas and co-workers.¹⁸ Thus, classical RRKM theory will be exact for a microcanonical ensemble if there is no recrossing, and the RRKM rate constant can be considered an upper bound to the classical unimolecular rate constant. In the following we will assume that the same situation is true for the quantum mechanical problem.¹⁰ We note that efforts have been

(23) K. J. Laidler and J. C. Polanyi in "Progress in Reaction Kinetics", G. Porter, Ed., Pergamon, Oxford, 1965, Vol. 3, p 1; K. J. Laidler, "Theories of Chemical Reaction Rates", McGraw-Hill, New York, 1969.

(24) E. Tschuikow-Roux, *J. Phys. Chem.*, **72**, 1009 (1968).

(25) E. V. Waage and B. S. Rabinovitch, *Chem. Rev.*, **70**, 377 (1970).

(26) E. Gorin, *Acta Physicochim URSS*, **9**, 691 (1938).

(27) W. Tsang, *J. Chem. Phys.*, **44**, 4283 (1966).

(28) W. Tsang, *Int. J. Chem. Kinet.*, **1**, 245 (1969).

(29) R. L. Johnson, W. L. Hase, and J. W. Simons, *J. Chem. Phys.*, **52**, 3911 (1970).

(30) W. L. Hase and J. W. Simons, *J. Chem. Phys.*, **54**, 1227 (1971).

(31) W. L. Hase, R. L. Johnson, and J. W. Simons, *Int. J. Chem. Kinet.*, **4**, 1 (1972).

(32) F. B. Growcock, W. L. Hase, and J. W. Simons, *J. Phys. Chem.*, **76**, 607 (1973).

(33) F. B. Growcock, W. L. Hase, and J. W. Simons, *Int. J. Chem. Kinet.*, **5**, 77 (1973).

(34) E. V. Waage and B. S. Rabinovitch, *Int. J. Chem. Kinet.*, **3**, 105 (1971).

(35) D. L. Bunker and M. Pattengill, *J. Chem. Phys.*, **48**, 772 (1968).

(36) W. L. Hase, *J. Chem. Phys.*, **57**, 730 (1972).

(37) H. S. Johnson, "Gas Phase Reaction Rate Theory", Ronald, New York, 1966.

(38) W. H. Wong and R. A. Marcus, *J. Chem. Phys.*, **55**, 5625 (1971).

(39) W. L. Hase, unpublished results.

(40) H. Gaedtke and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **77**, 24 (1973).

(41) M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **78**, 240 (1974).

(42) M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **81**, 329 (1977).

made to formulate a fully quantum transition-state theory.⁶

In variational microcanonical unimolecular rate theory the best upper bound to the unimolecular rate constant is found by minimizing the flux through the dividing surface.⁴³⁻⁴⁶ If all variations of the dividing surface in momenta and coordinate space are considered, the exact variational rate constant can be calculated.²² However, unconstrained variations of the dividing surfaces are impractical for a multidimensional system. On the basis of chemical intuition, the constraint that has been adopted for both unimolecular and bimolecular reactions is to assume the dividing surface is perpendicular to the reaction path r^+ . The *microcanonical variational criterion* is then⁴⁶ given by eq 4.

It is interesting to note that the microcanonical variational criterion eq 4 does not minimize the microcanonical unimolecular rate constant $k(E, J)$. This is because $k(E, J)$ depends upon the reactant density of states $N(E, J)$ in addition to $G(E^+, J)$. Since $N(E, J)$ decreases as r^+ is shortened, the minimum in $k(E, J)$ does not coincide with that for $G(E^+, J)$.

The reaction path is uniquely given by a trajectory that starts at the saddlepoint and moves toward reactants and products in infinitesimal steps, with its kinetic energy removed after each step.⁴⁷ In mass-weighted Cartesian coordinates, this trajectory traces out the steepest descent path from the saddlepoint and can be found by following the negative gradient from the saddlepoint. Miller and co-workers⁴⁸⁻⁵⁰ have defined normal coordinates for the $s - 1$ frequencies orthogonal to the reaction path $\nu_i(r^+)$. The frequencies are obtained by diagonalizing the projected force constant matrix, projecting out the reaction path and the overall translations and rotations. Also found along the reaction path are the three principal moments of inertia $I_i(r^+)$, the classical potential energy $V_{cl}(r^+)$, and the harmonic vibrational adiabatic potential $V_{va}(r^+)$ (eq 6), where E_z is the zero-point energy of the decomposing molecule.

$$V_{va}(r^+) = V_{cl}(r^+) + \sum_{i=1}^{s-1} h\nu_i(r^+)/2 - E_z \quad (6)$$

To illustrate the terms that influence the minimum in the sum of states, consider the classical harmonic sum of states

$$G(E^+) = \frac{\{E - V_{cl}(r^+) + \sum_{i=x,y,z} E_{ri} [1.0 - I_i/I_i(r^+)]\}^{s-1}}{(s-1)! \prod_{i=1}^{s-1} h\nu_i(r^+)} \quad (7)$$

(43) K. G. Kay, *J. Chem. Phys.*, **65**, 3813 (1976).

(44) B. C. Garrett and D. G. Truhlar, *J. Chem. Phys.*, **70**, 1593 (1979).

(45) P. Pechukas, *Ann. Rev. Phys. Chem.*, **32**, 159 (1981).

(46) For situations with multiple minima in $G(E^+, J)$ along the reaction path, some ambiguity may arise in choosing the critical configuration. It has been suggested that the minima at the largest r^+ be chosen: W. L. Hase and D. L. Bunker, *QCPE*, **11**, 234 (1973). Multiple extrema in the microcanonical flux along the reactive path can be used to define a "unified" statistical theory that uses the relative minima and maxima of flux to construct an approximate transmission coefficient: W. H. Miller in "Potential Energy Surfaces and Dynamics Calculations", D. G. Truhlar, Plenum, New York, 1981, p 65.

(47) K. Fukui, *J. Phys. Chem.*, **74**, (1975); S. Kato, H. Kato, and K. Fukui, *ibid.*, **99**, 684 (1977); H. F. Schaefer, *Chem. Br.*, **11**, 227 (1975); K. Morokuma and S. Kato in "Potential Energy Surfaces and Dynamics Calculations". D. G. Truhlar, Ed., Plenum, New York, 1981, p 243.

(48) W. H. Miller, N. C. Handy, and J. E. Adams, *J. Chem. Phys.*, **72**, 99 (1980).

(49) (a) S. K. Gray, W. H. Miller, Y. Yamaguchi, and H. F. Schaefer III, *J. Chem. Phys.* **73**, 2733 (1980); (b) *J. Am. Chem. Soc.*, **103**, 1900 (1981).

(50) Y. Osamura, H. F. Schaefer III, S. K. Gray, and W. H. Miller, *J. Am. Chem. Soc.*, **103**, 1904 (1981).

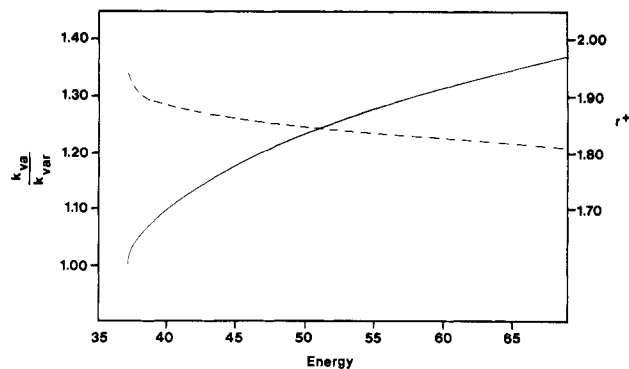


Figure 2. Variational results for ethyl radical dissociation: solid line, plot of the ratio of the vibrationally adiabatic rate constant to the variational rate constant vs. energy (kilocalories/mole); dashed line, plot of the rupturing C-H bond length (angstroms) at the variational dividing surface vs. energy.

where E_{ri} and I_i are the rotational energy and moment of inertia for an external rotational degree of freedom in the reactant. For values of E just above the saddlepoint energy, the numerator in eq 7 predominates in defining the minimum in $G(E^+)$. However, as the energy is increased changes in vibrational frequencies along the reaction path become more significant and influence the location of the minimum. Changes in the principal moments of inertia are important when E^+ is small and for situations with large amounts of external rotational energy.

Ethyl Radical Dissociation

Type 2 potential energy surfaces have a saddlepoint, i.e., a maximum in $V_{cl}(r^+)$, and this feature usually determines the location of the dividing surface. As an example, ethyl radical dissociation is considered. The reaction path and the $s - 1$ frequencies perpendicular to the reaction path were found as described above for an analytic potential published previously.⁵¹ This surface has a rather broad saddlepoint region and a small classical barrier of 3.50 kcal/mol for $H + C_2H_4$ recombination. Two bending vibrations associated with the rupturing CH bond undergo major frequency changes along the reaction path.

With use of harmonic state counting, the minimum in the quantum sum of states was determined as a function of E for $J = 0$. As the energy is increased, the dividing surface moves closer to the reactant minimum, but its displacement from the vibrationally adiabatic barrier is still small. (The vibrationally adiabatic barrier occurs at a C-H bond length of 1.94 Å and the classical saddlepoint at 2.00 Å.) This is illustrated in Figure 2 where the length of the rupturing CH bond at the dividing surface is plotted. Also shown in Figure 2 is the ratio of the rate constant calculated by fixing the dividing surface at the vibrationally adiabatic barrier to the variational one, k_{va}/k_{var} . One sees that the assumption of a fixed dividing surface is good for computing the unimolecular rate constant. Even at 30 kcal/mol above the vibrationally adiabatic threshold, the error is only 35%. The location of the vibrationally adiabatic barrier and the saddlepoint along r^+ are nearly identical, and fixing the dividing surfaces at the saddlepoint gives similar differences with the variational criterion as those in Figure 2.

(51) W. L. Hase, G. Mrowka, R. J. Brudzynski, and C. S. Sloane, *J. Chem. Phys.*, **69**, 3548 (1978); **72**, 6321 (1980).

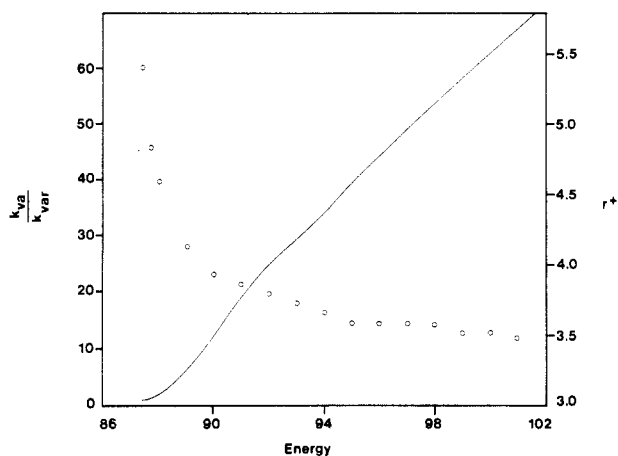


Figure 3. Variational results for ethane dissociation: solid line, same as in Figure 1; circles, values of the rupturing C-C bond length (angstroms) at the variational dividing surface vs. energy (kcal/mol).

Ethane Dissociation

In sharp contrast to the above example, the variational criterion is of utmost importance for type 1 surfaces, those without a saddlepoint. A particularly important example is a previous calculation for $C_2H_6 \rightarrow 2CH_3$ dissociation.⁵² A model reaction-path Hamiltonian was postulated by (i) assuming that stretching of the C-C bond defines the reaction path, with

$$V_{cl}(r^+) = D[1 - \exp\{-\beta(r^+ - r_0)\}]^2 \quad (8)$$

and (ii) attenuating the four CH_3 rocking frequencies by

$$\nu_{rock} = \nu_{rock}^0 \exp\{-\alpha(r^+ - r_0)\} \quad (9)$$

These rocking motions are the vibrations that undergo the major frequency changes along the reaction path. The exponential term in eq 9 results from a BEBO analysis^{36,40} in which the CCH bending force constant is given by $f = f^0 n$, where f^0 is the force constant at the equilibrium geometry and n is the C-C bond order. The parameter α was chosen so that the surface fits a chemical activation rate constant for ethane dissociation.⁵² A small vibrationally adiabatic barrier, 0.15 kcal/mol, for methyl radical recombination exists on the surface at a C-C distance of 5.3 Å.

Variational calculations were performed for this model Hamiltonian, and the same information is presented in Figure 3 for ethane dissociation, as in Figure 2 for ethyl radical dissociation. The differences between these figures are striking and important. For ethane dissociation r^+ is strongly dependent on E . Major differences exist between k_{va} and k_{var} , and serious errors would result in assuming a fixed dividing surface. Only for values of E near the vibrationally adiabatic barrier do k_{va} and k_{var} agree. As the energy is raised, k_{va} becomes significantly larger than k_{var} .

Direct Use of ab Initio Results: Formaldehyde Dissociation

Accurate ab initio calculations provide the information required to perform a unimolecular variational study. The reaction path can be traced by following the negative gradient from the saddlepoint, and with recent advances in computing analytic first⁵³ and second⁵⁴

(52) W. L. Hase, *J. Chem. Phys.*, **64**, 2442 (1976).

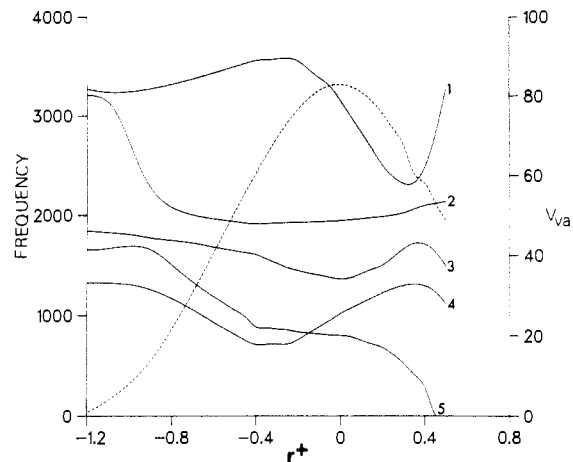


Figure 4. Information for the $H_2CO \rightarrow H_2 + CO$ variational calculation. The solid lines are plots of the five frequencies in reciprocal centimeters perpendicular to the reaction path (r^+) given in $\text{amu}^{1/2} \text{Å}$. The saddlepoint is at $r^+ = 0.0$. At the H_2CO equilibrium geometry $\nu_1, \nu_2, \nu_3, \nu_4,$ and ν_5 are the asymmetric CH stretch, symmetric CH stretch, CO stretch, out of plane bend, and CH_2 symmetric deformation, respectively. The information in this figure was supplied by Dr. Stephen K. Gray.

derivatives of the potential energy, it has become relatively easy to compute the frequencies for the $s - 1$ degrees of freedom perpendicular to the reaction path.^{48-50,55}

As an illustration of the use of ab initio results, calculations are reported for formaldehyde dissociation to hydrogen and carbon monoxide. Values for the $s - 1$ frequencies along the reaction path have been reported previously^{49b,56} and are plotted in Figure 4 vs. reaction coordinate for calculations at the DZ-SCF level.⁵⁷ Also shown in Figure 4 is the vibrationally adiabatic potential as determined from DZ-SCF calculations. This level of theory gives a vibrationally adiabatic barrier of 107.2 kcal/mol. In accord with recent estimates of the actual barrier,⁵⁸ all the DZ-SCF potential energies are uniformly scaled to give the barrier of 83.0 kcal/mol in Figure 4.

For this example the $J = 0$ situation is considered, and the information in Figure 4 gives the complete input for the variational calculation. Variational theory places the dividing surface at the saddlepoint for all energies 0–50 kcal/mol above the vibrationally adiabatic barrier. Higher energies, though not considered, are expected to yield the same result. Obviously, the shape and well-defined saddlepoint for formaldehyde dissociation overwhelms any frequency changes along the reaction path that might influence the location of the dividing surface.

Canonical Variational Criterion

If the reactant molecule has a distribution of internal

(53) P. Pulay in "Modern Theoretical Chemistry", H. F. Schaefer III, Ed., Plenum, New York, 1976, Vol. 3, p 153.

(54) J. A. Pople, R. Krishnan, H. B. Schlegel, and J. S. Binkley, *Int. J. Quantum Chem., Symp.*, **13**, 225 (1979).

(55) S. Kato and K. Morokuma, *J. Chem. Phys.*, **73**, 3900 (1980).

(56) K. Yamashita, T. Yamabe, and K. Fukui, *Chem. Phys. Lett.*, **84**, 123 (1981).

(57) B. A. Waite, S. K. Gray, and H. W. Miller, *J. Chem. Phys.*, **78**, 259 (1983).

(58) J. D. Goddard and H. F. Schaefer III, *J. Chem. Phys.*, **70**, 5117 (1979); L. B. Harding, H. B. Schlegel, R. Krishnan, and J. A. Pople, *J. Phys. Chem.*, **84**, 3394 (1980).

Table I
Comparison between Microcanonical and Canonical Variational Theory for Ethane Dissociation

temp, K	k_{uni}^{∞} , s ⁻¹	
	microcanonical	canonical
400	1.61×10^{-32}	1.92×10^{-32}
600	3.03×10^{-16}	3.45×10^{-16}
800	4.06×10^{-8}	4.36×10^{-8}
860	2.00×10^{-6}	2.14×10^{-6}
1000	2.83×10^{-3}	2.99×10^{-3}

energy and angular momentum, the average rate constant is given by

$$\langle k \rangle = \int \int k(E, J) P(J) P(E) dJ dE, \quad (10)$$

where continuous distributions are assumed. A particularly important distribution is the canonical Boltzmann distribution. Integrating $k(E, J)$ over this distribution give the high-pressure thermal unimolecular rate constant k_{uni}^{∞} .

For the general case the critical configuration's structure, frequencies, and potential energy E_0 will depend upon both E and J , and a numerical integration is required to solve eq 10. However, as illustrated above for ethyl radical dissociation, if the potential energy surface has a saddlepoint, it is often an accurate approximation to fix the dividing surface at this point. For such a situation the potential energy of the critical configuration E_0 is just the zero-point energy difference between the saddlepoint and the reactant. By assuming a fixed dividing surface, eq 10 becomes for a Boltzmann distribution the activated complex theory⁵⁹ expression:

$$k_{\text{uni}}^{\infty} = \frac{k_b T}{h} \frac{Q^+}{Q} \exp(-E_0/k_b T) \quad (11)$$

where Q^+ is the partition function for the $s - 1$ degrees of freedom on the dividing surface (an activated complex for the canonical ensemble), and Q is the partition function for the reactant.

Numerically integrating the double integral in eq 10 is laborious and not practical for general applications. A more convenient variational approach is to find the minimum in the canonical unimolecular rate constant along the reaction path

$$\partial k_{\text{uni}}^{\infty} / \partial r^+ = 0 \quad (12)$$

Equation 12 is referred to as the *canonical variational criterion* in contrast to the microcanonical criterion of eq 4. The dividing surface chosen by eq 12 is a compromise of those for the individual energies.

In the canonical approach, unimolecular rate constants are calculated along r^+ with use of eq 11. The variational unimolecular rate constant is then chosen according to eq 12. It is not obvious that eq 10 and the canonical variational method will give similar rate constants. One reason for this is that, in general, the activated complex chosen by eq 12 will have a potential energy *less* than the vibrationally adiabatic barrier. As a result, the partition function Q^+ in eq 11 will include states that do not have sufficient energy to dissociate adiabatically.^{60,61}

Ethane dissociation is the only unimolecular reaction for which canonical variational theory has been com-

Table II
Arrhenius Parameters for Ethane Dissociation Derived from the Canonical Variational Criterion

temp, K	r^+ , Å	E_0 , kcal/mol	A^{∞} , s ⁻¹	E_a^{∞} , kcal/mol
400	3.98	86.4	1.03×10^{17}	89.2
600	3.77	85.8	1.03×10^{17}	89.2
800	3.62	85.1	7.71×10^{16}	88.8
860	3.58	84.9	6.91×10^{16}	88.6
1000	3.50	84.4	5.41×10^{16}	88.1

pared to microcanonical variational theory in calculating k_{uni}^{∞} .⁵² Agreement is found between the two sets of rate constants, and a comparison is given in Table I. The reaction-path Hamiltonian used in the calculations is that given by eq 8 and 9 above.

As shown in Figure 3 the dividing surface for ethane moves nearer the ethane minimum as the energy is raised. The suspicion is then that the activated complex for the thermal dissociation of ethane become "tighter" as the temperature is raised. The results in Table II show that this is indeed the case. With increase in temperature the Arrhenius parameters decrease as suggested by the dependence of r^+ on temperature.

Maximum Free Energy Criterion

By writing eq 12 in its thermodynamic form (eq 13),

$$k_{\text{uni}}^{\infty} = \frac{k_b T}{h} K^+ = \frac{k_b T}{h} \exp(-\Delta G^+ / k_b T) \quad (13)$$

it is clear that the minimum in k_{uni}^{∞} occurs where ΔG^+ is a maximum. Thus, the canonical variational criterion is a *maximum free energy criterion*. The term ΔG^+ equals the free energy of the activated complex minus that of the reactant (a constant quantity), and the criterion of eq 12 is satisfied by finding the maximum in the free energy along the reaction path $G(r^+)$. To calculate $G(r^+)$, contributions to the free energy from the $s - 1$ degrees of freedom perpendicular to the reaction path (including internal rotation) are summed and added to the free energy of external rotation and the vibrationally adiabatic potential:

$$G(r^+) = G_{\text{vib}}(r^+) + G_{\text{ir}}(r^+) + G_r(r^+) + V_{\text{va}}(r^+) \quad (14)$$

For some situations one has to consider degrees of freedom changing from vibrations to free rotors along the reaction path.³⁶

Equation 14 is very useful in understanding the canonical variational criterion, since the origin of the maximum in $G(r^+)$ can be separated into contributions of free energy from particular degrees of freedom. For most molecules only a few degrees of freedom will have significant free energy changes along the reaction path. The use of $G(r^+)$ provides a very convenient means for analyzing the application of the canonical variational criterion to either a homologues series of molecules or different types of molecules.

Related Method

One of the major successes of variational rate theory is its ability to fit the temperature dependence of the dissociation and recombination rate constants for the ethane-methyl radical system.^{36,52,62} In contrast, the Gorin model²⁶ gives the incorrect temperature dependence for these rate constants. In the Gorin model the

(59) S. Gladstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes", McGraw-Hill, New York, 1941.

(60) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **83**, 1052 (1979).

(61) B. C. Garrett and D. G. Truhlar, *J. Phys. Chem.*, **84**, 805 (1980).

(62) M. Quack and J. Troe in "Specialist Periodical Report on Gas Kinetics and Energy Transfer", P. G. Ashmore and R. J. Donovan, Ed., The Chemical Society, London, 1977, Vol. 2, p 175.

activated complex is located at the rotational barrier, and its internal modes are simply the vibrations of the independent fragments. The six vibrations associated with the rupturing bond become the reaction coordinate, a one-dimensional rotor, and two two-dimensional rotors. To rectify the inadequacy of the Gorin model, it has been suggested that a hindrance parameter, η , be introduced for rotation of the two-dimensional rotors.⁶³ Since the interfragment distance at the rotational barrier decreases with increase in temperature, it is argued that the rotational hindrance should increase with temperature. A "tighter" activated complex results as temperature increases, and by use of η as an adjustable parameter, the temperature dependence of dissociation and recombination rate constants can be fit.

The similarity between the hindered Gorin model and variational unimolecular rate theory is that they both give "tighter" activated complexes with increase in temperature. However, there are major differences between the fundamental assumptions of these two methods. In the hindered Gorin model it is assumed that the dividing surface for thermally activated bond dissociations is located at the rotational barrier, an assumption that is not supported by trajectory calculations.^{35,64-66} In the variational theory a potential energy surface is first derived and then application of the variational criterion produces the energy and temperature dependence of the reaction rate. Since η is formulated as a function of temperature, the hindered Gorin model cannot be used to calculate the microcanonical unimolecular rate constant as a function of energy.

(63) S. W. Benson, "Thermochemical Kinetics", 2nd ed., Vol. 2, Wiley, New York, 1976; D. M. Golden and S. W. Benson in "Physical Chemical. An Advanced Treatise", H. Eyring, D. Henderson, and W. Jost, Ed., Academic Press, New York, 1978, Vol. 2, p 57.

(64) W. L. Hase and D.-F. Feng, *J. Chem. Phys.*, **61**, 4690 (1974); **64**, 651 (1976); C. S. Sloane and W. L. Hase, *ibid.*, **66**, 1523 (1977).

(65) R. J. Wolf and W. L. Hase, *J. Chem. Phys.*, **72**, 316 (1980); W. L. Hase and R. J. Wolf, *ibid.*, **75**, 3809 (1981).

(66) E. R. Grant and D. L. Bunker, *J. Chem. Phys.*, **68**, 628 (1978).

Conclusion

In this Account the importance of using the variational criterion to choose the dividing surface in statistical unimolecular rate theory is considered. For chemical reactions such as simple bond dissociations, which do not have saddlepoints, the variational criterion is a necessary to attain agreement between experiment and theory. If the surface has a well-defined saddlepoint, this feature will usually define the location of the dividing surface, and the variational criterion is unnecessary. However, as the saddlepoint region of the potential energy surface becomes broader and less pronounced, and if there are significant frequency changes along the reaction path, the variational criterion is accordingly more important in positioning the dividing surface.

Among chemical reactions without saddlepoints are many neutral dissociations that are important in combustion kinetics, such as C-C bond rupture in alkanes and O-O bond rupture in peroxides. There are also many ion dissociations without saddlepoints that are important in nucleation, solvation, and atmospheric kinetics, e.g., $\text{Li}^+(\text{H}_2\text{O})_5 \rightarrow \text{H}_2\text{O} + \text{Li}^+(\text{H}_2\text{O})_4$. The variational criterion is expected to be essential in calculating unimolecular rates for these processes.⁶⁷

What is impeding general application of variational unimolecular rate theory is the scarcity of ab initio information that can be used to derive potential energy surfaces. For simple bond dissociations, model surfaces have been constructed from a combination of Morse and BEBO functions. In future analyses it would be useful for comparisons if accurate ab initio calculations were available for several salient reactions as $\text{HOOH} \rightarrow 2\text{OH}$, $\text{CH}_4 \rightarrow \text{H} + \text{CH}_3$, and $\text{C}_2\text{H}_6 \rightarrow 2\text{CH}_3$. Knowledge of the form of these surfaces would be of much value to unimolecular kineticists.

The author's research in unimolecular reaction dynamics is supported by the National Science Foundation.

(67) W. J. Chesnavich, T. Su, and M. T. Bowers, *J. Chem. Phys.*, **72**, 2641 (1980).