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From the Time-Dependent, Multiple-Well Master Equation to Phenomenological Rate Coefficients

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We discuss at some length the relationship between solutions to the time-dependent, multiple-well master equation and a macroscopic description of the chemistry in terms of phenomenological rate coefficients. In so doing, we derive two different methods of obtaining the rate coefficients from the eigenvalues and eigenvectors of **G**, the transition matrix of the master equation. We apply the first of the two methods to the $C_2H_3 + C_2H_2$ and $C_3H_3 + C_3H_3$ reactions, problems we have treated previously using the "experimental" (or exponential-decay) approach, and obtain considerably more and somewhat different results than we obtained in our earlier work.

I. Introduction

Many reactions in combustion, particularly those involved in the formation of aromatic compounds, polycyclic aromatic compounds (PAH), and soot, are complicated processes that take place over multiple, interconnected potential wells.[1] Such reactions may be chemically activated, or they may be thermal dissociation/isomerization processes. Some of the former are "collisionless" in that the intermediate complexes are so short-lived that they effectively do not suffer any collisions under conditions that are normally of interest. Such reactions typically involve a small number of atoms and relatively shallow potential wells, resulting in small densities of states. The reaction between NH_2 and NO is the classic example of such a "collisionless" reaction.[1−3] However, intermediate complexes more commonly live long enough to suffer numerous collisions.[1,4] In such cases, any of a number of stabilized or bimolecular products may result. For such reactions, it is necessary to solve the time-dependent, multiple-well master equation in all its complexity in order to predict rate constants and product distributions.[1,4−17] However, obtaining rate-constant information from such an analysis has not proven to be a simple task.[4]

Let us illustrate concretely the issues involved in obtaining (product-specific) rate constants from solutions to the master equation in the general case. It is normally desirable to cast the master equation in the form

$$\frac{\mathrm{d}|w\rangle}{\mathrm{d}t} = \mathbf{G}|w\rangle \tag{1}$$

where $|w\rangle$ is a vector containing the populations of all of the relevant states and **G** is a real, symmetric matrix, the transition matrix of the master equation in this form. The solution to eq 1 can be written as

$$|w(t)\rangle = \sum_{j=0}^{N} \mathrm{e}^{\lambda_j t}|g_j\rangle\langle g_j|w(0)\rangle \tag{2}$$

where $|w(0)\rangle$ contains the initial condition and $|g_j\rangle$ and λ_j are the eigenvectors and eigenvalues of **G**, i.e., $\mathbf{G}|g_j\rangle = \lambda_j|g_j\rangle$, $j = 0, ..., N$. The operator $\hat{\mathrm{T}} = \sum_{j=0}^{N} \mathrm{e}^{\lambda_j t}|g_j\rangle\langle g_j|$ is the time evolution operator of the system − once the eigenvalues and eigenvectors of **G** are found, the time evolution of the state populations can be determined from eq 2 for *any* initial condition by operating on $|w(0)\rangle$ with $\hat{\mathrm{T}}$.

Typically, N (or $N + 1$) is a very large number. However, under conditions where one might expect to be able to define rate constants, only the "normal modes of relaxation" corresponding to algebraically the largest eigenvalues of **G** (i.e., the least negative ones) describe chemical changes.[18−23] The remainder describe the relaxation of the internal degrees of freedom of the chemical species under consideration. These latter degrees of freedom normally (but not always) relax much more rapidly than the chemical ones. Such a separation of time scales is generally thought to be a necessary condition for a phenomenological description of the chemistry to apply,[18−22] i.e., a description in terms of phenomenological rate constants and macroscopic rate laws. If there are S species, or chemical configurations, in a problem, there are

$$N_{\text{chem}} = S - 1 \tag{3}$$

chemically (or kinetically) significant eigenpairs (CSE's) of **G**[4] in addition to $\lambda_0 = 0$ and $|g_0\rangle$, which describe a state of complete thermal and chemical equilibrium. At least at low temperature, where the λ_j's are distinctly different in magnitude, each of the CSEs describes an "equilibration". The first of these normal modes to relax establishes chemical equilibrium between two species, although other products may be formed during the relaxation process. The second mode to relax describes the equilibration of these two species with a third, and so on. Clearly, it takes $S - 1$ such normal modes to relax the entire system to chemical equilibrium.

At the same time, for a problem with S distinct chemical configurations (or species), there are N_k forward rate constants, where

$$N_k = \sum_{n=1}^{S-1} n = \frac{S(S-1)}{2} \tag{4}$$

and an equal number of reverse rate constants or equilibrium constants.[4] If $S = 2$, i.e., one reactant and one product, both N_{chem} and N_k are equal to 1, and it is trivial to determine both

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the forward and reverse rate constants from λ_1, the lone chemically significant eigenvalue, and the equilibrium constant. However, if $S = 9$, as was the case in our recent investigation of the propargyl (C_3H_3) recombination reaction, $N_{\mathrm{chem}} = 8$ and $N_k = 36$! In the present article, we discuss how such rate constants are related to the CSEs in the general case. Specifically, we propose 2 methods of obtaining *all* of the rate constants in a given problem once **G** has been diagonalized at any temperature and pressure. We apply the first method to two problems that we have addressed previously, the $C_3H_3 + C_3H_3$ and $C_2H_3 + C_2H_2$ reactions, obtaining considerably more information than we were able to obtain before.

We should note at the outset that, in our previous work,[5−9] we have adopted the point of view of an experimental kineticist in looking for exponential decays of a "deficient" reactant in the time evolution of the system, associating such decay constants with pseudo-first-order rate constants and the products formed on the same time scale with the products of an elementary reaction. Of course, such an approach is valid and yields good rate constants as long as the chemically significant eigenvalues of **G** are well separated in magnitude. However, if the eigenvalues are close together (even within 1 or 2 orders of magnitude), the approach can be prone to error. This point is discussed below.

II. The Master Equation and Its Solution

For the purposes of the present discussion, it is useful to keep in mind a potential energy surface (PES) such as those shown diagrammatically in Figure 1 for C_2H_3+C_2H_2 and Figure 6 for C_3H_3+C_3H_3. The master equation for such problems takes the form of a set of coupled integro−differential equations:

$$\frac{\mathrm{d}n_i(E)}{\mathrm{d}t} = Z\int_{E_{0i}}^{\infty} P_i(E,E')n_i(E')\,\mathrm{d}E' - Zn_i(E) - \sum_{j\neq i}^{M} k_{ji}(E)n_i(E) + \sum_{j\neq i}^{M} k_{ij}(E)n_j(E) - k_{\mathrm{d}i}(E)n_i(E) + K_{\mathrm{R}i}k_{\mathrm{d}i}(E)F_i(E)n_{\mathrm{R}}n_{\mathrm{m}} - k_{\mathrm{p}i}(E)n_i(E) \quad (i = I, ..., M) \tag{5}$$

In these equations, t is the time, Z is the collision number per unit time, $n_i(E)\mathrm{d}E$ is the number density of molecules (or complexes) in well i with energy between E and $E + \mathrm{d}E$, E_{0i} is the ground-state energy for well i, M is the number of wells (three (III) in Figure 1 and seven (VII) in Figure 6), $P_i(E, E')$ is the probability that a molecule in well i with energy between E' and $E' + \mathrm{d}E'$ will be transferred by collision to a state with energy between E and $E + \mathrm{d}E$, $k_{ij}(E)$ is the microcanonical rate constant for isomerization from well j to well i, $k_{\mathrm{d}i}(E)$ and $k_{\mathrm{p}i}(E)$ are the microcanonical rate constants for dissociation from well i to the bimolecular "reactants" and products, respectively; n_{R} and n_{m} are the number densities, respectively, of the "deficient" and "excess" reactants, and $K_{\mathrm{R}i}$ is the equilibrium constant for stabilization of the reactants into well i. The function $F_i(E)$ is the equilibrium energy distribution in well i at temperature T:

$$F_i(\mathrm{E}) = \rho_i(E)\mathrm{e}^{-\beta E}/Q_i(\mathrm{T}) \tag{6}$$

where $Q_i(T)$ is the vibrational−rotational partition function for the ith well. In these definitions, and in the discussion below, we frequently refer to the bimolecular fragments on the left of Figures 1 and 6 as "reactants" and those on the right as "products", consistent with the terminology in our previous work, although either the bimolecular reactants or an isomer corresponding to any one of the wells may actually be the reactant in the results presented below. In any event, the bimolecular products are always assumed to be an "infinite sink", in which population can only accumulate and from which molecules can never return to the wells.

As in our previous work, we restrict ourselves to a situation in which the reacting species are highly dilute in an inert bath gas:

$$n_{\mathrm{B}} \gg n_{\mathrm{reac}} \tag{7}$$

where n_{B} is the number density of the bath gas (either N_2 or He in this work) and n_{reac} is the number density of the reactant, either n_{R} or that of one of the isomers of C_4H_5 shown in Figure 1 or of C_6H_6 shown in Figure 6. Generally we assume n_{m} to be of such a magnitude that the following inequalities hold:

$$n_{\mathrm{B}} \gg n_{\mathrm{m}} \gg n_{\mathrm{reac}} \tag{8}$$

However, for dissociation/isomerization processes, we could take $n_{\mathrm{m}} \ll n_{\mathrm{reac}}$ and still get the same results for rate constants.

The problem specification is completed by adding an equation for n_{R}:

$$\frac{\mathrm{d}n_{\mathrm{R}}}{\mathrm{d}t} = \sum_{i=I}^{M}\int_{E_{0i}}^{\infty} k_{di}(E)n_i(E)\,\mathrm{d}E - n_{\mathrm{R}}n_{\mathrm{m}}\sum_{i=I}^{M} K_{\mathrm{R}i}\int_{E_{0i}}^{\infty} k_{di}(E)F_i(E)\,\mathrm{d}E \tag{9}$$

Implicit in eq 9 is the assumption that the bimolecular reactants are maintained in thermal equilibrium throughout the course of the reaction even though the complexes are not.

As noted in the Introduction, it is convenient and useful to cast the problem posed by eqs 5 and 9 in a slightly different form.[5−9] First, let $X_{\mathrm{R}}(t) = n_{\mathrm{R}}(t)/n_{\mathrm{reac}}(0)$, $x_i(E,t) = n_i(E,t)/n_{\mathrm{reac}}(0)$, and $y_i(E,t) = x_i(E,t)/f_i(E)$, where $f_i^2(E) = F_i(E)Q_i(T)$. Then, after approximating the integrals in eqs 5 and 9 as discrete sums using the left-hand rectangle rule with an energy spacing δE, we can express them in the concise form given as eq 1 in the Introduction:

$$\frac{\mathrm{d}}{\mathrm{d}t}|w(t)\rangle = \mathbf{G}|w(t)\rangle$$

where $|w(t)\rangle$ is the vector

$$|w(t)\rangle = \left[y_I(E_{0I}), ...y_I(E_l), ...y_i(E_{0i}), ...y_i(E_l), ..., \left(\frac{n_{\mathrm{m}}}{Q_{\mathrm{Rm}}\delta E}\right)^{1/2} X_{\mathrm{R}}\right]^T \tag{10}$$

G is a real, symmetric matrix, and E_l in (10) is the energy of the lth grid point. Clearly, $|w(t)\rangle$ has $1 + \sum_{i=I}^{M} N_i$ components, where N_i is the number of grid points in the energy space of well i, and **G** is a square matrix of the same size.

From the solution vector at any time, one may obtain the relative macroscopic populations $X_{\mathrm{R}}(t)$, $X_{\mathrm{i}}(t)$, and $X_{\mathrm{p}}(t)$, where

$$X_i(t) = \int_{E_{0i}}^{\infty} x_i(E,t)\,\mathrm{d}E \tag{11}$$

and

$$X_{\mathrm{p}}(t) = 1 - X_{\mathrm{R}}(t) - \sum_{i=I}^{M} X_i(t) \tag{12}$$

The function $X_p(t)$ is the fraction of the initial reactant concentration that has formed bimolecular products at time t; obviously, it refers to either fragment. Equation 12 is a consequence of the conservation of mass; we impose it directly because the "infinite sink" approximation for the bimolecular products results in the removal of $X_p(t)$ from the vector of unknowns, $|w(t)\rangle$; thus, we must calculate $X_p(t)$ directly from eq 12.

As noted in the Introduction, the solution to eq 1 is

$$|w(t)\rangle = \sum_{j=1}^{N_I+...N_M+1} e^{\lambda_j t}|g_j\rangle\langle g_j|w(0)\rangle \tag{13}$$

Let us review some of the properties of this solution. Because **G** is Hermitian (real and symmetric), its eigenvectors are orthogonal, and its eigenvalues are real. However, not only are the λ_j's real, they must all be negative; otherwise the populations determined by eq 13 would go to infinity as $t \rightarrow \infty$. Note that the sum in eq 13 starts at $j = 1$ and not $j = 0$. The equilibrium eigenpair, λ_0 and $|g_0\rangle$, does not come out of our solution because of the "infinite sink" approximation. As a result, all of the terms in eq 13 go to zero as $t \rightarrow \infty$, and $X_p(\infty) = 1$ from eq 12. As long as no two of the λ_j's are equal, the terms in eq 13 are linearly independent functions of time. This result has important consequences. We can cast eq 12 in a different form by differentiating it with respect to time and then integrating it over some specific time interval, i.e.

$$\Delta X_R + \Delta X_p + \sum_{i=I}^{M} \Delta X_i = 0$$

Because of the linear independence of the terms in eq 13, this conservation law must apply not only globally but to each term individually.[22-23] Taking the time interval to be from $t = 0$ to $t = \infty$, we can write

$$\left(\Delta X_R + \Delta X_p + \sum_{i=I}^{M} \Delta X_i\right)_j = 0 \tag{14}$$

where the terms in this equation now refer to changes in relative concentrations of the various chemical components as a consequence of the time evolution of the jth eigenpair from $t = 0$ to $t = \infty$. In general, we are interested in applying this result only to the $(S - 1)$ chemically significant eigenpairs.

III. A Simple Method of Determining the Rate Coefficients

We are primarily interested in the rate constant regime, i.e., the regime where one can anticipate that a description of the chemistry in terms of macroscopic rate laws and phenomenological rate constants might apply. Consequently, we assume that the normal modes of **G** corresponding to relaxation of the internal energy relax much faster than the $S - 1$ modes that describe chemical change. Focusing on the chemical time scales, let us define λ_1 to be the largest eigenvalue of **G** (i.e., the least negative one), λ_2 to be the next largest, etc. Of course, $|g_1\rangle$, $|g_2\rangle$, ... are the corresponding eigenvectors. After the internal degrees of freedom have relaxed, the lth component of $|w(t)\rangle$ can be written as

$$w_l(t) = \sum_{j=1}^{N_{\rm chem}} e^{\lambda_j t} g_{jl} C_j^{(A)} \tag{15}$$

where g_{jl} is the lth component of the jth eigenvector of **G** and $C_j^{(A)} = \langle g_j|w_A(0)\rangle$ is the scalar product of $|g_j\rangle$ with the initial condition vector, $|w_A(0)\rangle$, corresponding to the "reactant" being A. For our purposes, $|w_A(0)\rangle$ always corresponds to a normalized Boltzmann distribution in well $A = I, ..., M$, or it corresponds to $X_R(0) = 1$.

First, consider the case where A corresponds to a well. Multiplying eq 15 by $f_i(E_l)$ and integrating (in discrete form) with respect to E over all l corresponding to well i ($i = I, ..., M$) results in

$$X_i(t) = \sum_{j=1}^{N_{\rm chem}} e^{\lambda_j t} C_j^{(A)} \delta E \sum_{l \in i} f_i(E_l) g_{jl} \tag{16}$$

Equation 16 can also be written as

$$X_i(t) = \sum_{j=1}^{N_{\rm chem}} e^{\lambda_j t}(-\Delta X_{ij}^{(A)}) \tag{17}$$

where

$$\Delta X_{ij}^{(A)} = -C_j^{(A)} \delta E \sum_{l \in i} f_i(E_l) g_{jl} \tag{18}$$

was defined above, except that now we have added the superscript A to distinguish different possible initial conditions. Differentiating eq 17 with respect to time, we get

$$\frac{dX_i}{dt} = \sum_{j=1}^{N_{\rm chem}} \lambda_j e^{\lambda_j t}(-\Delta X_{ij}^{(A)}) \tag{19}$$

Evaluating (19) at $t = 0$ yields the following result:

$$\frac{dX_i}{dt}(0) = -\sum_{j=1}^{N_{\rm chem}} \lambda_j \Delta X_{ij}^{(A)} \tag{19a}$$

Now, start with $i = A$ so that eq 19a applies to the reactant

$$\frac{dX_A}{dt}(0) = -\sum_{j=1}^{N_{\rm chem}} \lambda_j \Delta X_{Aj}^{(A)} \tag{20}$$

The macroscopic rate law that applies to X_A at $t = 0$ (when A is the reactant) is

$$\frac{dX_A}{dt}(0) = -k_{TA} X_A(0) \tag{21}$$

where k_{TA} is the total rate constant for removal of A. Comparing eqs 20 and 21 with $X_A(0) = 1$, we deduce a simple expression for k_{TA}

$$k_{TA} = \sum_{j=1}^{N_{\rm chem}} \lambda_j \Delta X_{Aj}^{(A)} \tag{22}$$

It should be kept in mind that macroscopic rate laws such as eq 21 do not actually apply at $t = 0$; instead, they refer to a time that is extremely short compared to the $S - 1$ chemical time scales but is long compared to the internal relaxation time scales.

Next, consider eq 19a with $i \neq A$ and compare it with the phenomenological rate law for X_i at $t = 0$ when A is the reactant:

$$\frac{\mathrm{d}X_i}{\mathrm{d}t}(0) = k_{Ai}X_A(0) = k_{Ai} \tag{23}$$

where k_{Ai} is the $A \rightarrow i$ rate constant. Equating the two expressions for $\mathrm{d}X_i(0)/\mathrm{d}t$, we get

$$k_{Ai} = -\sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta X_{ij}^{(A)} \tag{24}$$

If we want to calculate k_{AR}, the rate constant for producing bimolecular "reactants" from well A, we must consider eq 15 with $l = N_I + ... + N_M + 1$, i.e., the last component of the eigenvectors

$$\left(\frac{\mathrm{n_m}}{Q_{\mathrm{Rm}}\delta \mathrm{E}}\right)^{1/2} \mathrm{X_R(t)} = \sum_{\mathrm{j=1}}^{\mathrm{N_{chem}}} \mathrm{e}^{\lambda_j t} g_{jl} C_j^{(A)},$$

or

$$X_{\mathrm{R}}(t) = -\sum_{j=1}^{N_{\mathrm{chem}}} \mathrm{e}^{\lambda_j t} \Delta X_{\mathrm{R}j}^{(A)} \tag{25}$$

where

$$\Delta X_{\mathrm{R}j} = -\left(\frac{Q_{\mathrm{Rm}}\delta E}{n_{\mathrm{m}}}\right)^{1/2} g_{jl} C_j^{(A)} \tag{26}$$

As above, differentiating eq 25 with respect to time, evaluating the resulting expression at $t = 0$, and comparing that with the phenomenological rate law for X_{R} at $t = 0$, we get an expression for k_{AR} that is the same form as those derived above

$$k_{\mathrm{AR}} = -\sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta X_{\mathrm{R}j}^{(A)} \tag{27}$$

It should also be clear that one can calculate k_{Ap} from a similar expression

$$k_{Ap} = -\sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta X_{pj}^{(A)} \tag{28}$$

except that ΔX_{pj} must be evaluated from eq 14 with the other terms in (14) given by eqs 18 and 26.

If the reactant is R, the derivation of the rate constants is the same as those given above except that the phenomenological rate equations at $t = 0$ are

$$\frac{\mathrm{d}X_{\mathrm{R}}}{\mathrm{d}t}(0) = -k_{\mathrm{TR}} n_{\mathrm{m}} X_{\mathrm{R}}(0)$$

$$\frac{\mathrm{d}X_i}{\mathrm{d}t}(0) = k_{\mathrm{R}i} n_{\mathrm{m}} X_{\mathrm{R}}(0) \quad (i = I, ..., M) \tag{29}$$

and

$$\frac{\mathrm{d}X_p}{\mathrm{d}t}(0) = -k_{\mathrm{R}p} n_{\mathrm{m}} X_{\mathrm{R}}(0)$$

which results in the following expressions for the rate constants:

$$\begin{aligned} k_{\mathrm{TR}} &= \frac{1}{n_{\mathrm{m}}} \sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta X_{\mathrm{R}j}^{(\mathrm{R})} \\ k_{\mathrm{R}i} &= -\frac{1}{n_{\mathrm{m}}} \sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta \mathrm{X}_{ij}^{(\mathrm{R})} \\ k_{\mathrm{Rp}} &= -\frac{1}{n_{\mathrm{m}}} \sum_{j=1}^{N_{\mathrm{chem}}} \lambda_j\, \Delta X_{\mathrm{p}j}^{(\mathrm{R})} \end{aligned} \tag{30}$$

that is, there is simply an extra factor of $1/n_{\mathrm{m}}$ when the reactant is R, because the reaction is actually bimolecular in this case.

It is a remarkable, and somewhat surprising, result that all of the first-order and pseudo-first-order (e.g., $k_{\mathrm{R}i}n_{\mathrm{m}}$) rate constants can be expressed in such a simple, generic form, typified by eq 24. Let us show that rate constants for some well-known, simple cases reduce to this form.

Consider a simple isomerization or dissociation reaction, $\mathrm{A} \rightleftarrows \mathrm{B}$, for which K_{AB} is the equilibrium constant for the reaction as written. The rate constant for the forward reaction is[18−22]

$$k_{\mathrm{AB}} = -\frac{\lambda_1 K_{\mathrm{AB}}}{1 + K_{\mathrm{AB}}} \tag{31}$$

Of course, there is an analogous expression for the reverse rate constant that can be obtained from the detailed balance condition

$$\frac{k_{\mathrm{AB}}}{k_{\mathrm{BA}}} = K_{\mathrm{AB}} \tag{32}$$

Considering A to be the reactant, note that $K_{\mathrm{AB}} = n_{\mathrm{B}}(\infty)/n_{\mathrm{A}}(\infty)$ and $n_{\mathrm{A}}(\infty) + n_{\mathrm{B}}(\infty) = n_{\mathrm{A}}(0)$. Using these identities in eq 31, one gets

$$\begin{aligned} k_{\mathrm{AB}} &= -\lambda_1 \frac{n_{\mathrm{B}}(\infty)}{n_{\mathrm{A}}(0)} \\ &= -\lambda_1 \frac{-\Delta n_{\mathrm{A}}}{n_{\mathrm{A}}(0)} \\ &= \lambda_1 \Delta X_{\mathrm{A}} \end{aligned} \tag{33}$$

where $\Delta n_{\mathrm{A}} = n_{\mathrm{A}}(\infty) - n_{\mathrm{A}}(0)$ and $X_{\mathrm{A}} = n_{\mathrm{A}}/n_{\mathrm{A}}(0)$. Clearly, eq 33 is the equivalent of eq 22 for the special case where $S = 2$ and $N_{\mathrm{chem}} = 1$. Moreover, if the equilibrium constant becomes very large, $K_{\mathrm{AB}} \rightarrow \infty$ and $\Delta X_{\mathrm{A}} \rightarrow -1$. Such is generally assumed to be the case in studying high-temperature dissociation reactions. In such reactions, the rate constant takes the particularly simple form

$$k_{\mathrm{AB}} = -\lambda_1 \tag{34}$$

Clearly then, the well-known results given in eqs 31 and 34 are just special cases of the more general expressions derived above.

It may appear at first glance from the derivation given here that the thermal rate coefficients depend on the initial energy distribution of the reactant. However, that is not the case. The energy−relaxation eigenpairs always establish the appropriate distribution prior to the reaction taking place, thus eliminating any "initial-condition dependence" of the rate coefficients.

IV. A Different Approach

The seminal work on the topic of this article was done by Bartis and Widom[21] in the early 1970s and largely overlooked thereafter. Bartis and Widom take a completely different approach to the rate-constant problem than the one we have employed above. Although their expressions for the rate constants are more complicated and less physically appealing than those given in the previous section, their approach might be considered more general. It thus provides a foundation and a context for our analysis. Consequently, we believe it is worth considering in some detail.

Bartis and Widom consider a master equation that represents (macroscopically) a system of first-order chemical reactions, although the extension to pseudo first-order processes is trivial. Moreover, they consider the "full" master equation, not the contracted description that results from making an "infinite sink" approximation. This difference makes comparing their results with ours (numerically) problematic, although our approach is applicable generally with or without this approximation. Note that we could incorporate the bimolecular products into our master equation and retain linearity by taking one of the fragments to be in great excess. In the discussion below, the term "species" in such a case should be taken to mean the deficient product or reactant. However, the most important difference between our approach and that of Bartis and Widom is that the latter consider the time evolution of the system from a single initial condition (although that initial condition is arbitrary), whereas the approach we have taken above considers multiple initial conditions in the limit that $t = 0$.

On the chemical time scales, the solution to the master equation (analogous to eq 17) can be written as

$$X_i(t) = \sum_{j=0}^{N_{\mathrm{chem}}} a_{ij} \mathrm{e}^{\lambda_j t} \quad (i = I, ..., M, R, p) \tag{35}$$

where $a_{i0} = X_i(\infty)$ is the equilibrium population of the ith species and

$$a_{ij} = -\Delta X_{ij} \quad (j \neq 0) \tag{36}$$

We have removed the superscript from ΔX_{ij} because we are now restricting ourselves to a single (but arbitrary) initial condition. Differentiating eq 35 with respect to time, we get

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = \sum_{j=0}^{N_{\mathrm{chem}}} \lambda_j a_{ij} \mathrm{e}^{\lambda_j t} \tag{37}$$

It should be remembered that $\lambda_0 = 0$ so that the $j = 0$ term does not actually appear explicitly in this equation. Now, eq 35 can be written in the form

$$X_i = \sum_{j=0}^{N_{\mathrm{chem}}} a_{ij} \upsilon_j \tag{38}$$

where

$$\upsilon_j = \mathrm{e}^{\lambda_j t} \tag{39}$$

Equation 38 can be viewed as a set of linear algebraic equations for the S υ_j's, which in matrix form is

$$|\mathrm{X}\rangle = \mathbf{A}|\upsilon\rangle, \tag{40}$$

where $\mathbf{A}$ is the $S \times S$ matrix whose elements are a_{ij}. As long as $\mathbf{A}$ is not singular, we can solve eq 40 for $|\upsilon\rangle$:

$$|\upsilon\rangle = \mathbf{B}|X\rangle \tag{41}$$

where $\mathbf{B} = \mathbf{A}^{-1}$. In component form, eq 41 is

$$\upsilon_j = \sum_{l=1}^{S} b_{jl} X_l \tag{42}$$

where b_{jl} are the elements of $\mathbf{B}$ (i.e., $\mathbf{A}^{-1}$). Substituting eq 42 into eq 37, one obtains equations for the rates of formation of the populations in terms of the populations themselves:

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = \sum_{j=0}^{S-1} \sum_{l=1}^{S} \lambda_j a_{ij} b_{jl} X_l \tag{43}$$

Equation 43 is a closed system of first-order differential equations describing the time evolution of the S macroscopic populations. They have the mathematical structure of the phenomenological rate law

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = \sum_{l \neq i} k_{li} X_l - X_i \sum_{l \neq i} k_{il} \tag{44}$$

if we identify the first-order or pseudo first-order rate constants with

$$k_{li} = \sum_{j=0}^{S-1} \lambda_j a_{ij} b_{jl} \qquad l \neq i \tag{45}$$

and

$$k_{\mathrm{T}i} = \sum_{l \neq i} k_{il} = -\sum_{j=0}^{S-1} \lambda_j a_{ij} b_{ji}$$

where k_{li} is the $l \rightarrow i$ rate constant and $k_{\mathrm{T}i}$ is the total rate constant for removal of species i. We have used eqs 45 in conjunction with the infinite sink approximation to calculate rate constants in some selected cases and obtain results identical to those obtained using the methods of section III. However, to do so, we must "fill out" the $\mathbf{A}$ matrix by calculating ΔX_{pj} from eq 14, taking $X_i(\infty) = 0$ for $i \neq p$, and setting $X_p(\infty) = 1$, since these quantities do not come directly from the eigenvectors of our $\mathbf{G}$ matrix. In any event, this is *NOT* the approach taken by Bartis and Widom.

Bartis and Widom were not only interested in deriving expressions for rate constants, they were also interested in showing that those rate constants satisfy detailed balance (eq 32). This motivated them to derive an *approximate* orthogonality property satisfied by the a_{ij}'s:

$$\sum_{i=1}^{S} \frac{a_{ij} a_{ij'}}{a_{i0}} = \delta_{jj'} \sum_{i=1}^{S} \frac{{a_{ij}}^2}{a_{i0}} \tag{46}$$

It serves no purpose to derive this property here, although we comment briefly below on the assumption on which it is based.

Defining h_{ij} as

$$h_{ij} = \frac{a_{ij}/\sqrt{\mathrm{a}_{i0}}}{N_j} \tag{47}$$

where N_j is given by

$$N_j = \left(\sum_{i=1}^{S} {a_{ij}}^2 / a_{i0} \right)^{1/2} \tag{48}$$

equation 46 becomes

$$\sum_{i=1}^{S} h_{ij} h_{ij'} = \delta_{jj'} \tag{49}$$

or in matrix notation

$$\mathbf{H}^{\mathrm{T}}\mathbf{H} = \mathbf{I} \tag{50}$$

where **I** is the identity matrix. Thus $\mathbf{H}^{-1} = \mathbf{H}^{\mathrm{T}}$, and **H** is unitary. Solving (47) for a_{ij} and using the result in eqs 38 and 37, we obtain

$$X_i/\sqrt{a_{i0}} = \sum_{j=0}^{S-1} h_{ij} N_j v_j \tag{51}$$

and

$$\frac{\mathrm{d}}{\mathrm{d}t}(X_i/\sqrt{a_{i0}}) = \sum_{j=0}^{S-1} \lambda_j h_{ij} N_j v_j \tag{52}$$

In matrix notation, eq 51 can be written

$$|\mathrm{X}/\sqrt{a_0}\rangle = \mathrm{H}|\mathrm{N}v\rangle \tag{53}$$

Proceeding as before, assuming **H** is not singular

$$\begin{aligned} |\mathrm{N}v\rangle &= \mathbf{H}^{-1}|\mathrm{X}/\sqrt{a_0}\rangle \\ &= \mathbf{H}^{\mathrm{T}}|\mathrm{X}/\sqrt{a_0}\rangle \end{aligned} \tag{54}$$

In component form, eq 54 can be written as

$$\begin{aligned} N_j v_j &= \sum_{l=1}^{S} h_{jl}{}^{\mathrm{T}} X_l/\sqrt{a_{l0}} \\ &= \sum_{l=1}^{S} h_{lj} X_l/\sqrt{a_{l0}} \end{aligned} \tag{55}$$

Substituting $N_j v_j$ from eq 55 into eq 52, we get an expression analogous to eq 43 above

$$\frac{\mathrm{d}X_i}{\mathrm{d}t} = \sum_{l=1}^{S} \left(\frac{a_{i0}}{a_{l0}}\right)^{1/2} X_l \sum_{j=0}^{S-1} \lambda_j h_{ij} h_{lj} \tag{56}$$

For $l \neq i$, one can identify the $l \rightarrow i$ rate constant

$$k_{li} = \sqrt{K_{li}} \sum_{j=0}^{S-1} \lambda_j h_{ij} h_{lj} \tag{57}$$

where

$$K_{li} = \frac{a_{i0}}{a_{l0}} = \frac{X_i(\infty)}{X_l(\infty)}$$

The reverse rate constant can be obtained by interchanging i and l in eq 57, i.e.

$$k_{il} = \sqrt{K_{il}} \sum_{j=0}^{S-1} \lambda_j h_{ij} h_{lj}$$

and thus

$$\frac{k_{li}}{k_{il}} = \frac{\sqrt{K_{li}}}{\sqrt{K_{il}}} = K_{li} \tag{58}$$

since $K_{il} = 1/K_{li}$. Therefore, detailed balance is satisfied by the rate constants.

Applying the Bartis-Widom formulas (with the infinite sink approximation) for the rate constants (eq 57) to our problem is complicated by the appearance of $(a_{i0})^{1/2}$ in the denominator of the definition of h_{ij}, eq 47. With the infinite-sink approximation, $a_{i0} = 0$ for $i \neq p$, and $a_{p0} = 1$. Thus, the h_{ij}'s blow up for $i \neq p$. However, in our own derivation of eq 46, it is Q_i that appears rather than a_{i0}, and consequently, Q_i appears instead of a_{i0} in the denominator of the definition of h_{ij}. In the infinite sink approximation $Q_p \rightarrow \infty$ (another complication), but it may be possible to evaluate rate constants from eq 57 in this limit. In any event, we have not pursued this approach and have no particular interest in doing so. It is much easier to evaluate the rate constants from the expressions derived in the previous section, or from eq 45, than it is to evaluate them from eq 57. The value of the Bartis–Widom analysis is that it shows that the chemistry embedded in the multiple-well master equation reduces to a *unique* phenomenological description in terms of macroscopic rate laws and rate constants that *satisfy detailed balance*, at least as long as the energy relaxation eigenvalues are much smaller (more negative) than the chemically significant ones. Note that the uniqueness of solutions to the master equation, given a set of initial conditions, and the invertibility of **A** and **H** guarantee that the rate constants are unique.

The Bartis–Widom analysis justifies the results given in the previous section, in which it was *assumed* that a phenomenological description (satisfying detailed balance) would apply; it also justifies (or at least adds credibility to) the identification made in deriving eq 45. The infinite-sink approximation in the multiple-well case is a complication. However, it has been shown that, for simple dissociation/recombination reactions[24] and for bimolecular reactions giving bimolecular products over a single well,[25] the infinite sink approximation gives good rate constants that satisfy detailed balance. We expect that the derivations in these single-well cases can be extended to cover multiple wells. For the present, we content ourselves with checking our results numerically, where it is possible, to see if detailed balance is satisfied. All our checks indicate that it is.

Bartis and Widom's use of a quantum mechanical analogy to derive eq 46 obscures somewhat the assumption on which it is based. Stated simply, the assumption is that the formation (or removal) rate of molecules in any state of any species, through the propagation of any CSE, is proportional to the relative population of that state of that species in *thermal equilibrium*. If every chemical species remained in thermal equilibrium throughout the course of the reaction, this assumption would be satisfied exactly. However, that is not the case. Nevertheless, it is probably true that the results that derive from the assumption will be compromised only if states that are heavily populated at equilibrium have that population significantly perturbed by the reaction.[26] This is likely to happen only when the rate constant approximation itself begins to fail. Therefore, we expect eq 46 to hold over a wide range of conditions, as suggested by Bartis and Widom.

V. Application to $C_2H_3 + C_2H_2 \rightarrow$ Products

The potential energy surface (PES) used in our previous work[5] on this reaction is shown in Figure 1. For the rate constants presented below we have used a value of $E_{01} = 5.22$ kcal/mol,

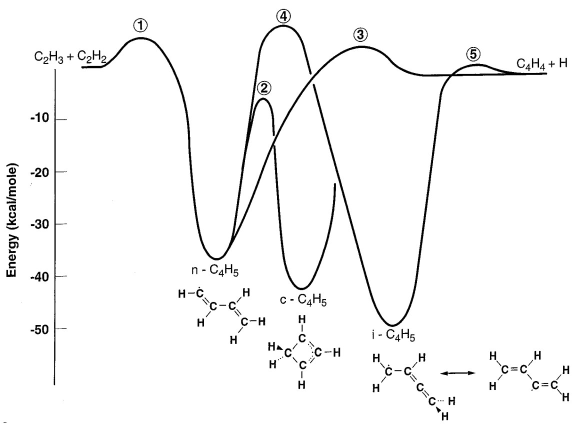

Figure 1. Potential energy surface for the $C_2H_3 + C_2H_2$ reaction.[5]

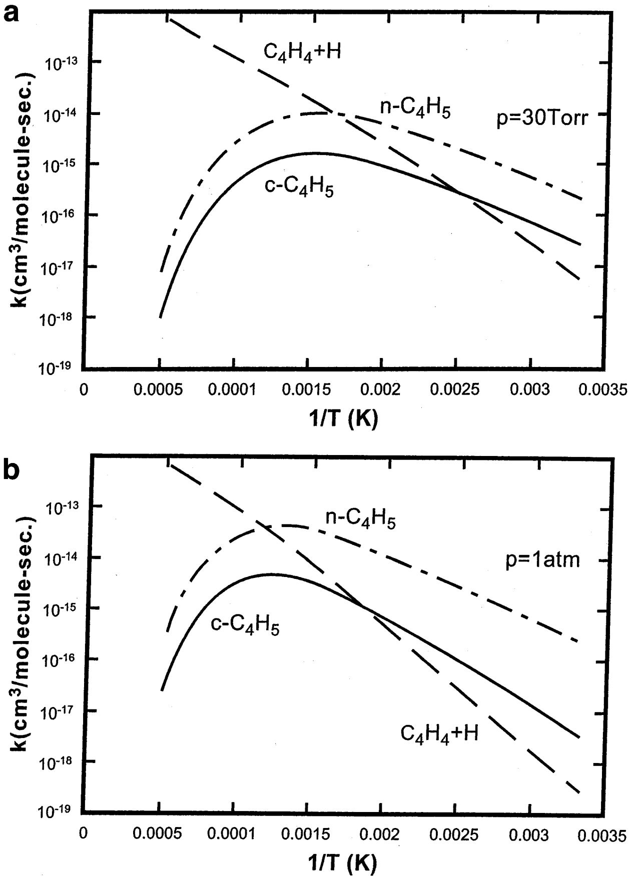

Figure 2. Thermal rate coefficients for $C_2H_3 + C_2H_2 \rightarrow$ products (a) $p = 30$ Torr (b) $p = 1$ atm.

where E_{01} is the threshold energy for transition state 1 (TS-1). This is the value of E_{01} for which we obtained good agreement with total rate-constant measurements over a wide range of temperatures and pressures in our previous analysis. Other PES parameters remain the same.

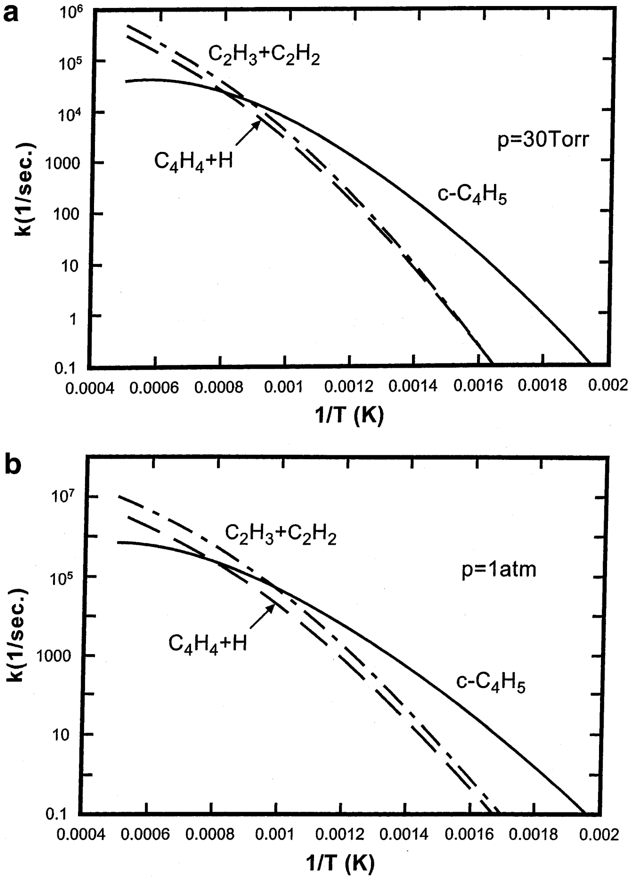

Figure 3. Thermal rate coefficients for isomerization and dissociation of n-C_4H_5 (a) $p = 30$ Torr (b) $p = 1$ atm.

Figures 2−5 show rate constants for all the possible reactions (except those where C_4H_4 + H are the reactants) obtained by the methods of section III for two different pressures, $p = 30$ Torr and $p = 1$ atm. The first pressure is typical of low-pressure flame experiments, and the second is that of normal, atmospheric-pressure combustion. The results for the $C_2H_3 + C_2H_2$ reaction are largely the same as those obtained in our previous work − n-C_4H_5 is the dominant product at low temperature for these pressures, and C_4H_4 + H is dominant at high temperature. However, the present results indicate that c-C_4H_5 is never the dominant product of the reaction, in conflict with our previous result, which showed that c-C_4H_5 was the dominant product at $T \approx 700$ K for $p >$ 1atm. This latter result was a consequence of a rapid n-$C_4H_5 \rightarrow c$-C_4H_5 thermal isomerization, whose time constant begins to be comparable to the characteristic time for $X_R(t)$ decay in this temperature range (both are $\approx 10^{-3}$ s). In general, the temperature range 650 K $< T <$ 900 K, where the eigenvalues in Figure 9 of ref 5 are all very close together in magnitude, is a regime of shifting equilibrium. First, the reaction $C_2H_3 + C_2H_2 \rightleftarrows n$-$C_4H_5$ begins to shift in favor of the reactants, and then $C_2H_3 + C_2H_2 \rightleftarrows c$-$C_4H_5$ follows suit. For $T >$ 900 K, the only observable products are C_4H_4 + H, primarily because of this equilibrium shift. These products are principally a consequence of the direct reaction, $C_2H_3 + C_2H_2 \rightarrow C_4H_4$ + H, although at very high pressure there is a contribution from the secondary dissociation of n-C_4H_5.

In our previous work, we did not obtain thermal rate coefficients for isomerization and dissociation, because the methods employed did not lend themselves to determining such rate constants. However, using the methods of section III, we can obtain them quite easily. Dissociation/isomerization rate constants are given for n-C_4H_5, c-C_4H_5, and i-C_4H_5 in Figures 3−5, respectively.

Interestingly, although it was to be expected, the n-$C_4H_5 \rightleftarrows c$-$C_4H_5$ isomerization is the dominant reaction for both c-C_4H_5 and n-C_4H_5 at both pressures up to $T \approx 1000$ K. For c-C_4H_5, isomerization is the dominant channel at all temperatures and pressures considered, whereas dissociation of n-C_4H_5 begins to be competitive with isomerization for $T >$ 1000 K. If one were interested in measuring the dissociation rate constant for either c-C_4H_5 or n-C_4H_5 directly at, for example, $T = 800$ K, it would be impossible to do. The n-$C_4H_5 \rightleftarrows c$-$C_4H_5$

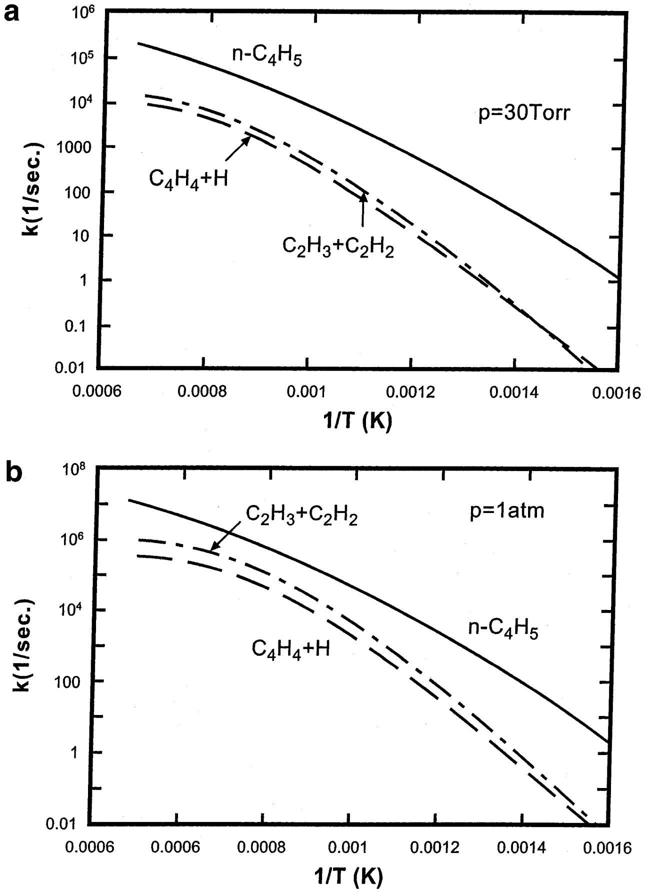

Figure 4. Thermal rate coefficients for isomerization and dissociation of *c*-C_4H_5 (a) $p = 30$ Torr (b) $p = 1$ atm.

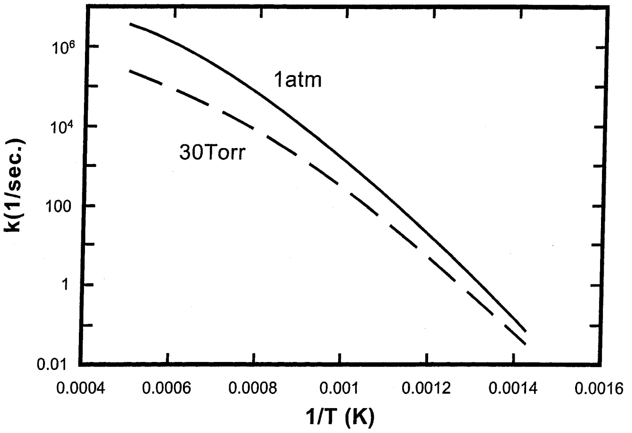

Figure 5. Thermal dissociation rate coefficient for *i*-$C_4H_5 \rightarrow C_4H_4$ + H. (a) $p = 30$ Torr (b) $p = 1$ atm.

isomerization equilibrates so rapidly that one can only measure the dissociation rate for the equilibrated pair, and this rate constant is given by $-\lambda_j$ for a single eigenpair. At $T = 800$ K, both *c*-C_4H_5 and *n*-C_4H_5 have nontrivial concentrations at equilibrium. However, at lower temperatures, equilibrium heavily favors *c*-C_4H_5, so its dissociation rate constant would be measurable at these temperatures (i.e., the dissociation of *c*-C_4H_5 dominates the dissociation of the equilibrated pair). Similarly, at temperatures much higher than 800 K, equilibrium favors *n*-C_4H_5, so that its dissociation rate constant could be measured under such conditions, at least if it were prepared as the reactant. Note that it is only the indicated dissociation rate constants at most that are measurable regardless of which isomer is prepared as the reactant. Similar circumstances exist for many hydrocarbons, which frequently have relatively low-lying isomerization barriers.

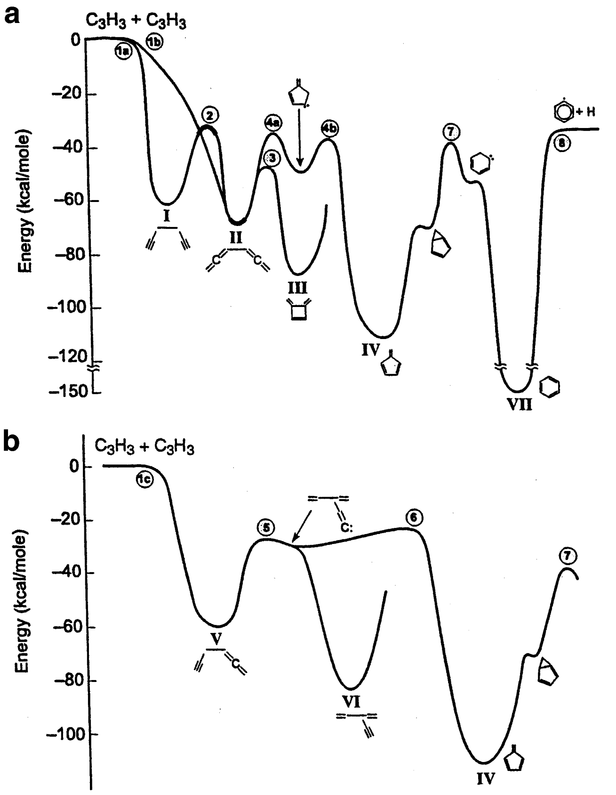

Figure 6. Potential energy surface for $C_3H_3 + C_3H_3 \rightarrow$ products.[8,27,28] (a) Head-to-head and tail-to-tail recombination. (b) Head-to-tail recombination. The CH_2 end of propargyl is the head; the CH end is the tail.

Although the two dissociation channels have similar rate constants, Figures 3 and 4 show that $C_2H_3 + C_2H_2$ is the favored channel for both *c*-C_4H_5 and *n*-C_4H_5 at the temperatures and pressures shown, more so at $p = 1$ atm than at $p = 30$ Torr. Increasing the pressure at any temperature increasingly favors the $C_2H_3 + C_2H_2$ channel. If one were to reduce the pressure to the point where the low-pressure limit is reached, the only products would be C_4H_4 + H, because they are the energetically favored channel, and the channel with the lowest threshold energy is the only observable one in the low-pressure limit.

Figure 5 shows rate constants for *i*-$C_4H_5 \rightarrow C_4H_4$ + H at $p = 30$ Torr and at $p = 1$ atm. As indicated previously,[4,5] TS-4 (Figure 1) makes *i*-C_4H_5 virtually inaccessible from C_2H_3 + C_2H_2, *n*-C_4H_5, or *c*-C_4H_5. Consequently, the only significant dissociation channel is C_4H_4 + H on this PES. However, we have explored the PES beyond what is described in ref 5 and find that the *i*-C_4H_5 dissociation rate may be affected by isomerization to isomers not shown in Figure 1. Nevertheless, we give the *i*-C_4H_5 dissociation rate constants here for completeness.

VI. Application to Propargyl Recombination

The BAC-MP4 potential energy surface[27,28] used in our previous work[8] on the $C_3H_3 + C_3H_3$ reaction is shown diagrammatically in Figure 6. We know now that this potential is not sufficiently complete to give good rate constants, particularly at high temperature.[4] However, this is the most complex problem we have attacked, and employing the new methodology on it is instructive, even though the results will soon be superseded by more accurate ones.

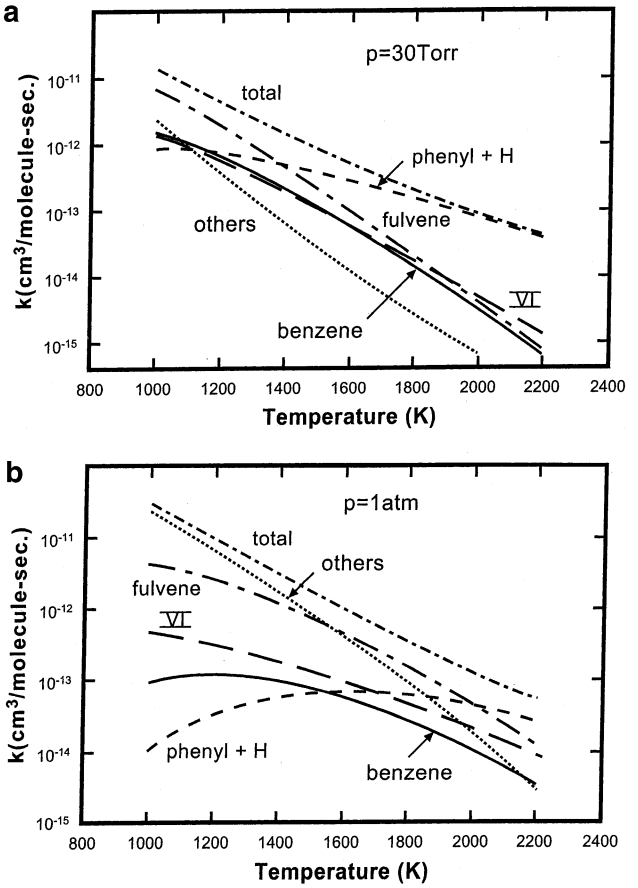

Figure 7. Thermal rate coefficients for $C_3H_3 + C_3H_3 \rightarrow$ products. (a) $p = 30$ Torr (b) $p = 1$ atm. "Others" indicates stabilization into wells I, II, III, and V.

Figure 7 shows rate constants as a function of temperature for $C_3H_3 + C_3H_3 \rightarrow$ products at the two pressures, 30 Torr and 1 atm. Figures 8−10 show isomerization/dissociation rate constants for benzene (well VII), fulvene (well IV), and 2-ethynyl-1,3 butadiene (well VI), the most stable isomers on the PES. Good eigenvalues and eigenvectors could be calculated only for $T \geq 1000$ K,[8] so only this temperature regime is considered here. The results are similar to those of our previous work, the most notable exception being *that benzene is never the dominant product*. At 30 Torr, the formation of fulvene is dominant from 1000 to about 1400 K, with phenyl + H taking over for $T > 1400$ K. At 1 atm, the early wells (particularly well III, dimethylene-cyclobutene) dominate up to $T \approx 1500$ K; fulvene dominates between 1500 and 2000 K, and phenyl + H is the primary product for $T > 2000$ K.

The appearance of benzene as a dominant product at $T \approx 1600$ K in our previous work is easy to understand from the present results. The characteristic time for $X_R(t)$ to decay ranges from 4 μs at 1000 K to 2.5 ms at 2000 K; it is approximately 0.6 ms at 1600 K. At 1600 K, fulvene isomerizes thermally to benzene with a time constant that is roughly the same as that for $X_R(t)$ to decay ($\approx$0.7 ms), whereas the characteristic time for benzene to dissociate to phenyl + H is 0.2 s. Consequently, on the time scale of $X_R(t)$ decay, benzene appears to be a stable product, but fulvene does not. Such multiple-step processes were mentioned as a possibility in our previous paper, but we could not sort out the rate constants at that time.

In our previous work, we discussed the concept of "stabilization limits". Although we were reluctant to make such a statement at the time, it appears that the vast majority of such

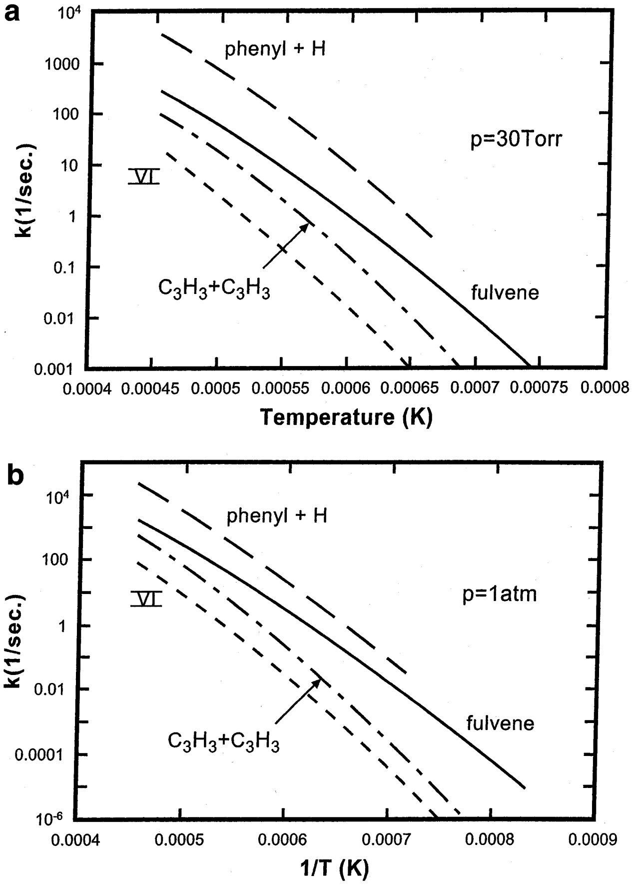

Figure 8. Thermal rate coefficients for benzene → products. (a) $p = 30$ Torr (b) $p = 1$ atm.

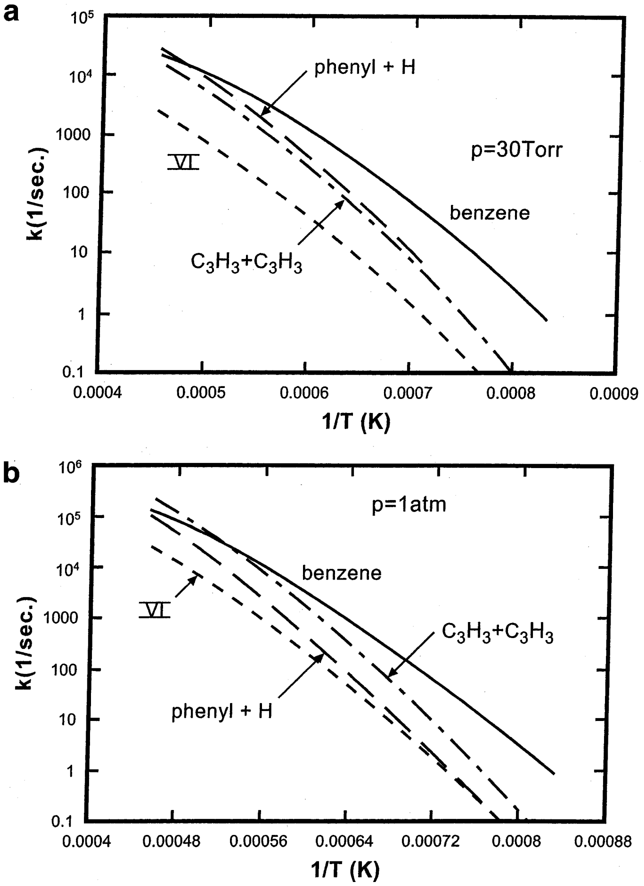

Figure 9. Thermal rate coefficients for fulvene → products. (a) $p = 30$ Torr (b) $p = 1$ atm.

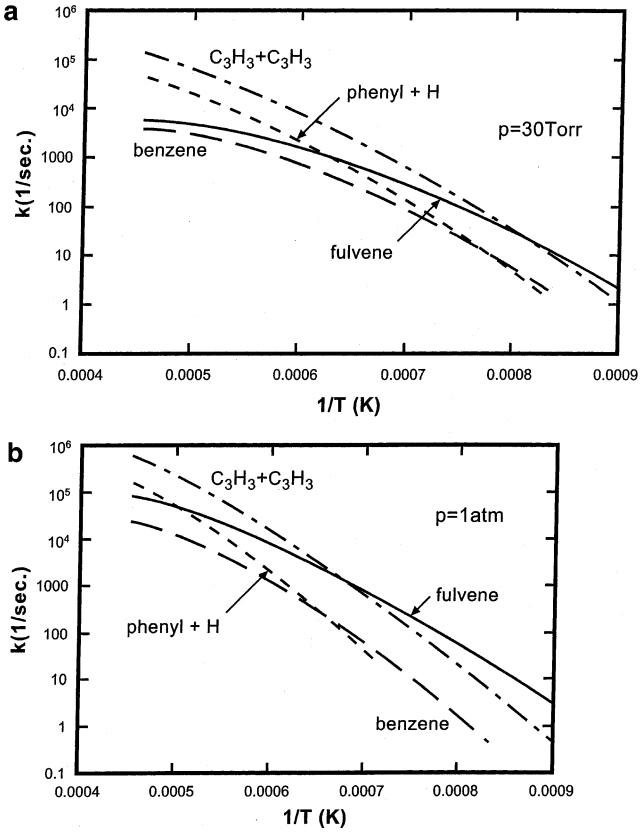

Figure 10. Thermal rate coefficients for 2-ethynyl-1,3 butadiene (well VI) → products. (a) $p = 30$ Torr (b) $p = 1$ atm.

limits are of macroscopic origin. They occur as a consequence of one of two phenomena:

1. There is a shift in equilibrium in favor of the reactants, so that population in a well is no longer stable with respect to dissociation back to reactants.

2. A temperature is reached beyond which a "stabilized" isomer thermally isomerizes to another well or to some set of dissociated products faster than it can be formed from the reactants. The two phenomena obviously are similar, but the former can result in an avoided crossing of the eigenvalue curves;[7,8] the latter does not.

VII. Concluding Remarks

In the past, it has not been a simple task to determine phenomenological rate coefficients from solutions to the time-dependent master equation for multiple-well problems. Of course, the major difficulty is determining whether a particular product is formed in a single elementary step or whether its formation is a consequence of two or more sequential reactions, with the first in the sequence controlling the overall rate. In the present article, we have provided two methods (section III and eq 45 of section IV) of calculating all $S(S - 1)/2$ independent rate constants from the eigenvalues and eigenvectors of $\mathbf{G}$, thus eliminating the above problem once and for all. The methods of section III are the simplest to apply, and we have reanalyzed our previous work on the $C_2H_3 + C_2H_2$ and $C_3H_3 + C_3H_3$ reactions using this approach, obtaining many new and somewhat different results. At the moment, it is not clear which of the two methods is actually better in practice. We expect to pursue this question in future applications.

In this article, we have avoided the issue of what happens at high temperature when one (or more) of the CSE's merges with what is essentially a continuum of energy-relaxation eigenvalues; we address this point in another article.[29] Such a crossing indicates that some isomerization or dissociation process equilibrates on a time scale comparable to that for internal-energy relaxation. Consequently, for our purposes, the two species involved cease to be distinct, and it is appropriate in the analysis to consider them as a single species. In such a case, S and N_{chem} are reduced by one, thus reducing the upper limit on the summations in section III by one and the size of the matrices in section IV by one row and one column. Otherwise, the rate-constant calculations proceed as described above.

In doing the calculations for this article, it became obvious to us that the "experimental" approach to determining rate coefficients, i.e., looking for exponential decays of reactants and rises for products, is prone to error in temperature regimes where the chemically significant eigenvalues are close together. Of course, there is the obvious problem that exponential decays may be hard to find. However, the problem is more severe than that. Suppose the reactant is R, and at some temperature and pressure $\Delta X_{R1} = -0.99$ for the eigenvector corresponding to λ_1. At first glance, one would expect to be able to calculate the rate coefficient from λ_1 and the product distribution from this eigenvector − the decay of R and the rise of products would be pretty good exponentials. However, it frequently happens that there is another eigenvalue, say λ_2, that is $\approx 100\lambda_1$ (for example) and for which $\Delta X_{R2} \approx -0.01$. Using the methods of section III, the contributions to the rate coefficient from these eigenpairs would be $-0.99\lambda_1$ and $-1.00\lambda_1$, respectively. By equating the exponential decay constant of the reactant with a pseudo-first-order rate constant, and thus obtaining the bimolecular rate coefficient, one makes an error of about a factor of 2. Such factor-of-2 errors are ubiquitous in these large, multiple-well problems with closely spaced eigenvalues. Of course, similar errors can occur in product distributions. The methods developed in this article alleviate this problem from a theoretical perspective, but such errors remain a problem for experiments.

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