Alternate Locations for the Dividing Surface of Transition State Theory. Implications for Application of the Theory

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Received January 14, 1974

Abstract: Eyring's absolute rate theory (ART) evaluates chemical reaction rates as the equilibrium flux of systems through a dividing surface (DS) which is located at a *definite place* in a potential energy volume in phase space. A transmission coefficient is used to take account of trajectories which are reflected and return to the reactant region. The ART DS is perpendicular to the transition state's unstable normal coordinate and its location is therefore determined by masses and the curvatures of the potential energy hypersurface (PES) at the saddlepoint. We show how an orthogonal transformation to coordinates other than the normal ones allows one to vary the orientation of the DS given the restrictions that it must pass through the saddlepoint of a PES with a minimum energy linear configuration. Given these restrictions, we prove that if the flux through the planar Cartesian DS is not corrected for reflected trajectories, or those which do not originate from the reactant region of phase space, and the small vibrations approximation (SVA) is employed to evaluate concentrations on the DS, the ART placement of the DS represents an *approximate upper limit* on the *minimum equilibrium* reaction *rate*. ART does not give a rigorous upper bound on the minimum rate due to the employment of the SVA and a planar Cartesian DS. We also show how to evaluate the SVA flux through a DS which is perpendicular to the path of the steepest descent at the saddlepoint. Implications for the application of ART are discussed. For systems characterized by a very unsymmetrical PES, the ART placement of the DS may render the use of the SVA unreasonable. In such cases, it is more reasonable in terms of the assumptions involved to estimate the rate using the steepest descent DS. Kinetic isotope effects for such systems are related in a sensitive manner to the orientation of the DS and may provide experimental support for the *utility* of other than ART locations. ART in its usual form gives *minimum* kinetic isotope effects of the type considered here. An examination of the assumptions involved in the evaluation of mean reaction cross sections within the framework of ART for a particular reaction indicates that the accurate mean cross section greatly exceeds the SVA value. The SVA value is, however, in comparatively good agreement with the corresponding classical mechanical trajectory result. In this sense, at least in this case, the SVA represents a poor but useful approximation. The considerations here result in a variational formulation of ART whose utility may be studied using the classical mechanical trajectory method.

E yring's absolute rate theory (ART)[1] has been applied with great success in quantitative studies of chemical reaction rates and isotope effects[2,3] and perhaps even more importantly as a conceptual framework for the qualitative discussion of structural and other factors which influence reaction velocities.[4]

We begin with a discussion of the formulation of ART and proceed to show that it represents a special case of a more general variational theory due to Keck.[5] We show that both theories give chemical reaction rates in terms of an integral over a dividing surface (DS) located in a potential energy volume in phase space at an intermediate position between reactants and products. In ART, the DS is of a special type and has a definite location. In Keck's theory, the DS is arbitrary in certain respects and is regarded as a trial surface which may be varied in both shape and location in order to place a minimum upper bound on the rate. Some

(1) H. Eyring, *J. Chem. Phys.*, **3**, 107 (1935); S. Glasstone, K. J. Laidler, and H. Eyring, "Theory of Rate Processes," McGraw-Hill, New York, N. Y., 1941; K. J. Laidler, "Theories of Chemical Reaction Rates," McGraw-Hill, New York, N. Y., 1969.

(2) J. Bigeleisen, F. S. Klein, R. E. Weston, and M. Wolfsberg, *J. Chem. Phys.*, **30**, 1340 (1959); A. Persky and F. S. Klein, *ibid.*, **44**, 3617 (1966); R. E. Weston, *Science*, **158**, 332 (1967); A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **47**, 1393 (1967); K. A. Quickert and D. J. Leroy, *ibid.*, **53**, 1325 (1970); M. J. Stern, A. Persky, and F. S. Klein, *ibid.*, **58**, 5697 (1973).

(3) D. J. Leroy, B. A. Ridley, and K. A. Quickert, *Discuss. Faraday Soc.*, **44**, 92 (1967).

(4) J. E. Leffler and E. Grunwald, "Rates and Equilibria in Organic Reactions," Wiley, New York, N. Y., 1963.

(5) J. C. Keck, *J. Chem. Phys.*, **32**, 1035 (1960); J. C. Keck, *Advan. Chem. Phys.*, **13**, 85 (1967).

difficulties involving the application of this theory are discussed. The two theories are compared to show that the *usual* interpretation of the ART transmission probability is deficient. The sense in which the minimum variational rate represents an upper bound on the true rate is explained. The conditions which must be satisfied to obtain the best variational rate are then examined in order to provide an interpretation for the ART rate. A method is given for varying the DS orientation within the framework of ART. The implications of the considerations given here for the application of ART are examined for a number of different potential energy hypersurfaces. The validity of the usual assumptions of ART is examined for a particular reaction by making comparisons involving accurate, small vibrations approximation (SVA), and trajectory mean cross sections.

ART

Basically, ART estimates reaction rates by placing a dividing volume (DV) within a potential energy volume in phase space at a definite location which is intermediate between reactants and products.[6] The DV passes through the saddlepoint (SP) of the potential energy hypersurface (PES) and has a definite orientation which may be expressed in terms of the variables which give the SP location. Phase points located within the DV correspond to transition states. The ART DV is perpendicular to the transition states unstable normal coordinate and its location is therefore determined by masses and curvatures of the PES at the SP. Using a classical model, ART then evaluates the reaction rate by multiplying the frequency $(\nu^{\ddagger})$ of crossing the DV by the *equilibrium* concentration of transition states and the transmission probability $\kappa^{\ddagger}$ at a given location within the DV; the total rate is obtained by integrating this product over the entire DV. According to this formulation $\nu^{\ddagger-1}$ is the lifetime of a given transition state and $\kappa^{\ddagger}$ is usually interpreted as the probability that a given phase point within the DV gives the desired reaction product; *i.e.*, it is zero or unity for a given phase point within the DV. In reality, $\nu^{\ddagger}$ and $\kappa^{\ddagger}$ depend upon all of the transition states coordinates and conjugate momenta except for those of the center of mass. In the usual application of ART, a number of additional assumptions are made; these will be discussed later.

To make our discussion more concrete, we will use the bimolecular exchange reaction $A + BC \rightarrow AB + C$ between an atom and a diatomic molecule as an example. When the transition state has a linear minimum energy configuration, the classical ART rate constant is given by the expression

$$k_{\text{r}} = \frac{Q_{\text{tran}}^{\ddagger}}{Q_A Q_{BC}} \int \ldots \int_{DV} \kappa^{\ddagger} \nu^{\ddagger} e^{-H/kT} \prod_i^6 \mathrm{d}q_i \mathrm{d}p_i \qquad (1)$$

where Q_A and Q_{BC} are the classical reactant partition functions per unit volume; $Q_{\text{tran}}^{\ddagger}$ is the translational partition function per unit volume for the transition state; H is the classical Hamiltonian; q_i and p_i, $i = 1-4$, correspond to the vibrational normal coordinates and their conjugate momenta; and q_i and p_i, $i = 5, 6$, are the Eckart rotational angles and their conjugate

(6) H. S. Johnston, "Gas Phase Reaction Rate Theory," Ronald Press, New York, N. Y., 1966, p 119.

momenta. In the notation used here, we consistently omit Planck's constant.

Keck's Variational Theory

Keck's[5] variational theory of chemical reaction rates is based on an approach originally used by Marcelin[7] and developed later by Wigner[8] and Horiuti.[9] His phase space theory result for the rate constant takes the form

$$k_{\text{r}} = \int_{DS}^{\mathbf{v}\cdot\mathbf{n}>0} \mathbf{v}\cdot\mathbf{n}\,\rho\,\mathrm{d}\sigma \qquad (2)$$

where $\mathrm{d}\sigma$ is an element on the dividing surface (DS); $\mathbf{v}$ is the generalized velocity of a representative phase point; $\mathbf{n}$ is the unit normal to $\mathrm{d}\sigma$; and ρ is the phase point density function. Keck points out that in the regions where the reactants interact, the DS is somewhat arbitrary in nature and must be regarded as a trial surface which is subject to arbitrary variations. It must not, however, have any holes. A hole is a route connecting initial and final states which does not encounter the DS. Keck argues that the equilibrium value for ρ $(\rho_e = e^{-H/kT}/Q_A Q_{BC})$ is the maximum value which is consistent with the conservation laws[10] and he uses this value to calculate an upper limit on the reaction rate. The rate given by eq 2 represents an upper limit for a number of reasons. Trajectories originating from the reactants may cross the surface a number of times; each crossing in the forward (product) direction for a single trajectory will contribute to the reaction rate on an equal basis. In addition, trajectories which originate from the products and cross and recross the surface will also be counted; *i.e.*, trajectories which do not originate in the reactant region of phase space will contribute to the reaction rate. Trajectories which form closed loops through the DS in the transition region will also contribute to the rate.

Keck's theory is a variational one in that one may *in principle* vary the location of the trial surface in order to find the position that gives a *minimum upper bound* on the rate.[11] For our example, eq 2 may be expressed as[12]

$$k_{\text{r}} = \frac{Q_{\text{tran}}^{\ddagger}}{Q_A Q_{BC}} \int \ldots \int_{DS} v_n \beta e^{-H/kT} \prod_i^5 \mathrm{d}q_i \prod_i^6 \mathrm{d}p_i \qquad (3)$$

where v_n is the velocity in phase space normal to the DS and β relates the differential surface area $\mathrm{d}\sigma$ to the position and momentum coordinates; *i.e.*, if $v_n = v_1 = \dot{q}_1$, then $\beta = 1$.

Comparing the Theories

It is interesting to compare eq 1 and 3. Consider the integration over q_1 and p_1, the unstable vibrational normal coordinate and its conjugate momentum, in eq 1. Transition state theory requires that $-\delta/2 < q_1 < +\delta/2$ where δ is a small length along q_1. Since the DV is perpendicular to q_1, $\nu^{\ddagger} = (\delta\mu_1)^{-1}p_1$ where μ_1 is

(7) R. Marcelin, *Ann. Phys. (Leipzig)*, **3**, 120 (1915).
(8) E. Wigner, *J. Chem. Phys.*, **5**, 720 (1937).
(9) J. Horiuti, *Bull. Chem. Soc. Jap.*, **13**, 210 (1938).
(10) This point will be taken up later.
(11) Some difficulties in this regard will be taken up at a later point.
(12) R. L. Jaffe, J. M. Henry, and J. B. Anderson, *J. Chem. Phys.*, **59**, 1128 (1973).

the reduced mass for motion along q_1.[13] Part of the hypervolume integral in eq 1 is given in eq 4. The

$$\int_{-\delta/2}^{+\delta/2} dq_1 \int_{-\infty}^{+\infty} \kappa^{\pm}(\delta\mu_1)^{-1}p_1 e^{-H/kT} dp_1 \qquad (4)$$

length δ must be small enough to ensure that the potential energy is constant to a good approximation. It is clear that δ cancels and eq 1 becomes

$$k_r = \frac{Q_{tran}^{\pm}}{Q_A Q_{BC}} \int \cdots \int_{DS} \kappa^{\pm}(\mu_1)^{-1}p_1 e^{-H/kT}\prod_i^5 dq_i \prod_i^6 dp_i \qquad (5)$$

Comparing eq 3 and 5, we note that both the transition state and variational formulations are essentially phase space theories which give the rate in terms of a hypersurface integral. In the former approach, a definite DS is specified; in the latter, a somewhat arbitrary trial surface is varied to place a minimum upper bound on the rate. Unfortunately, applications using the variational feature of Keck's theory have been restricted to the study of the recombination of attracting atoms in the presence of repulsive third bodies using a crude trial surface having one adjustable parameter.[5] The successful outcome of the study suggests that additional research using this approach is certainly warranted.

We prefer to discuss ART in terms of the concept of a dividing surface rather than a dividing volume. The latter is, however, more useful when one considers the conditions under which a classical treatment of motion across the transition region is appropriate. For example, δ must be small enough so that $\partial V/\partial q_1 \approx 0$ within DV where V is potential energy. At the same time, the validity of the classical treatment of motion along q_1 requires that the "width" of the transition region is large enough to allow the quantum mechanical uncertainty in thermal velocities ($\dot{q}_1$) to be small.[15]

The ART Transmission Probability and the Equilibrium Assumption in the Transition Region

A comparison of eq 3 and 5 makes it clear that the usual interpretation of the ART transmission probability, given earlier here, is deficient.[16] The transmission probability $\kappa^{\pm}$ in eq 5 depends upon five spatial and six momentum coordinates on the DS ($q_1 = 0$). If a reactive trajectory, originating from the reactants, crosses the DS a number of times while proceeding in the general direction of the product (forward), $\kappa^{\pm}$ must be 0 at all but one forward crossing in order to obtain the correct rate. For example, if a trajectory originating from the reac-

tants maps into the product region of phase space and intersects the DS three times, $\kappa^{\pm}$ must be zero at one of the two forward crossings. If this is not done, the trajectory will incorrectly contribute twice to the rate. For a nonreactive trajectory originating from the reactants which intersects the DS twice, $\kappa^{\pm}$ must be zero at the single forward crossing. Furthermore, $\kappa^{\pm}$ must be 0 for trajectories which originate from the product region of phase space and cross and recross the DS to attain the forward direction. $\kappa^{\pm}$ must also be zero for closed loop trajectories through the DS in the transition region. The proper values for $\kappa^{\pm}$ in eq 5 could be obtained by computing the appropriate classical mechanical trajectories (CMT). Even if these values are employed in eq 5, the ART rate would be larger than the true rate if as Keck suggests $\rho < \rho_e$ for certain regions on the DS.

Anderson[17] suggested that the classical phase space distributions in the transition region are the equilibrium ones ($\rho = \rho_e$) on any DS *provided* that trajectories moving in the direction of products which originate from reactants, products, and loops in the transition region are included. He supported his argument by example using collinear trajectories and did not regard the matter as proved. Recently, Mayer[18] stated that Anderson's suggestion is correct and is "an obvious consequence of the Liouville theorem of classical mechanics."

Conditions for the Best Variational Rate

Horiuti[9] has discussed the conditions which must be satisfied in order to obtain the minimum rate using the variational theory. His arguments are not entirely correct and are discussed here with some necessary modification.

The hypersurface integral appearing in eq 2 and 3 and Horiuti's eq 1 may be expressed in terms of our example as

$$\int \cdots \int_{DS} v_1 \exp\left\{-\frac{\mu_1 v_1^2}{2kT} - \frac{H'}{kT}\right\}\prod_i^5 dq_i \prod_i^6 dp_i \qquad (6)$$

where the q_i's are orthogonal curvilinear coordinates, the p_i's are their conjugate momenta, q_1 is perpendicular to the surface, and μ_1 is the reduced mass associated with q_1. One then integrates over positive values of $p_1 = \mu_1 v_1$ and over all momentum space for the remaining momenta. The variational requirement for a minimum is then given by the equation[9]

$$\int \cdots \int_{DS} \prod_i^5 (2\pi\mu_i kT)^{1/2} e^{-V/kT} \times$$

$$\left[-\frac{1}{kT}\frac{\partial V}{\partial q_1} + \sum_i^5 \rho_i^{-1}\right]\delta q_1 \prod_i^5 dq_i = 0 \qquad (7)$$

or

$$\frac{1}{kT}\frac{\partial V}{\partial q_1} = \sum_i^5 \rho_i^{-1} \qquad (8)$$

where the μ_i's are the reduced masses for the momenta, V is the potential energy on the DS, and the ρ_i's are the principal radii of curvature.[19]

(13) It is interesting to note that within the SVA, the conjugate momentum for a vibrational normal coordinate is simply the time derivative of the normal coordinate, i.e., $p_1 = \dot{q}_1$, $\mu_1 = 1$, and the contribution to the approximate SVA Hamiltonian due to normal coordinate 1 is simply $\frac{1}{2}(\dot{q}_1^2 + \lambda_1 q_1^2)$ where λ_1 is the eigenvalue for the unstable normal coordinate. The value of λ_1 is negative and the corresponding vibrational frequency, $\nu_1 = \lambda_1^{1/2}/2\pi$, is imaginary. When the exact Hamiltonian is formulated,[14] the relationship between $\dot{q}_1$ and p_1 is more complex due to the presence of Coriolis terms which account for vibrational–rotational interaction.

(14) L. Page, "Introduction to Theoretical Physics," 2nd ed, Van Nostrand, New York, N. Y., 1934, Chapter 2; C. Eckart, *Phys. Rev.*, 47, 552 (1935); E. B. Wilson, Jr., and J. B. Howard, *J. Chem. Phys.*, 4, 260 (1936); H. H. Nielsen, *Rev. Mod. Phys.*, 23, 90 (1951); E. B. Wilson, Jr., J. C. Decuis, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, Chapter 11.

(15) J. O. Hirschfelder and E. Wigner, *J. Chem. Phys.*, 7, 616 (1939).

(16) Hirschfelder and Wigner[15] and Anderson[17] have also taken up this point.

(17) J. B. Anderson, *J. Chem. Phys.*, 58, 4684 (1973).

(18) I. Mayer, *J. Chem. Phys.*, 60, 2564 (1974).

(19) G. James and R. C. James, "Mathematics Dictionary," multilingual ed, Van Nostrand, New York, N. Y., 1959.

If the orthogonal curvilinear coordinates and momenta used are those of ART (spherical polar, Eckart), it is clear that one *must* integrate over the orientational coordinates in order to carry out the integration over the momenta. These coordinates do not affect the potential energy and Horiuti's variational condition may be modified accordingly. It would appear that all one has to do is evaluate eq 3 with the conditions imposed by a modified version of eq 8 in order to obtain the best variational rate. A problem is encountered in this connection due to practical considerations involving the DS boundary conditions.

Anderson and coworkers[12] and Porter and coworkers[20] have evaluated reaction rates using eq 3. No variational condition was used. The points in configuration space were defined by the variables $\mathbf{R}$, $\mathbf{r}$, and θ where $\mathbf{R}$ is the vector connecting the BC center of mass to A, $\mathbf{r}$ is the BC vector, and θ is the angle formed by the intersection of $\mathbf{R}$ with $\mathbf{r}$. The spherical polar variables defining $\mathbf{R}$ and $\mathbf{r}$ and their conjugate momenta were used and the rate constant is given by

$$k = [2\pi kT/\mu_{A,BC}]^{1/2} R_t^2 \int_0^\circledast r^2 dr \times$$

$$\int_0^\pi \sin\theta e^{-V(r,R_t,\theta)/kT} d\theta \bigg/ \int_0^\circledast r^2 e^{-V_{BC}(r)/kT} dr \quad (9)$$

where R_t, the distance between A and the BC center of mass, defines the location of the DS. Porter and coworkers point out that the integrals which appear diverge when the circled limits are used due to the finite limit on the potential energy for dissociation. They showed that the value of the rate constant increased dramatically as the first circled limit was increased. On this basis, it appeared as though the arbitrary nature of the DS limit represented a serious handicap of the variational theory and combined phase space trajectory (CPST) studies of reaction rates. However, their DS location was not a good one for two reasons: (1) it had "holes," and (2) it extended into the product valley for near linear configurations. The dramatic increase in rate which accompanied an increase in the DS boundary was a consequence of the fact that many reflected trajectories originating in the product region of phase space made a contribution to the rate as the surface was extended. The handicap, associated with the surface boundary, is not a serious one. One must use a surface without holes and simply extend the surface boundary until the contribution to the rate due to an increase in the limit represents a small fraction of the rate. It may, however, be difficult to locate a proper DS of the type discussed here in the transition region for a very unsymmetrical PES which does not give an enormous overestimate for the rate. This would of course seriously reduce the efficiency of the CPST method.

We now consider ART in connection with Horiuti's formulation. When the integration over positive p_1 is carried out, one obtains the familar kT factor of ART provided that $v_1 = p_1/\mu_1$. The momentum p_1 is that of the transition state's unstable vibrational mode. Within the SVA, $\mu_1 = 1$ and $v_1 = p_1$[13] and all is well. However,

(20) R. N., Porter, D. L. Thompson, and L. M. Raff, *J. Chem. Phys.*, submitted for publication.

if one expresses the normal coordinates in terms of mass weighted Cartesian coordinates and includes vibration–rotation interaction terms in the Hamiltonian, it follows that[14]

$$v_1 = \dot{q}_1 = p_1 - \mathfrak{X}_1\omega_x - \mathfrak{Y}_1\omega_y - \mathfrak{Z}_1\omega_z \quad (10)$$

where the ω's are the components of the angular velocity of the rotating Eckart axes and their coefficients are determined by the transformation from normal to Cartesian coordinates as well as the particular values of the normal coordinates. ART assumes that $v_1 = p_1$, *i.e.*, that $\dot{q}_1$ is separable in this sense. The terms in the Hamiltonian that couple the momentum of the unstable vibrational normal coordinate with the other vibrational–rotational momenta are assumed to be negligible.

Horiuti calls the ART DS a Cartesian plane whose location is given by a particular value of q_1. The ART DS for our example reaction is actually 11-dimensional. The potential energy on the DS can, however, be resolved in a Cartesian plane. See ref 12. The RHS of eq 8 is on this basis zero and $\partial V/\partial q_1$ must be zero in order to satisfy the variational condition for the special case of a planar Cartesian surface. The value of the partial derivative at the SP is zero, *i.e.*, $q_1 = 0$. Within the separability assumption, ART gives the upper bound ($\kappa^\pm = 1$) on the minimum rate *for a planar Cartesian DS* whose location is given by a *particular* orthogonal coordinate *when that coordinate has its saddlepoint value.* ART in its usual form makes an additional assumption; the SVA is used to evaluate concentrations on the DS. We will show that within this approximation, the use of the normal coordinate for the unstable vibration as the particular orthogonal coordinate does provide an approximate upper bound on the minimum equilibrium rate. However, when the SVA is not employed, another orthogonal coordinate and consequently a different planar DS may give a lower rate. In other words, Horiuti's variational considerations are incomplete. The location of the DS may be changed by varying the form of the orthogonal coordinate as well as its value.

Alternate Locations for the Planar Dividing Surface

Consider eq 1 and the usual assumptions of ART. Degrees of freedom which do not influence the classical rate (through $\kappa^\pm$ or $\nu^\pm$) factor out as the appropriate partition functions.[6] We assume that $\kappa^\pm$, $\nu^\pm$, and the location of DV do not depend on the rotational and bending vibrational coordinates and therefore depend only upon the two stretching normal coordinates q_R and $q_1 = q_I$, which correspond to the transition state's real and imaginary (unstable) vibrational modes, respectively. The expression for the rate constant then becomes

$$k_r = \frac{Q_{tran}^\pm Q_{rot}^\pm (Q_b^\pm)^2}{Q_A Q_{BC}} \times$$

$$\int_{DV} \cdots \int \kappa^\pm \nu^\pm e^{-H'/kT} \prod_i^2 dq_i dp_i \quad (11)$$

where we have made the SVA and $Q_{rot}^\pm$ and $Q_b^\pm$ are the rotational and bending vibrational partition functions, respectively, and H' is the Hamiltonian for

the stretching modes. ART assumes that $\kappa^{\pm}$, $\nu^{\pm}$, and the location of DV depend upon q_I alone.

$$\kappa^{\pm} = \kappa^{\pm}(q_I, p_I) \tag{12}$$

$$\nu^{\pm} = \nu^{\pm}(q_I, p_I) \tag{13}$$

$$-\delta/2 \leqslant q_I = c_1{}^I \Delta R_1 + c_2{}^I \Delta R_2 \leqslant +\delta/2 \tag{14}$$

where δ is a small distance along q_I; ΔR_i, $i = 1$, 2, is the bond displacement internal coordinate; and the coefficients $c_1{}^I$ and $c_2{}^I$ are determined by a normal coordinate analysis, i.e., by the masses and second partial derivatives of the potential energy with respect to ΔR_1 and ΔR_2 at the saddlepoint. The satisfied equation corresponds to a thin strip of width δ on the collinear PES map. Since $q_I \approx 0$ within the strip, the potential energy within the strip is approximately that of the mode q_R. The Appendix gives a convenient method for finding the location of the ART DS which appears as a line on the collinear map. We use the symbol χ for $\Delta R_2/\Delta R_1$, the slope of the line. The value of χ corresponding to the ART DS is given by the expression

$$\chi_{ART} = -c_1{}^I/c_2{}^I \tag{15}$$

We now carry out an orthogonal transformation which serves to define two new coordinates q_{rc} and $q_\perp$.

$$q_{rc} = (\sin \phi)q_I + (\cos \phi)q_R \tag{16}$$

$$q_\perp = (-\cos \phi)q_I + (\sin \phi)q_R \tag{17}$$

where for our purposes $-\pi/2 \leqslant \phi \leqslant \pi/2$. Later, we will see that there are additional restrictions on the values of ϕ. The kinetic and potential energies for the stretching modes in the old and new coordinates are

$$2T = \dot{q}_I{}^2 + \dot{q}_R{}^2 = \dot{q}_{rc}{}^2 + \dot{q}_\perp{}^2 \tag{18}$$

$$2V = \lambda_I q_I{}^2 + \lambda_R q_R{}^2 = (\lambda_R \cos^2 \phi +$$
$$\lambda_I \sin^2 \phi)q_{rc}{}^2 + (\lambda_R \sin^2 \phi + \lambda_I \cos^2 \phi)q_\perp{}^2 +$$
$$2 \sin \phi \cos \phi(\lambda_R - \lambda_I)q_{rc}q_\perp \tag{19}$$

where $\lambda_R = 4\pi^2 \nu_R{}^2$ and $\lambda_I = 4\pi^2 \nu_I{}^2$ are the eigenvalues for the real and imaginary vibrations and ν_R and ν_I are the corresponding frequencies. The eigenvalue λ_I is negative and ν_I is therefore imaginary. Recall that within the SVA the time derivative of a normal coordinate gives the conjugate momentum for that coordinate.

The requirement for the position of the new DS is given by the equation[21]

$$-\delta/2 \leqslant q_{rc} \leqslant +\delta/2 \tag{20}$$

It follows that $q_{rc} \approx 0$ and $2V = \lambda_\perp q_\perp{}^2$ where $\lambda_\perp = \lambda_R$ $\sin^2 \phi + \lambda_I \cos^2 \phi = 4\pi^2 \nu_\perp{}^2$. We now assume that $\kappa^{\pm} = 1$ for $\dot{q}_{rc} > 0$ and $\nu^{\pm} = \dot{q}_{rc}/\delta$; the part of the rate constant integral involving $q_\perp$ and q_{rc} is then

$$\int_{-\infty}^{+\infty} e^{-\dot{q}_\perp{}^2/2kT}d\dot{q}_\perp \int_{-\infty}^{+\infty} e^{-\lambda_\perp q_\perp{}^2/2kT}dq_\perp \times$$
$$\int_{-\delta/2}^{+\delta/2} \delta^{-1}dq_{rc} \int_{0}^{\infty} \dot{q}_{rc}e^{-\dot{q}_{rc}{}^2/2kT}d\dot{q}_{rc} \tag{21}$$

(21) G. J. Wei and P. E. Yankwich, J. Chem. Phys., 58, 5552 (1973), discussed the effect of variations in reaction coordinate eigenvalue and eigenvector on the rate and hydrogen isotope effects of the reaction H + Cl₂ → HCl + Cl which has a nonlinear equilibrium configuration.

The variational requirement takes the form

$$\frac{\partial V}{\partial q_{rc}} = 0 = (\lambda_R \cos^2 \phi + \lambda_I \sin^2 \phi)q_{rc} +$$
$$\sin \phi \cos \phi(\lambda_R - \lambda_I)q_\perp \tag{22}$$

In order to satisfy the equation, the DS must pass through the SP ($q_{rc} = 0$) and ϕ must be 0 or $\pm \pi/2$ since $-\infty < q_\perp < +\infty$ on DS. Since $\lambda_\perp$ is the eigenvalue for the real vibration, it follows that

$$\lambda_R \sin^2 \phi + \lambda_I \cos^2 \phi > 0 \tag{23}$$

This places the following restrictions upon the orientation of the DS

$$\phi_\infty < \phi \leqslant \pi/2 \tag{24}$$

$$-\pi/2 \leqslant \phi < -\phi_\infty \tag{25}$$

where $\phi_\infty = \tan^{-1}(-\lambda_I/\lambda_R)^{1/2}$ and the rate is infinite at $\pm\phi_\infty$. The minimum SVA rate is therefore the ART one; i.e., $\phi = \pm \pi/2$ and $\lambda_\perp = \lambda_R$. The infinite rate at $\pm\phi_\infty$ is of a course a consequence of the SVA. The connection between ϕ and χ for a given DS is given by the expression

$$\chi = \frac{\Delta R_2}{\Delta R_1} = -\frac{c_1{}^I \tan \phi + c_1{}^R}{c_2{}^I \tan \phi + c_2{}^R} \tag{26}$$

or

$$\phi = \tan^{-1}\left[-\frac{c_1{}^R + \chi c_2{}^R}{c_1{}^I + \chi c_2{}^I}\right] \tag{27}$$

where $q_R = c_1{}^R \Delta R_1 + c_2{}^R \Delta R_2$ and a normal coordinate analysis provides the values of $c_1{}^R$ and $c_2{}^R$.

Integration of eq 21 provides the result $(kT)^2/\nu_\perp$. When the ART DS is used, $\nu_\perp = \nu_R$. Consequently, the classical rate alteration when an acceptable DS other than that of ART is used is simply $\nu_R/\nu_\perp$ ($\geqslant 1$). In the usual application of ART, the rate if formulated in terms of quantum mechanical partition functions. In this case, the rate alteration is simply

$$e^{h(\nu_R-\nu_\perp)/2kT}(1 - e^{-h\nu_R/kT})/(1 - e^{-h\nu_\perp/kT}) \tag{28}$$

When $\kappa^{\pm} = 1$ and the assumption involving the integration over p_1 is made, eq 1 may be expressed as

$$k_r = kTQ^{\pm}/Q_A Q_{BC} \tag{29}$$

where $Q^{\pm}$ is the classical transition state partition function excluding the contribution due to the reaction coordinate. $Q^{\pm}$ is usually evaluated employing the SVA approximation for the potential energy on the DS. It is worthwhile to note that $Q^{\pm}$ may be evaluated using the accurate potential energy using the expression[22]

$$kTQ^{\pm} = \left[\frac{kT}{2\pi}\right]^{1/2}(2\pi kT)^3\left[\frac{m_A m_B m_C}{m_A + m_B + m_C}\right]^{1/2}8\pi^2 \times$$

$$\int_{-\infty}^{+\infty}\int_{0}^{\pi} R_1{}^2(q_R)R_2{}^2(q_R)J(\Delta R_1, \Delta R_2/\theta, q_R) \sin \theta \times$$
$$e^{-V(q_R,\theta)/kT}d\theta dq_R \tag{30}$$

where the R's are the transition state bond lengths, θ is the angle which gives the deviation from linearity, and J is an appropriate Jacobian.[23] The SVA result for

(22) G. W. Koeppl, unpublished work. For the techniques involved, see ref 23.

(23) H. L. Strauss and E. Thiele, J. Chem. Phys., 46, 2473 (1967).

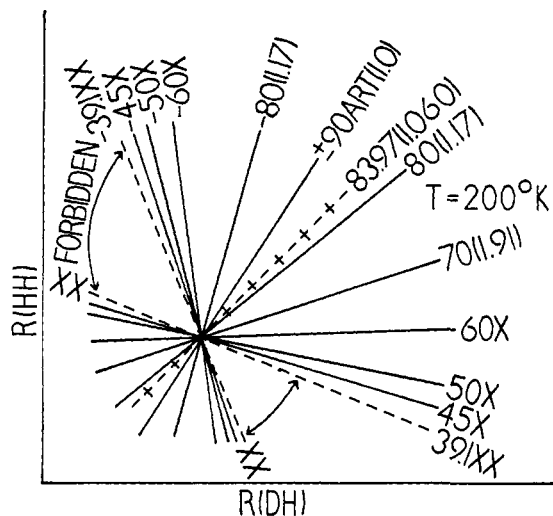**Figure 1.** Alternate dividing surfaces for the $D + H_2$ reaction. See text for explanation.

Figure 2. Alternate dividing surfaces for the $Cl + H_2$ reaction. See text for explanation.

J is $[(m_A + m_B + m_C)/m_A m_B m_C]^{1/2}$. Equation 30 reduces to that of the SVA under the proper conditions. For an alternate DS, one replaces q_R with $q_\perp$ and J with the expression appropriate for this coordinate. The integral in eq 30 diverges; one must use a practical limit for q_R.

Steepest Descent SVA Rates[24]

The SVA collinear transition state potential energy may be expressed as

$$2V = f_1 \Delta R_1{}^2 + f_2 \Delta R_2{}^2 + 2f_{12} \Delta R_1 \Delta R_2 \qquad (31)$$

where the f's are valence bond stretching force constants. We set this expression equal to zero and solve for the two values of $\Delta R_2/\Delta R_1 = \chi(\pm)$ which give the lines corresponding to $V = 0$ on the collinear PES.

$$\chi(\pm) = \frac{-f_{12} \pm (f_{12}{}^2 - f_1 f_2)^{1/2}}{f_2} \qquad (32)$$

The bisector of these lines gives the path of steepest descent at the saddlepoint. Let

$$S_1 = -[\chi(+)]^{-1} \qquad (33)$$

$$S_2 = -[\chi(-)]^{-1} \qquad (34)$$

The value of $\chi = \Delta R_2/\Delta R_1$ corresponding to a DS which is perpendicular to the path of steepest descent at the SP is

$$\chi(SD) = \frac{S_1(1 + S_2{}^2)^{1/2} + S_2(1 + S_1{}^2)^{1/2}}{(1 + S_1{}^2)^{1/2} + (1 + S_2{}^2)^{1/2}} \qquad (35)$$

This expression is valid provided that S_1 and S_2 have the same sign $(+)$. If one value is positive and the other negative, $\chi(SD)$ is given by the negative reciprocal of this expression.

Applications

We now consider the consequences of varying the orientation of the DS within the framework of ART.

(24) Leroy, *et al.*,[3] pointed out that the normal coordinate associated with the transition state's imaginary mode did not lie parallel to the path of steepest descent at the SP in the case of the $D + H_2$ and $H + D_2$ reactions. They discussed the consequences insofar as a tunneling correction was concerned.
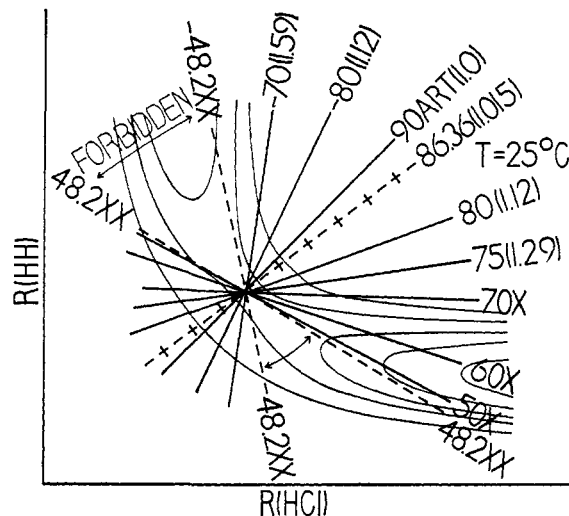
We examine a series of reactions. In the series, the potential energy surface changes from symmetric to very unsymmetric. See Table I for descriptive information for the surfaces and Table II for transition state

Table I. Descriptive Information for Reactions and Potential Energy Surfaces

Reaction	Surface type	Ref
$D + H_2$	Symmetrical harmonic surface corresponding to the best *ab initio* PES	*a, b*
$Cl + H_2$	Nearly symmetrical LEPS surface	*c*
$Br + H_2$	Unsymmetrical extended LEPS surface	*d*
$F + H_2$, $F + D_2$	Very unsymmetrical extended LEPS surface	*e, f*

a G. W. Koeppl, *J. Chem. Phys.*, **59**, 3425 (1973). *b* B. Liu, *ibid.*, **58**, 1925 (1973). *c* A. Persky and F. S. Klein, *ibid.*, **44**, 3617 (1966). *d* C. Paar, Ph.D. Thesis, California Institute of Technology, CALT-532-38, 1969. *e* J. T. Muckerman, Surface V, private communication. *f* G. W. Koeppl, *J. Chem. Phys.*, **60**, 1684 (1974).

Table II. Transition State Properties

Transition state	BrHH	FHH	ClHH	DHH
r_1, Å	1.4898	1.5413	1.4115	0.9297
r_2	1.1483	0.7618	0.9745	0.9297
E_c,[a] kcal mol^{-1}	20.854	1.0644	7.7592	9.50
f_1,[b] mdyn Å^{-1}	2.278	-0.0748	1.5677	1.02
f_2[b]	0.0643	4.9066	0.5700	1.02
f_{12}[b]	0.9382	0.4962	1.5105	1.47
f_b,[c] ergs $\times 10^{11}$	0.4058	0.0217	0.0774	0.0815

[a] Classical activation energy. [b] Valence bond stretching force constants. [c] Valence bending force constant.

properties. In Table III, we give the real and imaginary normal mode eigenvalues, the limiting values of ϕ $(\pm\phi_\infty)$, the normal mode values of γ (see Appendix), and the steepest descent rate alterations. In Figures 1–4, we show the consequences of using alternate DS's. The PES contours of the semiempirical surfaces are

Table III. Normal Coordinate Properties and Steepest Descent Rate Alterations

Reaction	$\lambda_R{}^a$	λ_1	$\pm\phi_\infty$, deg	γ, deg	χ_{ART}	χ(SD) (perpendicular to path of steepest descent)	QM rate alteration at χ(SD) (T, °K)
Br + HH	1.1817	−0.6267	±36.06	38.91	−0.2009	0.36677	1.153 (400)
Br + DD	0.6056	−0.3137	±35.74	39.28	−0.1980	0.36677	1.113 (400)
F + HH	8.7506	−0.07628	±5.334	42.82	−2.1427	10.139	15.82 (298.16)
F + DD	4.3804	−0.04181	±5.580	43.96	−2.1573	10.139	6.273 (298.16)
Cl + HH	1.0758	−1.3425	±48.17	64.70	0.9990	0.72287	1.015 (298.16)
Cl + DD	0.5641	−0.6755	±47.58	65.49	0.9645	0.72287	1.009 (298.16)
D + HH	1.8310	−1.2055	±39.06	86.02	0.6642	1.0	1.060 (200)
H + DD	1.8271	−0.7554	±32.74	3.700	1.6198	1.0	1.114 (200)

a Given in practical units (mdyn $\text{Å}^{-1}\text{amu}^{-1}$).

Figure 3. Alternate dividing surfaces for the Br + H_2 reaction. See text for explanation.
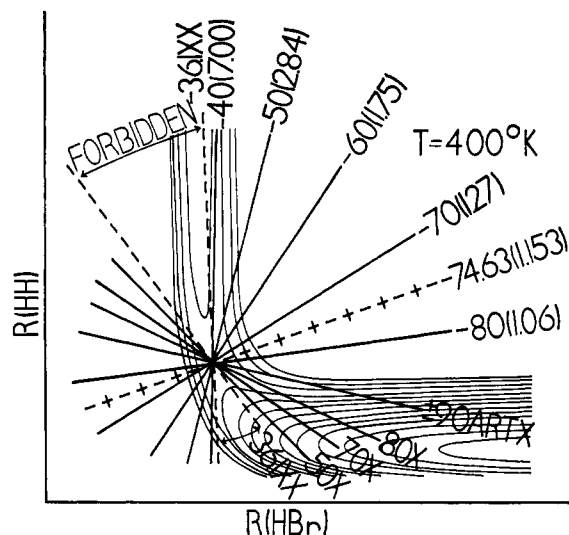

Figure 4. Alternate dividing surfaces for the F + H_2 reaction. See text for explanation.

given in the background. A DS which has an unacceptable potential energy for the $q_\perp$ mode is labeled with an X. The first number at the end of the DS line gives the value of ϕ; the second number gives the quantum mechanical (QM) alteration of the ART rate. The dashed lines indicate the limiting values for $\phi (\pm\phi_\infty)$ and have two X's at the ends. The DS formed by alternating + and − signs is perpendicular to the path of steepest descent at the SP. The figures show that the consequences of using alternate DS's are the most serious for very unsymmetrical potential energy surfaces such as that for F–H–H. For this reason we consider this system in more detail.

In Table IV, we give the rate alterations for the reactions F + H_2 and F + D_2. We give rate alterations both at the same values of ϕ and the same values of χ. In the absence of CMT studies, one has no means to decide whether in calculating kinetic isotope effects one should use the same transformation angle ϕ or the same DS position as measured by χ in making the rate comparison. We therefore report isotope effect alterations of both types. They do not differ greatly. It is important to point out that the ART SVA isotope effect is a minimum. The ART isotope effect is 1.64 at 25°; the experimental value is ca. 1.9.[25] The harmonic isotope effect alteration (QM) at $\phi = -70°$ based on the

(25) A. Persky, J. Chem. Phys., 59, 3612 (1973).

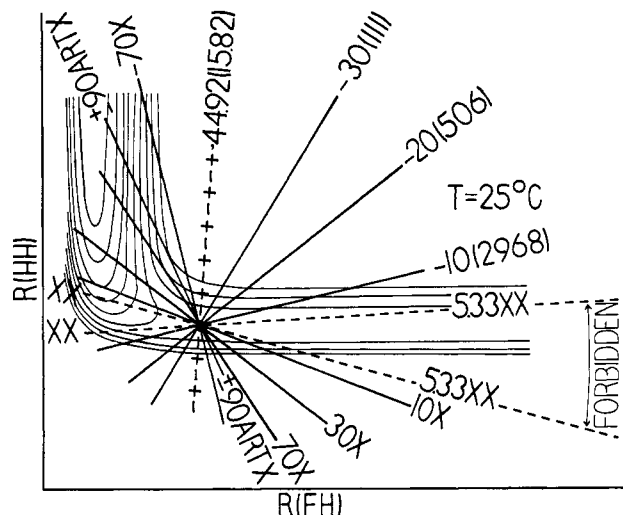same transformation angle for each reaction is 1.18; this correction brings the experimental and calculated isotope effects into agreement with no recourse to a tunneling correction at 25°. The steepest descent isotope effect alteration at $\phi = -44.92°$ for both reactions is 2.24. In Figure 5, we compare experimental,[25] ART, and −70° DS isotope effects.

In Figure 6, we give the potential energy for the $q_\perp$ mode along different DS's. The harmonic ART potential is in poor agreement with the PES result. The agreement is improved as the position of the DS is varied. As the potential along the DS becomes more acceptable, the alteration of the isotope effect becomes less acceptable in terms of agreement with the experimental value. The lack of agreement between experimental and theoretical isotope effects may be due of course to quite a number of reasons: (1) the limitations of SVA ART; (2) the use of an approximate PES as a basis for the SVA; (3) the calculations do not include an isotope effect on the classical transmission coefficient; (4) PES nonadialaticity (more than one PES may be important for this reaction); and/or (5) the lack of an appropriate quantum mechanical correction. Perhaps CMT studies will suggest a means for dealing with what we have referred to as an unacceptable DS potential for $q_\perp$. The elucidation of the correct explanation for the disagreement respresents a considerable challenge. The considerations here certainly

Table IV. Isotope Effects at Different Dividing Surfaces for the F + H₂ vs. F + D₂ Reactions[a]

$\tilde{\nu}_\perp$, cm⁻¹	χ	φ	Harmonic QM alteration	Harmonic classical alteration	Anharmonic classical alteration	Isotope effect on alterations QM	Isotope effect on alterations Classical anharmonic
H 3854*	−2.143	±90	1.0	1.0			
D 2727*	−2.143	89.67	1.0	1.0		1.0	
D 2727*	−2.157	±90	1.0	1.0		1.0	
H 3619*	−3.704	−70	1.761	1.065			
D 2578*	−3.704	−71.11	1.430	1.057		1.231	
D 2561*	−3.886	−70	1.493	1.065		1.180	
H 3333*	−6.653	−60	3.517	1.156			
D 2390*	−6.653	−61.36	2.255	1.141		1.559	
D 2358*	−7.596	−60	2.436	1.156		1.444	
H 2709	10.139	−44.92	15.82	1.422	1.866		
D 1966	10.139	−46.39	6.273	1.387	1.473	2.522	1.267
D 1916	7.674	−44.92	7.070	1.423	1.497	2.238	1.246
H 1902	1.784	−30	111.1	2.027	2.124		
D 1395	1.784	−31.22	24.89	1.955	1.963	4.464	1.082
D 1344	1.618	−30	28.18	2.029	2.036	3.942	1.043
H 1274	0.7755	−20	506.2	3.025	3.034		
D 940	0.7755	−20.89	75.36	2.901	2.910	6.717	1.043
D 893	0.7177	−20	83.48	3.035	3.044	6.064	0.997
H 568	0.2378	−10	2968	6.788	6.796		
D 420	0.2378	−10.46	300.8	6.490	6.497	9.867	1.046
D 394	0.2194	−10	326.9	6.918	6.919	9.079	0.982

[a] An asterisk indicates that the DS is unacceptable. The quantum mechanical (QM) alterations are for 25°C.
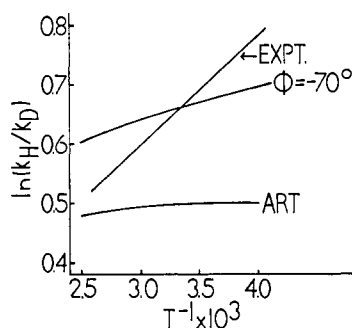

Figure 5. Comparison of experimental and theoretical isotope effects for the reactions F + H₂ vs. F + D₂.
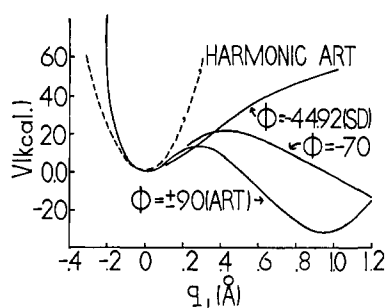

Figure 6. Potential energy along the dividing surface for F-H-H.

indicate that there is a great deal more ambiguity than is usually recognized in ART calculations of kinetic isotope effects.

Refined Treatment in Terms of Mean Reaction Cross Sections

It is desirable at this point to consider the error due to the SVA in ART applications of both the usual and alternate DS type. In order to do this without introducing any uncertainty via the DS boundary, we will make comparisons in terms of mean reaction cross sections which may be formulated in terms of convergent integrals.

Morokuma, Eu, and Karplus[26] have obtained expressions for the mean reaction probabilities and cross sections of ART which are a function of the total system energy. Their results are valid within the harmonic oscillator–rigid rotor approximation, i.e., the SVA. Their classical mean reaction cross section may be defined as

$$\bar{S}_r(E) = [\epsilon_I(E)]^{-1} \int \cdots \int_{\substack{\text{BC potential energy} \\ \text{phase volume}}} (E - E_{int}) H(E - E_{int}) \times$$

$$S_r(E - E_{int}; q_i, p_i, i = 1\text{–}3) \prod_i^3 dq_i dp_i \quad (36)$$

where

$$\epsilon_I(E) = \int \cdots \int_{\substack{\text{BC potential energy} \\ \text{phase volume}}} (E - E_{int}) \times$$

$$H(E - E_{int}) \prod_i^3 dq_i dp_i \quad (37)$$

where E is the total system energy; E_{int} is the internal energy of the reactant, BC; the q_i and p_i are the reactant internal coordinates and momenta; and $H(X)$ is the Heaviside step function, i.e., $H(X) = 1$ for $X > 0$ and 0 for $X < 0$. The ART result for $\bar{S}_r(E)$ may be evaluated readily if one assumes that $\kappa^\pm = 1$ and makes the approximation discussed earlier involving the integration over p_1. The classical expression for $\bar{S}_r(E)$ takes the form

$$\bar{S}_r(E) = [8\pi\mu_{A,BC}\epsilon_I(E)]^{-1} \times$$

$$\int \cdots \int_{\substack{\text{potential energy} \\ \text{phase volume on DS}}} H(E - E_c - E_{int}^\pm) \prod_i^5 dq_i dp_i \quad (38)$$

where $\mu_{A,BC}$ is the reduced mass for the reactants; E_c is the classical activation energy; $E_{int}^\pm$ is the internal

(26) K. Morokuma, B. C. Eu, and M. Karplus, J. Chem. Phys., 51, 5193 (1969); see also ref 29 and 31.

energy of the transition state; q_i and p_i, $i = 1$–3, correspond to the coordinates and momenta for the transition state's real stretching and bending Cartesian normal coordinates; and q_i and p_i, $i = 4, 5$, are the Eckart rotational angles and their conjugate momenta. When the mean cross section is desired for an alternate DS, $q_\perp$ is used in place of q_R. Equations 36–38 represent modifications of eq 19–21 of reference 26. The integral of eq 38 converges when the PES is unsymmetrical provided that the total energy does not exceed the appropriate dissociation energies.

We have evaluated $\bar{S}_r(E)$ at a total energy of 0.5 eV for the reaction[27]

$$H + HBr \longrightarrow H_2 + Br$$
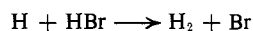
using eq 38 and a semiempirical PES studied by Paar.[28] A Monte-Carlo rather than a quadrature technique was employed to evaluate the integrals since this allows us to accurately estimate the error of the result. The accurate Hamiltonian was used to evaluate $E_{int}{}^{\mp 14}$ and no recourse was made to the SVA. The rather considerable details involved are given elsewhere.[27] Values of $\bar{S}_r(E)$ were computed for the steepest descent and ART dividing surfaces. Monte-Carlo points were selected until the error in $\bar{S}_r(E)$ was *ca.* 5%; this involved *ca.* 10^6 points. We have also evaluated the corresponding SVA-values using eq 57 of ref 26 and its alternate DS modification; *i.e.*, $\nu_\perp(SD)$ is used in place of ν_R. In addition, we have also evaluated $\bar{S}_r(E)$ using the classical mechanical trajectory method and a Monte-Carlo technique.[27]

The eq 38 accurate Hamiltonian ART, SVA ART, and trajectory values of $\bar{S}_r$ (0.5 eV) are 5338 ± 4.4%, 2.446, and 4.39 ± 10.7%, respectively in atomic units. The corresponding accurate average classical transmission coefficient of ART is therefore $8.22 \times 10^{-4} \pm 11.6\%$. The eq 38 and SVA steepest descent values of $\bar{S}_r$ (0.5 eV) are 9.301 ± 5.0% and 2.598 ($\chi(SD) = 2.726$, $\phi = -74.63°$). In this case at least, the results show that the SVA is a poor approximation indeed. However, the comparatively good agreement among the SVA ART, SVA steepest descent, and *trajectory* values indicates that, nevertheless, the SVA represents a *useful* approximation. The general validity of these findings must be investigated.[27]

Finally, inspection of Figure 3 indicates that the ART DS has "holes" and is improper for this reason. In addition, we point out that the eq 38 steepest descent DS cross section is much smaller than the corresponding ART value. The ART DS extends into the "product valley" of the potential energy surface. Many points, which correspond to trajectories which originate in the product region of phase space and are reflected, contribute to the eq 38 mean cross section. The harmonic approximation is a poor one indeed for this type of DS.

Conclusions

The ART DS is a planar Cartesian one which is perpendicular to the transition state's unstable normal coordinate. The location of the DS may be varied within the framework of ART by making an orthogonal transformation to coordinates other than the normal

ones. We applied the restrictions that it must pass through the saddlepoint of a potential energy hypersurface with a minimum energy linear configuration. With these restrictions, if the flux through the surface is not corrected for trajectories which are reflected or do not originate from the reactant region of phase space, and the SVA is employed to evaluate concentrations on the DS, the ART placement of the DS represents an approximate upper limit on the minimum equilibrium rate. ART does not give a rigorous upper bound on the minimum rate due to the employment of the SVA and a planar Cartesian DS. The SVA distorts the potential energy hypersurface. As a result, some allowed trajectories may be eliminated and some forbidden ones included.

ART does not give the SVA rate for a DS which is perpendicular to the path of steepest descent at the saddlepoint. When a DS other than that of ART is used, the potential energy contains a "cross term" even near the SP where the SVA represents a good approximation. We point this out since the importance of a separable reaction coordinate has been emphasized in the literature[15,29,30] in connection with dynamical considerations.

For systems characterized by a very unsymmetrical potential energy surface, the ART placement of the DS may render the use of the SVA particularly unreasonable. In such cases, it is more reasonable in terms of the assumptions involved to estimate the rate using the steepest descent DS. Kinetic isotope effects for such systems are related in a sensitive manner to the orientation of the DS and may provide experimental support for the utility of other than ART locations. The usual form of ART gives minimum kinetic isotope effects of the type considered here.

Further study of Horiuti's variational condition for minimum rates and its use in practice are desirable. The possibility of practical limitations arising due to the somewhat arbitrary DS boundary should be explored.

The generality of the findings in the final section here should be investigated.

Appendix

Location of the ART Dividing Surface. Consider three colinear atoms with masses m_1, m_2, and m_3 and relative Cartesian displacement coordinates z_1, z_2, and z_3. We define two coordinates q_1' and q_2' which serve as precursers to the normal coordinates.

$$q_1' = (m_1 m_3/\sigma)^{1/2}(z_1 - z_3)$$

$$q_2' = 2(m_2 \textstyle\sum)^{1/2}\left[z_2 - \frac{m_1 z_1 + m_3 z_3}{2m_2}\right]\Big/3\sigma^{1/2}$$

(27) G. Koeppl and M. Karplus, to be published.

(28) C. Paar, Ph.D. Thesis, California Institute of Technology, CALT-532-38, 1969.

(29) R. A. Marcus, *J. Chem. Phys.*, **45**, 2138, 2630 (1966); **46**, 959 (1967).

(30) L. Hofacker, *Z. Naturforsch. A*, **18**, 607 (1963); R. A. Marcus, *J. Chem. Phys.*, **43**, 1598 (1965).

where

$$\sigma = m_1 + m_3$$

$$\sum = m_1 + m_2 + m_3$$

In these coordinates, the vibrational kinetic energy for the stretching modes may be expressed as

$$2T = \dot{q}_1'^2 + \dot{q}_2'^2$$

The stretching vibrational potential energy may be conveniently expressed as

$$2V = f_1\Delta r_1^2 + f_2\Delta r_2^2 + 2f_{12}\Delta r_1\Delta r_2$$

where

$$\Delta r_1 = z_1 - z_2$$

$$\Delta r_2 = z_2 - z_3$$

In terms of q_1' and q_2', the potential energy has the form

$$2V = k_1 q_1'^2 + k_2 q_2'^2 + 2k_{12}q_1'q_2'$$

where

$$k_1 = m_3 f_1/m_1\sigma + m_1 f_2/m_3\sigma + 2f_{12}/\sigma$$

$$k_2 = \sum(f_1 + f_2 - 2f_{12})/m_2\sigma$$

$$k_{12} = \sum^{1/2}[m_1 f_2 - m_3 f_1 + f_{12}(m_3 - m_1)]/\sigma(m_1 m_2 m_3)^{1/2}$$

The total stretching vibrational energy may then be expressed as

$$2E = \dot{q}_1'^2 + \dot{q}_2'^2 + k_1 q_1'^2 + k_2 q_2'^2 + 2k_{12}q_1'q_2'$$

We now make an orthogonal transformation to what will become the normal coordinates.

$$q_1' = (\sin \gamma)q_1 + (\cos \gamma)q_2$$

$$q_2' = (-\cos \gamma)q_1 + (\sin \gamma)q_2$$

The cross term in the potential energy will vanish provided that the equation below is satisfied. The coordinates q_1 and q_2 are then the normal coordinates.

$$(k_1 - k_2) \sin \gamma \cos \gamma + k_{12}(\sin^2 \gamma - \cos^2 \gamma) = 0$$

The value of γ given by the correct choice of the sign in the expression below will satisfy this equation.

$$\gamma = \sin^{-1}\left[\frac{1}{\sqrt{2}}\left\{1 \pm \left[\frac{(k_1 - k_2)^2}{4k_{12}^2 + (k_1 - k_2)^2}\right]^{1/2}\right\}^{1/2}\right]$$

The eigenvalues of the normal coordinates which appear in the equation

$$2V = \lambda_1 q_1^2 + \lambda_2 q_2^2$$

are given by the equations

$$\lambda_1 = k_1 \sin^2 \gamma + k_2 \cos^2 \gamma - 2k_{12} \sin \gamma \cos \gamma = 4\pi^2\nu_1^2$$

$$\lambda_2 = k_1 \cos^2 \gamma + k_2 \sin^2 \gamma + 2k_{12} \sin \gamma \cos \gamma = 4\pi^2\nu_2^2$$

One of the eigenvalues will be negative and is denoted by λ_I in the main body of the paper, and the other will be positive and is denoted by λ_R.

The normal coordinates may be conveniently expressed in terms of the internal displacement coordinates Δr_1 and Δr_2.

$$q_1 = c_1^{(1)}\Delta r_1 + c_2^{(1)}\Delta r_2$$

$$q_2 = c_1^{(2)}\Delta r_1 + c_2^{(2)}\Delta r_2$$

The normal coordinates corresponding to the positive and negative eigenvalues will be denoted by R and I, respectively. The normal mode coefficients are given by the expressions

$$c_1^{(1)} = \left[\frac{m_1 m_3}{\sigma}\right]^{1/2} \sin \gamma + m_1\left[\frac{m_2}{\sigma\sum}\right]^{1/2} \cos \gamma$$

$$c_2^{(1)} = \left[\frac{m_1 m_3}{\sigma}\right]^{1/2} \sin \gamma - m_3\left[\frac{m_2}{\sigma\sum}\right]^{1/2} \cos \gamma$$

$$c_1^{(2)} = \left[\frac{m_1 m_3}{\sigma}\right]^{1/2} \cos \gamma - m_1\left[\frac{m_2}{\sigma\sum}\right]^{1/2} \sin \gamma$$

$$c_2^{(2)} = \left[\frac{m_1 m_3}{\sigma}\right]^{1/2} \cos \gamma + m_3\left[\frac{m_2}{\sigma\sum}\right]^{1/2} \sin \gamma$$