Branching Ratios in Activated Systems

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Branching between reaction channels in activated systems is often observed to vary with changes in the potential energy surface as $\Delta\ln(k_1/k_2) \propto \Delta(\Delta E_1^\ddagger - \Delta E_2^\ddagger)$. RRKM calculations demonstrate that in many, but not all, cases the log−linear relationship accurately describes branching in nonthermal distributions of reactants with energies well above the threshold for reaction. The origin of this relationship and conditions necessary for its validity can be understood in terms of quantum RRK theory.

I. Introduction

We recently investigated the competition between carbon and oxygen attack of chemically activated enolate ions at carbonyl groups and observed that branching between the two channels varies exponentially with the difference in the activation energies of the two pathways:[1]

$$\Delta\ln(k_1/k_2) \propto \Delta(\Delta E_1^\ddagger - \Delta E_2^\ddagger) \qquad (1)$$

Other investigators have reported similar findings for a series of activated reactions. Relationship 1 describes the dissociation of collisionally activated proton-bound dimer ions, and this forms the basis of Cooks' kinetic method[2−6] for determining the relative proton affinities of anions and neutral molecules. The kinetic method has subsequently been extended to a wide variety of other competitions.[6] Branching between channels in chemically activated systems has been studied previously by DePuy et al.,[7] who observed that the relative abundance of anionic alkyl leaving groups from nucleophilic attack at silane centers varies exponentially with the exothermicity of the reaction.

The observation of the log−linear relationship 1 for a series of related reactions is not altogether surprising. In their investigation of competing dissociations of activated alkyl radicals, Rabinovitch and co-workers[8,9] noted that in the classical limit the logarithm of the ratio of volumes in phase space depends directly on the energy difference between channels. Several authors have derived theoretical justifications for the validity of (1) in the kinetic method. Cooks and co-workers, working on the assumption of a thermal equilibrium between reactant ions, have used transition state theory to derive forms of (1) in terms of the relative enthalpies[2,3] and free energies[5] of the competing pathways. As pointed out by Cooks, however, the assumption of thermal equilibrium does not apply to isolated, chemically activated species. Recently, other workers[10,11] have assumed classical behavior in the form of quasi-equilibrium theory (QET) to justify (1) in microscopic systems without invoking thermal equilibrium.

While it is clear that relationship 1 may be generally descriptive, it is equally clear that it is not exact. The classical form, while qualitatively applicable in limiting cases, is still an approximation of the quantum mechanical form of the rate equation, and it does not accurately reflect the influence of quantized oscillators with specific frequencies. The branching ratio depends not only on energy difference but also on the total energy and angular momentum of the system.[12] Furthermore, reactants generally comprise a distribution of energies, and the effect of that distribution must be considered. Recently, Bojesen[10] has suggested that the size of the reacting species contributes to the observed branching ratio between available channels. A detailed analysis using a statistical theory such as phase space theory[13−15] or RRKM[15−17] theory is often used to infer the reaction potential energy surface from the observed kinetics.[8,9,18,19] Such an analysis can be cumbersome, and the use of the empirical relationship 1 to describe a series of related reactions is an attractive option. While its empirical success in such situations is promising, relationship 1 is often applied to a series of reactions in which few of the aforementioned factors are likely to remain completely constant. A more rigorous quantitative examination of its validity therefore seems appropriate.

In this paper, we use RRKM calculations to examine quantitatively how the branching ratio depends on various aspects of the potential energy surface for reactions of activated systems. We assume no form for the rate equation other than that dictated by statistical theory (see below); the reaction rate constants are calculated by direct count with only minor mathematical approximations whose quantitative effect on the results is negligible. As the goal of this work is to understand what appears to be a general phenomenon, we could, in principle, examine any arbitrary potential energy surface, whether real or artificially constructed. While we have performed calculations on several systems, we report results from a potential energy surface that is based on the reaction of enolate anions with trifluoroacetyl chloride in order to provide a physically meaningful context for the calculations. This approach also should facilitate comparison with other experimental systems. We use the RRKM results to assess the validity of relationship 1 for specific systems, and the relationship appears to hold for all of the systems that we have examined. Because specific calculations cannot prove a general relationship, we use quantum RRK theory to demonstrate the basis and limits of the validity of (1) without invoking either thermal equilibrium or classical behavior. We also quantitatively examine the relative influences of the many factors known to affect the branching ratio (entropy and enthalpy of activation, total energy of the system, and size of the system) and establish computationally that variations in these factors should be considered when using (1) to describe a series of results.

II. RRKM Calculations: Method

We use RRKM theory[15−17] to calculate the branching between two competing channels in an activated system. We consider kinetic reactions, in which the branching ratio (BR) between

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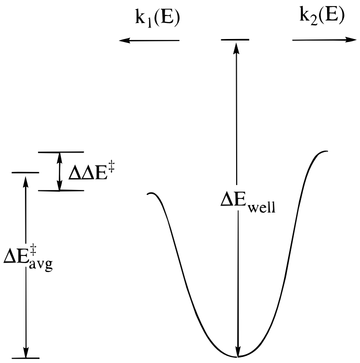

Figure 1. Potential energy surface employed to model the reaction of an activated complex with two channels. $\Delta E^\ddagger_{avg}$ is the average activation energy of the two channels relative to the bottom of the ion−molecule complex, $\Delta\Delta E^\ddagger$ is the difference in activation energies between the two channels, and ΔE_{well} is the activation of the complex relative to the bottom of the well. In practice, the reactants comprise a distribution of energies $P(E)$, and ΔE_{well} defines the minimum energy for which $P(E)$ is nonzero. In such cases, the branching ratio reflects a weighted average over that distribution.

the channels is determined by the relative rates for crossing their respective barriers and is independent of the relative exothermicity of the channels. For a system with total energy E,[20] the RRKM unimolecular reaction rate constant is given by

$$k(E) = \frac{G(E)}{hN(E)}$$

where $G(E)$ is the sum of states above the transition state and below total energy E, h is Planck's constant, and $N(E)$ is the density of states of the reactant at energy E. Because $N(E)$ is identical for reactions proceeding from the same ion−molecule complex,[21] the microcanonical fraction of reactants proceeding through one of two available channels is

$$\text{fraction}_1(E) = \frac{G_1(E)}{G_1(E) + G_2(E)} \tag{2}$$

The observed fraction of total products produced by channel 1 is then given by summing over the appropriate normalized energy distribution $P(E)$ of reactants that go to products:

$$\text{fraction}_1(\text{tot}) = \int \frac{G_1(E)}{G_1(E) + G_2(E)} P(E)\,\mathrm{d}E \tag{3}$$

and the observed branching ratio between the two channels is

$$\text{BR} = \frac{\text{fraction}_1(\text{tot})}{\text{fraction}_2(\text{tot})} = \frac{\int \frac{G_1(E)}{G_1(E) + G_2(E)} P(E)\,\mathrm{d}E}{\int \frac{G_2(E)}{G_1(E) + G_2(E)} P(E)\,\mathrm{d}E} \tag{4}$$

For convenience, we will subsequently refer to the observed BR of eq 4 as the *ensemble* BR for the energy distribution $P(E)$.

The RRKM calculations[22] model the reaction of enolate anions with trifluoroacetyl chloride, whose behavior inspired this study. Details of the calculations are given elsewhere.[12,23] The potential energy surface for the calculations is described in Figure 1. In our model, the activated complex has a normalized energy distribution $P(E)$ that is zero below an energy ΔE_{well} above the minimum in the reactant potential energy surface and Boltzmann above it. The two channels have an average activation energy of $\Delta E^\ddagger_{avg} = {}^1/_2(\Delta E^\ddagger_1 + \Delta E^\ddagger_2)$ relative to the bottom of the well, and the difference in their activation energies is defined as $\Delta\Delta E^\ddagger = \Delta E^\ddagger_1 - \Delta E^\ddagger_2$. The frequencies used in the RRKM calculations are listed in Table 1; we arbitrarily assign the more "loose", or entropically favorable, transition state to channel 2.[24,25] The frequencies are chosen to be loosely representative of the transacylation reactions studied previously in our lab, and they are taken from AM1 calculations[26] of acetone enolate and trifluoroacetyl chloride. Qualitatively similar behavior, however, is seen with other sets of frequencies, and we show below that the results are independent of the set of frequencies. The relative values of ΔE_{well} and $\Delta E^\ddagger_{avg}$ determine the net activation of the reactant complex. For this work, we arbitrarily fix ΔE_{well} at 19 kcal mol^{-1} and vary $\Delta E^\ddagger_{avg}$. Effects due to conservation of angular momentum are considered in the calculations, but these serve only to increase the apparent barriers to reaction and do not influence the conclusions of this study.

TABLE 1: Frequencies Used in RRKM Calculations

transition state 1		transition state 2	
frequency (cm^{-1})	degeneracy	frequency (cm^{-1})	degeneracy
28, 37, 48, 82	1	13, 39, 59, 64	1
116, 190, 247	1	129, 194, 233	1
303, 314, 338	1	265, 317, 326	1
347, 414, 441	1	345, 385, 442	1
484, 495, 518	1	490, 503, 556	1
559, 624, 699	1	564, 651, 805	1
752, 985, 1011	1	880, 953, 1001	1
1027, 1044	1	1075, 1094	1
1064, 1100	1	1100, 1168	1
1108, 1309	1	1229, 1296	1
1337, 1371	1	1340, 1364	1
1378, 1409	1	1368, 1380	1
1434, 1444	1	1412, 1428	1
1513, 1522	1	1504, 1513	1
1886, 3053	1	2972, 3007	1
3066, 3151	1	3060, 3064	1
3185, 3222	1	3077, 3154	1
201, 260, 728	deg	201, 260, 728	deg
997, 1422	deg	997, 1422	deg
2884, 2941	deg	2884, 2941	deg
1263	2 × deg	1263	2 × deg

III. RRKM Calculations: Results

We test relationship 1 by holding the mean activation energy $\Delta E^\ddagger_{avg}$ for the two channels fixed at 13 kcal mol^{-1} above the bottom of the well (6 kcal mol^{-1} below the activated complex). The choice of $\Delta E^\ddagger_{avg}$ is unconventional; it is more usual to fix the activation energy of one channel (ΔE_1, for example) and vary the other relative to it. When we used the latter convention, however, we observed that the logarithmic plot exhibits curvature across the range of $\Delta\Delta E^\ddagger$ examined here. The analysis in section IV demonstrates why the breakdown occurs and why the use of $\Delta E^\ddagger_{avg}$ is more appropriate for this study. $\Delta\Delta E^\ddagger$ is varied from −4 to 6 kcal mol^{-1}, and the branching ratio (BR) is calculated using RRKM theory. Results are plotted in Figure 2.

As seen in the characteristic graphs of Figure 2, the resulting data are exponential, and a logarithmic plot is linear. The generality of the linear behavior was tested by performing numerous other calculations in which the following characteristics of the sample system were changed: the magnitude and number of vibrational frequencies, the mean activation energy, and the distribution function $P(E)$. For each set of conditions, the plot of BR vs $\Delta\Delta E^\ddagger$ maintained an apparently exponential relationship across a range of several kcal mol^{-1} in $\Delta\Delta E^\ddagger$. The shape of the plot, however, does depend on the choice of initial

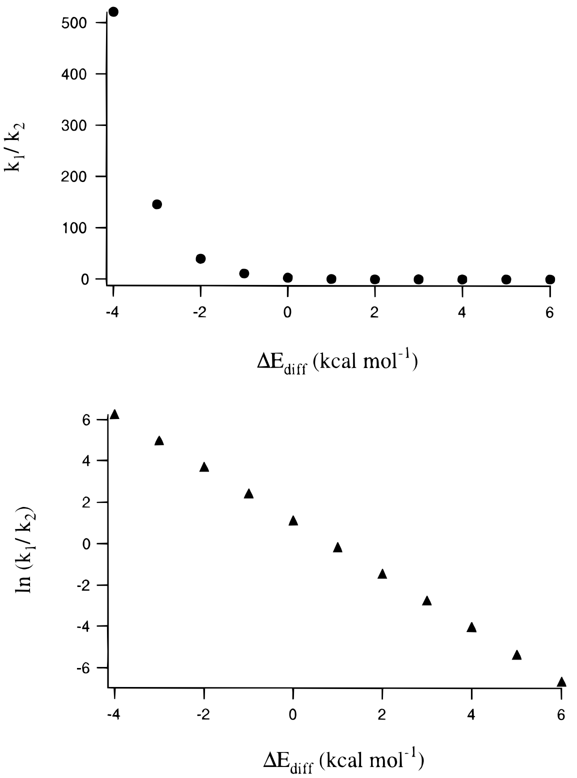

Figure 2. Plot of the branching ratio (top) and logarithm of the branching ratio (bottom) of two channels vs difference in energy of the transition states for the two competing reactions as calculated by RRKM theory. The input frequencies for the RRKM calculation are given in Table 1 (deg = 1), and $\Delta E^{\ddagger}_{avg} = 13$ kcal mol^{-1}.

TABLE 2: Slope of the Line Obtained by Plotting ln(BR) vs $\Delta\Delta E^{\ddagger}$ as a Function of $\Delta E^{\ddagger}_{avg}$ and deg, the Degeneracy of the Frequencies Representing a Methylene Group in Table 1

	methylene degeneracy			
$\Delta E^{\ddagger}_{avg}$	1	3	5	7
6	−1.10	−1.22	−1.32	−1.41
8	−1.18	−1.31	−1.41	−1.49
10	−1.29	−1.41	−1.50	−1.56
12	−1.41	−1.51	−1.58	−1.62
14	−1.53	−1.61	−1.64	−1.66

conditions; the magnitude of the dependence of the BR on $\Delta\Delta E^{\ddagger}$ varies from system to system. The dependence may be quantified conveniently by considering the slope of the lines from plots of ln(BR) vs $\Delta\Delta E^{\ddagger}$, which are quite linear.[27] Table 2 reports the slope of such plots as a function of $\Delta E^{\ddagger}_{avg}$ and input frequencies from Table 1.

Average Activation Energy. The columns in Table 2 show the variation in the slope of logarithmic plots of BR as a function of $\Delta\Delta E^{\ddagger}$ for values of $\Delta E^{\ddagger}_{avg}$ from 6 to 14 kcal mol^{-1}. The original plots of BR vs $\Delta\Delta E^{\ddagger}$ are omitted in the interest of space. Each of the plots is linear, however, showing that the exponential character remains across this range of $\Delta E^{\ddagger}_{avg}$ and input frequencies. The results, listed in Table 2, reflect several properties of the relationship between the BR and the reaction potential energy surface. First, the absolute value of the slope of the logarithmic plot increases monotonically with increasing activation energy; changes in $\Delta\Delta E^{\ddagger}$ have less influence in systems whose total energy is further above threshold. Second, changes in slope with $\Delta E^{\ddagger}_{avg}$ are less pronounced in larger systems. For the smallest system (one added methylene, 51 vibrational modes), the change in slope is 39% across the range of $\Delta E^{\ddagger}_{avg}$ examined, while in the largest system (seven added methylenes, 105 vibrational modes) the slope changes by only 18% across the same range of $\Delta E^{\ddagger}_{avg}$. Finally, the intercept of the plots is a constant for all plots (not shown); the BR for $\Delta\Delta E^{\ddagger} = 0$ has an approximately constant value of 3.0 for all values of $\Delta E^{\ddagger}_{avg}$. As expected, only differences due to the enthalpic component of the potential energy surface vary with the system energy. For systems that have identical enthalpic barriers, the BR depends only on the relative entropy and is independent of total energy.

Number and Magnitude of Vibrational Frequencies. The sum of states $G(E)$ and density of states $N(E)$ are inherently dependent on the number and frequencies of the active degrees of freedom in a system. While such effects have been considered implicitly in many calculations and the qualitative effects are well understood (e.g., increasing the size of a system increases its lifetime at a given total energy), it is interesting to examine the influence of the set of vibrational frequencies on the BR in the context of the problem under investigation. Bojesen[10] has recently published results of quasi-equilibrium theory (QET) calculations[28,29] in which he examines the BR between dissociating pathways of metastable proton-bound dimer ions. He finds that the BR is dependent on the size of the system (i.e., the number of “active modes”), but the QET calculations do not rigorously evaluate the relationship because they contain no specific information about the vibrational characteristics of the system. Furthermore, Bojesen’s calculations are specific to the dissociation of metastable ions of a particular range of lifetimes, and those lifetimes are themselves dependent on the size of the system. Our treatment is quite different, as we consider the total BR for all complexes regardless of their individual lifetimes.

Here, the effect of increased system size is tested with a series of RRKM calculations in which the original input data are modified to include additional frequencies of variable degeneracy (see Table 1). In order to give the modifications some physical relevance, we have chosen a set of additional frequencies that roughly correspond to those of additional methylene units in enolate anions, although the results are general even for frequencies that are not physically meaningful. Results are reported in the horizontal rows of Table 2. The slope change with added methylenes indicates that the additional size has a measurable influence on the observed BR and shows that applying relationship 1 to a series of reactions in which there is significant change in the structure of the reactants can be quantitatively misleading.

As the size (i.e., number of frequencies) increases, the BR becomes more sensitive to changes in $\Delta\Delta E^{\ddagger}$ (the logarithmic plot becomes more steep). It is interesting that the diagonals of Table 2 contain roughly constant values; simultaneously increasing $\Delta E^{\ddagger}_{avg}$ by 1 kcal mol^{-1} and adding an additional methylene unit causes very little change in the BR. The reason for this is discussed in section IV.

The BR is also sensitive to the magnitude of the frequencies in the calculations. If the frequency of a given oscillator is reduced, the BR becomes more sensitive to changes in $\Delta\Delta E^{\ddagger}$ (the logarithmic plot becomes more steep). The BR is especially sensitive to changes in the lower frequency modes (vide infra). In all of the cases examined, however, the dependence of the BR on $\Delta\Delta E^{\ddagger}$ remains exponential.

Reactant Energy Distribution Function. All of the results presented above were calculated for an ensemble of reactants whose initial energy distribution is given by the Boltzmann distribution, $P(E) \propto \rho(E)e^{-E/RT}$, where $\rho(E)$ is the density of states and T is the ambient temperature, shifted ΔE_{well} above the bottom of the reactant well. The Boltzmann distribution is largely responsible for exponential energy dependences in

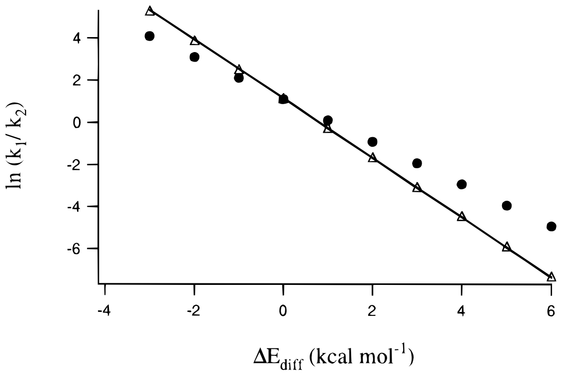

Figure 3. Plot of the branching ratio of two channels vs difference in energy of the transition states for two competing reactions as calculated by RRKM theory. The points represent calculations for microcanonical states which are either near the average energy (△) or greater than the average energy (●) of the entire ensemble. The line connects points calculated for the ensemble.

thermal systems, and so its effect on the energy dependence of chemically activated systems warrants investigation. Furthermore, many chemically activated systems (for example, species that are activated by either collisions or photochemical methods) do not comprise a shifted Boltzmann distribution as modeled in the calculations. The presence of a third channel, such as dissociation of the reactant complex formed in a bimolecular collision, will also have the effect of perturbing the initial energy distribution $P(E)$ for those reactants that proceed to reactants. The relationship between the ensemble BR and its microscopic components is therefore a central issue in interpreting the results presented above.

We therefore consider the branching ratio of a microcanonical system of specific energy as given in eq 2 or, alternatively, in eq 4 with $P(E) = \delta(E_0)$. A representative plot of the BR vs $\Delta\Delta E^\ddagger$ for two specific values of E is given in Figure 3. As is seen in Figure 3, the microcanonical ensemble yields an energy dependence that is fit extremely well by an exponential across the same range of energies studied previously; the behavior of the microcanonical BR is qualitatively and quantitatively very similar to that of the BR of the shifted Boltzmann ensemble. The slope of the ensemble BR plot is a weighted average of many microscopic BR's that possess unique exponential dependences on $\Delta\Delta E^\ddagger$. As seen in Figure 3, however, the BR for the distribution function $P(E)$ does not vary significantly from the microcanonical BR at the average energy of $P(E)$. Relationship 1, therefore, accurately describes the ensemble BR in spite of, rather than because of, the shifted Boltzmann distribution $P(E)$.

IV. Quantum RRK Theory

While the RRKM calculations cited above strongly support the theoretical validity of (1), they are not general, nor do they describe why such a relationship should be valid. As pointed out by Rabinovitch and in subsequent QET calculations by Bojesen and Grützmacher, such an energy dependence is clearly expected in the classical limit. While the general form of the energy dependence should not change upon going from quantum to classical behavior, the relevance of the classical approximation the exact RRKM form of the rate constant is not obvious. An alternate approach is to consider a simplified system in which all of the active oscillators in each transition state have identical frequencies of 1000 cm^{-1}. The results of an RRKM calculation for such a system with 20 vibrational degrees of freedom are presented in Figure 4, and the data are again described quite well by an exponential.

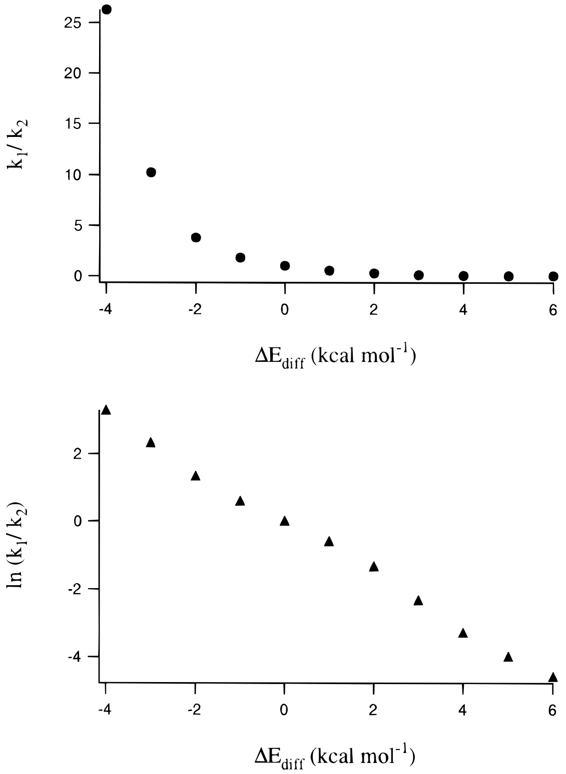

Figure 4. RRKM Calculations of the BR (top) and ln(BR) (bottom) vs $\Delta\Delta E^\ddagger$ for a system where both transition states have one 20-fold degenerate frequency of 1000 cm^{-1}. The slight curvature in plot b in the center of the plot is believed to be a computational artifact resulting from the high degeneracy of the system. $\Delta E^\ddagger_{\text{avg}} = 10$ kcal mol^{-1}.

This simplified RRKM calculation is essentially quantum RRK theory,[16,30] and a more descriptive analytical analysis is now possible. Consider a molecule consisting of s identical oscillators all having frequency ν. If E_1 is the critical energy for reaction, define $m_1 = E_1/h\nu$ to be the number of quanta in the reaction coordinate necessary to cross the reaction barrier. For a molecule with total energy E, $n = E/h\nu$ is then the total number of quanta in all oscillators.

It follows[16,30] that the rate constant k_1 is given by

$$k_1 = A_1 \frac{n!\,(n - m_1 + s - 1)!}{(n - m_1)!\,(n + s - 1)}$$

and the ratio of k_1/k_2 is then

$$\frac{k_1}{k_2} = \frac{A_1\,(n - m_1 + s - 1)!/(n - m_1)!}{A_2\,(n - m_2 + s - 1)!/(n - m_2)!} \tag{5}$$

Consider the case where $m_1 < m_2$, and let $\Delta m = m_1 - m_2$. The term $(n - m_2 + s - 1)!$ in the denominator cancels all but the Δm leading terms of the factorial $(n - m_1 + s - 1)!$ in the numerator, and the factorial $(n - m_2)!$ cancels all but Δm terms of $(n - m_1)!$. Defining $A' = A_1/A_2$, eq 5 can be rewritten with Δm terms in both the numerator and denominator.

$$\frac{k_1}{k_2} = A' \frac{(n - m_1 + s - 1)(n - m_1 + s - 2)...(n - m_2 + s)}{(n - m_1)(n - m_1 - 1)...(n - m_2 + 1)} \tag{6}$$

Now, if $\Delta m = m_1 - m_2$ is small relative to n, i.e., the critical energies are close to each other relative to the degree of activation of the system, then the individual terms in the numerator are all approximately equal to $(n - \bar{m} + s)$, where

$\bar{m} = {}^1/_2(m_1 + m_2)$. Likewise, each term in the denominator is very close to $(n - \bar{m})$. That $(n - \bar{m} + s)$ and $(n - \bar{m})$ are better approximations for the average value of the terms in the numerator and denominator than, for example, $(n - m_1 + s)$ or $(n - m_1)$ is the reason that $\Delta E^{\ddagger}_{\text{avg}}$ is a more appropriate choice than E_1 as the basis of the RRKM calculations presented in section III. Multiplying the Δm nearly identical terms in each of the numerator and denominator of eq 6, the expression may be rewritten as

$$\frac{k_1}{k_2} \approx A' \frac{(n - \bar{m} + s)^{\Delta m}}{(n - \bar{m})^{\Delta m}}$$

or

$$\frac{k_1}{k_2} \approx A' \left[\frac{(n - \bar{m} + s)}{(n - \bar{m})}\right]^{\Delta m}$$

and therefore

$$\ln\left(\frac{k_1}{k_2}\right) \approx \Delta m \ln\left[\frac{(n - \bar{m} + s)}{(n - \bar{m})}\right] + \ln(A') \qquad (7)$$

If $(n - \bar{m})$, A', and s do not vary for a series of reactions, and realizing that Δm is proportional to $\Delta\Delta E^{\ddagger}$, it follows that

$$\Delta \ln(k_1/k_2) \propto \Delta(\Delta E^{\ddagger}_1 - \Delta E^{\ddagger}_2)$$

Thus, we conclude that, for a series of similar reactions which are activated well above the critical energy and have similar activation energies, relationship 1 is valid.

V. Discussion

The derivation of eq 7 speaks directly to the validity of relationship 1 for a series of chemically activated reaction systems. In particular, it shows that (1) is not generally a valid means of comparing a series of reactions. In certain cases, however, the ratio of the combinatorial sum of states for two competing channels varies with the difference in activation energies of the respective channels in a manner that is nearly exponential. The statistical variation in the sum of states, and therefore the relative reaction rate constants, will be closest to an exponential when the following conditions are met: (a) The difference in the barrier heights, $\Delta\Delta E^{\ddagger}$, is small relative to the total energy above threshold in the activated system. (b) The relative activation entropies, A', for the two channels remains constant. (c) The difference $\Delta E_{\text{well}} - \Delta E^{\ddagger}_{\text{avg}}$ remains constant. (d) The size of the system remains constant.

While the above conditions will rarely, if ever, be satisfied exactly, eq 7 demonstrates that the dependence of the branching ratio on variations in any of these parameters is smaller than the dependence on the difference in the activation energies. Furthermore, eq 7 may be rewritten as follows:

$$\ln\left(\frac{k_1}{k_2}\right) \approx \Delta m \ln\left[1 + \left(\frac{s}{n - \bar{m}}\right)\right] + \ln(A') \qquad (8)$$

Equation 8 shows that conditions c and d, above, need not be satisfied independently if their ratio, $s/(n - \bar{m})$, is constant. It may be helpful to think of this ratio in terms of its inverse, $(n - \bar{m})/s$, which is the average number of quanta in each oscillator.[31] When the ratio varies, as in the columns or rows of Table 2, relationship 1 is not a valid description of the energy dependence of the BR. When this ratio is constant, the BR will vary logarithmically with $\Delta\Delta E^{\ddagger}$. This effect is manifested in the diagonal entries of Table 2, which are approximately constant when the system energy is increased 1 kcal mol^{-1} per added methylene group. Another consequence is seen by comparing the columns of Table 2, which show that the slope change as a function of $\Delta E^{\ddagger}_{\text{avg}}$ is greater for smaller systems. Addition of a given increment of energy will have more effect in a smaller system because the change in average quanta per oscillator will be be greater than in a larger system. When changes in $\Delta\Delta E^{\ddagger}$ are proportionally greater than changes in $\Delta E^{\ddagger}_{\text{avg}}$, total energy, and the relative activation entropies, the quasi-exponential dependence on $\Delta\Delta E^{\ddagger}$ will dominate the change in branching ratio. The RRKM calculations presented above are consistent with this picture of the relative influence of these parameters.

While this analysis is general, it is helpful to consider a specific case for illustrative purposes. For the series of transacylation reactions whose behavior inspired this study, $\Delta E^{\ddagger}_{\text{avg}}$ varies only slightly, as evidenced by the small change in reaction efficiencies (approximately $0.5 < \Phi_{\text{obs}} < 0.7$). Furthermore, the high efficiencies for reaction are indicative of low barriers or large energies above threshold for the activated complexes ($\Delta E_{\text{well}} \gg \Delta E^{\ddagger}_{\text{avg}}$). Finally, the relative activation entropies for carbon and oxygen nucleophilic addition should be relatively independent of the enolate substituent. It is therfore valid to describe the observed reactivity in this system by relationship 1.

VI. Conclusions

Many series of activated reactions have an observed branching ratio that appears to vary exponentially with the energy difference $\Delta\Delta E^{\ddagger}$ of the competing channels. RRKM calculations reproduce this observed relationship for certain systems but confirm that several other factors, including changes in the relative entropies of activation, size of the system, and degree of activation, influence the branching ratio. The log−linear relationship 1 should be used only with full consideration of these limits. Quantum RRK theory shows how the quasi-exponential dependence of the branching ratio on $\Delta\Delta E^{\ddagger}$ arises from the combinatorial form of the sum of states for an activated system and provides a semiquantitative means of assessing the relative importance of the many factors which influence branching in activated systems.

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(20) The sum of states is also constrained by conservation of angular momentum, and a rigorous treatment would have to include that condition. In this work, we assume that the moments of inertia of the competing channels are equal, so that the only consequence of conserving angular momentum is to reduce the total energy available to the system (i.e., increase the apparent barriers to reaction by equal amounts). This is likely to be an appropriate assumption for cases in which the two transition states have comparable structure and, for this work, facilitates interpretation of the relationship between the BR and other characteristics of the potential energy surface.

(21) While there may be two distinct complexes, interconversion between the complexes is expected to be extremely facile.

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(24) We could, in principle, have selected two transition states with identical frequencies and therefore identical entropies of activation. We choose to examine the more general system in which there are competing effects due to entropy and enthalpy.

(25) In the instance that the rate constant in the denominator is zero, the BR will be undefined. Switching the two rate constants so that the numerator is zero only temporarily avoids this problem, as the logarithm of the subsequent BR is then similarly undefined. The purpose of this paper, however, is to show how information about relative activation energies may be inferred from an observed BR. If either of the rate constants is zero, one cannot determine the relative activation energies of the two processes except to say that the total energy of the system lies between the critical energies of the reactions, and the subsequent analysis is irrelevant.

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(31) Although the average quanta per oscillator is not as easily defined for a distribution of oscillator frequencies, one may think of the quantity as an effective temperature of the system. Such a characterization, while not rigorously analogous to the temperatures described by Boltzmann distributions, facilitates a qualitative understanding of eq 7. For example, as the effective temperature increases, enthalpic contributions to the BR decrease. The concept of an effective temperature in activated systems has been discussed previously by Cooks[5,6] as a qualitative measure of the energy distribution in studies using the kinetic method. While Cooks' definition is more phenomenological, the RRK form in eq 8 may provide the basis for a more rigorous definition.