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A Stochastic Theory of Chemical Reaction Rates. II. Applications

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A formalism developed for the treatment of chainlike models of reaction dynamics is applied to simple reacting systems and generalized to treat a reaction with a branching process. The models can be solved exactly, and the overall rates of the reactions are studied as a function of the rates arising from different dynamical regimes involved in the microscopic mechanisms.

KEY WORDS: Stochastic models; chemical reactions; rate constants; isomerization; barrier crossings.

1. INTRODUCTION

Even for a superficially simple reaction like an isomerization between A and B species, the reaction dynamics often involves several different kinds of molecular motion; for example, the interconversion process may entail passage over a potential barrier and relaxation of a newly-formed species to its ground-state form. In the description of such processes it is convenient to focus on the dynamics of the system along a reaction coordinate; the behavior of this reactive degree of freedom may be complex due to its coupling to other degrees of freedom, like internal molecular or solvent motions. Except in the case of model systems where molecular

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dynamics computer simulations are possible, the precise nature of the influence of bath degrees of freedom on the reaction coordinate is not known; hence, it is useful to model the dynamics by a stochastic process, which ignores many of the details of the bath motion and concentrates instead on its statistical properties.

In this paper we study a number of stochastic models of barrier-crossing dynamics as an application of the general formalism developed in the preceding paper, hereafter referred to as I.(1) All of the reactions can be imagined as occurring between species defined by potential wells separated by barriers in a reaction coordinate. Both the activation and deactivation mechanism in the well regions as well as the dynamics on the barrier are assumed to be simple stochastic processes: activation and deactivation within the wells occurs by "collisions" with exponentially-distributed collision times, while the barrier dynamics is a random telegraph process[5] where the velocity changes sign with exponentially-distributed waiting times. While these stochastic processes are highly idealized and may not capture all features of real reaction rates, they have the advantage that they are exactly soluble and show how various regimes of different dynamical behavior couple and contribute to the overall rate of a reaction.

Three models are studied below: the first two are chainlike in character and the formalism of I can be applied directly; the results for these models are presented in Sections 2 and 3. The third model involves a branching process among three species and requires a generalization of the method; this calculation is presented in Section 4.

2. CROSSING OF A SIMPLE BARRIER

2.1. Model and Dynamics

As a first illustration of the general formalism presented in I, we calculate the rate coefficient for the interconversion between two species A and B separated by a flat barrier of length L. The time evolution of the model is simple and can be described by the motion of a "particle" representing the dynamics of the reaction coordinate subject to the following collision processes resulting from its coupling to the other degrees of freedom of the system: When the particle is in the barrier region $[0, L]$, it has speed $\pm v$, where the sign changes at stochastic times exponentially distributed with frequency Z; this is a random telegraph process. When the particle arrives in 0 it has speed $-v$, and there is a time τ_A such that if

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[5] See Kac(2) (based on 1956 notes from the Magnolia Petroleum Company colloquium lectures).

there is no collision (with collision frequency Z_A) in the time interval $[0, \tau_A]$, the particle is reflected and stays in 0 with the reverse speed $+v$. On the other hand, if there is a collision in $[0, \tau_A]$, the particle stays in state A forever (absorbing state). When the particle is in 0 with speed $+v$ it begins its random telegraph process in the barrier region. If the particle arrives in L with speed $+v$, the mechanism is the analog of that in A, with a time τ_B and collision frequency Z_B.

A schematic representation of this model as a double-well potential problem is shown in Fig. 1; its full dynamics was studied earlier,(3) but we show here that the general formalism of I provides a simple and direct route to the rate constant, and we give a physical interpretation of the overall rate constant in terms of partial rate constants for the various dynamical regions.

We can interpret this model in the framework of the general chainlike models in the following way: The regime X_0 contains three states, $X_0 = \{A^-, 0^+, 0^-\}$, where A^- is identified with the stable A species, which is taken to be an absorbing state. In the case of a reactivation mechanism from the "bottom of the well," a fourth state A^+ could be added to X_0. Similarly, the regime X_2 contains three states, $X_2 = \{L^+, L^-, B^+\}$, where B^+ is the stable (absorbing) B species. Again, B^- could be added if there is a reactivation process in B. The regime $X_1 = [0, L] \times \{1, -1\}$ is the phase space of the barrier region $[0, L]$ with two possible speeds.

2.2. The Overall Rate Constant k

We can use Eqs. (I.3.8) and (I.3.9) directly to compute the rate constant k characterizing the interconversion process. Taking the dividing surface at 0, we can calculate $k = k_{0B}$ by letting $0 = A$, $i = 0$, $n = i + 1 = L$, and $n + 1 = B$ in these formulas, and obtain

$$\begin{aligned} \frac{1}{k} &= \frac{1}{k_{0A}^{\text{eff}}} + \frac{1}{k_{0L}} + \frac{1}{k_{LB}^{\text{eff}}} \\ \frac{1}{k_{0L}} &= \frac{1}{k_{0L}^{\text{TST}}} + \frac{1}{k_{0L}^{\text{eff}}} \end{aligned} \tag{2.1}$$

and

$$\frac{1}{k} = \frac{q_A}{vq_0}\left(\frac{1}{S_{0A}} - 1\right) + \frac{q_A}{vq_0} + \frac{q_A}{vq_0}\left(\frac{1}{S_{0L}} - 1\right) + \frac{q_A}{vq_0}\left(\frac{1}{S_{LB}} - 1\right) \tag{2.2}$$

where S_{ij} is the transmission coefficient defined in I and we have taken $q_0 = q_L$.

It is not difficult to compute the required transmission coefficients. By definition, S_{0A} is the probability that the particle starting from 0^- at time $t=0$ is absorbed by A^- at some time; this is exactly the probability to have a collision in the time interval $[0, \tau_A]$. For exponentially distributed collisions with frequency Z_A, the probability to have no collision in $[0, \tau_A]$ is $\exp(-Z_A\tau_A)$, so that

$$S_{0A} = 1 - \exp(-Z_A\tau_A) \tag{2.3}$$

By a similar argument we have

$$S_{LB} = 1 - \exp(-Z_B\tau_B) \tag{2.4}$$

It is interesting to note that we can use the general formalism of Part I, even to compute S_{0L}. We divide the barrier region $[0, L]$ into a sequence of small segments

$$[0, L] = [0, \Delta X] \cup [\Delta X, 2\,\Delta X] \cup \cdots \cup [(n-1)\,\Delta X, n\,\Delta X]$$

with $n\,\Delta X = L$. Inside each segment $[j\,\Delta X, (j+1)\,\Delta X]$ the particle starting from $j\,\Delta X$ with speed $+v$ is transmitted to $(j+1)\,\Delta X$ if no collision occurs during the time $(\Delta X)/v$, and reflected back to $j\,\Delta X$ if there is one collision. Neglecting $(\Delta X)^2$ terms, we get

$$S_{j\,\Delta X,\,(j+1)\,\Delta X} = 1 - Z\frac{\Delta X}{v} = S_{(j+1)\,\Delta X,\,j\,\Delta X}$$

This implies that in the barrier $q_j = q_{j+1}$ and by Eq. (I.2.12)

$$\frac{1}{S_{0L}} - 1 = \sum_{j=0}^{n-1}\left(\frac{1}{S_{j\,\Delta X,\,(j+1)\,\Delta X}} - 1\right) = \sum_{j=0}^{n-1}\frac{Z\,\Delta X\,v^{-1}}{1 - Z\,\Delta X\,v^{-1}} \tag{2.5}$$

so that

$$S_{0L} = \left(1 + \frac{ZL}{v}\right)^{-1} \tag{2.6}$$

Of course, there are other, more standard ways to obtain (2.6), using well-known information on the random telegraph process (see, for instance, ref. 2).

Using these expressions for the transmission coefficients S_{ij}, we can write Eqs. (2.1) and (2.2) for k in a physically transparent form. First, we can identify k_{0L}^{TST} as the transition state theory (TST) rate constant for crossing the barrier and thus the TST rate constant k^{TST} for the overall reaction:

$$k^{\mathrm{TST}} = k_{0L}^{\mathrm{TST}} = \frac{q_0 v}{q_A} \tag{2.7}$$

The partition function ratio q_0/q_A is just

$$q_0/q_A = e^{-\beta E_A}/v\tau_A \tag{2.8}$$

where E_A is the activation energy from the A well bottom; the factor $v\tau_A$ arises from the fact that 0 is a point while the A well has a finite length $v\tau_A$ (cf. Fig. 1 and the final remark in Section I.3.1). Thus, the TST rate constant is

$$k^{\mathrm{TST}} = \frac{1}{\tau_A} e^{-\beta E_A} \tag{2.9}$$

In this simple model, τ_A^{-1} also represents an attempt frequency at the barrier. The effective rate constant k_{0A}^{eff} in Eq. (2.1) can be interpreted as an activation rate constant for well A:

$$k_{W,A}^{\mathrm{act}} = k_{0A}^{\mathrm{eff}} = \frac{vq_0}{q_A}\left(\frac{1}{S_{0A}} - 1\right)^{-1} = \frac{e^{-\beta E_A}}{\tau_A}\left(\frac{1 - e^{-Z_A\tau_A}}{e^{-Z_A\tau_A}}\right) \tag{2.10}$$

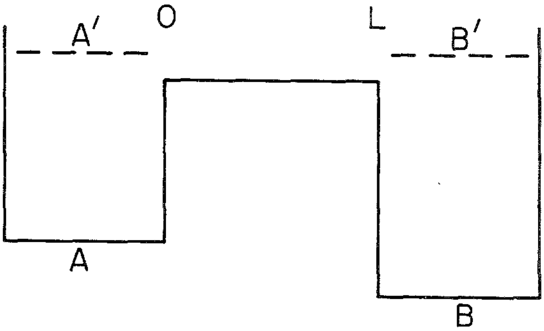

Fig. 1. Schematic representation of a simple barrier-crossing model involving interconversion of A and B species connected by a barrier of length L. The states A' and B' represent excited states in each well; when the system is in these states it may return to the barrier region or be deactivated and form stable A or B species.

A deactivation rate constant from energies at the level of 0 can be defined from the detailed balance relation

$$\begin{aligned} k_{W,A}^{\text{deact}} &= k_{W,A}^{\text{act}} K_A^{\text{eq}} \tau_A = k_{W,A}^{\text{act}} \left(\frac{q_A}{q_0}\right) \tau_A \\ &= \frac{1}{\tau_A} \left(\frac{1 - e^{-Z_A \tau_A}}{e^{-Z_A \tau_A}}\right) \end{aligned} \tag{2.11}$$

[The factor of τ_A appearing in the first line of Eq. (2.11) accounts for the finite length of the A well at its top.] A similar set of the rate constants can be defined for well B with the replacement of A by B in Eqs. (2.10) and (2.11) and are related to the term involving S_{LB} in Eq. (2.2).

Finally, the effective rate constant k_{0L}^{eff} for the barrier involving S_{0L} is a rate constant for diffusive motion in the barrier region, defined as

$$\begin{aligned} k_D^{\text{barr}} = k_{0L}^{\text{eff}} &= \frac{v q_0}{q_A} \left(\frac{1}{S_{0L}} - 1\right)^{-1} = k^{\text{TST}} \frac{v}{ZL} \\ &= k^{\text{TST}} \frac{D}{vL} \end{aligned} \tag{2.12}$$

where the identification of the diffusion coefficient D is made from a consideration$^{(2)}$ of the random telegraph equations in the diffusion limit where $v \to \infty$, $Z \to \infty$, and $D = v^2/Z$ is fixed. Recall that Kramers' formula$^{(4)}$ for the rate constant k^{KR} for barrier crossing dynamics in the strong friction or diffusive limit has the form $k^{KR} = k^{\text{TST}} w_b m/\zeta$, where w_b is the barrier frequency and ζ the friction coefficient. Equation (2.12) is just of this form if we relate the diffusion coefficient to the friction coefficient by the Einstein relation$^{(4)}$ $D = k_B T/\zeta$ and identify $k_B T/mvL$ with the barrier frequency.

In terms of the partial rate constants just described, we can write k in the form

$$\frac{1}{k} = \frac{1}{k_{W,A}^{\text{act}}} + \frac{1}{k^{\text{TST}}} + \frac{1}{k_D^{\text{barr}}} + \frac{1}{K_{BA}^{\text{eq}} k_{W,B}^{\text{act}}} \tag{2.13}$$

where K_{BA}^{eq} is the $A \rightleftharpoons B$ equilibrium constant q_B/q_A.

2.3. Discussion of *k*

Equation (2.13), which has the general form originally derived via SSP theory$^{(5,6)}$ and applied to isomerization reactions,$^{(6)}$ expresses the additivity of the reciprocal rate coefficients characterizing the various regimes. First, $k^{\mathrm{act}}_{W,A}$, Eq. (2.10), governs the activation from the reactant A up to the barrier. Next,

$$\frac{1}{k_{\mathrm{barr}}} = \frac{1}{k^{\mathrm{TST}}} + \frac{1}{k^{\mathrm{barr}}_{D}} \tag{2.14}$$

governs the motion in the barrier region. If this is very slow, then $k_{\mathrm{barr}} \to k^{\mathrm{barr}}_{D}$.

Finally, $K^{\mathrm{eq}}_{BA} k^{\mathrm{act}}_{W,B}$ governs the rate of the stabilization to form B after the barrier passage. It is perhaps most natural to consider this a deactivation step. In terms of the deactivation rate constant

$$k^{\mathrm{deac}}_{W,B} = (1 - e^{-Z_B\tau_B})/\tau_B e^{-Z_B\tau_B}$$

one has

$$\begin{aligned} K^{\mathrm{eq}}_{BA} k^{\mathrm{act}}_{W,B} &= \frac{q_B}{q_A}\,\frac{v q_0}{q_D}\,\frac{(1 - e^{-Z_B\tau_B})}{\tau_B e^{-Z_B\tau_B}} \\ &= k^{\mathrm{TST}} \tau_B k^{\mathrm{deact}}_{W,B} \end{aligned} \tag{2.15}$$

This is most readily interpreted by considering Eq. (2.13) when activation out of A and diffusion across the barrier are fast and deactivation in B is very slow. Then we have

$$\frac{1}{k} \to \frac{1}{k^{\mathrm{TST}} \tau_B k^{\mathrm{deact}}_{W,B}} \tag{2.16}$$

or $k = k^{\mathrm{TST}} \tau_B k^{\mathrm{deact}}_{W,B}$. Then the k^{TST} factor describes the rate constant for arriving over the B well (containing the activation energy factor $e^{-\beta E_A}$) and the factor

$$\tau_B k^{\mathrm{deact}}_{W,B} = \frac{1 - e^{-Z_B\tau_B}}{e^{-Z_B\tau_B}} \tag{2.17}$$

gives the probability of deactivation.

Under ordinary circumstances, the well activation and deactivation contributions will only be of importance when these steps are slow, e.g., at low to moderate density; otherwise the barrier passage is rate limiting and $k^{\mathrm{act}}_{W,A}$ and $K^{\mathrm{eq}}_{BA} k^{\mathrm{act}}_{W,B}$ drop out of k. At such densities, the collision frequencies will be low enough that $Z_A\tau_A$ and $Z_B\tau_B$ are both much less than unity. Then we have, for example,

$$k^{\mathrm{act}}_{W,A} = \left(\frac{1 - e^{-Z_A\tau_A}}{\tau_A e^{-Z_A\tau_A}}\right) e^{-\beta E_A} \to Z_A e^{-\beta E_A} \tag{2.18}$$

which is the standard form of a "strong-collision" activation rate constant.$^{(5,7,8)}$ For a symmetric isomerization ($E_A = E_B$, $Z_A = Z_B$, etc.), use of this in Eq. (2.13) gives

$$\frac{1}{k} = \frac{2}{k_{SC}^{\text{act}}} + \frac{1}{k^{\text{TST}}} + \frac{1}{k_D^{\text{eff}}} \tag{2.19}$$

where $k_{SC}^{\text{act}} = Ze^{-\beta E_A}$. This expression$^{(9,10)}$ has recently been found to fairly accurately describe the rate of a model isomerization in a BGK stochastic computer simulation.$^{(10)}$

3. CROSSING OF A BARRIER WITH SEVERAL CHANNELS

It is not difficult to extend the simple barrier-crossing model of Section 2 to allow for the possibility that there are several channels connecting the A and B states. This could, for example, serve to model certain structural effects in an isomerization, in which barrier passage occurs with different internal configurations of the isomerizing species. Other examples can be imagined in which the reacting species encounters different medium (e.g., solvent) configurations on the way to products.

We suppose that there are r channel states having common extremities 0 and L but possibly of different length. When the particle starts at 0 with speed $+v$, it chooses channel j with probability p_j, while if it starts from L with speed $-v$ it chooses channel j with probability p'_j; subsequent to the choice it begins a random telegraph motion in the jth channel. If a particle in channel j arrives at 0 with speed $-v$, it goes into regime X_0, where it may be deactivated or return to 0^+, where the same mechanism as in Section 2 operates. This reaction model is depicted symbolically in Fig. 2. We take $q_0 = q_L$.

The definitions of the regimes X_0 and X_2 are unchanged from Section 2, and the regime X_1 will be described in terms of the four states $X_1 = \{0^+, 0^-, L^+, L^-\}$. The formal expression for the rate constant is identical to that Eq. (2.2); however, S_{0L} is different from Eq. (2.6). S_{0L} is the probability that the particle is absorbed by L^+, knowing that it started from 0^+ (with speed $+v$). But, starting from 0^+, the probability of choosing channel j is p_j and in channel j there is a probability $S_{0,L}^{(j)}$ (L_j is the length of channel j) to be absorbed at the other end of the channel. Trajectories coming back to 0^- are not counted, since this is an absorbing state for X_1. Then, we have

$$S_{0L} = \sum_{j=1}^{r} p_j S_{0,L_j}^{(j)} \tag{3.1}$$

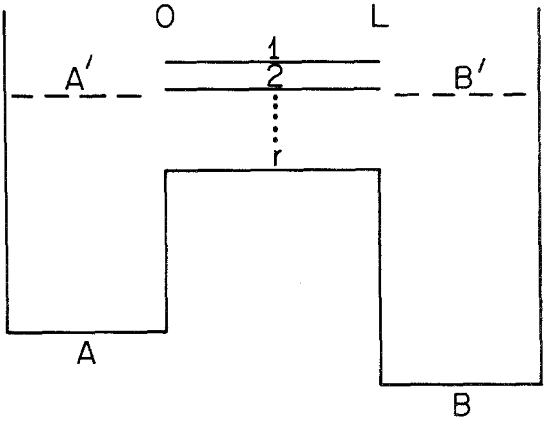

Fig. 2. Model with r barrier channels connecting wells A and B.

and in the same way

$$S_{L0}=\sum_{j=1}^{r} p_j' S_{0,L_j}^{(j)} \tag{3.2}$$

We may then write $k=k_{0B}$ as

$$\frac{1}{k}=\frac{1}{k_{W,A}^{\mathrm{act}}}+\frac{1}{k^{\mathrm{TST}}}+\frac{1}{\tilde{k}_D^{\mathrm{barr}}}+\frac{1}{K_{AB}^{\mathrm{eq}}k_{W,B}^{\mathrm{act}}} \tag{3.3}$$

where

$$\frac{1}{\tilde{k}_D^{\mathrm{barr}}}\equiv\frac{q_A}{q_0 v}\left(\frac{1}{S_{0L}}-1\right) \tag{3.4}$$

Thus, the only difference between Eq. (3.3) and (2.13) is the replacement of k_D^{barr} by a new diffusive barrier rate constant $\tilde{k}_D^{\mathrm{barr}}$ that takes into account averaging over the possible channels. The new rate constant $\tilde{k}_D^{\mathrm{barr}}$ can be shown to have a simple additive form. With Eqs. (3.4), (3.2), and the analogue

$$S_{0,L_j}=\left(1+\frac{Z_j L_j}{v}\right)^{-1} \tag{3.5}$$

of Eq. (2.6), we find that

$$\tilde{k}_D^{\mathrm{barr}}=k^{\mathrm{TST}}\sum_{j=1}^{r}\mathscr{P}_j D_j/vL_j \tag{3.6}$$

where $D_j = v^2/Z_j$ is the diffusion constant in channel j and

$$\mathscr{P}_j = \frac{p_j(1 + D_j/vL_j)^{-1}}{\sum_j p_j(1 + D_j/vL_j)^{-1}} \tag{3.7}$$

is an effective probability for channel j. Equation (3.6) has the property that if diffusion in a particular channel i is much faster than in the others, it will dominate the rate, i.e., $\tilde{k}_D^{\text{barr}} \to k^{\text{TST}}(D_i/vL_i)$. This reflects the fact that the channels j are parallel routes across the barrier.

4. MODEL WITH TWO CHANNELS AND THREE WELLS

While the formalism in I is restricted to chainlike models, it is nonetheless possible to use similar ideas to treat a broader class of problems. Branching processes frequently arise in the study of reaction mechanisms, and it is of interest to study microscopic models that incorporate such a feature.(11,12) As an example, we compute the rate constant for a system of three species denoted S, A, and B, which are coupled by two barriers: S and A are connected by the barrier $[0, L_A]$, S and B are connected by the barrier $[0, L_B]$, while A and B are not directly coupled to each other; they are coupled only through S. The schematic picture is given in Fig. 3.

The dynamical evolution is as follows: the deactivation mechanism in the wells is exactly the same as in the other models, with (Z_A, τ_A), (Z_B, τ_B), and (Z_S, τ_S) the collision frequencies and characteristic times for each well. When the particle arrives at 0^+ (with speed $+v$) it chooses barrier $[0, L_A]$ with probability p_A and barrier $[0, L_B]$ with probability p_B and once it has chosen a barrier it begins a random telegraph process with collision frequency Z_A or Z_B in the barrier region. It can then arrive, say, at L_A^+ and become deactivated or come back in L_A^-. If it arrives in 0^-, it can become deactivated and fall in S or come back to 0^+.

The model is not chainlike, because there is a bifurcation point at 0; in fact, the point 0^+ has to be split into two points 0_A^+ and 0_B^+, which are phase points corresponding to the particle with speed $+v$ at the beginning of the barrier leading from 0 to A or 0 to B, respectively. There are five dynamical regimes in this model: $X_B = \{S^-, S^+, 0^-, 0_A^+, 0_B^+\}$, where S^- is identified with the bottom of well S; $X_A = \{A^+, A^-, L_A^+, L_A^-\}$ and $X_B = \{B^+, B^-, L_B^+, L_B^-\}$, where A^+ and B^+ are identified with the bottoms of wells A and B, respectively; and $X_{0A} = [0, L_A] \times \{+v, -v\}$ and $X_{0B} = [0, L_B] \times \{+v, -v\}$, the phase space regions corresponding to the two barriers. In the above specification we have made the identification $0_A^- \equiv 0_B^- \equiv 0^-$.

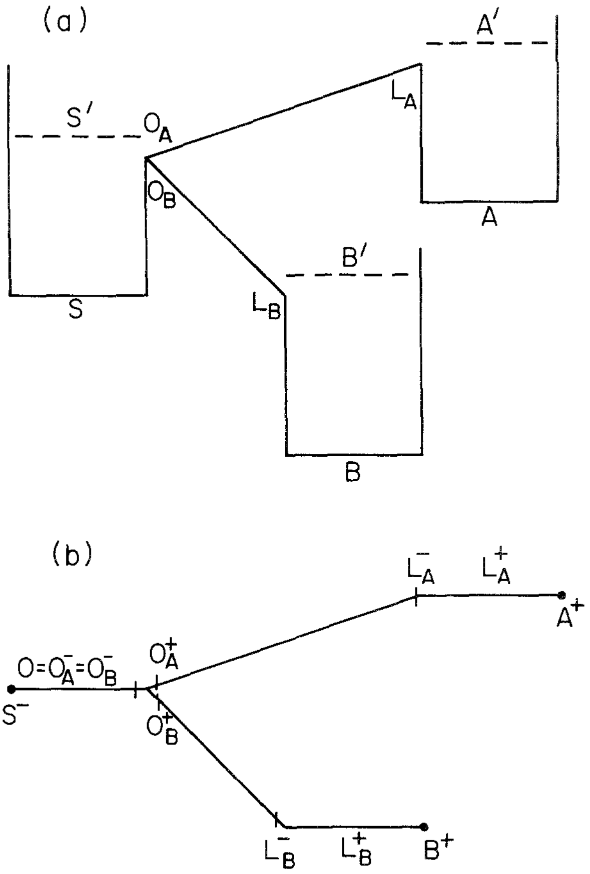

Fig. 3. (a) Schematic picture of the branching model involving two barriers and three wells. (b) Representation in terms of the states of the stochastic model.

4.1. Rate Constant Calculation

Consider a regime X_n and define $S_n(k\,|\,l)$ to be the transmission coefficient or probability to be absorbed by k at some time, starting from l, and staying inside X_n. For region X_0, with absorbing states 0_A^+, 0_B^+, and S^-, we may define the transmission coefficients $S_0(S^-\,|\,0^-)$, $S_0(0_A^+\,|\,0^-)$, and $S_0(0_B^+\,|\,0^-)$. It is clear that

$$S_0(0_A^+\,|\,0^-)=p_A(1-S_0(S^-\,|\,0^-)) \tag{4.1}$$

and

$$S_0(0_B^+\,|\,0^-)=p_B(1-S_0(S^-\,|\,0^-)) \tag{4.2}$$

Next, we define a regime X_1 to be a union of the other regimes, $X_1 = X_A \cup X_B \cup X_{0A} \cup X_{0B}$. This regime has absorbing states 0^-, A^+, and B^+, and we define the transmission coefficients $S_1(A^+ \mid 0_A^+)$, $S_1(B^+ \mid 0_A^+)$, and $S_1(0^- \mid 0_A^+)$, and an analogous set of quantities with $A \to B$ and $B \to A$. Note that $S_1(B^+ \mid 0_A^+) = 0$, since the barrier $[0, L_A]$ cannot communicate with $[0, L_B]$ inside X_1, except through 0^-, which is absorbing for X_1; thus, $1 - S_1(A^+ \mid 0_A^+) = S_1(0^- \mid 0_A^+)$.

Let $P(A^+, \infty \mid l)$ be the probability to be absorbed by A^+ at some time, starting from $l = 0_A^+$, 0_B^+, or 0^-, the evolution taking place in the whole system $X_0 \cup X_1$. The flux of particles absorbed at A^+, measured at 0, may be written in terms of these probabilities as

$$\Phi(0, A) = v[p_A P(A^+, \infty \mid 0_A^+) + p_B P(A^+, \infty \mid 0_B^+) - P(A^+, \infty \mid 0^-)] \tag{4.3}$$

This flux definition is the analog of that introduced for the chainlike models. The rate constant $k_A = k_{0A}$ for the production of A from reactant S can be expressed in terms of this flux as

$$k_A = \frac{q_0}{q_s} \Phi(0, A) \tag{4.4}$$

An analogous expression can be written for the rate constant characterizing the production of B.

Next, we outline the calculation of $\Phi(0, A)$. We may write

$$P(A^+, \infty \mid 0_A^+) = S_1(A^+ \mid 0_A^+) + P(A^+, \infty \mid 0^-)\, S_1(0^- \mid 0_A^+) \tag{4.5}$$

$$P(A^+, \infty \mid 0_B^+) = P(A^+, \infty \mid 0^-)\, S_1(0^- \mid 0_B^+) \tag{4.6}$$

$$\begin{aligned} P(A^+, \infty \mid 0^-) = {} & P(A^+, \infty \mid 0_A^+)\, S_0(0_A^+ \mid 0^-) \\ & + P(A^+, \infty \mid 0_B^+)\, S_0(0_B^+ \mid 0^-) \end{aligned} \tag{4.7}$$

These equations follow directly from the definitions of the quantities; for example, to establish Eq. (4.5), we can say that the probability to go from 0_A^+ to A^+ splits into the probability to go from 0_A^+ to A^+ without leaving $X_1(S_1(A^+ \mid 0_A^+))$, and the probability to go from 0_A^+ to A^+ when the particle leaves X_1 and enters X_0 (X_0 is entered through state 0^-). Equations (4.5)–(4.7) may be manipulated to yield

$$P(A^+, \infty \mid 0^-) = [p_a P(A^+, \infty \mid 0_A^+) + p_B P(A^+, \infty \mid 0_B^+)][1 - S_0(S^- \mid 0^-)] \tag{4.8}$$

and

$$\begin{aligned}&[p_A P(A^+, \infty \,|\, 0_A^+) + p_B P(A^+, \infty \,|\, 0_B^+)]^{-1}\\ &\quad = [p_A S_1(A^+ \,|\, 0_A^+)]^{-1} \{1 - [1 - S_0(S^- \,|\, 0^-)]\\ &\quad\quad \times [p_A S_1(0^- \,|\, 0_A^+) + p_B S_1(0^- \,|\, 0_B^+)]\}\end{aligned} \tag{4.9}$$

Substitution of Eqs. (4.8) and (4.9) into (4.3) yields

$$\begin{aligned}\frac{1}{k_A} &= \frac{q_s}{q_0} \frac{1}{\Phi(0, A)}\\ &= \frac{q_s}{q_0 v}\left(\frac{1}{S_0(S^- \,|\, 0^-)} - 1\right) + \frac{1}{p_A} \frac{q_s}{q_0 v} \frac{1}{S_1(A^+ \,|\, 0_A^+)}\\ &\quad + \frac{p_B}{p_A} \frac{q_s}{q_0 v} \frac{1}{S_1(A^+ \,|\, 0_A^+)}\left(\frac{1}{S_0(S^- \,|\, 0^-)} - 1\right) S_1(B^+ \,|\, 0_B^+)\end{aligned} \tag{4.10}$$

where we have used the fact that $1 - S_1(B^+ \,|\, 0_B^+) = S_1(0^- \,|\, 0_B^+)$ and $p_A + p_B = 1$.

The transmission coefficients may be expressed in terms of the rate coefficients defined in Section 2. The activation rate constant for well S is given by

$$\frac{1}{k_{W,S}^{\text{act}}} = \frac{q_s}{v q_0}\left(\frac{1}{S_0(S^- \,|\, 0^-)} - 1\right) \tag{4.11}$$

$S_1(A^+ \,|\, 0_A^+)$ is also simply related to the rate constants introduced earlier by

$$\begin{aligned}\frac{q_s}{v q_0} \frac{1}{S_1(A^+ \,|\, 0_A^+)} &= \frac{q_s}{v q_0}\left(\frac{1}{S_{0_A L_A}} - 1\right) + \frac{q_s}{v q_0} + \frac{q_s}{v q_0}\left(\frac{1}{S_{L_A, A}} - 1\right)\\ &\equiv \frac{1}{k_{D,A}^{\text{barr}}} + \frac{1}{k^{\text{TST}}} + \frac{K_{S0}^{\text{eq}}}{K_{AS}^{\text{eq}}} \frac{1}{k_{W,A}^{\text{act}}}\end{aligned} \tag{4.12}$$

where $K_{S0}^{\text{eq}} = q_s/q_0$ and $K_{AS}^{\text{eq}} = q_A/q_S$. There is an analogous expression for $S_1(B^+ \,|\, 0_B^+)$, which has the form of Eq. (4.12) with A replaced by B. Using these results, we may write k_A^{-1} as

$$\frac{1}{k_A} = \frac{1}{k_{W,S}^{\text{act}}} + \frac{1}{p_A} \frac{1}{k_A'} + \frac{p_B}{p_A} \frac{k_B'}{k_A'} \frac{1}{k_{W,S}^{\text{act}}} \tag{4.13}$$

where

$$\frac{1}{k'_\alpha}=\frac{1}{k^{\text{barr}}_{D,\alpha}}+\frac{1}{k^{\text{TST}}}+\frac{K^{\text{eq}}_{S0}}{K^{\text{eq}}_{\alpha S}}\frac{1}{k^{\text{act}}_{W,\alpha}}, \qquad \alpha=A, B \tag{4.14}$$

The k'_α are the rate constants for independent production of either A or B subsequent to activation out of the reactant well. We may write Eq. (4.13) as

$$k_A=\frac{p_A k'_A}{1+(p_A k'_A+p_B k'_B)/k^{\text{act}}_{W,S}} \tag{4.15}$$

This expression clearly shows the influence of the B channel on the rate constant for the passage from O to A. In the absence of the second channel, $p_B=0$ and $p_A=1$, and the results is identical to Eq. (2.13) for a single-channel reaction; however, the presence of channel B influences the dynamics, since particles can explore this channel before being absorbed by A; this leads to a reduction of the rate constant for the $S \to A$ reaction. Finally, the generalization of Eq. (4.15) to any number of products is obvious.

5. CONCLUSION

The calculations presented in this paper demonstrate how the overall rate of a reaction depends on the rates of passage through intermediate regimes on the way from reactants to products. The simplicity of the assumed stochastic model, along with the general formalism developed in I, permit a detailed investigation of this connection between the microscopic dynamics and the macroscopic rate law. The calculations also show that a variety of processes, including branching mechanisms and interactions among several channels, can be treated by this formalism.

For the chainlike models the explicit calculations of the stochastic process yield a simple addition formula for the reciprocals of the rate constants; this is a direct consequence of the formalism developed in I. The calculations of the rate constant for the branching process show that this simple type of law can break down when nonconsecutive steps are introduced in the microscopic mechanism. Nonetheless, related addition formulas can be found.

The random telegraph process used in these calculations is a simplification of the stochastic dynamics of a reaction coordinate of a real system; however, its simplicity allows a direct calculation of the rate constants for the various regimes, and the physical content of the theory can be illustrated without lengthy calculations. The stochastic processes that occur in the different regimes depend on the specific system under study. The main advantage of the formalism presented here is that the possibly complex stochastic motion in the full system can be analyzed in terms of processes occurring in dynamically distinct regimes; the explicit calculations presented here demonstrate this point.

It is worth noting that there is another class of rate processes where the methods developed in these papers could be applied. These are noise-induced transitions between macroscopic bistable states in far-from-equilibrium chemical systems.(13) The evolution equations are stochastic versions of the macroscopic rate laws. These transitions may involve barrier-crossing dynamics, and dynamically distinct regimes may be identified. If the transition rate is driven by externally applied noise, then the choice of stochastic dynamics can be controlled by the investigator and it is possible to implement a Poisson-dichotomous noise process like that considered in these model calculations. Thus, while our calculations have largely heuristic value for the study of microscopic reaction kinetics, they may be of direct value for other types of rate process.

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