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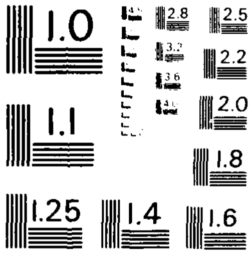

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The Transfer of Atoms, Ions and Molecular Groups in Solution. Part III. Monte Carlo methods for the evaluation of rate constants

by

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We illustrate the method by considering the reactive inversion of a bent A-B-A molecule in a two-dimensional system of disk-like solvent. We determine the activation energy for the transformation to a linear transiton state, and we are able to keep a tally of the average adiabaticity of the reaction. These results indicate that the extention of the method to more realistic systems ought to yield valuable information about the mechanisms of reactions in condensed phases.

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Abstract

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Introduction

In a preceeding paper[1] the transition state theory, as formulated by Marcus,[2] was examined for the purpose of finding algorithms which can be used to develop computational forms for the theory. To that end, an arbitrary system was viewed as composed of a definite reactive subsystem which is surrounded by an environment. The local microscopic dynamics of the reactive subsystem can be examined in isolation. Adjustments in these dynamics can be accounted for as the local subsystem is placed into the remainder of the solution. Such a decomposition of an arbitrary system seems to imply the operation of weak to moderately weak couplings. However, a reactive subsystem can be defined so that a sufficient amount of solvent is included with the reactant(s) to encompass all species which experience large displacements in the course of a reactive transition. Thus, a range of strengths of interaction between the reactant(s) and the local solvent in the surroundings can be accounted for.

In this paper we continue to consider the construction of a computational form of the transition state theory. We examine the transition state theory in a form which makes evident the mode of application of the Monte Carlo method in order to evaluate certain average values such as the energy of activation and the pre-exponential factor. By examining a simple two-dimensional reactive system, it is possible to see the emergence of some of the limits on and limitations of a Monte Carlo method of simulating reactive systems.

Equilibrium Statistics and the Development of the Rate Constant

As was noted in Part I,[1] the Marcus transition state theory *admits Monte Carlo techniques* for the purpose of carrying out various averages, but it is not immediately evident how this is possible. The abstract form of Marcus's original treatment disguises, to some extent, an underlying simplicity. This simplicity is revealled by changing to a more model-dependent, less abstract formulation. The work of Glyde[3] on the self-diffusion of argon suggests the essential steps one needs to take in order to establish contact with the Monte Carlo methods of averaging.

In the following paragraphs the transition state theory is outlined for both the adiabatic and diabatic limits. This sketch of the theory immediately suggests the proper approach to take in order to carry out the Monte Carlo methods of averaging or optimization.

The definition of an adiabatic transfer was considered in Part I. If a reaction proceeds through the transition state *via* an *adiabatic* path, the transfer species then occupies a state of local, transient, and *stable* mechanical equilibrium for the instant it resides in the configuration of the transition state. Furthermore, an adiabatic path for a reaction is one on which the transfer species always occupies a state of local, transient, and stable mechanical equilibrium at every point along the path. In other words, in the adiabatic limit, fluctuations in the configuration of the entire system define new states into which the transfer species moves. This movement can be defined, for the purpose of thermodynamic argument, to take place reversibly. Thus, the transfer-species adiabatically follows a migrating position of equilibrium. Changes in the configuration of the environment carry the transfer-species from its initial to its final location.

The diabatic limit, in contrast, applies to those configurations for which it is impossible to define a state of local, stable mechanical equilibrium at the transition point. The migrating species must then tunnel through the narrow remaining barrier. As an example, one can consider the passage of an atom or ion through an annular opening in a cryptate.[4] If the effective radius of the annulus is less than a critical value, it is not possible for the migrating species to occupy a position of equilibrium at the centre of the ring-like structure. However, if the effective radius increases, a stable position of equilibrium can result. For the diabatic limit, therefore, it is possible to define a Born-Oppenheimer type of separation of the local reactive modes from the remaining modes of the environment.[1] As will become evident for the Monte Carlo simulations, the use of a Born-Oppenheimer type of separation of local reactive modes from the modes of the environment has a direct bearing only on the evaluation of the matrix elements which are associated with the transfer. The calculation of the activation energy with the use of Monte Carlo techniques is operationally the same in the diabatic and adiabatic limits.

The total Hamiltonian operator for the system is divided into two parts:

$$H = H_t + H_{env} \qquad (1)$$

for which H_t is the Hamiltonian operator for the transfer species and H_{env} is associated with all other species. The operator for the transfer-species, H_t, is the sum of the kinetic and potential energy operators:

$$H_t = T + V. \qquad (2)$$

This operator is one-dimensional in the coordinate which coincides with the transfer-axis. The potential energy operator V spans the initial and final configurations; it is, for example, a potential energy function with a double minimum. Solutions in the Born-Oppenheimer approximation are constructed with the use of basis functions $\phi_{a\gamma}$ and $\phi_{b\delta}$ which satisfy the local, model Hamiltonian operators

$$H_a = T + V_a$$
$$H_b = T + V_b \qquad (3)$$

with

$$H_a\phi_{a\gamma} = \epsilon_{a\gamma}\phi_{a\gamma}$$
$$H_b\phi_{b\delta} = \epsilon_{b\delta}\phi_{b\delta} \qquad (4)$$

and the indices a and b specify the physical locations of the initial and final states. The indices γ and δ specify energy states for the transfer-species at the locations a and b. For example, V_a and V_b can be local harmonic oscillator potentials Thus, $\phi_{a\gamma}$ and $\phi_{b\delta}$ are the usual solutions to the one-dimensional

Schrödinger equation for the oscillator. In terms of these solutions and in terms of the potential energy operators V_a and V_b, one has

$$H_t = H_a + V - V_a$$
$$= H_b + V - V_b \qquad (5)$$

where now the combinations $V - V_a$ and $V - V_b$ operate as perturbations.

The complete eigenvalue problem is written

$$H\Psi = E\Psi \qquad (6)$$

with the state function expanded in terms of a basis set in the $\phi_{a\gamma}$ and $\phi_{b\delta}$:

$$\Psi = \sum_{i,\gamma} X_{i\gamma}\phi_{i\gamma}. \qquad (7)$$

In the usual manner, it is now possible to find sets of equations with which to determine the expansion coefficients $X_{i\gamma}$. One finds

$$H_{i\gamma,i\gamma}X_{i\gamma} = \sum_{j,\delta}{}' L_{i\gamma,j\delta}X_{j\delta} \qquad (7)$$

where the prime on the summation excludes $i\gamma = j\delta$. The L-matrix elements are defined by

$$L_{i\gamma,j\delta} = \sum_{k,\epsilon} S^{-1}_{i\gamma,k\epsilon}V^{j}_{k\epsilon,j\delta}, \qquad (8)$$

here $S^{-1}_{i\gamma,k\epsilon}$ is an element of the inverse overlap matrix. Roman indices cover the initial and final locations (*a* and *b*) while Greek indices cover local energy states. The matrix element $V^{j}_{k\epsilon,j\delta}$ is

$$V^{j}_{k\epsilon,j\delta} = \langle k\epsilon|V - V_j|j\delta\rangle + \langle k\epsilon|V_{env}|j\delta\rangle \qquad (9)$$

In defining the L-matrix elements, we have ignored the contribution from the kinetic energy operators of the environment which operate in the space of the transfer species. It is not altogether clear that this is generally permissible for vibrational problems as it may be for electron transfer.[5] It is of course relatively simple to amend the formalism to include these T-operators in the definition of the L-matrix elements; indeed, one need only add T_{env} *to* $V-V_j$ *in eqn (9). Finally,* the diagonal element $H_{i\gamma,i\gamma}$ is given by

$$H_{i\gamma,i\gamma} = E - \epsilon_{i\gamma} - L_{i\gamma,i\gamma} - T_{env}. \qquad (10)$$

Adiabatic solutions $X^{0}_{i\gamma}$ are defined by the solutions to the equation

$$H_{i\gamma,i\gamma}X^{0}_{i\gamma} = 0. \qquad (11)$$

The non-diagonal terms $L_{i\gamma,j\delta}$ account for the tunnel-transfer of the migrating species when the transfer takes place in the diabatic limit.

From the first order, time-dependent perturbation theory, the quantum mechanical transition probability is given by

$$w = \frac{2\pi}{\hbar Q} \sum_{i\gamma, f\delta} \exp(-\beta E_{i\gamma}) |L_{i\gamma, f\delta}|^2 \delta(E_{i\gamma} - E_{f\delta}) \qquad (12)$$

where the energies $E_{i\gamma}$ and $E_{f\delta}$ are the total energies of the entire system in its initial and final states, and γ and δ specify the state of the transfer species. In eqn (12) Q is the partition function

$$Q = \sum_{i\gamma} \exp(-\beta E_{i\gamma}). \qquad (13)$$

By virtue of arguments which have been presented in detail elsewhere,[6] it is possible to equate the transition probability in the diabatic limit with the rate constant:

$$k_d = w$$

where now k_d stands for the rate constant in the diabatic limit. The work of creating the initial state and various other energies which enter the activation energy appear automatically in a general analysis.

We now assume that the environment (which can include the non-reactive vibrational modes of the molecular framework in a molecule which undergoes a transformation) can be treated in the classical limit. Therefore, the summations can be replaced by integrations with the result that the rate constant now is expressed as

$$k_d = \frac{2\pi}{\hbar Q} \int d\dot{r}\, dr\, \exp(-\beta H_i) |L_{i\gamma, f\delta}|^2 \delta(V_i - V_f) \qquad (14)$$

The integration involves the 3N velocities and coordinates of the

N species in the system. H_i is now a classical Hamilton function for the system in its initial state. The energy difference in the delta function, $E_{i\gamma} - E_{f\delta}$, is replaced by the difference in the potential energy functions in the initial and final states as the kinetic energy terms cancel.[1,7]

The integrations over the velocities in Q and k_d can be carried out immediately. As there is no isolated velocity $\dot{x}_\ell^\alpha$ in the expression, the contributions due to the kinetic energies cancel. The rate constant is

$$k_d = \frac{2\pi}{\hbar q} \int d\underline{r}\, \exp(-\beta V_i) |L_{i\gamma, f\delta}|^2 \delta(V_i - V_f) \qquad (15)$$

with

$$q = \int d\underline{r}\, \exp(-\beta V_i). \qquad (16)$$

At this point, we make the assumption, parallel to the assumption made by Glyde,[3] that the major contributions to the integral in eqn (16) come from terms in the exponent which are near to V_{i0}, the initial equilibrium potential energy. Thus, on expanding about V_{i0}, one finds

$$V_i = V_{i0} + \tfrac{1}{2} \sum A_{\ell\alpha, m\beta} x_\ell^\alpha x_m^\beta \qquad (17)$$

with

$$A_{\ell\alpha, m\beta} = \partial^2 V_i / \partial x_\ell^\alpha \partial x_m^\beta \Big|_0 \qquad (18)$$

The integration over $\underline{r}$ yields for q

$$q = (2\pi/\beta)^{3N/2}|A|^{-\frac{1}{2}} \exp(-\beta V_{i0}) \tag{19}$$

where $|A|$ is the determinant of the matrix of second derivatives. The expression for the rate constant is

$$k_d = \frac{2\pi}{\hbar}(2\pi/\beta)^{3N/2}|A|^{\frac{1}{2}} \int d\underline{r} \exp(-\beta(V_i - V_{i0}))|L_{i\gamma,f\delta}|^2\delta(V_i - V_f) \tag{20}$$

Write the delta function as[7]

$$\delta(V_i - V_f) = \frac{1}{|\Delta F|}\delta(x^{\alpha}_{i\ell} - x^{\alpha}_{f\ell}) \tag{21}$$

with

$$|\Delta F| = \left|\partial(V_i - V_f)/\partial x^{\alpha}_{\ell}|_0\right| \tag{22}$$

which is the difference in the slopes of the initial and final potential energy functions evaluated at the transition point. Effectively, this quantity is the difference in force which is experienced by the transfer species as it passes from one potential energy surface to the other in the transfer region. The single coordinate which is involved in the integration over the delta function is x^{α}_{ℓ}. The integration which involves the delta function has the effect of freezing the value of x^{α}_{ℓ} for the transfer species at that value which corresponds to the transfer point. Thus,

$$k_d = \frac{2\pi}{\hbar|\Delta F|}(2\pi/\beta)^{3N/2}|A|^{\frac{1}{2}}\int d\underline{s} \exp[-\beta(V(\ldots x^{\alpha}_{\ell},\ldots) - V_{i0})] \times |L_{i\gamma,f\delta}|^2 \tag{23}$$

where $d\underline{s}$ is the surface element in the reaction hyperspace. For this analysis it is easily defined; it is

$$d\underline{s} = \Pi' dx^{\alpha}_{i} \tag{24}$$

where the prime excludes the single coordinate which is associated with the transfer coordinate, x^{α}_{ℓ}.

We assume that the Condon approximation applies. The matrix element $|L_{i\gamma,f\delta}|^2$ now can be removed from the integration. Further, we assume that the major contributions to the integrals over the x^{α}_{i} come from terms in the vicinity of the single minimum $V^{\dagger}$ in the transition state. Thus,

$$V(\ldots x^{\alpha}_{0}\ldots) = V^{\dagger} + \tfrac{1}{2}\sum{}' A^{\dagger}_{\ell m}x^{\alpha}_{\ell}x^{\beta}_{m} \tag{25}$$

and the rate constant finally is

$$k_d = \frac{\sqrt{2\pi\beta}}{\hbar}\,\frac{|A|^{\frac{1}{2}}_{3N}}{|A^{\dagger}|^{\frac{1}{2}}_{3N-1}}\,\frac{|L_{i\gamma,f\delta}|^2}{|\Delta F|}\exp(-\beta(V^{\dagger} - V_{i0})). \tag{26}$$

By way of contrast, following Glyde's analysis [3] with the modifications introduced here, one finds k_{ad}, the rate constant in the adiabatic limit, is given by

$$k_{ad} = (2\pi m)^{-\frac{1}{2}} \frac{|A|_{3N}^{\frac{1}{2}}}{|A^{\dagger}|_{3N-1}^{\frac{1}{2}}} \exp(-\beta(V^{\dagger} - V_{i0})). \qquad (27)$$

It *is necessary* to note the fact that the ratio $|A|_{3N}^{\frac{1}{2}}/|A^{\dagger}|_{3N-1}^{\frac{1}{2}}$ in the adiabatic limit will not be the same as the similar expression in the diabatic limit, cf. eqn (26). However, one expects the difference to be (usually) relatively small.

Beacuse of the difference in dimensions of the ratio of generalized force constant determinants A, it is easy to see that

$$|A|_{3N}^{\frac{1}{2}}/|A^{\dagger}|_{3N-1}^{\frac{1}{2}} = (m/2\pi)^{\frac{1}{2}}\omega_E \qquad (28)$$

is effectively a single force constant. The frequency ω_E is an effective frequency which can be assigned to the transfer. As Glyde noted[3] *for the self-diffusion of* argon, it is an Einstein-like frequency. With the restriction that the ratio of force constant determinants is essentially the same for the diabatic and adiabatic limits, it is possible to express the diabatic limit as

$$\begin{aligned} k_d &= (2\pi m_e)^{-\frac{1}{2}} \frac{|A|_{3N}^{\frac{1}{2}}}{|A^{\dagger}|_{3N-1}^{\frac{1}{2}}} \exp(-\beta(V^{\dagger} - V_{i0})) \qquad (29) \\ &= (m/m_d)^{\frac{1}{2}}\omega_E \exp(-\beta(V^{\dagger} - V_{i0})) \end{aligned}$$

The effective mass is then defined by

$$\sqrt{m_e} = \frac{\hbar|\Delta F|}{2\pi\sqrt{\beta}|L_{i\gamma,f\delta}|^2} \qquad (30)$$

The diabatic mass m_d is just

$$m_d = 4m_e. \qquad (31)$$

An Estimate of the Pre-exponential Factor

The simplest estimate of the size of the pre-exponential factor is made with the use of the model of intersecting harmonic *oscillator* potential energy functions. It is clear from our other investigations[1,8] that the diabatic limit occurs, as mentioned, in those instances for which *stable mechanical equilibrium* cannot be found for the transfer species in the transition state. It is equally clear from our investigations[8] that these conditions depend strongly upon the dominant contribution of repulsive forces for some particular configuration of the system. Thus, in more graphic, physical terms, it is easy to see that a model of intersecting harmonic oscillator potential energy functions is an adequate representation, in simple terms, of an actual interplay of potential energy functions in the region of strong repulsive interaction

For the simple one-dimensional oscillator, the potential energy function is

$$V = \tfrac{1}{2}m\omega^2(z - z_0)^2 \qquad (32)$$

on the transfer axis. The force is

$$F = -m\omega^2(z - z_0) \qquad (33)$$

The location of the point of intersection, a cusp, is given by

$$z_{int} = z_{i0} - \frac{\delta}{1-\alpha^2} \pm \frac{1}{1-\alpha^2}\left\{(1-\alpha^2)(2E_0/m\omega_i^2-\delta^2) + \delta^2\right\}^{\frac{1}{2}} \tag{34}$$

where

$$\alpha = \omega_f/\omega_i \tag{35}$$

and

$$\delta = z_{f0} - z_{i0} \tag{36}$$

E_0 is the difference in zero-point energies for the two wells.

If $\omega_f = \omega_i$, such that $\alpha=1$, then

$$z_{int} = z_{i0} + \frac{1}{2\delta}(2E_0/m\omega_i^2 - \delta^2), \tag{37}$$

and if $E_0 = 0$, then $z_{int} = \frac{1}{2}R_{ab}$, where R_{ab} is the distance between the locations of the initial and final states.

In a similar manner, one finds that the difference $F_i - F_f$ is

$$F_i - F_f = m\omega_f^2(z_{int}(\alpha^2-1) + z_{i0} - \alpha^2 z_{f0}) \tag{38}$$

For the case of a totally symmetric system,

$$|\Delta F| = 2\omega\sqrt{m\hbar\omega}\,\zeta \tag{39}$$

where ζ is $\sqrt{m\omega/\hbar}\,z_0$, and z_0 is the distance from the minimum to the cusp.

We found in Part II[8] that

$$L_{if} = -\frac{1}{\sqrt{\pi}}\hbar\omega\zeta e^{-\zeta^2}. \tag{40}$$

In terms of this quantity, and in term the estimate of $|\Delta F|$ for the intersecting oscillator potent , one finds that the effective mass, m_e, is given by

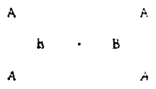
$$\sqrt{m_e} = \sqrt{m}\,\frac{e^{2\zeta^2}}{\sqrt{8\hbar\omega\zeta}}\ . \tag{41}$$

In view of the definition of the distance ζ, it is clear from eqn (41) that the effective mass increases dramatically with increasing distance between the minimum of the potential and the maximum of the barrier. This, of course, is a result which is well-established in the lore of chemistry. In addition, one sees that the effective mass increases with temperature as $T^{\frac{1}{2}}$. This result can be attributed to the increase in the mean displacement of an oscillating particle as the temperature increases.

Monte Carlo Methods Implied by the Formal Expression for the Rate Constant

To begin, a reactive transition evolves as a fluctuation from the thermodynamic state of equilibrium. Thus, one prepares the system in an initial state according to the method devised originally by Metropolis, *et al.*[9] Given a centrally located reactant which is surrounded by solvent, the entire system is allowed to come to equilibrium. Each atom in the entire system of reactant(s) and solvent individually is displaced a random distance along an axis. If the displacement results in a lower overall energy, it is kept and the sampling proceeds to the next coordinate and to subsequent atoms. If, on the other hand, the displacement results in an increase in the energy, the displacement is kept only if the Boltzmann weighting factor is less than a randomly generated number which lies in the range of zero to one. In this manner, a Markov chain is constructed.[9] The process of sampling continues until the average energy settles on a stable, central value. At this point the system is in an appropriate initial state for the reaction.

Consider as an example a simple two-dimensional reactive system which consists of a non-linear ABA molecule which is immersed in a solvent of disk-like atoms. The reaction involves a simple inversion



in much the same manner as is the case for the inversion of ammonia.[10] The preparation of the initial state for the system in all likelihood places a molecule of solvent at or near to the location for the B-species in the final state. Thus, as is the case for the solid state,[3] here as well it is necessary to form a vacancy into which B can migrate. The work which is required to form this vacancy is part of the energy of activation.

A Monte Carlo simulation of the formation of the vacancy can be carried out, in principle, in several different ways. The following, however, seems to be the simplest and most direct. One merely continues to execute Metropolis samples for the Monte Carlo simulation. The simulation continues beginning with the system in its initial state of thermodynamic (and Monte Carlo) equilibrium. It is apparent that there can be molecules of solvent which lie in the region where one wants to create a vacancy. A test therefore is needed to see if any molecule must be moved. If a molecule occupies the space where a vacancy should be, then it is necessary to determine whether a randomly generated displacement will move that molecule from the location of the required vacancy. In addition, the move can only occur if it satisfies the criteria imposed for the Metropolis sampling. On the other hand, if a vacancy already exists or nearly exists (i.e., a molecule lies close to but not over the location of the vacancy), then it is necessary to test each displacement for each molecule of solvent to make sure that no molecule moves into the location of the vacancy.

The Monte Carlo simulation is carried out with the restriction that a vacancy form until the energy of the system stabilizes. The state for which there exists a vacancy into which the transfer-species can migrate therefore defines the initial state for the reactive transition.

The determination of the energy of the transition state is the final part of the simulation of the reaction. Again, there are several ways the simulation could be carried out. One way, theoretically the soundest, is to continue to generate configurations for which the reaction is allowed, i.e., the vacancy remains. For such a configuration, assuming a linear trajectory to the final state through the transition state, the transfer-species is placed at the point of maximum energy. This point should lie between the initial and final positions and should also lie within the reactive species or system of reactants. With the reactive system "frozen" in this transition-configuration, the environment is allowed to relax to a lowest possible energy. The energy which is determined in this manner corresponds to a transition state energy for the single configuration. This process must be carried out a sufficient number of times in order to get a statistical sample. Moreover, for each transition state configuration, it is necessary to determine whether the transfer species is in a state of mechanical equilibrium. Such a calculation clearly consumes much more computer time than either of the two preceeding preparatory computations.

A less accurate, approximate approach is the following; its accuracy, as will be evident, depends upon the degree to which the reactive system and its molecular framework is insulated or isolated from the environment. The technique is simple. Consider the reactive system in the absence of the surrounding environment. Determine, on the basis of reasonable intuition and perhaps an optimization, the location of a probable position for the transfer-species in the transition state. For the ABA example, a reasonable choice is to place the B-species on the A-A axis, thus creating a linear transition configuration. Now, with the reactant system "frozen" in this configuration, the environment is allowed to interact and come to a new state of equilibrium. The energy which is found in this manner corresponds to the energy of the transition state.

The activation energy is simply the energy of the transition state less the energy of the original, initial state of equilibrium.

In spite of the approximate nature of this approach to the determination of the energy of the transition state, it is possible that some adjustment of the reactive system can be made in order to obtain a more accurate value of the energy. For the ABA system, for example, it is possible that a slightly bent configuration corresponds to the true transition state. Such a calculation can be carried out and tests can be included in order to ensure that the Monte Carlo simulation does not merely regenerate the thermodynamic initial or final states.

So far, only a brief mention has been made of the determination of mechanical stability for the transfer-species in the transition state. It is clear that for the last approach to the determination of the energy of the transition state, each configuration which is generated as the system stabilizes about an energy can be tested for mechanical stability. Configurations which indicate a mechanically unstable transition state correspond to cases for which a diabatic transition, with tunnelling, applies. It is a simple matter to tally the diabatic versus adiabatic configurations. It is a less simple matter to remove the transfer-species to a position on the reactive trajectory for which a state of mechanical equilibrium does exist and from there to determine the probability for tunnelling. However, such calculations can be carried out. It is possible, therefore, to obtain an appropriate form for the pre-exponential factor.

One should note the fact that the activation energy for a configuration for which a diabatic transfer holds must be determined still with the transfer species in the transition state configuration, even though this configuration is mechanically unstable.

An interesting result of these simulations is the statistical definition of an adiabatic *versus* diabatic limit for a reaction. Consider an individual configuration for the transition state. From that which has been stated here, and in part I, it is clear that the transfer corresponds to one either in the adiabatic or diabatic limit. At the microscopic level, there is no gradation of diabaticity; the reaction is either diabatic or it is adiabatic. However, in a statistical sense, for a given reactive system it is possible that the Monte Carlo simulations will generate configurations for which a fully adiabatic transfer applies part of the time and for the remainder of the configurations a diabatic limit applies. The overall value of the pre-exponential factor therefore must reflect a statistical balance between the two extreme limits. Thus, one sees that a given reactive system can exhibit a type of transfer which corresponds overall to a statistical weight of the diabatic against the adiabatic limit. That this is indeed the case is already evident in a Landau-Zener type of analysis.[11] The difficulty in applying the Landau-Zener analysis to any system which undergoes a reaction which belongs between the extremes of diabaticity and adiabaticity is well known. Monte Carlo methods of simulation and averaging, on the other hand, provide the means to investigate the shades of diabaticity which one expects for real systems.

Algorithms for Determining Mechanical Stability in the Transition State

One can test for mechanical stability of the transfer-species

in the transition state configuration, the test is carried out in the classical limit. It is necessary simply to determine the sign of the second order coefficient in the Taylor expansion for the motion of the particle along the transfer axis. The expansion uses pair-wise interactions between the transfer-species and each atom of the reactant(s) and the solvent.

The symmetry-adaptable Taylor series for a general scalar function $g(\underline{r})$ is[12]

$$g(\underline{r}+\underline{R}) = \sqrt{4\pi}\sum_{n=0}^{\infty}(r^n/n!)\sum_{\ell}(-i)^{n+\ell}A_{n\ell}P_\ell(\hat{R}\cdot\hat{r})I_{n\ell}(R) \tag{42}$$

in which[12]

$$\begin{aligned} A_{n\ell} &= 0 && \text{for } \ell > n \text{ and } n-\ell \text{ odd} \\ &= \frac{(2\ell+1)n!(n-\ell+1)!!}{(n-\ell+1)!(n+\ell+1)!!} && \text{for } \ell \le n \text{ and } n-\ell \text{ even} \end{aligned} \tag{43}$$

and

$$I_{n\ell}(R) = \frac{1}{(2\pi)^3}\int_0^{\infty} dk\; k^{n+2}f(k)j_\ell(kR) \tag{44}$$

In eqn (44) $j_\ell(kR)$ is the spherical Bessel function of the first kind,[13] and $f(k)$ is given by[12]

$$f(k) = 4\pi\int_0^{\infty}dr\; r^2g(r)j_0(kr). \tag{45}$$

In eqn (42), $P_\ell(\hat{R}\cdot\hat{r})$ is the Legendre polynomial of order ℓ and $\hat{R}\cdot\hat{r}$ is the scalar product of the unit vectors for R and r. it is the

the cosine of the angle between the vectors.

When the z-axis is specified to be the transfer axis, eqn (42) reduces to

$$g(\underset{\sim}{r}+\underset{\sim}{R}) = \sqrt{4\pi} \sum_{n=0}^{\infty} \sum_{\ell=0} \frac{z^n}{n!}(-i)^{n+\ell} A_{n\ell} P_\ell(\cos\theta_R) I_{n\ell}(R) \qquad (46)$$

where now, θ_R is the angle between the location of the source and the z-axis.

Mechanical stability for the motion *along* the z-axis at the location of the transition state is guaranteed if

$$g_2(R) = \sqrt{4\pi} \sum_{\ell=0}^{2} (-i)^{\ell+2} A_{2\ell} P_\ell(\cos\theta_R) I_{2\ell}(R)$$

$$= -\frac{\sqrt{4\pi}}{3}\left\{I_{20}(R) - 2P_2(\cos\theta_R) I_{22}(R)\right\} \qquad (47)$$

is greater than zero.

In order to determine if the transfer-species occupies a state which is mechanically stable in the transition state, it is necessary to evaluate $g_2(R_i)$ for each species in the system. Thus,

$$g_2 = \sum_i{}' g_2(R_i) > 0 \qquad (48)$$

where, clearly, the prime on the summation excludes the transfer-species. As an example, consider a system of particles associated through the interaction of the Mie potential:

$$V(r) = -A/r^6 + B/r^{12} \qquad (49)$$

The general expansion of a potential of the form $1/r^q$ is[14]

$$\frac{1}{|\underset{\sim}{r}+\underset{\sim}{R}|^q} = \frac{1}{(q-2)!R^q} \sum_{n,\ell} A_{n\ell} P_\ell(\cos\theta_R)(-z/R)^n \frac{(q+n+2+\ell)!!(q+n-2-\ell)!}{n!(q+n-2-\ell)!!} \qquad (50)$$

The condition for stability is derived simply from eqn (50), it is

$$g_2 = -\sum_i R_i^{-8}\left(\left[5 + 16P_2(\cos\theta_{R_i})\right]A_i - \left[22 + 56P_2(\cos\theta_{R_i})\right]\frac{B_i}{R_i^6}\right) \qquad (51)$$

$$> 0.$$

An expression of this type is no more difficult to evaluate, and consumes about the same amount of computer time, as the evaluation of each of the individual pair-wise contributions to the energy of the system.

Computational Aspects of the Monte Carlo Simulation of a Reactive Transfer in the ABA System

The system is two-dimensional and consists of a bent A-B-A molecule which is immersed in a solvent of uniform disks. The origin of the coordinate system is located initially at the mid-point of the A-A axis. The B-species is located at a perpendicularly displaced point over this midpoint. The solvent is distributed about the solute in concentric circles the radii of which are multiples of the solvent diameter; the first radius includes an effective radius for the solute. No form of optimization is used to construct this initial configuration.

The system is equilibrated first at 4K, this step is suggested in a similar treatment which was carried out by Simons.[14] The equilibration is accomplished in approximately 60,000 cycles of the Monte Carlo simulation. The temperature is then raised to 300K. The simulation is allowed to proceed through approximately 20,000 cycles. At that point, memory of the initial energy and configuration of the system is erased and a new equilibration is sought in approximately 60,000 cycles. At the end of the equilibration at 300K, the system is considered to be prepared in an initial state. It is evident that the system has reached a state of equilibrium at a given temperature when the fluctuations in the energy diminish and an essentially stable, almost constant value of the energy is reproduced every thousand cycles or so.

Although emphasis has been placed on the process of forming a vacancy into which the migrating species can transfer, this is not altogether a necessary step in the simulation. It is possible, in fact, merely to seek good configurations for the transition state. The activation energy is simply the difference between the absolute energy of the transition state and the energy of the initial state. Nevertheless, it appears to hasten the convergence of the simulation to optimal configurations and values for the energy if the step to find the vacancy is included. This process is carried out as follows. To begin, a test is carried out to see if a molecule of solvent occupies a position in the eventual location of the migrating B-species. If the test proves to be positive, the molecule of solvent is displaced along the y-axis (the transfer direction) until an appropriate void is created. With the molecule of solvent held rigidly in this position, the remaining solvent is allowed to equilibrate about the solute and its vacancy with the temperature at 300K.

Once the vacancy is created, an initial attempt to form the transition state is made. The transition state is prepared simply by moving the B-species to the origin of coordinates at the midpoint on the A-A axis. The A-species are allowed to equilibrate only along the bond axis; this is done in order to prevent the re-establishment of the initial state or the establishment of the final state. The solvent equilibrates as usual. The entire process is again carried out at 300K. With the generation of each configuration in the process of equilibration, the transition state is tested to see if the transfer species occupies a position which is mechanically stable. If the transfer species alone occupies a position within a configuration and the species is mechanically stable in that position, the transfer is termed adiabatic. The average adiabaticity is determined.

The running average of any quantity is kept with the use of the simple recursion relation:

$$\bar{F}_N = \frac{1}{N}(f_N + (N-1)\bar{F}_{N-1}) \qquad (52)$$

where f_N is the value of F (any measurable quantity) for the N-th individual configuration, and $\bar{F}_{N-1}$ and $\bar{F}_N$ are the average values after N-1 and N cycles respectively. With the use of this recurrence relation for the average, it is easy to see the emergence of a relatively stable value for any quantity which is averaged. It is also easy to see the effect of long-term memory, especially when the simulation is programmed to evaluate averages over smaller subcollections of randomly generated configurations.

In addition to the details of the calculation which have been described above, we included a circular boundary with a radius equal to the distance of the outermost molecule of solvent from the coordinate origin plus one solvent diameter. The interaction between any species and the wall of this container was taken to be infinitely repulsive.

The potential energy which was used throughout the simulation was the Lennard-Jones/Mie potential:

$$V(r) = D[(r_0/r)^{12} - 2(r_0/r)^6] \qquad (53)$$

where D is the dissociation energy and r_0 is a diatomic, equilibrium bond distance. The dissociation energy for the A-B bond was taken to be 5.0×10^{-19}J and the dissociation energy for the A-A was half that value, 2.5×10^{-19}J. For simplicity, the dissociation energy for the interaction between solvent and between each atom of the solute, A and B, and the solvent was taken to be 9×10^{-20}J. The equilibrium distance, r_0, for the A-B bond was kept a constant 0.1nm. In contrast, the bond distance for the two A-species was allowed to run from a minimum value of 0.1nm (allowing, in vacuum, an almost equilaterially triangular molecule) to 0.2nm. The solvent-solvent and solvent-solute atom distance was taken to be 0.3nm which is approximately the van der Waals separation for water.

Results of the Calculation

As intuition and experience leads one to suspect, the activation

energy decreases as the distance between the two A-species increases. it becomes energetically less costly to move the migrating B-species into the configuration of the transition state. As the data indicate, when the A-A bond distance is allowed to equilibrate in the transition state, the result is generally an adiabatic transfer. It is clear that the adiabaticity of the transfer increases as the fundamental A-A distance increases.

The question naturally arises with these types of simulations as to whether the number of molecules of solvent which surround the solute is sufficiently large to account accurately for the effect of the solvent on the activation. In order to test the adequacy of the account of the solvent, an additional layer was considered. The result of the simulation, which took more than twice the time on the computer the original calculation took, was identical to the result with the smaller sample of solvent. It appears, for the size of solute, A-B-A, which we considered, two distinct layers of solvent in concentric circles are sufficient to estimate the energy of activation.

The calculations also reveal more than Table 1 alone shows. It is clear in examining the evolution of the adiabaticity as the system moves toward an optimal value for the transition state that the initial adiabaticity is small; this is illustrated in Table 2. Adiabaticity grows as the A-A bondlength expands to accomodate the enclosed B-species. This occurence suggests that if, for the reason of a constraint due to a larger and more complicated, effectively rigid molecular geometry, a molecule cannot easily expand to accomodate a transfer species in a state of mechanical equilibrium in the configuration of the transition state, then the heavy-centre transfer will tend to be diabatic. The relative inflexibility of a molecular framework, therefore, is surely an obvious limitation on the adiabaticity of any heavy-centre atom or molecular group transfer.

Discussion

It is appropriate to consider at least briefly the comparison between the theory which is developed in this paper and the transition state theory of reactions in the gas phase as formulated by several people, especially, Miller[15] and Pechukas.[16]

First of all, an assumption is made here that there is separability in the quantal limit in the sense of the Born-Oppenheimer approximation. This is an essential assumption, for it prescribes the form which the expression for the transition probability (and hence the rate constant) must take. The development of each expression for the rate constant in the diabatic and adiabatic limits proceeds strictly governed by the limitations which are dictated by assuming the classical limit for all degrees of freedom which are associated with the solvent. The single quantum mechanical contribution to the expression for the rate constant in the diabatic limit arises from the need to consider tunnelling across the residual barrier to the transfer.

In principle, all the difficulties which are inherent in the gas phase theory[16] of the transition state are also contained in the theory for the condensed phases as well. Because we have chosen to examine the classical limit for the environmental contributions, the expression for the rate constant in that limit

is well-defined; this is also the case for the gas phase.[16] As long as the Born-Oppenheimer approximation applies to a transfer, the transition probability (from second order time-dependent perturbation theory) also applies. The classical limit for the environmental contributions also applies. However, in the limit of strong interactions, where quantal limits also apply, the theory which is developed here is inappropriate. Thus, it is incorrect to attempt to apply our results to highly endo- or exothermic reactions. It is well-known, also, from the theory of the electron transfer reaction that a more appropriate (but, perhaps not yet entirely accurate) form for the rate constant arises from the proper consideration of the saddle point integration which enters the theory.[17] Such an analysis has not yet been carried out for these heavy-centre transfers. Moreover, it is not immediately clear how such an analysis should be carried out in order to derive expressions for the rate constant which lend themselves immediately to Monte Carlo simulation.

It is evident, therefore, that the results which we have presented for the simulation of rate constants for heavy-centre transfers in the condensed phase must be considered in the context of the limits which define the problem. The transfers which we are able to consider are those for which the enthalpy of reaction is in the so-called "normal" range; the reactions can be neither highly exothermic nor highly endothermic. Finally, it is mandatory that the reactions be considered to take place in the classical limit with reference to all the possible dynamical contributions from the solvent.

Table 1

A. (2.5/0.100/5.0/0.100)*

$E_0 = -54.87$ (at 300K)

$E_v = -53.85$

$E_t = -51.65$

$E_a = 3.22$ (448 kJ mol^{-1})

(final adiabaticity: 0.98)

B. (2.5/0.125/5.0/0.100)

$E_0 = -54.36$

$E_v = -53.82$

$E_t = -51.55$

$E_a = 2.86$ (439 kJ mol^{-1})

(final adiabaticity: 0.88)

C. (2.5/0.180/5.0/0.100)

$E_0 = -54.42$

$E_v = -53.85$

$E_t = - 53.43$

$E_a = 0.99$ (153 kJ mol^{-1})

(final adiabaticity: 0.88)

D. (2.5/0.200/5.0/0.100)

$E_0 = -54.33$

$E_v = -54.27$

$E_t = -54.20$

$E_a = 0.13$ (20 kJ mol^{-1})

(final adiabaticity: 0.99)

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*The notation ($D_{AA}/R_{AA}/D_{AB}/R_{AB}$) indicates the parameters used for the solute: D_{AA} is the A-A dissociation energy, D_{AB} is the A-B bond dissociation energy, R_{AA} is the A-A equilibrium pairwise separation in the gas phase, and finally R_{AB} is the equilibrium A-B separation. The energies are given in Joules$\times 10^{19}$ and the distances in nm.

Table 2 The growth of adiabaticity for (2.5/0.180/5.0/0/100)

Cycles	E	Adiabaticity
2,625	-52.27	0.0015
4,375	-52.89	0.39
6,125	-53.12	0.48
7,875	-53.22	0.59
9,625	-53.33	0.66
11,375	-53.36	0.71
13,125	-53.38	0.75
14,875	-53.38	0.78
16,625	-53.40	0.80
18,375	-53.43	0.82

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