Some Observations Concerning Detailed Balance in Association/Dissociation Reactions

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In this article we discuss the chemical kinetics of reversible association/dissociation reactions at great length. We find that, as long as the characteristic time for internal-energy relaxation is faster (not necessarily much faster) than that for chemical reaction, there will be a period of time, perhaps only late in the reaction but before equilibrium is reached, during which phenomenological rate laws will apply with rate coefficients that satisfy detailed balance. The nonequilibrium factor, f_{ne}, originally introduced by Smith, McEwan, and Gilbert (*J. Chem. Phys*. **1989**, 90, 4265−4273) is *not* a measure of the degree to which detailed balance is satisfied by the association and dissociation rate coefficients. It is simply the fractional contribution to the "long-time" association rate coefficient, k_{add}, of the slowest-relaxing eigenmode of the system. That is, $1 - f_{ne}$ is the fractional contribution to the same rate coefficient of the internal-energy relaxation modes. The standard practice of taking the dissociation rate coefficient, k_d, to be equal to that for irreversible dissociation is accurate as long as $\gamma \equiv K_{eq}n_m(1 - f_{ne}) \ll 1$, where K_{eq} is the equilibrium constant for the association reaction, and n_m is the concentration of the excess reactant under pseudo first-order conditions for the association reaction. Both rate coefficients, k_{add} and k_d, show a very weak composition dependence, i.e., dependence on n_m.

I. Introduction

It is common practice in chemical kinetics to identify the thermal dissociation rate coefficient, k_d, of a molecule with (the negative of) the largest eigenvalue (least negative) of the transition matrix of the master equation (ME) governing its *irreversible* dissociation.[1−4] It is equally common to calculate the reverse association (recombination) rate coefficient, k_{add}, from the detailed balance condition,

$$\frac{k_{add}}{k_d} = K_{eq}, \tag{1}$$

where K_{eq} is the equilibrium constant for the association reaction. However, both of these practices have only been justified qualitatively. The use of eq 1 to calculate k_{add} was discussed extensively in the 1950s and 1960s,[5−16] at least for the dissociation of diatomic molecules. Particularly important contributions were made by Rice,[5,6] Keck and Carrier,[10] and Widom.[11]

Rice[5,6] used microscopic reversibility and the statistical independence of dissociation and recombination processes in a dilute gas mixture to argue convincingly that eq 1 should be satisfied even if k_d is substantially smaller than its equilibrium value. The latter effect was (and is) known to occur, because the populations of highly excited molecules are depleted below their equilibrium values during the steady-state dissociation process, at least at low pressure. Keck and Carrier provided a somewhat more quantitative justification of eq 1, but they and Rice relied heavily on the condition,

$$\tau_v \ll \tau_r, \tag{2}$$

to make their arguments. In eq 2, τ_v is the vibrational relaxation time and τ_r is a characteristic time for reaction to occur. Widom's paper, which is one of the most lucid and insightful ever written about chemical kinetics, is limited to discussing first-order processes. However, even though he emphasized the condition given by eq 2, from his analysis it is clear that this condition is too restrictive. We discuss this point below. In fact, the discussion in section III of this article might be considered to be just an extension of Widom's analysis to *pseudo* first-order processes.

In 1989, Smith, McEwan, and Gilbert[1,2] made an ambitious and laudable attempt to identify rigorously if and when eq 1 was satisfied quantitatively for association/dissociation reactions, not limiting their discussion to diatomic molecules. In a later paper,[17] Smith and co-workers also discussed detailed balance for the case where a set of bimolecular products may be formed from the collision complex. Under the same conditions as those discussed above, Smith, McEwan, and Gilbert derived the rate equation (in our terminology),

$$\frac{dn_C(t)}{dt} = -k_u n_C(t) + f_{ne} k_u K_{eq} n_m(t) n_R(t), \tag{3}$$

where t is the time, and n_R, n_m, and n_C are the concentrations of the reactants and products of the association reaction R + m $\rightleftarrows$ C. The factor f_{ne}, the "nonequilibrium factor," is a function of the steady-state energy distribution, $c(E)$, of the dissociating molecule during its *irreversible* dissociation, i.e.

$$f_{ne} = \left(\int_0^\infty c(E)\, dE\right)^2 \Big/ \left(\int_0^\infty \frac{c^2(E)}{F(E)}\, dE\right)^2, \tag{4}$$

where $F(E)$ is the equilibrium energy distribution. The rate coefficient k_u (not necessarily equal to k_d under all conditions) is that for the *irreversible* dissociation of C,

$$k_u = -\xi_1, \tag{5}$$

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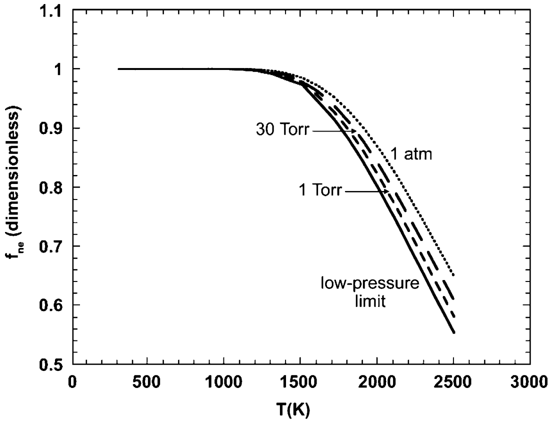

Figure 1. Nonequilibrium factor, f_{ne} (defined in eq 4), as a function of temperature and pressure for vinyl dissociation. Details of the calculations are given in ref 4.

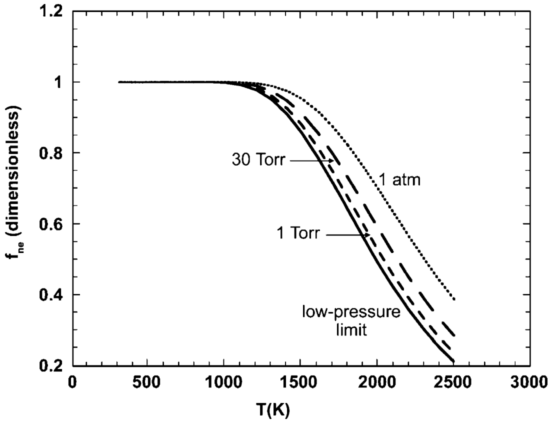

Figure 2. Nonequilibrium factor, f_{ne} (defined in eq 4), as a function of temperature and pressure for ethyl dissociation. Details of the calculations are given in ref 4.

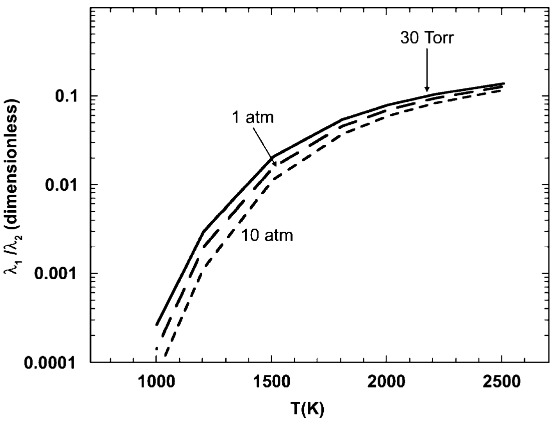

Figure 3. Characteristic time ratio, λ_1/λ_2, for vinyl dissociation as a function of temperature and pressure.

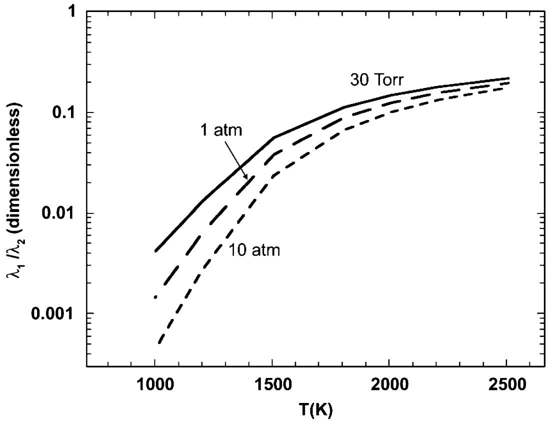

Figure 4. Characteristic time ratio, λ_1/λ_2, for ethyl dissociation as a function of temperature and pressure.

where ξ_1 is the eigenvalue mentioned in the first paragraph above. If the steady-state distribution is normalized, i.e.

$$\int_0^\infty c(E)\,\mathrm{d}E = 1, \tag{6}$$

f_{ne} can be written as

$$f_{ne} = 1/\left(\int_0^\infty \frac{c(E)}{F(E)} c(E)\,\mathrm{d}E\right). \tag{7}$$

From eq 7 the physical significance of f_{ne} is clear: its deviation from unity measures the degree to which dissociation perturbs the equilibrium population distribution of the dissociating molecule. If the only states whose populations are depleted by dissociation are those that are not heavily populated at equilibrium, $f_{ne} = 1$ to a high degree of accuracy.[3] Of course this is frequently the case.

The implication of eq 3 is that $k_d = k_u$ and $k_{add} = f_{ne}K_{eq}k_u$. Taken together, these two relations imply that eq 1 is satisfied if, and only if, f_{ne} is equal to unity. This result is at odds with the prior work of Rice, Keck and Carrier, and Widom. Viewing eq 3 from a slightly different perspective, let us simply take its limit as $t \rightarrow \infty$ and get

$$f_{ne}K_{eq} = \frac{n_C(\infty)}{n_m(\infty)n_R(\infty)}. \tag{8}$$

Clearly, eq 8 can be valid only if $f_{ne} = 1$, otherwise the reacting system would not approach equilibrium at long times. There are only 2 possibilities: either the rate law given by eq 3 is not valid at long times or it is valid only if $f_{ne} = 1$. We discuss this point at length in section IV.

Smith et al.[1,2] emphasize the point that f_{ne} is almost always equal to unity. However, that is not really the case, particularly for weakly bound free radicals at high temperature. In a recent investigation of vinyl and ethyl dissociation over a wide range of temperatures and pressures,[4] we found the results for f_{ne} shown in Figures 1 and 2. At temperatures just above 1000 K, f_{ne} begins to deviate from unity for both radicals, so much so that one would conclude from the Smith et al. analysis that eq 1 is not satisfied even approximately at temperatures typical of combustion processes. Somewhat surprisingly, these deviations begin to occur at τ_v/τ_r values as small as 10^{-2} . This point is illustrated in Figures 3 and 4, where we have plotted λ_1/λ_2 for the 2 molecules; $\lambda_1$and λ_2 are the 2 least negative eigenvalues of the transition matrix G for the reversible association/dissociation problem, described in section III. We can identify $(1/|\lambda_1|)$ with τ_r and $(1/|\lambda_2|)$ with τ_v.

Clearly, the issue described above is an important one for modeling combustion kinetics. Generally speaking, f_{ne} depends on the proximity of the peak in the equilibrium internal-energy distribution of the dissociating molecule to the threshold energy for dissociation. The closer these 2 energies are together, the more likely it is that states that are highly populated at equilibrium will have those populations perturbed by reaction.[3] Thus, larger (high density of states), weakly bound, free radicals will be affected even more than C_2H_3 and C_2H_5. Tsang et al.[18] have discussed the limiting case where the peak in the thermal internal-energy distribution lies well *above* the dissociation threshold. In such cases it is impossible to distinguish between τ_v and τ_r, and consequently it is impossible to define a dissociation rate coefficient.

In the following discussion we are able to reconcile the conflicting results alluded to above. The main result of the present article is contained in section IV, where we rederive the Smith et al. rate equation correcting a flaw in their analysis. In the process, we are able to offer an extended (different) interpretation of f_{ne} and to define a condition under which $k_d = k_u$. However, to understand these results, one must have a firm grasp of both the reversible and irreversible dissociation problems. We provide this background in sections II and III.

II. Irreversible Dissociation

In this section we consider the *irreversible* dissociation of a molecule C,

$$\mathrm{C} \rightarrow \mathrm{R} + \mathrm{m}. \tag{R1}$$

By the term "irreversible" we mean that the products are removed from the gas mixture as soon as they are formed, so that the reverse association process plays no role in the analysis. In this and the following sections we also assume that the initial reactant (or reactants) is immersed in an inert bath gas, so that energy-transferring collisions of C with the bath gas are the only ones that need to be considered. These are standard assumptions that define the irreversible, unimolecular dissociation problem. In addition, we consider only a one-dimensional master equation in which the total internal energy E is the independent variable. This facilitates comparisons with the solutions to the reversible ME, where only 1-d solutions are readily obtainable. This latter restriction is justified further by our observation that 1-d and 2-d solutions (where E and the total angular momentum quantum number are the independent variables) give very similar results at high temperatures.[3,4]

Under the conditions described in the previous paragraph, one can write the master equation as

$$\frac{\mathrm{d}n(E)}{\mathrm{d}t} = \mathrm{Z}\int_0^\infty P(E,E')n(E')\,\mathrm{d}E' - \mathrm{Z}n(E) - k(E)n(E), \tag{9}$$

where $n(E)\,\mathrm{d}E$ is the concentration of C with energy between E and $E + \mathrm{d}E$, Z is the collision rate, $k(E)$ is the microcanonical (RRKM) rate coefficient for the molecule, and $P(E,E')$ is the probability that a collision will transfer the molecule from a state with energy between E' and $E' + \mathrm{d}E'$ to one with energy between E and $E + \mathrm{d}E$. It is convenient to normalize eq 9 by dividing through by the initial concentration of the reactant, n_0. Equation 9 then becomes

$$\frac{\mathrm{d}x(E)}{\mathrm{d}t} = \mathrm{Z}\int_0^\infty P(E,E')x(E')\,\mathrm{d}E' - \mathrm{Z}x(E) - k(E)x(E), \tag{10}$$

where $x(E) = n(E)/n_0$.

The functions $P(E',E)$ and $P(E,E')$ are related through microscopic reversibility,

$$P(E',E)F(E) = P(E,E')F(E'), \tag{11}$$

where $F(E)$ is the equilibrium energy distribution,

$$F(E) = \rho(E)\mathrm{e}^{-\beta E}/Q(T), \tag{12}$$

$\rho(E)$ is the vibrational−rotational density of states of C, $Q(T)$ is the corresponding partition function, $\beta = (1/k_BT)$, k_B is Boltzmann's constant, and T is the temperature of the bath gas. Introducing the function $f(E)$ through the definition,

$$f^2(E) = \rho(E)\mathrm{e}^{-\beta \mathrm{E}} = F(E)Q(T), \tag{13}$$

one can write the microscopic reversibility condition (eq 11) in the symmetric form,

$$P(E',E)\frac{f(E)}{f(E')} = P(E,E')\frac{f(E')}{f(E)}. \tag{14}$$

Then, defining a new dependent variable,

$$y(E) = x(E)/f(E), \tag{15}$$

the master equation can be written in the form,

$$\frac{\mathrm{d}y(E)}{\mathrm{d}t} = \mathrm{Z}\int_0^\infty \left\{P(E,E')\frac{f(E')}{f(E)} - \left[1 + \frac{k(E')}{\mathrm{Z}}\right]\delta(E - E')\right\}y(E')\,\mathrm{d}E', \tag{16}$$

where $\delta(E - E')$ is the Dirac delta function. In view of eq 14, the kernel of this integral is symmetric with respect to interchanging E and E', making the integral operator Hermitian. Approximating the integral in eq 16 as a discrete sum with a fixed energy spacing δE and multiplying through by δE, the ME reduces to the simple vector equation,

$$\frac{\mathrm{d}|y\rangle}{\mathrm{d}t} = G'|y\rangle, \tag{17}$$

where $|y\rangle$ is the vector whose components are

$$y_i = y(E_i)\delta E, \tag{18}$$

and G' is a matrix whose elements are

$$G'_{ij} = \mathrm{Z}\left\{P(E_i,E_j)\frac{f(E_j)}{f(E_i)}\delta E - \left[1 + \frac{k(E_j)}{\mathrm{Z}}\right]\delta_{ij}\right\}. \tag{19}$$

Like the kernel of the integral in eq 16, G'_{ij} is real and symmetric, and thus Hermitian. This property greatly facilitates the solution of eq 17, which can be solved in exactly the same way as one obtains the general solution of the time-dependent Schrodinger equation in quantum mechanics. The general solution of eq 17 so obtained is

$$|y(t)\rangle = \sum_{j=1}^{N} \mathrm{e}^{\xi_j t}|g'_j\rangle\langle g'_j|y(0)\rangle, \tag{20}$$

where N is the number of grid points in the energy space, and $|y(0)\rangle$ is the initial condition vector. The ξ_j's are the eigenvalues and the $|g'_j\rangle$'s the *orthonormal* eigenvectors of G', i.e.

$$G'|g'_j\rangle = \xi_j|g'_j\rangle. \tag{21}$$

Because of the Hermiticity of G' the ξ_j's are real, and they must necessarily be negative, $\xi_j < 0$ for all j; otherwise the solution given in eq 20 would blow up as $t \rightarrow \infty$. Also because of the Hermiticity of G', the $|g'_j\rangle$ are orthogonal, and the solution of the ME leading to eq 20 requires that the $|g'_j\rangle$ be normalized so that

$$\langle g'_i|g'_j\rangle = \delta_{ij}. \tag{22}$$

Let us look at the solution to the ME, eq 20, more carefully. Absorbing the scalar coefficients, $\langle g_j'|y(0)\rangle$, into the eigenvectors, we can write

$$|y(t)\rangle = \left|\frac{x(t)}{f}\right\rangle = \sum_{j=1}^{N} e^{\xi_j t}|\psi_j\rangle, \tag{23}$$

where $|\psi_j\rangle = |g_j'\rangle\langle g_j'|y(0)\rangle$. The $|\psi_j\rangle$'s are still eigenvectors of G' with the eigenvalues ξ_j, and they are orthogonal. However, unlike the $|g_j'\rangle$'s, they are not normalized, and they depend on the initial condition. Writing eq 23 in terms of components,

$$\frac{x_i(t)}{f_i} = \sum_{j=1}^{N} e^{\xi_j t}\psi_{ij}, \tag{24a}$$

where $x_i(t) = x(E_i,t)\delta E$ and $f_i = f(E_i)$, or

$$x_i(t) = \sum_{j=1}^{N} e^{\xi_j t} f_i \psi_{ij} = \sum_{j=1}^{N} e^{\xi_j t} c_{ij}. \tag{24b}$$

In eq 24b, we have defined the components of a vector $|c_j\rangle$ as $c_{ij} = f_i\psi_{ij}$. Thus the vectors $|c_j\rangle$ and $|\psi_j\rangle$ are related by

$$|c_j\rangle = |f\psi_j\rangle \text{ or } |\psi_j\rangle = \left|\frac{c_j}{f}\right\rangle. \tag{25}$$

Finally, the population distribution can be written in vector form as

$$|x(t)\rangle = \sum_{j=1}^{N} e^{\xi_j t}|c_j\rangle. \tag{26}$$

The vector $|c_j\rangle$ has an important physical interpretation. One can write

$$|c_j\rangle = |-\Delta x_j\rangle \tag{27a}$$

or

$$c_{ij} = -\Delta x_{ij}, \tag{27b}$$

where Δx_{ij} is the change in population of the ith energy level that accompanies the time evolution of the jth eigenpair from $t = 0$ to ∞. After the "transients", or fast-relaxation modes (corresponding to vibrational−rotational relaxation), die out,

$$|x(t)\rangle = e^{\xi_1 t}|c_1\rangle. \tag{28}$$

If $|\xi_1| \ll |\xi_2|$, implying that there is no significant dissociation during the vibrational/rotational, or internal energy (IE), relaxation period, we have the result,

$$\sum_{i=1}^{N} c_{i1} = -\sum_{i=1}^{N} \Delta x_{i1} = 1$$

and

$$\sum_{i=1}^{N} c_{ij} = -\sum_{i=1}^{N} \Delta x_{ij} = 0 \text{ for } j > 1. \tag{29}$$

Thus, $|c_1\rangle$ is the steady-state energy distribution of C during the dissociation process as long as $|\xi_1| \ll |\xi_2|$. It is still *proportional* to the steady-state distribution as long as ξ_1 has not merged with the IE relaxation eigenvalues, *even if there is significant dissociation from* $j \geq 2$; $|c_1\rangle$ simply needs to be rescaled so that $\sum_{i=1}^{N} c_{i1} = 1$.

Note that the ξ_j's are related *physically* to the corresponding λ_j's mentioned in the Introduction and very crudely, $\xi_j \approx \lambda_j$ (except for $j = 1$). However, mathematically ξ_j and λ_j are eigenvalues of 2 different matrices, G' and G, the transition matrices of the ME's describing the *irreversible* and *reversible* dissociation problems, respectively. G and G' are different in that G has one more dimension than G', i.e., G is an $(N + 1)$ x $(N + 1)$ matrix and G' is N x N. We will continue to make the appropriate distinctions between them. Nevertheless, both $|\lambda_1| \ll |\lambda_2|$ and $|\xi_1| \ll |\xi_2|$ mean the same thing, that internal-energy relaxation is much faster than chemical relaxation.

Summing eq 26 over all components, one obtains

$$X_C(t) = \sum_{j=1}^{N} e^{\xi_j t}(-\Delta X_{Cj}), \tag{30}$$

where ΔX_{C_j} is the change in the normalized concentration of C induced by the jth eigenpair. After all the higher-eigenvalue terms have died out,

$$X_C(t) = -\Delta X_{C_1} e^{\xi_1 t}. \tag{31}$$

Differentiating eq 31 with respect to t, we get

$$\frac{dX_C(t)}{dt} = -\xi_1 \Delta X_{C_1} e^{\xi_1 t}, \tag{32}$$

and using the definition of the unimolecular rate coefficient,

$$k_u(T,p) \equiv -\frac{1}{X_C}\frac{dX_C}{dt} = -\frac{(-\xi_1 \Delta X_{C_1} e^{\xi_1 t})}{(-\Delta X_{C_1} e^{\xi_1 t})}$$

or

$$k_u = -\xi_1. \tag{33}$$

Equation 33 just gives the well-known relationship between the unimolecular rate coefficient for the irreversible problem and ξ_1 mentioned in the Introduction. Note that this result *does not require* $|\xi_1| \ll |\xi_2|$. As long as ξ_1 has not been absorbed into the continuum of IE relaxation eigenvalues, even if there is a large amount of dissociation during the IE relaxation period, there will be some period of time during which eqs 31 and 33 will apply, although this time period may produce a very small amount of dissociation. If this latter condition is not satisfied, separate IE relaxation and dissociation time periods are not distinguishable, and all the dissociation occurs as part of the IE relaxation process.

Understanding the derivation given above, even its more subtle points, is important to understanding the analysis described in section IV. In this vein, we need one more result. For an *irreversible dissociation*,

$$-\frac{dX_C}{dt} = \sum_{j=1}^{N} \int_0^{\infty} dE\, c_j(E) k(E) e^{\xi_j t}, \tag{34}$$

where for convenience we have shifted back to a continuous (integral) formulation of the problem from a discrete one (using sums). We hope that the relation between the 2 formulations is clear. Defining an "average rate coefficient" as

$$\bar{\mathrm{k}}_{\mathrm{j}} \equiv \int_0^\infty \mathrm{k(E)c_j(E)dE}\Big/\int_0^\infty \mathrm{c_j(E)dE}, \qquad (35)$$

eq 34 becomes

$$-\frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t} = \sum_{j=1}^{N}[\bar{k}_j\int_0^\infty c_j(E)\ \mathrm{d}E]\mathrm{e}^{\xi_j t}. \qquad (36)$$

Integrating this equation with respect to time, we get

$$-\Delta X_{\mathrm{C}} = 1 = \sum_{j=1}^{N}[\bar{k}_j\int_0^\infty c_j(E)\ \mathrm{d}E]/|\xi_j|. \qquad (37)$$

Each term on the right-hand-side of eq 37 can be identified as $-\Delta X_{\mathrm{C}_j}$, the contribution of the jth eigenvector of G' to the decay of the concentration of C,

$$-\Delta X_{\mathrm{C}_j} = [\bar{k}_j\int_0^\infty c_j(E)\ \mathrm{d}E]/|\xi_j|. \qquad (38)$$

Now from eq 27 we know that

$$\int_0^\infty c_j(E)\ \mathrm{d}E = -\int_0^\infty \Delta x_j(E)\ \mathrm{d}E = -\Delta X_{\mathrm{C}_j} \qquad (39)$$

Consequently, it follows from eqs 38 and 39 that

$$\bar{k}_j = |\xi_j| = -\xi_j, \qquad (40)$$

an important result that we need below. Note that if there is no dissociation from the higher eigenvectors, $\int_0^\infty c_1(E)\ \mathrm{d}E = 1$, and we have the intuitively obvious result,

$$\bar{k}_1 = \int_0^\infty k(E)c_1(E)\ \mathrm{d}E = -\xi_1 = k_{\mathrm{u}}, \qquad (41)$$

where, as noted above, $c_1(E)$ is the steady-state energy distribution of C during the dissociation phase of the relaxation process. However, it is the general result, eq 40, that proves useful below.

III. Reversible Association/Dissociation Reaction: Homogeneous Formulation

The most accurate, rigorous way of handling the association/dissociation problem is to treat it reversibly. In so doing, we generally view the reaction as going in the association direction, although our results do not depend on this being the case. To simplify the problem, we assume that we have pseudo first-order conditions,

$$n_{\mathrm{R}} \ll n_{\mathrm{m}} \ll n_{\mathrm{d}}, \qquad (42)$$

where n_{d} is the concentration of the diluent. The master equation (analogous to eq 9) can be written as

$$\frac{\mathrm{d}n(E)}{\mathrm{d}t} = Z\int_0^\infty P(E,E')n(E')\ \mathrm{d}E' - Zn(E) - k(E)n(E) + k_{\mathrm{a}}(E)[\rho_{\mathrm{Rm}}(E)\mathrm{e}^{-\beta E}/Q_{\mathrm{Rm}}]n_{\mathrm{R}}n_{\mathrm{m}}, \qquad (43)$$

where $\rho_{\mathrm{Rm}}(E)$ is the density of states (including relative translation motion) of the $R + m$ fragments, Q_{Rm} is the corresponding partition function, and $k_{\mathrm{a}}(E)$ is the microcanonical association rate coefficient. In formulating eq 43, it has been assumed that R and m are maintained in thermal equilibrium, consistent with eq 42.

Recasting the problem in the same way we did for the irreversible dissociation, and using microscopic reversibility to reformulate the last term in eq 43 in terms of the properties of C (rather than those of R and m), we can write the ME as

$$\frac{\mathrm{d}y(E)}{\mathrm{d}t} = Z\int_0^\infty \left\{P(E,E')\frac{f(E')}{f(E)} - \left[1 + \frac{k(E)}{Z}\right]\delta(E - E')\right\}y(E')\ \mathrm{d}E' + \frac{K_{\mathrm{eq}}}{Q}k(E)f(E)n_{\mathrm{m}}X_{\mathrm{R}}(t). \qquad (44)$$

The present problem is a special case of the more general, multiple-well problem we have treated previously;[19−23] so we adopt the same procedure as before and write a rate equation for $X_{\mathrm{R}}(t)$ (n_{m} = constant),

$$\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t} = \int_0^\infty k(E)x(E)\ \mathrm{d}E - X_{\mathrm{R}}(t)n_{\mathrm{m}}K_{\mathrm{eq}}\int_0^\infty k(E)F(E)\ \mathrm{d}E$$

or

$$\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t} = \int_0^\infty k(E)f(E)y(E)\ \mathrm{d}E - X_{\mathrm{R}}(t)n_{\mathrm{m}}K_{\mathrm{eq}}\int_0^\infty k(E)F(E)\ \mathrm{d}E. \qquad (45)$$

Writing the integrals in eq 45 as discrete sums and multiplying through by $(n_{\mathrm{m}}/(Q_{\mathrm{Rm}}\delta E))^{1/2}$, eq 45 becomes

$$\frac{\mathrm{d}}{\mathrm{d}t}\left[X_{\mathrm{R}}(t)\left(\frac{n_{\mathrm{m}}}{Q_{\mathrm{Rm}}\delta E}\right)^{1/2}\right] = \sum_{i=1}^{N}y(E_i)k(E_i)f(E_i)\left(\frac{n_{\mathrm{m}}\delta E}{Q_{\mathrm{Rm}}}\right)^{1/2} - \left[X_{\mathrm{R}}(t)\left(\frac{n_{\mathrm{m}}}{Q_{\mathrm{Rm}}\delta E}\right)^{1/2}\right]n_{\mathrm{m}}K_{\mathrm{eq}}\sum_{i=1}^{N}k(E_i)F(E_i)\delta E. \qquad (46)$$

After discretizing, eq 44 we can write it as

$$\frac{\mathrm{d}y(E_i)}{\mathrm{d}t} = Z\sum_{j=1}^{N}\left\{P(E_i,E_j)\frac{f(E_j)\delta E}{f(E_i)} - \left[1 + \frac{k(E_j)}{Z}\right]\delta_{ij}\right\}y(E_j) + \left(\frac{n_{\mathrm{m}}\delta E}{Q_{\mathrm{Rm}}}\right)^{1/2}k(E_i)f(E_i)\left[\left(\frac{n_{\mathrm{m}}}{Q_{\mathrm{Rm}}\delta E}\right)^{1/2}X_{\mathrm{R}}(t)\right]. \qquad (47)$$

Now we have the form that we want - the coefficient of $(n_{\mathrm{m}}/(Q_{\mathrm{Rm}}\delta E))^{1/2}X_{\mathrm{R}}(t)$ in eq 47 is identical to that of $y(E_i)$ in eq 46. To keep the present formulation as close as possible to that for the irreversible dissociation, it is useful to multiply both eqs 46 and 47 by δE.

The manipulations just described allow us to combine eqs 46 and 47 into one vector equation, a generalized master equation, of the form,

$$\frac{\mathrm{d}|w(t)\rangle}{\mathrm{d}t} = G|w(t)\rangle, \qquad (48)$$

where

$$|w\rangle = \left[\frac{x(0)}{f(0)}\delta E,\ldots,\frac{x(E_i)\delta E}{f(E_i)},\ldots,\left(\frac{n_{\mathrm{m}}\delta E}{Q_{\mathrm{Rm}}}\right)^{1/2}X_{\mathrm{R}}\right]^{\mathrm{T}}, \qquad (49)$$

and the transition matrix G again is Hermitian. Thus, we can write the solution to eq 49 in terms of the eigenvalues and eigenvectors of G, $G|g_j\rangle = \lambda_j|g_j\rangle$, as we did for the irreversible dissociation problem,

$$|w(t)\rangle = \sum_{j=0}^{N}\mathrm{e}^{\lambda_j t}|g_j\rangle\langle g_j|w(0)\rangle. \qquad (50)$$

Formally, the only difference between this solution and that given by eq 20 is that eq 50 includes an eigenpair corresponding to $\lambda_0 = 0$. Thus, eq 50 approaches a constant vector $|w(\infty)\rangle$ as $t \rightarrow \infty$ that corresponds to a state of complete chemical and thermal equilibrium, whereas eq 20 approaches the null vector at long times.

From eq 50, we can obtain the energy level populations of C, $x_i = x(E_i)\delta E$, as a vector,

$$|x(t)\rangle = \sum_{j=0}^{N} |c_j\rangle\, e^{\lambda_j t}, \tag{51}$$

where $|c_j\rangle$ is formally the same as before (eq 27) for $j \geq 1$ and $c_{i0} = x_i(\infty)$, the equilibrium population. Note that $|x(t)\rangle$ has N components, whereas $|w(t)\rangle$ has $N + 1$, i.e., $|x(t)\rangle$ is a vector in a subspace of one less dimension than that defined by the eigenvectors of G. After the transients have died out, i.e., all the terms involving $j \geq 2$, one can write eq 51 as

$$|x(t)\rangle = \sum_{j=0}^{1} |c_j\rangle e^{\lambda_j t} = |x(\infty)\rangle + |c_1\rangle e^{\lambda_1 t}$$

$$|x(t)\rangle = |x(\infty)\rangle + |-\Delta x_1\rangle e^{\lambda_1 t}. \tag{52}$$

Summing the components of $|x(t)\rangle$, we get from eq 52 that

$$X_C(t) = X_C(\infty) - \Delta X_{C_1} e^{\lambda_1 t}. \tag{53a}$$

Similarly, from the last component of $|w\rangle$, we arrive at

$$X_R(t) = X_R(\infty) - \Delta X_{R_1} e^{\lambda_1 t}. \tag{53b}$$

Equations 53 are applicable for any and all initial conditions, although the values of the ΔX's depend on what the initial conditions are.

If $|\lambda_1| \ll |\lambda_2|$, which we take to mean that the difference between the 2 magnitudes is sufficiently different that there is no significant contribution to reaction from $|g_j\rangle$, $j \geq 2$, we can apply the "initial-rate" method of Klippenstein and Miller[19,20] to obtain the rate coefficients k_d and k_{add}. This method requires that internal-energy relaxation be complete before any reaction takes place. Essentially, one must be able to identify unambiguously a time, $t = 0$, when IE relaxation is over but none of the reactant has disappeared. Applying this method, we obtain for the rate coefficients

$$k_{CR} = -\lambda_1 \Delta X_{R_1}^{(C)} = -\lambda_1 X_R(\infty)$$

and (54)

$$k_{RC} = -\lambda_1 \Delta X_{C_1}^{(R)} = -\lambda_1 X_C(\infty),$$

where k_{CR} is the C → R rate coefficient, and k_{RC} is the pseudo first-order R → C rate coefficient. The superscripts on the ΔX's in eq 54 indicate the reactant, i.e., the initial condition, in the calculation. Note that the second substitutions in these equations are valid only if *all* the reaction occurs through $|g_1\rangle$.

Since k_{RC} is pseudo first order, $k_{RC} = k_{add} n_m$ and we have

$$\frac{k_{RC}}{k_{CR}} = \frac{k_{add} n_m}{k_d} = \frac{X_C(\infty)}{X_R(\infty)}, \tag{55}$$

or

$$\frac{k_{add}}{k_d} = \frac{X_C(\infty)}{n_m X_R(\infty)} = \frac{n_C(\infty)}{n_m n_R(\infty)} = K_{eq}. \tag{56}$$

Note that in the second substitution, even though the rate coefficients were calculated for different initial conditions, they are presumed to be universally valid. Therefore, in any particular case, we can multiply both numerator and denominator by the appropriate normalization constant. Thus, we find that detailed balance is satisfied, at least under the assumptions employed. However, it should be clear that *this result is predicated on there being no reaction from the higher eigenvectors*. Otherwise, the second substitution in eqs 54 is not valid.

A more satisfactory approach to the rate-coefficient problem is the "long-time" method of Klippenstein and Miller.[19,20] Note that eqs 53 are valid after all the $e^{\lambda_j t}(j \geq 2)$ terms have died out, regardless of whether these terms bring about any chemical change. The only requirement for their validity is that λ_1 has not yet been absorbed in the continuum of IE- relaxation eigenvalues[20] (not necessarily $|\lambda_1| \ll |\lambda_2|$), in which case there will be a time period, perhaps very short and perhaps only late during the course of the reaction, but before equilibrium is attained, where eqs 53 are applicable. This last phase of the reaction may be responsible for only a small fraction of the chemical change.

We can write eqs 53 as

$$\begin{aligned} X_C(t) &= a_{11} + a_{12} e^{\lambda_1 t} \\ X_R(t) &= a_{21} + a_{22} e^{\lambda_1 t} \end{aligned} \tag{57}$$

and regard the coefficients a_{ij} as elements of a matrix A

$$A = \begin{bmatrix} a_{11} & a_{12} \\ a_{21} & a_{22} \end{bmatrix} = \begin{bmatrix} X_C(\infty) & -\Delta X_{C_1} \\ X_R(\infty) & -\Delta X_{R_1} \end{bmatrix} \tag{58}$$

whose inverse is B

$$B = A^{-1} = \begin{bmatrix} b_{11} & b_{12} \\ b_{21} & b_{22} \end{bmatrix} = \begin{bmatrix} a_{22}/d_A & -a_{12}/d_A \\ -a_{21}/d_A & a_{11}/d_A \end{bmatrix} \tag{59}$$

where $d_A = a_{11}a_{22} - a_{12}a_{21}$ is the determinant of A. The long-time method recognizes that eqs 57 (or 53) are the *unique solution* to a system of first-order rate equations whose rate coefficients are

$$k_{CR} = \lambda_1 a_{22} b_{21}$$

and (60)

$$k_{RC} = \lambda_1 a_{12} b_{22}$$

Using the conservation condition, $\Delta X_{R_1} = -\Delta X_{C_1}$, d_A becomes $d_A = \Delta X_{C_1} = -\Delta X_{R_1}$, and we get

$$\begin{aligned} k_{CR} &= \lambda_1 \Delta X_{C_1} \left[\frac{-X_R(\infty)}{X_C(\infty)\Delta X_{C_1} - (-\Delta X_{C_1})X_R(\infty)} \right] \\ &= -\lambda_1 \frac{X_R(\infty)}{X_C(\infty) + X_R(\infty)}, \end{aligned}$$

or $k_{CR} = -\lambda_1 X_R(\infty)$, since $X_C(\infty) + X_R(\infty) = 1$. Similarly,

$$k_{\mathrm{RC}} = \lambda_1(-\Delta X_{\mathrm{C}_1})\frac{X_{\mathrm{C}}(\infty)}{\Delta X_{\mathrm{C}_1}}$$
$$= -\lambda_1 X_{\mathrm{C}}(\infty).$$

These expressions for k_{CR} and k_{RC} are identical to those given in eq 54. Thus we deduce that the rate coefficients calculated by this method satisfy the detailed-balance condition, eq 1. It follows that, as long as IE relaxation is complete before chemical relaxation is complete (not necessarily $|\lambda_1| \ll |\lambda_2|$), the concentrations of R and C obey phenomenological rate equations with rate coefficients that satisfy detailed balance. The period of time during which this occurs before equilibrium is achieved may be extremely small, i.e., the fraction of the reactant consumed during this period may be small, but there will always exist a rate-coefficient period during which detailed balance is satisfied.

Before we close out our discussion of this method of treating the reversible association/dissociation problem, we want to establish one last result. Consider a "recombination experiment" in which initially there is only R. The long-time, pseudo first-order, addition rate coefficient is given by

$$k_{\mathrm{RC}} = n_{\mathrm{m}}k_{\mathrm{add}} = -\lambda_1 X_{\mathrm{C}}(\infty)$$
$$= -\lambda_1\sum_{j=1}^{N}\Delta X_{\mathrm{C_j}}^{(\mathrm{R})}$$
$$= \lambda_1\sum_{\mathrm{j=1}}^{\mathrm{N}}\Delta \mathrm{X}_{\mathrm{R_j}}^{(\mathrm{R})} \qquad (61)$$

Thus, the contribution to the long-time addition rate coefficient of each eigenpair is directly proportional to its contribution to the overall change in composition.

IV. Association/Dissociation Problem: Inhomogeneous Treatment

There are 2 ways of treating the association/dissociation problem mathematically. As we did in the last section, one can absorb $\mathrm{X_R}$ into the vector of unknowns and create a system of *homogeneous* differential equations. Alternatively, one may take the last term on the RHS of eq 43 as a source term, or inhomogeneity, in the master equation. The first method is superior for practical calculations and is easily generalizable to multiple-well problems; it has the advantage of treating bimolecular fragments and stabilized adducts as equals in calculating thermal rate coefficients.[19−24] However, the source-term method has been employed several times in the past.[1,2,24−26] In fact, it is the method used by Smith et al.[1,2] in the work discussed in the Introduction of this article. This method, when viewed in conjunction with the results discussed above, can yield important insights into the association/dissociation problem.

Starting with eq 44, we write the integral as a discrete sum with constant energy interval δE, and multiply through by δE. The ME then can be written in the vector form,

$$\frac{\mathrm{d}|y\rangle}{\mathrm{d}t} = G'|y\rangle + \left[\frac{K_{\mathrm{eq}}}{Q(T)}\right]|\varphi\rangle n_{\mathrm{m}}X_{\mathrm{R}}(t), \qquad (62)$$

where the components of $|\varphi\rangle$ are

$$\varphi_i = k(E_i)f(E_i)\delta E. \qquad (63)$$

Following Smith et al. (and Schranz and Nordholm[25] before them), we can use the vector equivalent of an integrating factor to solve eq 62, viz

$$|y(t)\rangle = \mathrm{e}^{G't}\left(\int_0^t \mathrm{e}^{-G's}\frac{K_{\mathrm{eq}}}{Q(T)}|\varphi\rangle n_{\mathrm{m}}X_{\mathrm{R}}(s)\,\mathrm{d}s + |y(0)\rangle\right).$$

Consistent with our general approach of viewing the reaction from the addition direction, we can take $|y(0)\rangle = |0\rangle$. However, ultimately we will derive a rate equation analogous to eq 3, which should not depend on initial conditions anyway. Then we have

$$|y(t)\rangle = \frac{K_{\mathrm{eq}}}{Q}\int_0^{\mathrm{t}} \mathrm{e}^{G'(t-s)}|\varphi\rangle n_{\mathrm{m}}X_{\mathrm{R}}(s)\,\mathrm{d}s, \qquad (64)$$

where the operator $\mathrm{e}^{G'(t-s)}$ operates on $|\varphi\rangle$. Continuing to follow Smith et al., we expand $|\varphi\rangle$ in terms of the eigenvectors of G', using the $|\psi_j\rangle$'s instead of the $|\mathrm{g_j}\rangle$'s even though the former are not normalized and depend on the initial conditions. Then

$$|\varphi\rangle = \sum_{j=1}^{N}\beta_j|\psi_j\rangle,$$

where

$$\beta_j = \frac{\langle\psi_j|\varphi\rangle}{\langle\psi_j|\psi_j\rangle}, \qquad (65)$$

and eq 64 becomes

$$|y(t)\rangle = \frac{K_{\mathrm{eq}}}{Q}\sum_{j=1}^{N}\int_0^t \mathrm{e}^{\xi_j(t-s)}\beta_j|\psi_j\rangle n_{\mathrm{m}}X_{\mathrm{R}}(s)\,\mathrm{d}s,$$

or

$$|x(t)\rangle = \frac{K_{\mathrm{eq}}}{Q}\sum_{j=1}^{N}\beta_j|\mathrm{c}_j\rangle\int_0^t \mathrm{e}^{\xi_j(t-s)}n_{\mathrm{m}}X_{\mathrm{R}}(s)\,\mathrm{d}s, \qquad (66)$$

where $|\mathrm{c}_j\rangle$, of course, refers to the irreversible dissociation problem discussed in section II.

Now let us calculate β_j. Using the relationships introduced in section II, we have

$$\langle\psi_j|\psi_j\rangle = \sum_{i=1}^{N}\frac{c_j^{\,2}(E_i)(\delta E)^2}{f^2(E_i)}$$

and

$$\langle\psi_j|\varphi\rangle = \sum_{i=1}^{N}\frac{c_j(E_i)k(E_i)f(E_i)(\delta E)^2}{f(E_i)}$$
$$= \bar{k}_j\delta E\sum_{i=1}^{N}c_j(E_i)\delta E.$$

Thus β_{j} reduces to

$$\beta_j = \frac{\bar{k}_j\sum_{i=1}^{N}c_{ij}}{\sum_{i=1}^{N}c_{ij}^{\,2}/(F_iQ)}, \qquad (67)$$

where $F_i = F(E_i)\delta E$. Substituting this expression for β_j into eq 66 and summing $|x(t)\rangle$ from eq 66 over all components, one obtains an expression for $X_{\mathrm{C}}(t)$,

$$X_{\mathrm{C}}(t) = K_{\mathrm{eq}}\sum_{j=1}^{N}\bar{k}_j f_{\mathrm{ne}}^{(j)}\int_0^t \mathrm{e}^{\xi_j(t-s)} n_{\mathrm{m}} X_{\mathrm{R}}(s)\,\mathrm{d}s, \tag{68}$$

where

$$f_{\mathrm{ne}}^{(j)} \equiv \frac{\left(\sum_{i=1}^{N} c_{ij}\right)^2}{\sum_{i=1}^{N} c_{ij}^{\ 2}/F_i}. \tag{69}$$

Note that $f_{\mathrm{ne}}^{(j)}$ is a generalization of the f_{ne} discussed in the Introduction. In fact, if there is no contribution to reaction from the higher eigenvectors of G', $|c_1\rangle$ becomes the steady-state energy distribution during the *dissociation* process, $\sum_{i=1}^{N} c_{i1} = 1$, and $f_{\mathrm{ne}}^{(1)} = f_{\mathrm{ne}}$. We use f_{ne} and $f_{\mathrm{ne}}^{(1)}$ interchangeably in the following analysis. It is an extremely important parameter, but we defer a discussion of its physical significance until we have completed our derivation of the rate law.

It is convenient and physically appealing to write eq 68 as

$$X_{\mathrm{C}}(t) = \sum_{j=1}^{N} X_{\mathrm{C}}^{(j)}(t), \tag{70}$$

where

$$X_{\mathrm{C}}^{(j)} = K_{\mathrm{eq}}\,\bar{k}_j\, f_{\mathrm{ne}}^{(j)}\int_0^t \mathrm{e}^{\xi_j(t-s)} n_{\mathrm{m}} X_{\mathrm{R}}(s)\,\mathrm{d}s \tag{71}$$

is the contribution of the jth eigenpair of G' to the population of the addition product at time t during our recombination experiment. The flaw in the Smith, et al. analysis was to identify $X_{\mathrm{C}}(t)$ with $X_{\mathrm{C}}^{(1)}(t)$ under all conditions. Note that this is equivalent to assuming $f_{\mathrm{ne}}^{(j)} = 0$ for $j \geq 2$ and (to be shown below) $f_{\mathrm{ne}}^{(1)} \equiv f_{\mathrm{ne}} = 1$. We know, however, from the previous section that, even if there is substantial reaction that occurs as part of the IE relaxation process, i.e., $X_{\mathrm{C}}^{(j)} \neq 0$ for $j \geq 2$, there is still a period of time during which phenomenological rate laws apply and the detailed balance condition is satisfied. Consequently, we do not want to limit our discussion to the special case $X_{\mathrm{C}}(t) = X_{\mathrm{C}}^{(1)}(t)$.

Differentiating eq 68 with respect to time, using eqs 33 and 70, and rearranging, we arrive at

$$\frac{\mathrm{d}X_{\mathrm{C}}(t)}{\mathrm{d}t} = -k_{\mathrm{u}}X_{\mathrm{C}}(t) + \sum_{j=2}^{N}(\xi_j - \xi_1)X_{\mathrm{C}}^{(j)} + k_{\mathrm{u}}K_{\mathrm{eq}}n_{\mathrm{m}}X_{\mathrm{R}}(t)\left(\sum_{j=1}^{N}\frac{\bar{k}_j f_{\mathrm{ne}}^{(j)}}{k_{\mathrm{u}}}\right). \tag{72}$$

Up to this point our analysis is *exact*, i.e., equation 72 is an *exact consequence* of the master equation. We have not yet even invoked the assumption n_{m} = constant; eq 72 could equally well apply for $n_{\mathrm{m}} = n_{\mathrm{m}}(t)$. However, to make further progress we must evaluate $X_{\mathrm{C}}^{(j)}(t)$. We can do this, at least approximately, by integrating by parts if n_{m} = constant. This approximation, of course, is the same as that made in section III (i.e., pseudo first-order conditions). Integrating the integral in eq 71 by parts twice, we have

$$\int_0^t \mathrm{d}s\, \mathrm{e}^{\xi_j(t-s)} n_{\mathrm{m}}X_{\mathrm{R}}(s) = \frac{n_{\mathrm{m}}X_{\mathrm{R}}(t)}{|\xi_j|} - \frac{n_{\mathrm{m}}X_{\mathrm{R}}(0)}{|\xi_j|}\mathrm{e}^{\xi_j t} - \frac{n_{\mathrm{m}}}{|\xi_j|^2}\frac{\mathrm{d}X_{\mathrm{R}}(t)}{\mathrm{d}t} + \frac{n_{\mathrm{m}}}{|\xi_j|^2}\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t}(0)\mathrm{e}^{\xi_j t} + \frac{n_{\mathrm{m}}}{|\xi_j|^2}\mathrm{e}^{\xi_j t}\int_0^t \mathrm{e}^{-\xi_j s}\frac{\mathrm{d}X_{\mathrm{R}}{}^2(s)}{\mathrm{d}s^2}\mathrm{d}s. \tag{73}$$

This process of successively integrating by parts generates a power series in $(1/|\xi_j|)$. Terminating the series with the $(1/|\xi_j|^2)$ term results ultimately in a first-order correction to the rate coefficients in the small parameter ξ_1/ξ_j, $j \geq 2$. This approximation is adequate for our purposes. Nevertheless, we consider the complete series in the Appendix. Also, we consider only the long-time behavior of the solution, i.e., after the $\mathrm{e}^{\xi_j t}$ terms, $j \geq 2$, have died out. This approximation is consistent with obtaining analogues to the long-time rate coefficients discussed in the last section.

Then we have, for $j \geq 2$,

$$X_{\mathrm{C}}^{(j)}(t) \approx K_{\mathrm{eq}}n_{\mathrm{m}}\bar{k}_j f_{\mathrm{ne}}^{(j)}\left(\frac{X_{\mathrm{R}}(t)}{|\xi_j|} - \frac{1}{|\xi_j|^2}\frac{\mathrm{d}X_{\mathrm{R}}(t)}{\mathrm{d}t}\right).$$

Using eq 40, this becomes

$$X_{\mathrm{C}}^{(j)}(t) \approx K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}\left(X_{\mathrm{R}}(t) - \frac{1}{|\xi_j|}\frac{\mathrm{d}X_{\mathrm{R}}(t)}{\mathrm{d}t}\right). \tag{74}$$

Note that here $K_{\mathrm{eq}}n_{\mathrm{m}}$ acts like an effective or pseudo first-order equilibrium constant. Now we can substitute eq 74 into eq 72 and obtain, again using eq 40,

$$\frac{\mathrm{d}X_{\mathrm{C}}(t)}{\mathrm{d}t} = -k_{\mathrm{u}}X_{\mathrm{C}}(t) + \sum_{j=2}^{N}(\xi_j - \xi_1)K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}\left[X_{\mathrm{R}}(t) - \frac{1}{|\xi_j|}\frac{\mathrm{d}X_{\mathrm{R}}(t)}{\mathrm{d}t}\right] + k_{\mathrm{u}}K_{\mathrm{eq}}n_{\mathrm{m}}X_{\mathrm{R}}(t)\left[f_{\mathrm{ne}}^{(1)} + \sum_{j=2}^{N}\frac{\bar{k}_j f_{\mathrm{ne}}^{(j)}}{k_{\mathrm{u}}}\right]. \tag{75}$$

We obtain the final form of our rate law by combining the $X_{\mathrm{R}}(t)$ term in the brackets with the last term on the RHS of eq 75, utilizing the conservation condition $\mathrm{d}X_{\mathrm{R}}(t)/\mathrm{d}t = -\mathrm{d}X_{\mathrm{C}}(t)/\mathrm{d}t$, and combining the resulting $\mathrm{d}X_{\mathrm{C}}(t)/\mathrm{d}t$ term on the RHS with the LHS (left-hand side) of eq 75. After simplifying and rearranging, eq 75 becomes

$$\frac{\mathrm{d}X_{\mathrm{C}}(t)}{\mathrm{d}t} = -k_{\mathrm{d}}X_{\mathrm{C}}(t) + k_{\mathrm{add}}n_{\mathrm{m}}X_{\mathrm{R}}(t), \tag{76}$$

i.e. the standard form for an association/dissociation reaction, where

$$k_{\mathrm{d}} = k_{\mathrm{u}}/\left[1 + K_{\mathrm{eq}}n_{\mathrm{m}}\sum_{j=2}^{N}\left(1 - \frac{\xi_1}{\xi_j}\right)f_{\mathrm{ne}}^{(j)}\right], \tag{77}$$

and

$$k_{\mathrm{add}} = k_{\mathrm{u}}K_{\mathrm{eq}}\left(\sum_{j=1}^{N} f_{\mathrm{ne}}^{(j)}\right)/\left[1 + K_{\mathrm{eq}}n_{\mathrm{m}}\sum_{j=2}^{N}\left(1 - \frac{\xi_1}{\xi_j}\right)f_{\mathrm{ne}}^{(j)}\right] \tag{78}$$

The rate coefficients given by eqs 77 and 78 are good to first

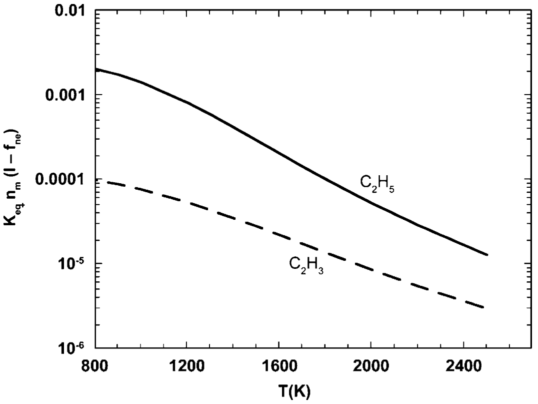

Figure 5. Small parameter, $\gamma \equiv K_{eq}n_m(1 - f_{ne})$, as a function of temperature for C_2H_3 and C_2H_5 dissociation at a pressure of $p = 30$ Torr and p_m ($= n_mk_BT$) of 1 Torr.

order in (ξ_1/ξ_j) for any j. Figures 1 and 2 show that such an approximation should be a reasonable representation of the C_2H_3 and C_2H_5 dissociations we have studied previously, so we shall use those reactions to illustrate our results. The rate coefficients given by eqs 77 and 78 have 2 immediate consequences:

1. Detailed balance is satisfied if, and only if,

$$\sum_{j=1}^{N} f_{\text{ne}}^{(j)} = 1. \tag{79}$$

We argue below that this must indeed always be the case in the rate-coefficient regime.

2. The dissociation rate coefficient k_d is approximately equal to k_u, the unimolecular rate coefficient for the *irreversible* dissociation problem ($k_u = -\xi_1$), if

$$K_{\text{eq}}n_{\text{m}}\sum_{j=2}^{N}\left(1 - \frac{\xi_1}{\xi_j}\right)f_{\text{ne}}^{(j)} \ll 1. \tag{80}$$

Let us look at the second condition first and assume that eq 79 is satisfied. Our goal is to provide a criterion for the applicability of $k_d = k_u$ that depends only on $|c_1\rangle$, and *not* on the higher eigenvectors. Then we have

$$\begin{aligned}\sum_{j=2}^{N}\left(1 - \frac{\xi_1}{\xi_j}\right)f_{\text{ne}}^{(j)} &\le (1 - f_{\text{ne}}^{(1)}) \\ &\le (1 - \text{f}_{\text{ne}}),\end{aligned} \tag{81}$$

and eq 80 becomes

$$\gamma \equiv K_{\text{eq}}n_{\text{m}}(1 - f_{\text{ne}}) \ll 1 \tag{82}$$

for the applicability of the substitution $k_d = k_u$. In Figure 5, we have plotted the parameter γ as a function of temperature for both C_2H_3 and C_2H_5 at a pressure of $p = 30$ Torr and $p_m = 1$ Torr, where $p_m = n_mk_BT$. This is a fairly typical condition. The plot shows clearly that indeed $\gamma_{C_2H_3}$ and $\gamma_{C_2H_5}$ are small compared to unity. The figure does not show results below 800 K, because f_{ne} becomes so close to 1 at low T that the difference $(1 - f_{ne})$ is unreliably small. Nevertheless, the indications are that both $\gamma_{C_2H_3}$ and $\gamma_{C_2H_5}$ flatten out and remain small at low temperatures.

Equations 77 and 78 show that both k_d and k_{add} have a weak composition dependence, i.e., dependence on n_m. Such a dependence was not anticipated, but it is confirmed by accurate calculations using the methods of section III. In any event, it seems safe to conclude that the condition given by eq 82 is a sufficient condition for the applicability of $k_d = k_u$. One probably makes virtually no error in identifying k_d with k_u under any ordinary experimental condition.

From eq 78 one can see that $f_{\text{ne}}^{(j)}$ is at least proportional to the fractional contribution of the jth eigenvector of G' to the addition rate coefficient. Since under "normal" conditions, $f_{\text{ne}}^{(1)} = 1$, it seems reasonable to conjecture that the other $f_{\text{ne}}^{(j)}$'s are normally zero and compensate to satisfy eq 79 when f_{ne} begins to deviate from unity. Moreover, we can write $f_{\text{ne}}^{(j)}$ as

$$f_{\text{ne}}^{(j)} = \frac{\left(\sum_{i=1}^{N}\Delta x_{ij}\right)^2}{\sum_{i=1}^{N}(\Delta x_{ij})^2/F_i} = \frac{(\Delta X_{C_j})^2}{\sum_{i=1}^{N}(\Delta x_{ij})^2/F_i}. \tag{83}$$

As discussed in section II, it is most common that virtually all of the dissociation of C comes from $j = 1$. In such cases $\Delta X_{C_1} = -1$, and $f_{\text{ne}}^{(1)}$ is extremely close to unity. If $\Delta X_{C_1} \neq -1$, there must be some compensation from other eigenvectors, because the condition

$$\sum_{j=1}^{N}\Delta X_{C_j} = -1 \tag{84}$$

must always be rigorously satisfied. Equation 83 shows, at least qualitatively, that the $f_{\text{ne}}^{(j)}$'s will have a similar compensating effect. In fact, one might take eq 79 to be the analogue of the conservation condition, eq 84, for the recombination rate coefficient. That is, eq 79 is to recombination what eq 84 is to irreversible dissociation.

In section III, we showed that the long-time rate coefficients always satisfy detailed balance as long as such rate coefficients can be reasonably defined. Comparison of those results with the ones given here provide compelling evidence that eq 79 is satisfied under the same conditions. Let us make a quantitative comparison between the 2 methods.

The analysis at the end of section III indicates that the fraction of the long-time recombination rate coefficient provided by $j = 1$ is $\Delta X_{C_1}^{(R)}/X_C(\infty)$, whereas the analysis of this section indicates that the same fraction is given by $f_{\text{ne}}^{(1)} = f_{ne}$. Even though the eigenvectors of G and G' are mathematically different, as emphasized above, in both cases $j = 1$ corresponds (nominally) to chemical reaction and $j \geq 2$ corresponds to IE relaxation. That is, even though the $j = 1$ eigenvectors in the 2 cases are formally different, they are physically equivalent. This suggests strongly that $f_{ne} = \Delta X_{C_1}^{(R)}/X_C(\infty)$.

We compare these two quantities for C_2H_3 and C_2H_5 under a variety of conditions in Table 1. The agreement is remarkably good, probably within the numerical uncertainty of the calculations. This result provides quantitative confirmation of our interpretation of f_{ne} as the fraction of the association rate coefficient contributed by $|g_1'\rangle$, or $|c_1\rangle$. More importantly, perhaps, $1 - f_{ne}$ is the fractional contribution of the IE − relaxation eigenpairs to the long-time association rate coefficient. If $f_{ne} \neq 1$, chemical reaction will take place as part of the internal-energy relaxation process. Thus, f_{ne} is an important physical quantity characterizing association/dissociation reactions, but its deviation from unity does not indicate that detailed balance is not satisfied. Detailed balance is always satisfied as long as one can rationally define phenomenological rate coefficients.

TABLE 1

T(K)	f_{ne}	$\Delta X^{\mathrm{R}}_{\mathrm{C}_1}/X_{\mathrm{C}}(\infty)$
C_2H_3 $p = 30$ Torr $p_{\mathrm{m}} = 1$ Torr		
1000	1.000	1.000
1200	0.998	0.998
1500	0.977	0.974
1800	0.907	0.900
2000	0.831	0.820
2200	0.739	0.726
2500	0.592	0.578
C_2H_5 $p = 30$ Torr $p_{\mathrm{m}} = 1$ Torr		
1000	0.999	0.999
1200	0.989	0.989
1500	0.908	0.905
1800	0.726	0.721
2000	0.581	0.575
2200	0.444	0.438
2500	0.278	0.274
C_2H_3 $p = 30$ Torr $p_{\mathrm{m}} = 10^{-2}$ Torr		
1000	0.998	0.998
1200	0.982	0.980
1500	0.872	0.866
1800	0.663	0.653
2000	0.551	0.502
2200	0.376	0.368
2500	0.224	0.218

A point that has been implicitly assumed in the foregoing discussion is that f_{ne} is independent of scaling. For example, if a large amount of dissociation occurs through $j \geq 2$ in the irreversible dissociation problem, $\sum_{i=1}^{N} c_{i1} \neq 1$, and the interpretation of f_{ne} given in the Introduction would appear not to be strictly correct. However, one can see clearly from the definition of f_{ne} that we can always multiply $|c_1\rangle$ by any constant (forcing $\sum_{i=1}^{N} c_{i1} = 1$, and thus establishing the interpretation of $|c_1\rangle$ as a steady-state energy distribution) without changing the value of f_{ne}. Thus, f_{ne} can be viewed as a property of the steady-state energy distribution of the dissociating molecule even when substantial dissociation comes from the IE-relaxation eigenvectors.

To summarize qualitatively, the parameter f_{ne} is a measure of the deviation from equilibrium of the steady-state distribution that emerges during the last stages of dissociation in the irreversible dissociation problem. The deviation of f_{ne} from unity is an indication that reaction is interfering with the collisional processes that try to establish the equilibrium distribution. This happens when the temperature is raised to the point where the peak of the thermal (equilibrium) energy distribution is sufficiently close to the dissociation threshold that the populations of states that are highly populated at equilibrium are affected by the process. Of course, a value of $f_{\mathrm{ne}} < 1$ indicates that some dissociation occurs as a consequence of the fast eigenmodes, i.e., those nominally associated with vibrational/rotational relaxation. Such rapid dissociation perturbs the steady-state distribution that evolves at long times. In more quantitative terms, if $\Delta X_{\mathrm{C}_1} = -1$, essentially all the dissociation takes place through the slowest relaxing eigenmode of the transition matrix, and the steady-state distribution that emerges at long times is very close to the equilibrium distribution, as indicated by $f_{\mathrm{ne}} = 1$. If $\Delta X_{\mathrm{C}_1} \neq -1$, the steady-state distribution will deviate significantly from equilibrium, making $f_{\mathrm{ne}} < 1$.

This coupling of IE relaxation and dissociation manifests itself in the association rate coefficient as a distribution of the $f^{(j)}_{\mathrm{ne}}$'s such that $f^{(1)}_{\mathrm{ne}} \neq 1$. However, the $f^{(j)}_{\mathrm{ne}}$'s are constrained by nature to satisfy eq 79 and ensure that detailed balance is satisfied.

V. Concluding Remarks

In this article, we have approached the association/dissociation problem from 2 different perspectives and arrived at some important conclusions.

1. As long as the characteristic time for vibrational/rotational relaxation, τ_{v}, is smaller than that for reaction, τ_{r}, i.e., $\tau_{\mathrm{v}} < \tau_{\mathrm{r}}$ and not necessarily $\tau_{\mathrm{v}} \ll \tau_{\mathrm{r}}$, there will be a time period (perhaps only late in the reaction) during which a phenomenological description of the kinetics will apply, and the associated rate coefficients will satisfy detailed balance, eq 1. This is true even if only a small fraction of the initial reactant is consumed during this period.

2. The nonequilibrium parameter f_{ne}, originally introduced by Smith et al.,[1,2] does not measure the degree to which detailed balance is satisfied. Instead, it represents the contribution of the slowest relaxing eigenmode of the system to the long-time association rate coefficient. The quantity $1 - f_{\mathrm{ne}}$ thus represents the contribution to the same rate coefficient of the internal-energy relaxation modes.

3. The long-time dissociation rate coefficient, k_{d}, is equal to that obtained from the irreversible dissociation problem, $k_{\mathrm{u}} = -\xi_1$, at least under conditions where $K_{\mathrm{eq}} n_{\mathrm{m}}(1 - f_{\mathrm{ne}}) \ll 1$, which is satisfied under almost all ordinary experimental conditions. Thus, we find that the standard procedure of calculating the dissociation rate coefficient from the steady-state distribution obtained from the master equation for irreversible association, then calculating the reverse association rate coefficient from detailed balance, is valid as long as one interprets the rate coefficients correctly. The parameter f_{ne}, obtained from the same steady-state distribution, provides important information about the degree of coupling between reaction and internal-energy relaxation.

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Appendix

In this appendix, we want to show that higher-order terms in the expansion of $X^{(j)}_{\mathrm{C}}(t)$ in powers of $(1/\xi_j)$, eq 74, do not change the conclusions drawn in section IV. If we continue to integrate by parts in eq 73 and neglect the $e^{\xi_j t}$ terms, we get

$$X^{(j)}_{\mathrm{C}}(t) = K_{\mathrm{eq}} n_{\mathrm{m}} f^{(j)}_{\mathrm{ne}} [X_{\mathrm{R}}(t) + \frac{1}{\xi_j}\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t} + \frac{1}{\xi_j^{\,2}}\frac{\mathrm{d}^2 X_{\mathrm{R}}}{\mathrm{d}t^2} + ...$$

$$= K_{\mathrm{eq}} n_{\mathrm{m}} f^{(j)}_{\mathrm{ne}} \left[X_{\mathrm{R}}(t) + \sum_{n=1}^{\infty} \frac{1}{\xi_j^{n}} \frac{\mathrm{d}^n X_{\mathrm{R}}}{\mathrm{d}t^n} \right]. \qquad (A.1)$$

To evaluate the *second and higher derivatives* in eq A.1, we make use of only the dominant terms in $\mathrm{d}X_{\mathrm{R}}/\mathrm{d}t$,

$$\begin{aligned}\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t} &= -\frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t} = k_{\mathrm{d}}X_{\mathrm{C}} - k_{\mathrm{d}}K_{\mathrm{eq}}n_{\mathrm{m}}X_{\mathrm{R}} \\ &\approx -\xi_1 X_{\mathrm{C}} + \xi_1 K_{\mathrm{eq}}n_{\mathrm{m}}X_{\mathrm{R}} = -\xi_1(X_{\mathrm{C}} - K_{\mathrm{eq}}n_{\mathrm{m}}X_{\mathrm{R}}).\end{aligned} \tag{A.2}$$

Then we can approximate the higher order derivatives of X_{R} as

$$\frac{\mathrm{d}^n X_{\mathrm{R}}}{\mathrm{d}t^n} = -\xi_1^{n-1}(1 + K_{\mathrm{eq}}n_{\mathrm{m}})^{n-1}\frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t} \tag{A.3}$$

for $n \geq 2$.

Using these results one can evaluate the second term on the RHS of eq 72 as

$$\begin{aligned}\sum_{j=2}^{N}(\xi_j - \xi_1)\, X_{\mathrm{C}}^{(j)} &= \sum_{j=2}^{N}(\xi_j - \xi_1)\, K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}X_{\mathrm{R}} + \\ &\sum_{j=2}^{N}(\xi_j - \xi_1)\, K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}\left[-\frac{1}{\xi_j} - \sum_{n=2}^{\infty}\frac{\xi_1^{n-1}}{\xi_j^{n}}(1 + K_{\mathrm{eq}}n_{\mathrm{m}})^{n-1}\right]\frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t}.\end{aligned} \tag{A.4}$$

The term in this equation involving X_{R} goes through as before. However, we can now evaluate the coefficient of $\mathrm{d}X_{\mathrm{C}}/\mathrm{d}t$ corresponding to the jth eigenvalue of G' in closed form, and thus get a somewhat better approximation to k_{d} and k_{add} than we obtained in the main text of this article,

$$\begin{aligned}K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}(\xi_j - \xi_1)&\left[-\frac{1}{\xi_j} - \sum_{n=2}^{\infty}\frac{\xi_1^{n-1}}{\xi_j^{n}}(1 + K_{\mathrm{eq}}n_{\mathrm{m}})^{n-1}\right] \\ &= -K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}\left(\frac{\xi_j - \xi_1}{\xi_j}\right)\left[1 + \sum_{n=1}^{\infty}\left(\frac{\xi_1}{\xi_j}\right)^{n}(1 + K_{\mathrm{eq}}n_{\mathrm{m}})^{n}\right] \\ &= -K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}\left(\frac{\xi_j - \xi_1}{\xi_j}\right)\sum_{n=0}^{\infty}\left(\frac{\xi_1}{\xi_j}\right)^{n}(1 + K_{\mathrm{eq}}n_{\mathrm{m}})^{n}.\end{aligned} \tag{A.5}$$

As long as $(1 + K_{\mathrm{eq}}n_{\mathrm{m}})(\xi_1/\xi_j) < 1$, which generally is the case, the series in A.5 converges to $1/(1 - (1 + K_{\mathrm{eq}}n_{\mathrm{m}})\xi_1/\xi_j)$. Substituting these results back into eq A.4 and simplifying one obtains

$$\begin{aligned}\sum_{j=2}^{N}(\xi_j - \xi_1)X_{\mathrm{C}}^{(j)} &= \sum_{j=2}^{N}(\xi_j - \xi_1)K_{\mathrm{eq}}n_{\mathrm{m}}f_{\mathrm{ne}}^{(j)}X_{\mathrm{R}} - \\ &K_{\mathrm{eq}}n_{\mathrm{m}}\frac{\mathrm{d}X_{\mathrm{C}}}{\mathrm{d}t}\sum_{j=2}^{N}\left[\frac{f_{\mathrm{ne}}^{(j)}}{1 - (K_{\mathrm{eq}}n_{\mathrm{m}}\xi_1/\xi_j)/\left(1 - \dfrac{\xi_1}{\xi_j}\right)}\right].\end{aligned} \tag{A.6}$$

Using eq A.6 in eq 72 and carrying through the derivation as before, we get the following expressions for the rate coefficients k_{d} and k_{add}:

$$k_{\mathrm{d}} = k_{\mathrm{u}}/\left\{1 + K_{\mathrm{eq}}n_{\mathrm{m}}\sum_{j=2}^{N}\left[\frac{f_{\mathrm{ne}}^{(j)}}{1 - (K_{\mathrm{eq}}n_{\mathrm{m}}\xi_1/\xi_j)/\left(1 - \dfrac{\xi_1}{\xi_j}\right)}\right]\right\} \tag{A.7}$$

and

$$k_{\mathrm{add}} = k_{\mathrm{u}}K_{\mathrm{eq}}\left(\sum_{j=1}^{N}f_{\mathrm{ne}}^{(j)}\right)/\left\{1 + K_{\mathrm{eq}}n_{\mathrm{m}}\sum_{j=2}^{N}\left[\frac{f_{\mathrm{ne}}^{(j)}}{1 - (K_{\mathrm{eq}}n_{\mathrm{m}}\xi_1/\xi_j)/\left(1 - \dfrac{\xi_1}{\xi_j}\right)}\right]\right\}. \tag{A.8}$$

As expected, the higher-order terms in our expansion A.1 change k_{d} and k_{add} by the same factor, so that detailed balance is still satisfied. Moreover, it is almost always the case that

$$\frac{K_{\mathrm{eq}}n_{\mathrm{m}}\dfrac{\xi_1}{\xi_j}}{1 - \xi_1/\xi_j} \ll 1 \tag{A.9}$$

Let us use our results on C_2H_5 dissociation and recombination with $p = 30$ Torr and $p_{\mathrm{m}} = 1$ Torr to illustrate this point. At 400 K, $K_{\mathrm{eq}}n_{\mathrm{m}} \approx 10^{12}$ but $(\xi_1/\xi_2) \approx 10^{-14}$, whereas at 2000 K, $K_{\mathrm{eq}}n_{\mathrm{m}} \approx 10^{-4}$and $(\xi_1/\xi_2) \approx 0.1$. In both cases A.9 is satisfied, as it seems virtually always to be. (Note that these numbers also confirm that the geometric series in eq A.5 converges in these cases.) With the approximation A.9, the denominator in the 2 rate coefficient expressions becomes

$$\begin{aligned}1 + K_{\mathrm{eq}}n_{\mathrm{m}}\sum_{j=2}^{N}f_{\mathrm{ne}}^{(j)} &= 1 + K_{\mathrm{eq}}n_{\mathrm{m}}(1 - f_{\mathrm{ne}}) \\ &= 1 + \gamma,\end{aligned}$$

where γ is the same small parameter we discussed in the main text of the article.

References and Notes

(1) Smith, S. C.; McEwan, M. J.; Gilbert, R. J. *J. Chem Phys.* **1989**, *90*, 4265−4273.

(2) Gilbert, R. G.; Smith, S. C. *Theory of Unimolecular and Recombination Reactions*; Blackwell Scientific Publications: Oxford, U.K., 1990; Chapter 6.

(3) Miller, J. A.; Klippenstein, S. J.; Raffy, C. *J. Phys. Chem.* **2002**, *106*, 4904−4913.

(4) Miller, J. A.; Klippenstein, S. J. *Phys Chem. Chem. Phys.* **2004**, *6*, 1192−1202.

(5) Rice, O. K. *J. Phys. Chem.* **1961**, *65*, 1972−1976.

(6) Rice, O. K. *J. Phys. Chem.* **1963**, *67*, 1733−1735.

(7) Nikitin, E. E.; Sokolov, N. D. *J. Chem. Phys.* **1959**, *31*, 1371−1375.

(8) Pritchard, H. O. *J. Phys. Chem.* **1961**, *65*, 504−510.

(9) Pritchard, H. O. *J. Phys. Chem.* **1962**, *66*, 2111−2113.

(10) Keck, J. C.; Carrier, G. F. *J. Chem. Phys.* **1965**, *43*, 2284−2298.

(11) Widom, B. *Science* **1965**, *148*, 1555−1560.

(12) Snider, N. S. *J. Chem. Phys.* **1965**, *42*, 548.

(13) Pyun, C. W.; Ross, J. *J. Chem. Phys.* **1964**, *40*, 2572.

(14) Nikitin, E. E. *Kinetika i Kataliz* **1962**, *3*, 830.

(15) Widom, B. *J. Chem. Phys.* **1961**, *34*, 2050−2056.

(16) Polanyi, J. C. *J. Chem. Phys.* **1959**, *31*, 1338.

(17) Smith, S. C.; McEwan, M. J.; Brauman, J. I., *J. Phys. Chem. A* **1997**, *101*, 7311−7314.

(18) Tsang, W.; Bedanov, V.; Zachariah, M. R. *J. Phys. Chem.* **1996**, *100*, 4011−4018.

(19) Klippenstein, S. J.; Miller, J. A. *J. Phys. Chem. A* **2002**, *106*, 9267−9277.

(20) Miller, J. A.; Klippenstein, S. J. *J. Phys. Chem. A* **2003**, *107*, 2680−2692.

(21) Miller, J. A.; Klippenstein, S. J.; Robertson, S. H. *J. Phys. Chem. A* **2000**, *104*, 7525−7536; see also *J. Phys. Chem. A* **2000**, *104*, 9806.

(22) Miller, J. A.; Klippenstein, S. J.; Robertson, S. H. *Proc. Combust. Inst.* **2000**, *28*, 1479−1486.

(23) Miller, J. A.; Klippenstein, S. J. *Int. J. Chem. Kinet.* **2001**, *33*, 654−668.

(24) Pilling, M. J.; Robertson, S. H. *Annual Rev. Phys. Chem.* **2003**, *54*, 245−275.

(25) Schranz, H. W.; Nordholm, S. *Chem. Phys.* **1984**, *87*, 163.

(26) Knyazev, V. D.; Tsang, W. *J. Phys. Chem. A* **1999**, *103*, 3944−3954.