Analytical Rate Expression for Association Reactions with Classical Rocking Motions: Application to CH_3 Recombination

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The rates of barrier-free association reactions are primarily controlled by two features of the potential energy surface—the attraction, $V_o(R)$, between the reactants in their most favorable angular orientation, and the product, $\Pi_j(V''_j(R))$, of the force constants, $V''_j(R)$, for rocking a reactant away from its most favorable orientation at a fixed internuclear distance, R. The product of the rocking force constants in n angular coordinates can be expressed as a quadratic function of the attractive potential, $(\Pi_j(V''_j(R))/R^4)^{1/n} = -aV_o + bV_o^2$. When canonical variational transition-state theory is applied to a potential surface expressed in this form and the rocking motions are treated as classical harmonic oscillators, the rate constant can be expressed as an analytical function of the parameters a and b, of the temperature, and of the average relative velocity of the reactants. The rate constant has a positive activation energy at low temperatures, where the linear term in a dominates; reaches a maximum at a temperature equal to $2a/((n^2 - 1)\, bk_B)$; and declines at high temperatures, or where the quadratic term above dominates. When applied to the reaction $2CH_3 \rightarrow C_2H_6$, the theory underestimates the rate constant at low temperatures but correctly predicts the decline in rate constant at higher temperatures.

I. Introduction

Association reactions are more difficult to understand than most other types of reactions.[1,2] Because there is usually no potential energy barrier to surmount, it is difficult to identify a single transition state for the reaction. The reaction rate is affected by the potential energies over a range of geometries in a multidimensional system. Variational transition-state theory (VTST)[1−3] can be used to determine rate constants for these reactions, but the theory is difficult conceptually. It requires users to seek a geometry with a maximum free energy, whereas chemists are used to systems that seek a minimum free energy. Except in a few cases where potential energies are proportional to inverse powers of internuclear distance, analytical expressions are not obtained. Usually one must perform calculations for a number of different distances between the reactants and obtains as the result an array of rate constants as a function of distance and temperature. This additional level of effort and difficulty is enough to convince many workers not to use the method. It also makes it difficult to see a direct relationship between particular features of the potential energy surface and the rate.

Often the potential energy is a strong and complicated function of the geometry. Various methods have been tried to simplify and rationalize this dependence. Johnston[4] suggested that vibrational frequencies would depend exponentially on the length, R, of the forming bond. Benson[5] restricted motion to regions where the van der Waals radii of nonbonding atoms would not intersect. Following these leads, investigations have formulated a number of expressions to state the potential energy as a function of internuclear distances and bond angles.[6,7]

In the present article I will take a different approach. Instead of expressing potential energy as a function of R and angles, the rocking force constants and R will be expressed as a function of the potential energy, $V_o(R)$, along the reaction path. The dependence will then be weaker and, I will postulate, can be expressed as a simple quadratic function. Canonical VTST (CVTST) will be applied, on the assumption that conserved vibrational frequencies and moments of inertia of the fragments do not change. The rocking vibrational modes will be treated as classical harmonic oscillators. The resulting expression for the rate constant is simple enough to be differentiated analytically and leads to an expression for the CVTST rate constant in closed form. The rate constant at a particular temperature does not need to be evaluated at more than one geometry.

The method will be presented in the next section. In section III, it will be applied to the recombination of methyl radicals, $2\ CH_3 \rightarrow C_2H_6$ (reaction A). The results will be discussed in the final section.

II. Theory

Transition-state theory (TST)[5] assumes an equilibrium between reactants and complexes moving in the forward direction. CVTST[1−3] assumes that passage through a bottleneck at a common distance limits the rate for all quantum states of the reactants.

The degrees of freedom in the reactants can be divided into conserved modes and transitional modes.[8] Generally the vibrational frequencies in the reactants do not change greatly as the reactants start to approach each other; these vibrational modes are considered to be conserved modes. The transitional modes start as translations or rotations in the reactants. Three translational degrees of freedom transform to translation of the center of mass of the transition state and contribute only a mass quotient to the rate expression. One translational mode in the reactants becomes the reaction coordinate, which contributes k_BT/h. Two translational modes become the end-over-end rotations of the complex, which can be treated as a "pseudo-diatomic".[9] These rotations contribute the factor of R^2 to the

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rate expression, where R is now defined more generally as the distance between the centers of mass of the reactants at the bottleneck.

The transformation of the rotations of the reactants will be the focus of attention in this article. Molecules may have either 0, 2, or 3 rotational degrees of freedom. For example, where one reactant is an atom and the other is linear, there are 2 rotational modes in the reactants. If the complex is linear, both of these will transform to degenerate, bending, vibrational modes in the complex. If the complex is nonlinear, the complex will have one new bending mode and a third rotational mode. If both reactants are nonlinear, their 6 rotational degrees of freedom will become 1 overall rotation of the complex, 1 internal rotational or torsional mode, and 4 bending vibrations. These bending vibrations, originating as between 1 and 4 rotational modes of the reactants, are the "rocking motions" of the title.

One can obtain an expression for the rate constant for these different cases by starting with the familiar, simple collision theory.[5,10,11]

$$k(T,R) = p(R)\pi R^2 u_r \exp(C)/\sigma_{12} \tag{1}$$

Here $p(R)$ is called the steric factor, and $\sigma_{12} = 1$ for unlike reactants or 2 for like reactants. The average relative velocity is represented by u_r. C is the potential energy divided by a Boltzmann energy:

$$C = -V(R)/k_BT \tag{2}$$

Collision theory is usually derived in a different way than TST is, but the assumptions are similar. Both theories are statistical and assume a Boltzmann distribution. If the steric factor is taken as unity, collision theory is a version of TST for the special case in which the potential energy of interaction between the approaching reactants is independent of their angles of orientation.

If less-drastic simplifications are made, some of the features of TST can be retained but still be expressed in collision theory form by incorporating them in the steric factor. For example, $p(R)$ could be expanded as a product as follows:[10,11]

$$p(R) = B_E B_\theta(R)... \tag{3}$$

Here B_E is the quotient of electronic partition functions between the transition state and the reactants. For example, two doublet radicals have a 1-in-4 chance of coming together as a singlet, so reaction A would have a B_E value of $^1/_4$. $B_\theta(R)$ is the ratio of partition functions for hindered and free motions of the fragments with respect to the tumbling or rocking angles, θ_i. The dots indicate that factors for other degrees of freedom (such as the umbrella motion in CH_3) could also be included. Such factors will not be included in this work, which will focus on the factor, $B_\theta(R)$.

For a linear reactant, l, such as CN, the partition function for free rotation is[2,5]

$$Q_{f,l} = 8\pi^2 I_l k_BT/(\sigma_l h^2) \tag{4}$$

The moment of inertia, I_l, refers to motion of the linear fragment about its own center of mass. The symmetry number, σ_l, of linear radicals would be 1 or 2. A strong hindering potential would transform the rotational partition function above into the partition function for two degenerate vibrations, when the axis of a linear reactant in its most favorable orientation coincides with the line joining the centers of mass of the two reactants. The classical expression for such a partition function is[5]

$$Q_{v,l} = (k_BT/h\nu_l)^2 \tag{5}$$

Here the vibration frequency, ν_l, is given by

$$\nu_l = (2\pi)^{-1}\,(V''_l(R)/I_l)^{1/2} \tag{6}$$

The bending force constant, V''_l, is defined as follows:

$$V''_l(R) = \frac{\partial^2 V(R,\theta_1)}{\partial {\theta_1}^2} \tag{7}$$

We may also assume that the potential energy could be described by a harmonic function[2]

$$V(R,\theta_1) = V_o(R) + {}^1/_2 V''_l(R)\,{\theta_1}^2 \tag{8}$$

$V_o(R)$ is the potential energy when the reactant is in its most favorable orientation, that is, when the rocking angle, θ_1, is zero. The moment of inertia, I_l, serves as an effective mass in eq 6, because the force constant, $V''_l(R)$, is the second derivative with respect to angle, instead of the more familiar derivative with respect to distance.[11] Combining eqs 4−6, one can obtain an expression for the ratio of hindered and free partition functions for the angular motion of one linear radical.

$$B_{\theta l} = \sigma_l/2D_l \tag{9}$$

Here D_l is defined as follows:

$$D_l = V''_l(R)/k_BT \tag{10}$$

Note that D_l is defined here to be twice as great as the D of Darvesh et al.[12] One of the convenient aspects of eq 9 is its lack of dependence on the moment of inertia, I_l. As long as the rocking motions are adequately described as classical harmonic oscillators and the internal geometry of the reactant does not change significantly, the moment of inertia cancels out.

If a reactant, n, is nonlinear, its free rotational partition function will be[2]

$$Q_{f,n} = 2^{4.5}\pi^{3.5}(k_BT)^{1.5}(I_xI_yI_z)^{0.5}/(h^3\sigma_n) \tag{11}$$

Here the three moments of inertia relate to motion about the three principal axes of rotation. For reaction A, the barrier to rotation about the carbon−carbon axis is very small; accordingly, this motion can be treated as a free internal rotation. If we suppose that motion about the axis joining the reactants can be treated similarly for other reactions, the partition function for this dimension becomes[5]

$$Q_{x,n} = (2\pi)^{1.5}(I_xk_BT)^{0.5}/h\sigma_x \tag{12}$$

Where two nonlinear reactants combine, and where the axis joining their centers of mass coincides with their x-axes, the x components of their rotational partition functions will transform into an internal rotational partition function, as above, and a partition function for overall rotation of the pair about the x-axis. The two partition functions will have the form of eq 12, but with different moments of inertia, the product of which will be the same as that of the independent reactants. These degrees of freedom then cancel out between reactants and transition state.[10,12] The free tumbling motion of a nonlinear reactant about its y- and z-axes would transform in the transition state into 2 rocking vibrational motions, which may not be degenerate. The classical partition functions of such motions have the following form:[5]

$$Q_{yz,n} = (k_B T/h\nu_y)(k_B T/h\nu_z) \tag{13}$$

Here the frequencies can be calculated by using analogues of eq 6; for example:

$$\nu_y = (2\pi)^{-1} (V''_y(R)/I_y)^{1/2} \tag{14}$$

where $V''_y(R)$ gives the dependence of potential energy on rotation about the y-axis. Combining eqs 11−14 yields the following expression for the contribution of a nonlinear reactant to the steric factor:

$$B_{\theta n} = \sigma_{yzn}/2(D_y D_z)^{1/2} \tag{15}$$

Here σ_{yzn} is the ratio of σ_n, the overall symmetry number of the reactant, to σ_{xn}, the symmetry number for rotation about the x-axis. It is equal to the number of equivalent paths by which the reactant can be approached. For a planar methyl radical, with 2 equivalent faces, $\sigma_{xyn} = 2$. D_y and D_z are defined as in eq 10. Thus eq 9 is a version of eq 15 for the special case where the vibrational frequencies are degenerate. Note that in both eqs 9 and 15, a principal axis of the reactant must coincide with the line joining the centers of mass of the reactants.

We can now obtain a VTST expression for combination of the species considered above. Combining eqs 1, 3, and 15, we obtain:

$$k(T,R) = (\pi R^2 u_r B_E \exp(C)/\sigma_{12})\, \Pi_i(\sigma_{yzi}/2(D_{yi}D_{zi})^{1/2}) \tag{16}$$

Here the subscript i labels the two combining reactants. An atomic reactant will just contribute a factor of unity (1) to this product. The product $\Pi_i\, \sigma_{yzi}$ should correspond to the reaction path degeneracy, σ_p, for the process. The exponent C should now be generalized as follows:

$$C = -V_o(R)/k_B T \tag{17}$$

$V_o(R)$ is now the potential energy along the minimum energy path, when both reactants are in their lowest energy orientation. The denominator of the product in eq 16 can be reexpressed as follows:

$$\Pi_i(D_{yi}D_{zi})^{1/2} = \Pi_i(V''_{yi}(R)V''_{zi}(R)/k_B^{\,2}T^2)^{1/2} \tag{18}$$

In eq 16 the three quantities R, C, and the product of the D's vary as the reactants approach. The relationship between these quantities is often not a simple function, especially where ab initio potential energies are available. In CVTST the usual approach is to express C and D as separate functions of R and calculate $k(T,R)$ at several distances. Instead, in the present article, R and D will be lumped together, leaving just two quantities, $(R^2/\Pi_i(D_{yi}D_{zi})^{1/2})$ and $\exp(C)$, to affect the rate. The parameter of the potential energy surface contained in $(R^2/\Pi_i(D_{yi}D_{zi})^{1/2})$ is $\Pi_i(V''_{yi}(R)V''_{zi}(R))^{1/2}/R^2$, which is a measure of the tightness of the transition state. The parameter in C is $V_o(R)$.

As a second change from the usual practice, I will express $\Pi_i(V''_{yi}V''_{zi})^{1/2}/R^2$ as a function of V_o, instead of as a function of R. To symbolize this change, R has been dropped from the parentheses following V_o and V''. V'' is still defined by eq 7 and V_o is still the potential energy along the minimum energy path. It is reasonable to express $\Pi_i(V''_{yi}V''_{zi})^{1/2}/R^2$ as a power series in V_o. At long distances, both V_o and V'' (and hence $\Pi_i(V''_{yi}V''_{zi})^{1/2}/R^2$) are zero, so the power series should not need to include a constant term. For simplicity in this article, the power series will be truncated at two terms, a linear term and a quadratic term.

$$((\Pi_j V''_j)/R^4)^{1/n} = -aV_o + bV_o^{\,2} \tag{19}$$

Also for simplicity, the subscript j now labels the individual rocking modes instead of the individual reactants, and n is the number of rocking modes. According to this expression, as the attractive potential, V_o, becomes more negative as reactants approach, the bending potential, V''_j, (divided by $R^{4/n}$) at first increases proportionally, according to the first term. This behavior would be reasonable where the strongest interaction between the fragments is covalent bonding, which would weaken if the fragments are bent away from their most favorable orientation. In ion−dipole attractions, V'' would also be expected to be proportional to V_o.[5] At closer distances, repulsion between nonbonded atoms could become more significant, and the quadratic term in eq 19 would allow flexibility in the form of the bending potential.

If eq 19 is substituted into eq 16,

$$k(T,R) = \pi B_E u_r(\sigma_p/\sigma_{12}) \exp(C)/2^{n/2}(aC + bk_BTC^2)^{n/2} \tag{20}$$

and differentiated with respect to C, one can determine the value of C at the distance where the rate constant is a minimum.

$$C_{\min} = (n/2)[1 - x + (1 + x^2)^{1/2}], \quad x = a/nbk_BT \tag{21}$$

Here x is a dimensionless parameter, dependent only on the temperature and properties of the potential energy surface. If eq 21 is then substituted into eq 20, the following expressions are obtained for the rate constant.

$$\begin{aligned} k(T) &= \pi B_E u_r(\sigma_p/\sigma_{12}) \exp(n[1 - x + (1 + x^2)^{1/2}]/2)/ \\ &\qquad [n^2bk_BT(1 + (1 + x^2)^{1/2})]^{n/2} \\ &= \pi B_E u_r(\sigma_p/\sigma_{12}) \exp(n[1 - x + (1 + x^2)^{1/2}]/2)/ \\ &\qquad [na(x^{-1} + (1 + x^{-2})^{1/2})]^{n/2} \end{aligned} \tag{22}$$

These expressions are the central result of this article. They are analytical expressions for the CVTST rate constant; they can be applied to determine the rate constant at a particular temperature by a single calculation; there is no need to calculate $k(T,R)$ at several values of R and then minimize.

At sufficiently low temperatures, x will become much greater than unity, and eq 22 can be expressed in the following limiting form:

$$k(T\rightarrow 0) = \pi B_E u_r(\sigma_p/\sigma_{12})(\mathrm{e}/na)^{n/2} \tag{23}$$

where e is the base of natural logarithms. The opposite limit occurs at high temperatures:

$$k(x\rightarrow 0) = \pi B_E u_r(\sigma_p/\sigma_{12})(\mathrm{e}/n)^n/(2bk_BT)^{n/2} \tag{24}$$

The Arrhenius activation energy for the full expression of eq 22 is

$$E_A = -nk_BT[1 - n^{-1} - x + x^2/(1 + (1 + x^2)^{1/2})] \tag{25}$$

Between the extremes of eqs 23 and 24, eq 25 indicates that the rate for reactions with 2 or more rocking modes would go

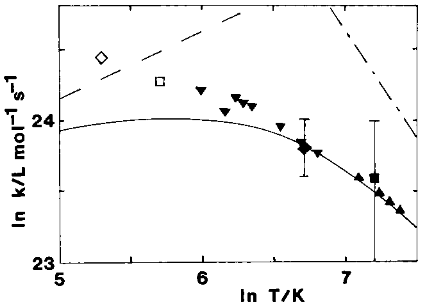

Figure 1. Temperature dependence of the rate constant for reaction A. Lines, theoretical: —, eq 22; - - -, eq 23; -·-, eq 24. Points, experimental: ▲, ref *13*; ■, ref *14*; ◆, ref *15*; □, ref *16*; ▼, ref *17*; ◇, ref *18*.

through a maximum, $k_{\max}$, at temperature $T_{\max}$.

$$T_{\max} = 2a/((n^2 - 1)bk_B) \qquad (26)$$

$$k_{\max} = 4B_E(\sigma_p/\sigma_{12}) \times [(\pi/b\mu)e^{n+1}(n-1)^{n-1}/((n+1)^{n+1}(a)^{n-1}n^n)]^{1/2} \qquad (27)$$

where μ is the reduced mass for the colliding radicals. For reactions in which the linear term in the potential energy equation (eq 19) dominates, $T_{\max}$ will tend to be large. Where $T_{\max}$ is above the experimental temperature range, k will increase with temperature, as u_r in eq 23 depends on $T^{1/2}$. Where the quadratic term in eq 19 dominates and there is more than one rocking mode, $T_{\max}$ will be small, and k will decrease with increasing temperature, approximately as in eq 24.

III. Application to Reaction A

Reaction A has been selected as a typical recombination reaction for comparison. First the parameters a and b will be evaluated, next the rate constant will be calculated and compared with experimental outcome, and then the assumptions made in section II will be revisited.

The ab initio calculations of Darvesh et al.[12] enable determination of the parameters a and b in eq 19. At a carbon−carbon distance of 4 Å, Darvesh et al. determined the electronic energies for an eclipsed geometry with both methyl radicals face to face and for a geometry with 1 of the methyl radicals tilted at an angle of $\pi/6$. Assuming a dependence on $\theta_1{}^2$, the value of V'' is calculated to be 4.8 kJ mol^{-1} rad^{-2}. At a distance of 3 Å, energies were calculated for 2 geometries with 1 methyl tilted by $\pi/6$, leading to an average value of V'' of 73 kJ mol^{-1} rad^{-2}. (Geometries with $\theta = \pi/2$ were also included in those authors' work,[12] but these would have a much lower Boltzmann weighting.) Substituting the above values in eq 19 and combining the simultaneous equations for the 2 distances, I found coefficient a to equal 0.304 Å^{-1} rad^{-2} and b equalled 0.0147 mol kJ^{-1} Å^{-1} rad^{-2}.

Substituting the coefficients into eq 22 and calculating rate constants as a function of temperature gives the results shown as the solid line in Figure 1, which is in the form of a double-logarithmic plot. At low temperatures, the rate constant is predicted to be almost independent of temperature. The curve is slightly convex upward, with a maximum rate constant at 332 K, as given by eq 26. At higher temperatures, the rate constant drops more sharply, and at 2000 K is only 42% of that near room temperature.

Experimental work on this reaction has been summarized by Hwang et al.[13] The values they recommend are shown as the points in Figure 1. Also shown is the value of Walter et al.[18] for 200 K. Note that experiment and theory are in excellent agreement at high temperatures. At moderate and low temperatures, the experimental rate constants are faster than the present theoretical predictions. Some earlier experimental measurements near room temperature are slower than those shown, and some are even slower than the theoretical curve. However, the most recent and most sophisticated measurements are faster than the theoretical predictions.

The low-temperature approximation, eq 23, is shown as the dashed line in Figure 1. This expression predicts a rate 37% faster than the full expression (eq 22) at 200 K. The expressions diverge at higher temperatures. The high-temperature limiting approximation, eq 24, is illustrated as the dashed and dotted line with a slope of −3/2. This rate is 79% faster at 2000 K than that obtained with the full expression and diverges further at lower temperatures.

Many assumptions have been made in deriving eq 22; these will be examined in turn.

TST assumes that the reacting complexes are in equilibrium with the reactants. Failure of this assumption leads to a pressure-dependent rate constant.[1,2] The rate constants shown in Figure 1 have been measured close to their high-pressure limit, indicating that the equilibrium assumption should not lead to significant error.

TST also assumes that complexes that have passed the critical value of R do not separate again but always become stable products. This assumption is the subject of intensive investigation.[1,2,19] Because CVTST gives an upper limit to the rate,[3] this assumption could not account for the fact that theoretical rates are less than the experimental values at low temperatures.

The present approach assumed that the geometry and internal force field of the methyl radicals are unchanged from the reactants to the critical complex. Robertson et al.[7] have calculated geometries and frequencies for this reaction at various values of R. The only significant change in frequency they found for a "conserved mode" occurred for the umbrella-bending modes of the radicals. Tightening of these modes would reduce the rate at high temperatures by 24% compared with the present calculation. At the same time, the moment of inertia of each methyl group would increase because of an increase in C−H bond length and a reduction in the HCH angles, and this would increase the rate at high temperatures by 12%. The net reduction in rate from both changes would be 12%.

The present approach also assumed that the torsional motion could be treated as a free rotation. Darvesh et al.[12] found the barrier to internal rotation to be 0.01 kJ mol^{-1} at 4 Å and 0.28 kJ mol^{-1} at 3 Å. In both cases the barrier is <1% of the attractive potential, V_o, at the same distance. In Robertson et al.,[7] geometries were optimized and the torsional barrier dropped to 0.4% of the attractive potential.

The simple harmonic model described in eq 22 treats the rocking motion by classical mechanics instead of quantum mechanics. However, the rocking frequencies are low and the product of 4 classical rocking partition functions exceeds the product of 4 quantal values[5] by only 3−5%, depending on the temperature and the value of R.

Darvesh et al.[12] found that a sinusoidal dependence on θ_1 and θ_2 represented the ab initio results at 4 Å better than did the harmonic dependence assumed herein. The partition function[11] at 200 K for a sinusoidal dependence of potential energy on θ is 20% greater than the partition function for a harmonic dependence. Since there are two angles, θ_1 and θ_2, here the effect would be a factor of 1.45, which is sufficient to explain almost all the difference between experiment and theory at low temperatures in Figure 1.

A quadratic dependence has been assumed for V''/R as a function of V_o. It is difficult to tell whether this is accurate, since Darvesh et al.[12] made ab initio calculations for small changes of θ at only 2 values of R. Robertson et al.[7] calculated vibrational frequencies with a 3−21G basis set at several values of R and indicated a mixing between internal coordinates in the normal vibrational modes. The square roots of the products of the vibrational frequencies (excluding the torsional frequency discussed above) have been fit to a quadratic of the form of eq 19. For 3 values of R between 3 and 4 Å, the correlation coefficient of the fit was 0.995, although individual data points differed from the fit by up to 27%. It appears that a cubic term would improve the fit.

In summary, some of the assumptions have a major impact and others a minor impact. The nonrecrossing assumption is common to all versions of CVTST. Lack of knowledge of the form of the potential energy surface affects all dynamical theories at present. Changes in the internal moments of inertia and in the umbrella modes would change the rate, although these changes could be folded into eq 19. Weak rocking motions may be better treated as hindered rotations than as vibrations. The latter problem accounts for most of the discrepancy between experiment and theory at low temperatures; the agreement at high temperatures is encouraging.

IV. Discussion

The central result of this work is eq 22, which provides an analytical expression for the rate constant of an association reaction. The parameters needed are defined in Section II. The relative velocity can be readily calculated from the masses of the reactants, the electronic factor from their degeneracies, and the values of σ from their symmetry. The parameters a, b, and x require knowledge of the potential energy of interaction. Equation 22 is accurate, provided (1) the rocking motions can be well described as classical harmonic oscillators, (2) the conserved vibrational frequencies and internal moments of inertia do not change greatly, and (3) the variation of force constants with attractive potential can be described by eq 19. The method should not be used if these conditions are not met.

Several antecedents to this method have also treated the rocking motions classically. Benson[5] used a restricted rotor model in which there was no change in potential energy for small rocking motions, but large amplitude rocks were prevented by hard-sphere repulsions between atoms on adjacent radicals. Hase[3d] adopted a semiclassical state density in a CVTST study of the reverse of reaction A. Quack and Troe[20] interpolated classical harmonic oscillator partition functions in a CVTST study of several association reactions, including reaction A. Wardlaw and Marcus[6c] numerically integrated more complex rocking potentials over 6 orientational angles for reaction A. More complete surveys may be found in recent reviews.[1,2]

Robertson et al.[21] applied a "configuration integral" to obtain an average Boltzmann factor over as many as 5 orientational angles. Although more cumbersome, the method has several advantages over the present approach. It allows for more-complex potential energy functions, including terms that depend on more than 1 angle at a time. Angles are correctly given a weight proportional to sin θ, instead of the weight of θ implicit in the present approach.[12] The limits of integration prevent double-counting of areas with large values of θ, (the magnitude of this effect was considered by Darvesh et al.[12]).

Troe[22] and co-workers, to account for the effect of rocking potentials on rates, developed a "thermal rigidity factor", defined as the ratio of the rate determined with a rocking potential included to the rate determined with the rocking motion reduced to a free rotation. The bottleneck may occur at different distances, R, when the rocking potential is included and excluded, so there is no simple relationship between the rigidity factor and eq 22. Their method is capable of handling complex potential functions, but the algebra is difficult. A report just published[23] on valence interactions between atoms and linear rotors includes cases where the reaction coordinate does not coincide with the axis of the rotor. The dependence on $a^{-n/2}$ found in eq 22 in the present work is paralleled by a dependence on the anisotropy to the power $-n/2$ by Maergoiz et al.[23] A common approximation[22,23] is that the ratio of the exponential attenuation factor, α, of the rocking modes to the Morse parameter, β, is 0.5. Neglecting the dependence on R, this corresponds to taking the second term in b in eq 19 as zero. Troe[22] has noted that valence potentials may have a stronger anisotropy at shorter distances, which corresponds to a positive value of b in the present notation.

The novelty of the present method lies in the grouping of the interfragment distance, R, and the rocking force constants, V'', expressing their quotient as a function of the attractive potential, V_o, by means of eq 19. This linking of R and V'' may remind readers of the linking of R and V_o for calculating a centrifugal potential[5] in other versions of CVTST.

It is instructive to consider the magnitudes of the variables in eq 16 as the internuclear distance changes from 3 to 4 Å in reaction A. At 2000 K, exp(C) decreases by a factor of 5.6 from 3 to 4 Å. At 200 K, exp(C) decreases by a factor of 2.8 $\times$ 10^7. The inverse product of the force constants, $\Pi_i(\sigma_{yzi}/2(D_{yi}D_{zi})^{1/2})$, increases by a factor of 231. R^2 increases by a factor of 1.78. Thus the force constants have a much greater influence on reaction A than does the factor of R^2.

Equation 22 is simple and transparent and can assist our understanding of the factors controlling the rates of association reactions. The location of the bottleneck is primarily decided by a struggle between the rocking force constants and the attractive forces.[19−23] At short distances, the rocking forces are large and restrictive, but the Boltzmann factor enhances the association. At low temperatures, energetic effects are most important. The exponential factor in eq 20 would become too large at short internuclear distances, so the bottleneck occurs at long distances. Here the rocking potential, V'', is small and is dominated by the linear term in a in eq 19. At high temperatures, entropic effects dominate; the bottleneck occurs where the force constants are strongest, that is, at short distances. Neither the high- nor low-temperature limiting approximation is particularly useful for reaction A, for which the value of $T_{\max}$ is within the experimental temperature range. The transition from eq 23 to eq 24 occurs over a very wide range of temperatures.

The low-temperature approximation is likely to be more useful where V''/R is a linear function of V_o, and $T_{\max}$ is above the experimental temperature range. An example could be atom−radical reactions or recombination of linear species, where interactions between nonbonded atoms could be less.

The only property of the potential surface appearing in the low-temperature approximation (23) is a. Note that the term in a in eq 19 dominates at small values of V_o, i.e., at long distances. In other words, the low-temperature rate is dominated by the behavior of the potential energy surface at long distances, where the interactions are weak. Where thermal energies are small, these weak interactions are important. The greater the dependence of potential energy on angle (the greater the value of *a)*, the slower the rate—another example of the general rule that a tight transition state gives a slow rate.[5] These statements lead to the following reexpression of eq 23:

$$k(T\rightarrow 0) = \pi B_E u_r(\sigma_p/\sigma_{12})(e/n)^{n/2} \times [\lim(V_o\rightarrow 0)(R^2 V_o^{n/2}/(\Pi_j V''_j{}^{1/2}))] \quad (28)$$

The force constant, V'', is a measure of the narrowness of the reaction channel. The width of the valley with respect to 1 rocking angle could be defined as $\Delta\theta_j$, the range of values of θ_j for which the potential energy is <0. Equation 8 may be solved to find $\Delta\theta_j$ as follows:

$$\Delta\theta_j = 8^{1/2}|V_o/V''_j|^{1/2} \quad (29)$$

This quotient also appears in eq 28, which may be rearranged to give

$$k(T\rightarrow 0) = \pi B_E u_r(\sigma_p/\sigma_{12})(e/2^3 n)^{n/2} \times [\lim(V_o\rightarrow 0)(R^2\ \Pi_j\ \Delta\theta_j)] \quad (30)$$

Thus the rate is proportional to the product of the widths of the valley with respect to each rocking angle, where the valley widths are measured in radians. If there are only 2 rocking angles, as with the reaction of H with CH_3, and if $\Delta\theta_j$ is small, then $R\Delta\theta_j$ is approximately equal to the valley width in Ångstroms, and the rate is proportional to the product of these widths or to the cross-sectional area of the entrance valley, or, in effect, to the area of the target.

The temperature dependence of the low-temperature limiting expression (eq 23) is entirely due to the average relative velocity, u_r. As with simple collision theory, the low-temperature rate is proportional to $T^{1/2}$. (Note the slope of 1/2 for the dashed line in Figure 1.) The Arrhenius activation energy at the low-temperature limit is $^1/_2 k_BT$, indicating that reacting pairs have slightly more energy on average than random pairs of radicals. Pairs of radicals with very little relative translational energy do not collide very often and so have a low probability of reacting. The heat capacity of activation,[5] dE_A/dT, in this limit is $^1/_2 k_B$, indicating that an Arrhenius plot would be curved and concave upward.

In the high-temperature limit, described by eq 24, the rate is limited only by the other coefficient, *b*, in eq 19. This coefficient describes the way the reaction valley becomes narrower as the attractive potential increases: the faster the valley becomes narrow, the slower the rate. The high-temperature rate is limited by the width of the inner reaches of the reaction channel. Equation 24 is also likely to be useful for reactions with small or zero values of *a*, for example, where the long-range attraction is dominated by dispersion forces, ion−ion forces, or ion-induced dipole forces.[1]

The rate constant in the high temperature equation (eq 24) depends on $T^{-(n-1)/2}$. A negative temperature dependence has been observed experimentally for several reactions with multiple rocking modes,[1,2] such as reaction A. As we can see, this behavior can be expected when the valley becomes narrower at shorter internuclear distances. The limiting activation energy at high temperature is $-(n-1)k_BT/2$, indicating that reactants with more than average energy are less likely to react. (Where there is only 1 rocking mode, the activation energy would be 0.) Two types of energetic reactants are less likely to react: Pairs of reactants with a lot of *relative translational energy* are likely to have a large relative angular momentum, which would create a centrifugal force at short distances, resisting reaction; reactants that are *rotating rapidly* will have this motion changed to a rocking vibrational motion at short distances. In the latter case, the spacing between quantum levels will increase; to stay in the same quantum state, or keep the same angular momentum, radicals will have to put more energy into rocking. These two types of extra energy requirements, centrifugal or rocking, constitute effective barriers to reaction and will slow the reaction rate. Now, because both large amounts of translational angular momentum and of tumbling angular momentum work against reaction, low-energy molecules have a better chance of reacting than high-energy ones. The average energy of reacting complexes is less than that of all reactant pairs, and the activation energy is negative. The lower probability of reaction for high-energy species leads to a narrower distribution of energies among reacting complexes than among the general population of reactants. This narrower energy distribution gives a negative heat capacity of activation, $-(n-1)k_B/2$. An Arrhenius plot for a reaction with multiple rocking modes would be convex upward at high temperatures.

The present results can provide guidance for ab initio calculations. The factor in square brackets in eq 21, $[1 - x + (1 + x^2)^{1/2}]$, varies only between 1.0 and 2.0. Accordingly, the value of the potential energy on the reaction coordinate at the variational transition state, $V_{o,vts}$, varies only between $-nk_BT/2$ and $-nk_BT$.

$$-nk_BT/2 > V_{o,vts} > -nk_BT \quad (31)$$

This should provide a useful rule of thumb for ab initio calculations on association reactions. Once the range of temperatures for which rate constants are desired is established, the range of values of V_o needed can be found. Low-level calculations can establish the relevant values of *R*, and then more-accurate calculations can find values of V_o and V''. Further quantum chemical calculations on association reactions would be desirable. It should be useful to test the accuracy of truncating at two terms the series expansion of the potential surface in eq 19.

This method could be extended if *R* were determined from V_o by an expression such as a Morse potential. It has been shown here that *R* does not change the rate constant greatly, so inaccuracies in this expression should not be detrimental. The combination of the Morse potential and eqs 8 and 19 ought to provide a simple potential energy surface, which could then be used for microcanonical-VTST (μVTST) calculations or classical trajectory calculations.[1] Either method would provide a way of testing the accuracy of the assumption that species that pass the critical value of *R* do not reappear as reactants. In the case of μVTST, one might be able to find analytical expressions for the positions and heights of the adiabatic barriers for individual quantum states.

In future work, this method can be tested on other reactions. The method could be extended to include variations in conserved vibrational frequencies and internal moments of inertia with V_o in eq 19. Transition states where the axes of the fragments do not coincide with the interfragment axis could be included.[23] The algebra for dissociation reactions could be worked out. The present calculation could also be reversed, and the temperature dependence of experimental rate constants could be used to learn about the potential energy surface for an association−dissociation process.[24]

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