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Phase Space Prediction of Product Branching Ratios: Canonical Competitive Nonstatistical Model

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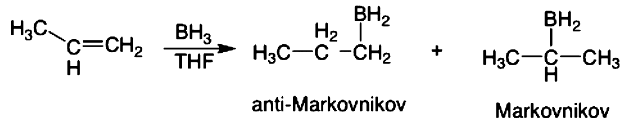
Abstract: We present a new model for predicting branching ratios of chemical reactions when a branching of the reaction path occurs after the dynamical bottleneck, including the case where it occurs after an intermediate. The model is based on combining nonstatistical phase space theory for the direct component of a reaction with variational transition-state theory for an indirect component of reaction. The competition between direct and indirect processes is treated by an extension of the unified statistical model. This new method provides a way to understand the factors that control this kind of chemical reaction and to perform calculations using high-level electronic structure methods for complex systems. The model is based on quantized energy levels of transition states and products, and it involves the same information as required for calculating transition-state rate constants and equilibrium constants plus a phenomenological relaxation time, which was taken from previous work. For the textbook reaction of the hydroboration of propene by BH_3 it has recently been inferred that the selectivity can only be understood by consideration of dynamical trajectories. However, the calculated branching fraction of this prototype reaction increases from 2%−3% when calculated under the inappropriate assumption of complete equilibration of the intermediate to from 8%−9% when calculated with the new theory, which requires only limited information about the system and does not involve running trajectories. The calculated result is in reasonable agreement with experiment (∼10%).

Introduction

The addition of HX to an alkene has been studied for a long time, and it is conventional to label the products as Markovnikov[1] (M) or anti-Markovnikov[2] (anti-M). This was originally understood in terms of an acid mechanism, where H^+ adds first, or a radical mechanism, where $X^•$ adds first. In the former case the more stable carbocation is obtained if H^+ adds to the least substituted end of the double bond, and in the latter case the more stable radical is obtained if $X^•$ adds first to the first least substituted end of the double bond.[3] For the case where X is BH_2 (Scheme 1), Brown and Zweifel[4] found 6−7% M, and they explained the result by a four-center transition state where $H^{\delta-}BH_2^{\delta+}$ interacts most favorably with the alkene when BH_2 is partially bonded to the least substituted end of the double bond because that end is more electronegative. Lipscomb and co-workers[5] studied the addition of BH_3 (hydroboration) computationally and found M and anti-M π complexes followed by M and anti-M transition states. They concluded that: "The observed regioselectivity of the hydroboration reaction is reflected in the differences in the stability of the transition states". However, their transition states were lower in energy than the reactant, and they did not compute free energies to see whether the association reaction or the post-complex transition states provided the overall dynamical bottleneck. Oyola and Singleton[6] recently performed much more quantitatively reliable calculations that included estimates of the free energies, and they found for the hydroboration of propene with BH_3 that the association bottleneck is overall rate determining.

Scheme 1



Rate processes when a branching of the reaction path occurs after the dynamical bottleneck are an important challenge for theory because in such a case transition-state theory only predicts the sum of the rate constants for the two branches. The hydroboration reaction was studied by Oyola and Singleton[6] using transition-state theory and trajectory calculations. They concluded the following: "In this most 'textbook' of reactions, transition state theory fails and the selectivity can only be understood by consideration of dynamics trajectories".[6] "For reactions exhibiting dynamic effects, chemistry must develop new qualitative ideas to account for reactivity and selectivity."[7]

In the present article we will present a qualitative theory not involving dynamical trajectories that accounts for the experi-

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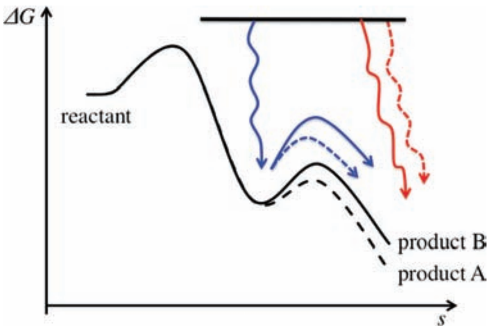
10.1021/ja904405v CCC: $40.75

Scheme 2



mental branching ratio in this prototype experiment. The dynamical model underlying the new theory is illustrated in Scheme 2, which shows a reaction with an overall dynamical bottleneck (a maximum of the free energy of activation profile) that is followed by a branching into two possible products. As the system proceeds along the reaction path, it is partially equilibrated by intramolecular vibrational relaxation[8] (IVR) and possibly also by collisions with a bath. Some fraction of the ensemble members can become equilibrated as an intermediate, and the reaction of the equilibrated intermediate is controlled by the two transition states leading to the two possible products. This is called the indirect mechanism. Some other fraction of the ensemble members retain a significant amount of energy in the reaction coordinate until after passing the second bottleneck region, and they react by a direct mechanism. In reality, there is a range of partial equilibration, but our model shall represent this as a mixture of two limiting cases. The indirect mechanism will be calculated by transition-state theory,[9] the direct mechanism will be calculated by nonstatistical phase space theory[10,11] (one could also use the statistical phase space theory,[12] but this is not recommended in the general case), and the competition between the two mechanisms will be calculated by the unified statistical theory.[13,14] The reaction coordinate in Scheme 1 is a general progress variable, not a minimum energy path; there is no implication that the dynamics of either the direct or the indirect reaction follows the minimum energy path. The new model is called the canonical competitive nonstatistical model (CCNM), where "nonstatistical" refers not only to the nonstatistical phase space calculation of the direct component but also to the competition of two mechanisms that is not included in the canonical unified statistical model.

Theory

Previously we presented, for reactions that have the general shape of free energy profile shown in Figure 1, a competitive canonical unified statistical (CCUS) model,[15] which is a generalization of the canonical[14,16] unified statistical[13] (CUS) model based on the probability branching analysis of Hirschfelder and Wigner.[17] Here we improve the model and use it to calculate the branching ratio of anti-M and M products in the hydroboration of propene with BH_3.

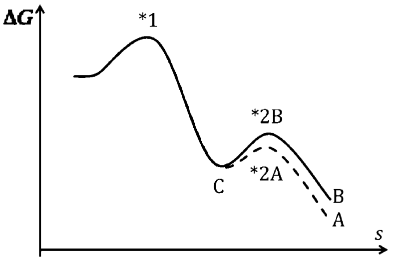


Figure 1. Schematic diagram of the generalized free energy of activation profile vs reaction coordinate (s). The dynamical bottlenecks are labeled with an asterisk (*), the complex succeeding the first bottleneck is labeled C, and the products are labeled A and B.

In the CCUS model,[15] the system is assumed to be fully equilibrated by the time it reaches the second set of bottlenecks. This assumption is invalid because some fraction of the collisions, which we call direct collisions, may pass through the second bottleneck region without being significantly impeded. For the direct collisions, the second bottleneck may be irrelevant to the branching ratio. The collisions that lead to a thermally equilibrated complex before passage through the second bottleneck region are called indirect collisions.

Phase space theories, either statistical[12] or nonstatistical,[10,11] although easy to apply, can be used to provide valuable insight into the detailed dynamics of chemical reactions by analyzing the quantitative extent of their success or failure and the effect of changing kinematic variables on their predictions.[18] Therefore, we propose a canonical competitive nonstatistical model by assuming that direct collisions can be modeled by nonstatistical phase space theory and indirect collisions are controlled by the second set of dynamical bottlenecks. The total rate (k_{tot}) is the sum of a direct component (k_{dir}) and an indirect component (k_{ind}) and is calculated by[15]

$$\frac{1}{k_{\mathrm{tot}}} = \frac{1}{k_{*1}} - \frac{1}{k_{\mathrm{C}}} + \frac{1}{k_{*2}} \tag{1}$$

where k_i denotes the reactive flux coefficient for a dividing surface at location i (i = *1, C, *2A, and *2B; see Figure 1) and $k_{*2} \equiv \min(k_{\mathrm{C}}, k_{*2\mathrm{A}}+k_{*2\mathrm{B}})$. For a gas-phase reaction, as a result of the potential energy release, if in fact Boltzmann distributions are formed at C and *2, their temperatures will be different than that for *1, and this would have to be considered.

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More generally we note that the temperature is not constant or even well defined for post-transition-state dynamics in the gas phase. For a reaction in liquid-phase solution where collisions with the bath as well as IVR contribute to equilibration, the limiting case is that the temperature of the complex is the same as the bath temperature, but in general, it is not clear how quickly a canonical ensemble is formed or whether it is useful to describe the trajectory ensemble by a temperature. Comparison to experiment is required to determine if it is useful to model temperature as done here.

For the reactive flux contributed by direct collisions the derivation of the unified statistical model (see eq 2.19 in ref 13) shows, upon changing[14] from a microcanonical to a canonical formulation, that

$$k_{\mathrm{dir}} = k_{*1}k_{*2}/k_{\mathrm{C}} \tag{2}$$

Let the branching ratio for the direct component of the reactive flux be called $R_{\mathrm{A/B}}$. For the branching ratio of the indirect component of the reactive flux, it is natural to assume

$$\left.\frac{k_{\mathrm{A}}}{k_{\mathrm{B}}}\right|_{\mathrm{ind}} = \frac{k_{*2\mathrm{A}}}{k_{*2\mathrm{B}}} \tag{3}$$

Then simple algebra shows that the total reaction rate constants for the two branches are given by

$$k_{\mathrm{A}}^{\mathrm{CCNM}} = \frac{R_{\mathrm{A/B}}}{1 + R_{\mathrm{A/B}}}k_{\mathrm{dir}} + \frac{k_{*2\mathrm{A}}}{k_{*2\mathrm{A}} + k_{*2\mathrm{B}}}(k_{\mathrm{tot}} - k_{\mathrm{dir}}) \tag{4}$$

$$k_{\mathrm{B}}^{\mathrm{CCNM}} = \frac{1}{1 + R_{\mathrm{A/B}}}k_{\mathrm{dir}} + \frac{k_{*2\mathrm{B}}}{k_{*2\mathrm{A}} + k_{*2\mathrm{B}}}(k_{\mathrm{tot}} - k_{\mathrm{dir}}) \tag{5}$$

Note that eqs 4 and 5 approximate the real reaction by a mixture of limiting cases. Also note that the earlier and less convincing CCUS model[15] is equivalent to setting k_{dir} equal to 0, in which case $R_{\mathrm{A/B}}$ is not needed.

Now we turn to the estimation of the ratio $R_{\mathrm{A/B}}$ without classical trajectories. This is the least reliable part of the calculation, but it is instructive to show that progress can be made on general grounds by statistical or nonstatistical phase space theory, that is, by statistical or nonstatistical weighting of product energy levels, which are the quantized analogs of volumes in phase space. The simplest approximation is statistical phase space theory[12] in which $R_{\mathrm{A/B}}$ is simply the equilibrium constant $K_{\mathrm{A/B}}$. A more accurate estimation can be made by a nonstatistical phase space theory.[10,11]

For unimolecular products, the equilibrium constant is

$$K_{\mathrm{A/B}} = \frac{Q_{\mathrm{A}}}{Q_{\mathrm{B}}}e^{-(V_{\mathrm{A}}-V_{\mathrm{B}})/RT} \tag{6}$$

where R is the gas constant, T is the temperature, and Q_{X} (where $\mathrm{X} = \mathrm{A}$ or B) is the partition function of X with the zero of energy at the corresponding local minimum V_{X} of the potential energy surface. Note that for unimolecular products Q_{X} may be approximated as

$$Q_{\mathrm{X}} = Q_{\mathrm{X,F}}Q_{\mathrm{X},\perp} \tag{7}$$

where $Q_{\mathrm{X,F}}$ is the partition function of the mode corresponding to the reaction coordinate s, which is a bound vibration at the product (we call it mode F), and $Q_{X,\perp}$ is the partition function of the other modes (i.e., those orthogonal to s). Note that according to basic statistical mechanics

$$Q_{\mathrm{X,F}} = \sum_{n_{\mathrm{F}}} e^{-\varepsilon_{n_{\mathrm{F}}}/RT} \tag{8}$$

where $\varepsilon_{n_{\mathrm{F}}}$ is the vibrational energy in mode F with quantum number n_{F}. We will use n to denote the full set of quantum numbers of the product (including n_{F}).

The leading correction to the statistical theory is that product states are not coupled to the complex if there is not enough time for energy transfer. By detailed balance this limits the product space that is accessible by direct collisions, and it has been suggested that a given product state n be weighted by[10,11]

$$\theta_n = 1 - e^{-\tau_n/\tau_{\mathrm{relax}}} \tag{9}$$

where τ_{relax} is a characteristic energy relaxation time (the reciprocal of a characteristic frequency) and τ_n is the duration of the relevant part of the collision. We approximate the duration as

$$\tau_{n_{\mathrm{F}}} = \frac{l}{v_{n_{\mathrm{F}}}} = \frac{l}{\sqrt{2E_{n_{\mathrm{F}}/\mu}}} \tag{10}$$

where l is a characteristic distance in coordinates scaled to a reduced mass μ, $v_{n_{\mathrm{F}}}$ is a characteristic velocity in the reaction coordinate for reaction coordinate quantum number n_{F}, and $E_{n_{\mathrm{F}}}$ is a characteristic kinetic energy in the reaction coordinate for that n_{F}. The nonstatistical factor of eq 9 is called the sticking coefficient. We take μ as 1 amu (the results are independent of μ because of the coordinate scaling[16,19]), l as $s_{\mathrm{product}} - s_{\mathrm{TS1}}$, and $E_{n_{\mathrm{F}}}$ as

$$E_{n_{\mathrm{F}}} = V^{\mathrm{TS1}} + \bar{E}^{\mathrm{TS1}} - \left(V^{\mathrm{product}} + \bar{E}_{\perp}^{\mathrm{product}} + \varepsilon_{n_{\mathrm{F}}}\right) \tag{11}$$

where $\bar{E}^{\mathrm{TS1}}$ is the thermal rovibrational energy plus zero-point energy at TS1 and $\bar{E}_{\perp}^{\mathrm{product}}$ is the product thermal rovibrational energy plus zero-point energy excluding the contributions of mode F. Since $\theta_{n_{\mathrm{F}}}$ depends only on n_{F} (not on the other quantum numbers that specify n), we can obtain $R_{\mathrm{A/B}}$ from $K_{\mathrm{A/B}}$ by replacing $Q_{\mathrm{X,F}}$ by

$$Q_{\mathrm{X,F}}^{\mathrm{nonstat}} \equiv \sum_{n_{\mathrm{F}}} \theta_{n_{\mathrm{F}}} e^{-\varepsilon_{n_{\mathrm{F}}}/RT} \tag{12}$$

Note that if $\tau_{\mathrm{relax}} = 0$ (instantaneous energy relaxation), we recover the statistical result. Note also that temperature considerations similar to those discussed for the complex after eq 1 also apply to the products.

Calculations

We use the harmonic oscillator, rigid rotator approximation to evaluate $\varepsilon_{n_{\mathrm{F}}}$ and all vibration−rotation partition functions. All vibrations are quantized. Following Oyola and Singleton,[6] we assume that for the indirect reaction, the temperature of C and hence the temperature at the second bottleneck region is the same as the temperature at the first bottleneck region, which is assumed, as usual, to be the temperature of the reactants. The product temperature is also assumed to be equal to the reactant temperature. Except for this temperature consideration, all calculations were performed for the gas phase. The calcula-

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tions would be more realistic if solvation effects on the free energies were included; however, there are no optimized parameters available for boron in otherwise applicable solvation models, so solvation effects are not included in the present calculations.

The association reaction is barrierless, and the reactive flux coefficient k_{*1} was taken from the NOSADDLE-type[20] calculation of ref 6. The reactive flux coefficient k_C was calculated from the generalized free energy of activation[21,22] at the complex, and the reactive flux coefficients at the second set of transition states were calculated by conventional transition-state theory[9] (TST) and by canonical variational transition-state theory[16,21,22] (CVT) with small-curvature tunneling[23] (SCT); these dynamical fluxes were calculated by using the variational transition-state theory with interpolated single-point energies (VTST-ISPE) algorithm[24] for dual-level direct dynamics (no trajectories are calculated). The B3LYP/6-31(d) method, which was validated for the relative barrier heights of *2A and *2B by Oyola and Singleton,[6] was used for geometry optimizations and for the lower level of dual-level direct dynamics. Although the difference of the anti-M and M barrier heights calculated by the B3LYP/6-31G(d) method agree well with CCSD(T)/aug-cc-pVQZ//aug-cc-pVDZ values,[6] the absolute barrier heights calculated by B3LYP/6-31G(d) are higher than these coupled cluster values by about 2 kcal/mol. Therefore, the energies of stationary points were corrected by G3SX(MP3),[25] which has been validated previously.[26] The resulting dual-level VTST-ISPE direct dynamics calculation is denoted as G3SX(MP3)//B3LYP/6-31G(d). The G3SX(MP3)//B3LYP/6-31G(d) calculations agree with CCSD(T)/aug-cc-pVQZ//aug-cc-pVDZ values[6] within 0.4 kcal/mol for the two saddle points at the second bottleneck and for the complex. The direct branching ratio was calculated either by using statistical theory or by adding nonstatistical effects to the reaction coordinate mode. With $\mu = 1$ amu we found $l = 10.2$ Å. Following ref 10 we set $\tau_{\text{relax}} = 100$ fs.

Table 1 lists the calculated branching ratios.

Table 1. G3SX(MP3)//B3LYP/6-31G(d) CCNM Branching Ratio for Propene Using Various Approximations for Calculating the Reactive Flux Coefficients at TS2 and the Direct Branching Ratio at Temperature 298 K

k_{2X}	statistics[a]	% Markovnikov
TST	$k_{\text{dir}} = 0^b$	1.7%
CVT/SCT	$k_{\text{dir}} = 0$	2.6%
TST	statistical	8.5%
CVT/SCT	statistical	7.4%
TST	nonstatistical	8.7%
CVT/SCT	nonstatistical	7.6%[c]
trajectories[d]		10−13%
experiment[e]		7%
experiment[f]		10%

[a] Partition functions of products. [b] CCUS. [c] Final result of the present model. [d] Reference 6; gas-phase trajectories (without G3SX(MP3) correction) started with quantized vibrational energies at the overall variational transition state gave 13%; trajectories in which solvent was included at an unspecified pressure yielded 10−11%. [e] For undeuterated 1-butene from ref 4. [f] For propene-d_6 from ref 6.

Discussion

Before considering the results, it is useful to discuss the physical models behind using a phase space theory in its either statistical or nonstatistical formulations. One possible justification would be the presence of a long-lived complex, but here we use phase space theory for the direct component of the reaction. (The direct component can be long lived, but it need not be; the crucial phenomenological distinction between direct and indirect in the present theory is that the direct component is not governed by reaction of an equilibrated complex.) The justification when there is not a long-lived complex is strong coupling—not a long lifetime.[27] The leading nonstatistical correction is lack of time for various reactant and product states to couple to the strong interaction region (which has been discussed elsewhere[28]), but the time scale involved here is a time scale for strong coupling, not the much longer times associated with long-lived complexes. An analogous consideration was raised in Gao and Marcus's paper[29] on nonstatistical effects in the ozone reaction, where "it is argued that the effective [density of quantum states] might be less than the statistical value... This... should be only the density of the quantum states of the... molecule that are sufficiently dynamically coupled to the... 'exit channels'..." A limitation of that paper is that it did not give any prescription for calculating the reduced weight to be assigned to each region of phase space. The present paper (building on the 1966 and 1975 papers already cited[10,11] and on the canonical[14,16] unified statistical model[13]) begins the process of making such ideas more quantitative by providing a testable nonstatistical theory that for at least one prototype case gets a reasonable answer. Note though that Marcus' overall approach is quite different from that used here in that he deals explicitly with the coupling of states of the complex to the entrance and exit channels, whereas we deal with the coupling of states in the entrance and exit channels to the strong-interaction region; this difference in approaches makes the present theory manageable even for complex reactions. The simple nonstatistical factor (sticking coefficient) used here is not the final answer for all reactions, but we think it will often

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be a dominant nonstatistical factor, and the present theory provides a framework for testing hypotheses involving other nonstatistical factors.

Table 1 shows that the variational and tunneling effects are quite small for the reactive flux coefficients at the second set of bottlenecks. We also found that the nonstatistical partition functions are reduced to about one-half of the statistical ones, but the nonstatistical factors change %M by only about one percentage point. Because the anti-M product has a lower energy than the M product, the duration of the relevant collision that leads to anti-M product is shorter. Therefore, the nonstatistical effect is greater for the partition function of the anti-M product. Hence, the predicted %M is slightly increased, but the magnitude of the nonstatistical effect on the product ratio is quite small for this hydroboration reaction because the energy difference between the two products is very small (1.2 kcal/mol) compared to the maximum energy release in this reaction (because $V_{\mathrm{TS1}} - V_{\mathrm{product}} \geq 29.3$ kcal/mol). When the energy difference between two products is comparable to the energy release, the nonstatistical effect will have a large effect on the branching ratio.

Table 1 shows that under the inappropriate assumption that the system is fully thermally equilibrated to the complex ($k_{\mathrm{dir}} = 0$), TST predicts 2% of the M product, which agrees with the calculations of Oyola and Singleton.[6] Considering the excess energy that is available from initial conditions, the system can pass directly to products after going through the first transition state. Including this in the CCNM model (with the full CVT/SCT calculations for the indirect contributions) yields 66% direct reaction and 8% M, which qualitatively agrees with the experimental value of 10%. Agreement with experiment is better when using the less complete conventional TST for the indirect contributions because in that case 83% of the reaction is direct. Note that $R_{\mathrm{A/B}}$ is very sensitive to the energy difference of the two products, because this energy difference is exponentiated in eq 6. Thus, %M is uncertain by as much as a few percentage points due to uncertainties in the input energetic parameters. In light of this sensitivity, the calculated branching ratio agrees with experiment within the reliability of the electronic structure calculations and the experiment.

Table 1 also shows the results of trajectory calculations reported in ref 6. These calculations also provide a qualitatively correct prediction of %M. Oyola and Singleton found that 25% of the trajectories yield product within 800 fs and 39% yield product within 800−5000 fs; these numbers cannot be compared to the present calculations because the present model does not predict the lifetime distribution. Trajectory calculations[30] have both advantages and disadvantages. Advantages are that they do not require a model of the reaction, they often predict qualitatively correct product energy distributions, and they can be analyzed to gain insight into the atomic motions that lead from reactants to transition state to products. Some disadvantages are that they can be expensive even when an analytic reactive potential energy surface is available, they become even more expensive when direct dynamics is employed, and they do not include quantum effects, especially zero-point energy and tunneling. Zero-point energy is not fully conserved during the true (quantal) dynamics, because the system is not in a stationary state, but we also know that vibrational actions are approximately conserved.[31] In classical trajectories, the local action variables are the analogs of the local vibrational quantum numbers, and the less conserved nature of the classical action variables as compared to the local quantum numbers is illustrated by the fact that trajectory calculations begun with quantization at a position earlier than the dynamical bottleneck do not give quantitative predictions of reaction thresholds and reaction rates[32] because, even if beginning with quantized vibrational action variables, they do not maintain the approximate conservation well enough; this is called nonadiabatic leak.[33,34] It is well known that nonadiabatic leak is important at dynamical bottlenecks and products (for example, it can allow reaction at energies where reaction is energetically forbidden[35] or dynamically forbidden in the quantum mechanical dynamics, although the latter error is sometimes partially compensated by cancellation of errors due to the neglect of tunneling[33,36]), but it is also important at other stages of the trajectories because it leads to the wrong distribution of energies in the various degrees of freedom, and that influences the dynamical outcomes, potentially having significant effects on branching ratios. One can alleviate nonadiabatic leak by starting the trajectories with zero-point energy at the dynamical bottleneck,[37] as done in ref 6, but in a case like the present one, with two bottleneck regions, starting the trajectories properly quantized at ***1** will not lead to properly quantized trajectories at ***2A** or ***2B** or at whatever other geometries are important for determining the product ratio. If the ensemble member does not move from the location where quantization is enforced to products (or to the region of the potential surface that determines the product ratio) on a fast time scale, the trajectory may not give the correct dynamics for this ensemble member because of nonquantal (i.e., unphysical) vibrational energy flow. Nevertheless, good agreement with experiment has been found in some cases for simulations of exothermic, barrierless reactions and of predissociations on repulsive potential energy surfaces,[38] and it is quite possible that the trajectory calculations of ref 6 give a qualitiatively correct result for

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the present example because they incorporate the physics properly. Our advancement of a qualitative theory should not be interpreted as a criticism of trajectory calculations in general or of those in ref 6 but rather as a response to the explicit[7] and implicit[6,39] pleas for qualitative theories that describe a broader class of reactions.

Louderaj et al. recently reviewed comparisons of trajectory calculations to experiment for post-transition-state dynamics.[39] They emphasized how trajectory calculations can illustrate the nature of the dynamics, and they pointed out that "widely used paradigms and model theories for interpreting reaction kinetics and dynamics are often inaccurate". To broaden the range of model theories available to the experimentalist, we sought a theory that includes quantization at all dynamical bottlenecks and products and that can be used to conveniently predict branching ratios that require consideration of motions following the overall dynamical bottleneck but without the cost of trajectories. The calculations using the CCNM model show that the branching ratio for the prototype competitive hydroboration reaction whose fate is determined after the bottleneck can be estimated without trajectories by using quantities readily available from electronic structure theory; in particular the theory involves the stability of the complex, generalized transition-state theory calculations at the dynamical bottlenecks, equilibrium constants of the two products, the vibrational frequencies of the product modes that correlate with the reaction coordinate, and one phenomenological constant (τ_{relax}) whose value in the present case was taken as a nominal value from previous work.

The fact that the effect of the sticking coefficient (i.e., nonstatistical factor of eq 9) has only a small effect on the calculated %M is both a minus and a plus for the present application of the theory. On the minus side, the experiment does not provide evidence for the quantitative evaluation of the nonstatistical factor and hence does not discriminate decisively between the statistical and nonstatistical versions of the phase space component. Two other aspects of this result are on the plus side though: (i) the only parameter of the theory over and above those needed to calculate transition-state theory rate constants (such as CVT/SCT rate constants) and equilibrium constants is the phenomenological relaxation time τ_{relax}, and the present results are not sensitive to this parameter; (ii) it is well known from extensive experience with phase space theory that it often overestimates the coupling of incoming and outgoing states to the strong interaction region; therefore, it is encouraging that the theory works even when an attempt is made to remove that deficiency (and the factors involved are not insignificant, with the partition functions reduced by about a factor of 2), making it less likely that the theory is working by a cancelation of errors.

If the theory is considered more broadly for a variety of reactions, an area for further study would be justification for the use of a single phenomenological relaxation time for coupling of the reaction coordinate motion to the remaining degrees of freedom. This is clearly an idealization; nevertheless, this type of coupling and relaxation can be studied by trajectory calculations in the gas phase or the condensed phase or by analytical nonlinear mechanics.[8,28]

In the present work, we proposed a new method based on combining nonstatistical phase space theory for the direct reaction with variational transition-state theory for the indirect reaction for predicting branching ratios of chemical reactions when a branching of the reaction path occurs after the dynamical bottleneck. This new method provides a way to understand the factors that control this kind of chemical reaction and to perform calculations using high-level electronic structure methods for complex systems. The calculated branching fraction of the hydrobroation of propene with BH_3 increases from 2%–3% when calculated under the inappropriate assumption of complete equilibration of the intermediate to from 8%–9% when calculated with the new CCNM theory, which involves both direct and indirect reaction, requires only limited information about the system, and does not involve running trajectories. Furthermore, because the model—unlike classical trajectory calculations—is based on quantized energy levels of transition states and products, it is applicable to kinetic isotope effects, which are a powerful mechanistic tool. One cannot exclude the fact that the success of a model in providing qualitatively correct results for a one or a limited number of cases is fortuitous; therefore, tests of the model on diverse reactions and on kinetic isotope effects would be interesting to learn how general the new model is and to learn when additional nonstatistical effects need to be invoked.

Concluding Remarks

The essence of the present approach is treating the direct part of the reaction by a nonstatistical phase space theory. Even when such a theory does not yield quantitatively accurate results (and it will certainly not be correct for all reactions, especially if one limits oneself to the present simple formulation of the sticking coefficient), it can still offer insights, just as we gain insight when we test whether a product ratio agrees with that predicted by conventional transition-state theory or whether it agrees with a value simply predicted by thermodynamics. In the present case the only nonstatistical factor included in the canonical competitive nonstatistical model is eq 9, and although the sums of nonstatistical factors times Boltzmann constants differ significantly from the statistical values, the product branching ratio in the present case is not sensitive to the nonstatistical factors; however, in other cases it can be more sensitive, and one might need more detailed nonstatistical considerations. In such cases the present treatment provides a framework in which such additional nonstatistical hypotheses might be tested against experiment (by altering eq 9). Despite the simplicity of the present treatment, the present results are encouraging in accounting for the product ratio in the prototype reaction of the hydroboration of propene.

As stated above, there are some reactions where the present method is expected to be less successful. This includes cases where the product ratio differs greatly from both the direct and indirect predictions. By sorting reactions into those where the product ratio can be accounted for by a simple statistical or nonstatistical calculation and those where it cannot be so explained, we begin to get a greater understanding of which reactions involve specific dynamical features and which do not. In this first application we

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already found that a case previously thought to be explainable only by trajectory calculations can be explained by a simple competitive model using either a statistical phase space theory or a nonstatistical one for the direct contribution.

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Supporting Information Available: Geometries, energies, reactive flux coefficients, statistical and nonstatistical partition functions, equilibrium constants, computational details, software references, and a paragraph of additional discussion. This material is available free of charge via the Internet at http://pubs.acs.org.

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