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Computer Construction of Detailed Chemical Kinetic Models for Gas-Phase Reactors

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The combustion, oxidation, and pyrolysis chemistry of even simple light hydrocarbons can be extremely complex, involving hundreds or thousands of kinetically significant species. Even relatively minor species can play an important role in the formation of undesirable emissions and byproducts, and their properties and reactions need to be modeled in some detail in order to make accurate predictions. In many technologically important applications, the reaction chemistry is closely coupled with the mixing and heat flow, dramatically increasing the computational difficulty. The most reasonable way to deal with this complexity is to use a computer not only to solve the simulation numerically, but also to construct the model in the first place. We are developing the methods needed to make this sort of computer-aided kinetic modeling feasible for real systems. The computer is used to calculate most of the molecular properties and rate parameters in the model by a variety of quantum- and group-additivity-based techniques. We summarize our new computer methods for modeling the pressure dependence (falloff and chemical activation) of gas-phase reactions. Our approach to determining the optimal reduced kinetic models for various reaction conditions is discussed. Adaptive-chemistry methods that allow one to solve detailed macroscopic reacting flow simulations involving hundreds of species are outlined.

I. Introduction

Many technologically important reactions (e.g., partial oxidation, combustion, cracking, halogenation) proceed via very complex nonlinear chemistry involving hundreds of kinetically significant reaction intermediates. Often, this complex chemistry is strongly coupled with heat and mass transport and fluid dynamics. Because constructing and solving detailed simulations of the reactors would be impractical and because such simulations would require a large number of generally unknown thermochemical and kinetic parameters, these processes have historically been modeled empirically, using severely oversimplified chemistry. These empirical models are usually satisfactory for interpolations, e.g., for finding the locally optimal set point and for control around that set point. Yet, they do not provide accurate extrapolations and often miss critical features of the physics and chemistry going on inside the reactors, so they are of little use (and are often even misleading) in designing a new process or reactor operating away from that set point. More detailed and reliable simulations are clearly required.

It now appears to be feasible to use computers to construct the needed detailed chemistry models, to couple them with complex fluid dynamics, to reliably compute the many kinetic parameters needed, and to numerically solve these large-scale simulations. In this paper, we summarize some of our recent progress toward achieving this goal and highlight some of the remaining obstacles to be overcome.

II. Computer Construction of Chemical Kinetic Models

A. Background. The potential advantages of using computers to construct kinetic models (as well as to construct and solve the corresponding differential equations) have been recognized for many years, and about a dozen groups have actually written software that can generate complex kinetic schemes given only the reactants and some information about the reaction conditions.^{1–13} Note the very important distinction between these scheme-generation codes and more conventional kinetic-modeling programs such as CHEMKIN,¹⁴ which require the user to provide the list of kinetically significant species and reactions.

Most of the scheme-generation codes represent molecules by their valence-bond connectivities, and so

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clearly, they would have difficulties with weakly bonded complexes and other nonclassical structures. However, this representation is very well suited to hydrocarbon chemistry. To our knowledge, all of the existing kinetic-model-construction codes are based on planar graphs (i.e., there is no attempt to keep track of stereoisomers and other essentially three-dimensional information). For very complicated feeds, a simplified approach that lumps together all isomers having the same functional groups (but in a different order) is more practical and has been used quite successfully. The simplified approach is, of course, only useful if one does not require the isomer information, and it has been most successful for systems in which the overall reaction conditions do not change much with the typical range of variations in the feed.^{15–19}

Once one has decided on a molecular representation, the key issue is how the computer should decide which chemical species belong in the kinetic model and which can be ignored. A key advance in this area was our rate-based algorithm,¹² which tests the kinetic significance of each species before it is added to the model and so naturally terminates model construction when all the important species have been added. When this algorithm converges, the user can be sure that

$$d[X]/dt < \text{rtol} \times R_{\text{char}}(t) \quad 0 < t < t_{\text{simulation}} \quad (1)$$

for all species X excluded from the model, where $R_{\text{char}}(t)$ is some characteristic reaction rate of the species included in the model and rtol is a user-specified tolerance. The key is to have the computer identify all additional “edge” species that can be reached in a single elementary step reaction from the species in the model. This algorithm has been demonstrated to be robust even for systems with multistep catalytic amplification loops.²⁰ Other rate-based species-selection algorithms have also been devised.²¹ Note that the rate-based algorithms construct distinct kinetic models (with different species and reactions) for different reaction conditions, as they should—the model should change as the chemistry changes.

B. Recent Advances. Our new model-construction program XMG¹³ uses the valence-bond planar-graph representation of molecules and the rate-based species-selection algorithm mentioned above.¹² After the molecular structures have been represented and the structures belonging in the simulation have been selected, the main remaining issues are the methods for calculating the thermochemistry of each structure and the reaction rates between all these species. In the 1997 version, called NetGen,¹² we used Benson-style group additivity (as implemented in the NIST Structures and Properties software) and MOPAC semiempirical electronic structure calculations for the thermochemistry, along with a relatively small set of very rough reaction-family rate-estimation rules based on linear free energy relationships (aka LFER, Evans–Polanyi, Semenov, and Hammett equations). The rough rate rules and the thermochemistry used were not in precise agreement, i.e., this version did not enforce microscopic reversibility.

The new model-generation software package XMG also uses group additivity for thermochemistry and the reaction-family concept for rate estimation, but these modules have been completely rewritten for higher accuracy. The thermochemistry is now based on the approach used in the THERM program of Bozzelli and co-workers,²² implemented through the new GAPP

program and interface.²³ The most important difference is that the thermochemistry of radicals is now computed using the HBI approach instead of the Benson method, requiring many fewer group parameters and using more extended groups to reflect accurately neighboring-group effects on resonantly stabilized radicals. As before, the software searches a library of high-quality thermochemical data first before relying on the group additivity estimates.

The reaction families in XMG are more narrowly defined than in the older software, and the rate-estimation rules can therefore be much more specific and accurate. XMG also uses library rates where they are available. The rate estimates now always satisfy microscopic reversibility, i.e., for each reaction

$$k_{\text{backward}}(T) = k_{\text{forward}}(T)/K_{\text{eq}}(T) \quad (2)$$

where $K_{\text{eq}}(T)$ is computed from the thermochemistry. The effects of pressure (falloff, chemical activation) on the rates can now be computed. The rate estimates are discussed in more detail in section V.

C. Issues for the Future. *1. Handling Complexity.* We can now generate kinetic models for extremely complex processes. The challenge for the future is how to test and use these large models effectively. One never has enough experimental information to thoroughly test these models, which predict concentration profiles for hundreds of species, most of which are short-lived intermediates. Also, it is very difficult at present for a human to use all of the output from the model, or even to compare two very large kinetic models. We are currently developing tools to simplify some of these tasks, but much more effort will ultimately be required.

2. Uncertainty Propagation. To perform useful quantitative comparisons between experimental measurements and our kinetic model predictions, confidence intervals are needed for the model predictions. Because the structure of the model depends on the rate estimates, these error bars must take structural uncertainty into account. We are presently developing an algorithm that drives XMG to construct a kinetic model large enough that its structure does not change when one varies the rate parameters within their error bars, so that conventional uncertainty propagation techniques^{2,24,25} can be used.

3. Time-Dependence of Kinetic Models. Chemistry changes with time as reactants are converted into products, so, in general, larger kinetic models are required for long-time (i.e., high-conversion) simulations than for shorter simulations. In some applications, such as the split-operator reacting flow simulations discussed below, the kinetic models need to be accurate only over very short time periods, whereas in other cases, it is desirable to have a single model valid all the way from reactants to products. It is perfectly feasible to have the computer switch kinetic models when the chemistry changes, and we have used this approach to speed up combustion chemistry simulations (Figure 1), where we use different models for preignition, flame, and exhaust chemistry. When the switch is done at the appropriate time, the results are numerically identical to simulations done using the full chemistry (the union of the three models) over the whole course of the simulation. We are currently addressing the tricky issues of deciding when to switch models and what simulation time or extent of conversion to specify when constructing a model (see section IV).

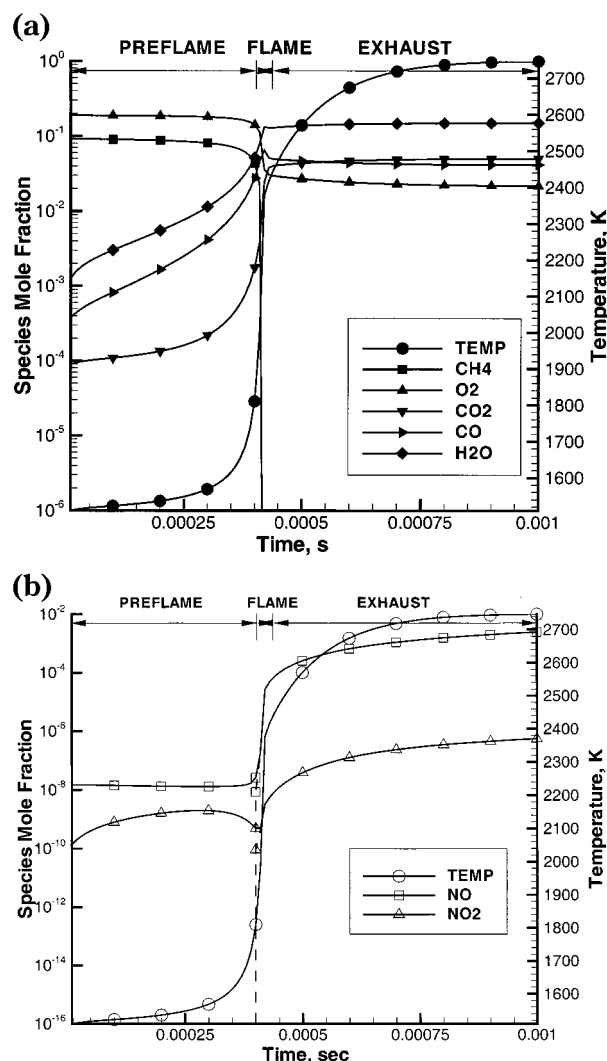


Figure 1. Comparison between a perfectly mixed methane–air simulation done using the complete kinetic model (solid lines) and that done using three reduced models (for preignition, flame, and exhaust chemistry) with the computer dynamically switching the kinetic models according to the instantaneous temperature. The computation using the reduced models (dashed lines) is significantly faster but just as accurate. For the major species, the dashed line exactly overlaps the solid line. The small discrepancies in Figure 1b arise because the reduced model for preignition does not include NO_x .

III. Adaptive Chemistry for Reacting Flow Simulations

A. Adaptive-Chemistry Concept and Motivation.

Reacting flow simulations are most valuable for reactors with large concentration or temperature gradients, where one expects the chemistry to be dramatically different in different spatial regions (or at different times in a dynamic simulation). However, most reacting flow simulations are performed using the same chemistry model at all spatial mesh positions and at all times. (It is implicitly assumed that this chemistry model is accurate over the whole range of conditions sampled by the reacting flow, although this assumption is often uncertain and is never tested.) Much higher efficiency is possible by adapting the chemistry in much the same way that modern simulations use adaptive time steps and adaptive mesh refinement. The idea in all three cases is to use a great deal of detail when necessary but to use a less-detailed description whenever possible

without sacrificing accuracy. The adaptive-chemistry approach of ignoring chemical species when they are insignificant is very advantageous, as the best methods for solving the chemistry equations and for computing the multicomponent diffusion coefficients both scale superlinearly with the number of chemical species considered.

B. Adaptive-Chemistry Algorithm for Steady Multidimensional Flows. We have implemented this adaptive-chemistry concept^{26,27} into an existing CFD code for two-dimensional steady laminar or turbulent reacting flows. At each macroiteration, the computer selects the chemistry model appropriate for each finite volume based on the current estimate of the state variables (concentrations, temperature, etc.) there. The CFD code then steps forward by one or more time steps Δt_{flow} (converging to a steady-state solution at long times). The chemistry model is solved over each period Δt_{flow} using a stiff ODE solver,²⁸ while the flow equations are solved using a preconditioned diagonalized ADI approach using upwind differencing.^{29,30} The operator-splitting strategy used is particularly appropriate for finding accurate steady-state solutions when the chemical kinetic equations are stiff. After convergence with the given chemistry models is reached, the appropriateness of the kinetic model for each finite volume's reaction conditions is checked, and if any are inappropriate, the next macroiteration begins.

Our algorithm is similar in motivation but considerably different in execution from the ISAT/ILDM algorithms of Pope, Maas, and co-workers^{31,32} and the PRISM algorithm of Frenklach, Brown, and co-workers.³³ Most basically, our chemistry models are systems of differential equations, whereas those authors use algebraic fits. This fundamental difference leads to numerous other differences between our algorithm and theirs.

As an example of how our adaptive-chemistry algorithm works, the kinetic models used in each zone of a H_2/O_2 burner simulation at final convergence are displayed in Figure 2.

C. Issues for the Future. 1. *Error Control on Both Chemistry and Flow.* At present, we are checking the accuracy of our adaptive-chemistry algorithm by actually running the full-chemistry calculation for comparison. In the long run, of course, methods are needed for bounding the uncertainties in the adaptive-chemistry calculation without ever having to run a full-chemistry calculation. This will require deriving a quantitative bound on the errors that arise as a result of using an incomplete chemistry model, computing how these errors propagate in the reacting flow simulation, and ultimately using these bounds for dynamic error control of the adaptive chemistry and other parts of the computation.

2. *Dynamic Multidimensional Simulations with Adaptive Meshes.* The adaptive-chemistry algorithm presented above was based on a particular CFD code designed for steady-state simulations using a fixed mesh. It is straightforward to incorporate our adaptive-chemistry approach into any CFD code using operator splitting to separate the fast chemistry from the fluid dynamics. We are currently collaborating with several other groups to incorporate adaptive-chemistry into their state-of-the-art software. Special numerical and kinetic-model-construction issues arise for time-dependent calculations (see ref 29).

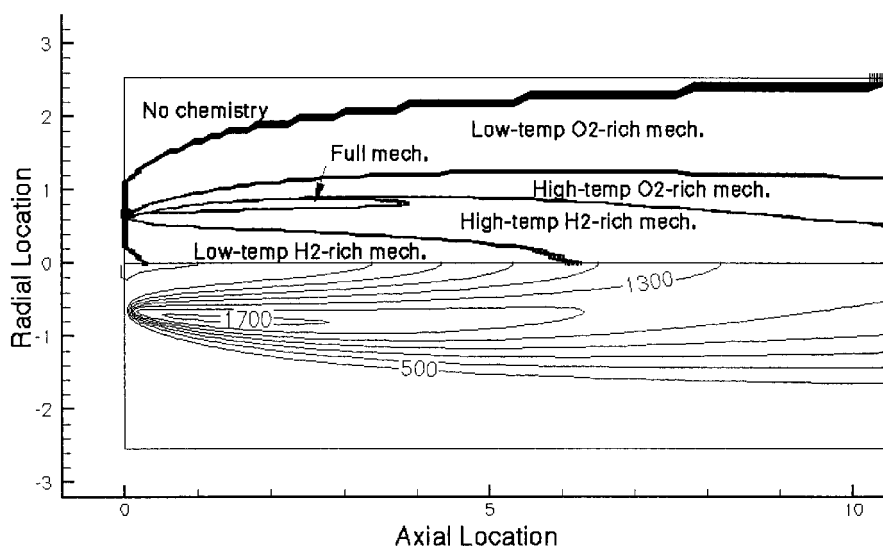


Figure 2. Top: Kinetic models used in each zone of an axisymmetric laminar H_2/O_2 burner simulation at final convergence of the adaptive-chemistry algorithm. Bottom: Corresponding temperature field. The results using the adaptive-chemistry technique precisely match those made using the complete chemical kinetic model everywhere. The full model need only be used in a narrow zone where the temperature is high and the fuel/air ratio is near stoichiometric.

3. Reduced Kinetic Model Libraries. The adaptive-chemistry approach is only useful if one has a set of reduced kinetic models available that accurately reproduce the full chemistry in some reaction regime important in the reacting flow. In principle, these models could be generated whenever needed using XMG, or produced by reducing a very large mechanism, but current software for both scheme generation and scheme reduction appear to be too slow for incorporation inside an adaptive-chemistry code—certainly, one would not want to have to generate a kinetic model for every finite element in a big simulation at each macroiteration! Instead, we have been pregenerating libraries of reduced models appropriate to different reaction conditions likely to be encountered during the simulation. Each of these mechanisms must have its “range of validity” determined and stored in the library as well, so the adaptive-chemistry algorithm will know when to use each mechanism. At present, there does not appear to be any efficient way to perform model reduction, despite considerable prior and ongoing research in this area. We discuss our new method for finding locally optimal reduced models below. The range of validity problem has arisen before^{31,33} for small models created from the reduction of a larger model. In this case, one generally compares the small model’s predictions with the larger model’s predictions. However, there is no way at present to confirm that the large model is actually valid over the whole range of reaction conditions. As discussed in section IV, the approach can be very different if one is starting from a model generated by XMG rather than some hypothetical perfectly accurate large model.

IV. Constructing Libraries of Reduced Kinetic Models

A. Efficient Method for Kinetic Model Reduction. Many researchers have attempted to find an optimal method for reducing large kinetic models. In the usual formulation of the problem, it is assumed that one somehow has constructed a large model that is both accurate and complete for the reaction conditions of

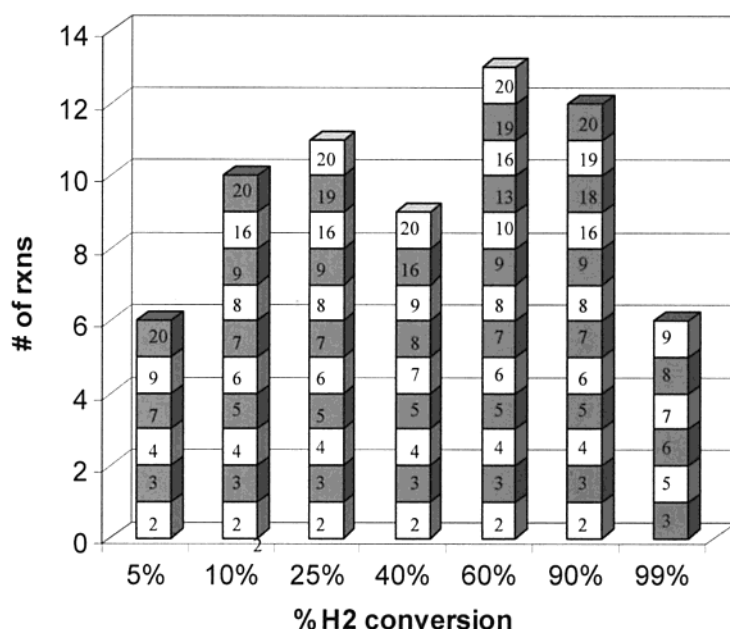
interest. The goal is to construct a much smaller model that essentially reproduces the large model. The problem is usually formulated as^{34,35}

$$\begin{aligned} \min \sum y_k \quad & k = 1, \dots, N_{\text{reactions}} \\ \text{s.t.} \quad & \int \|\mathbf{Z}_{\text{small}}(t; \mathbf{y}) - \mathbf{Z}_{\text{big}}(t)\| dt < \text{tol} \\ d\mathbf{Z}_{\text{big},j}/dt = \sum \eta_{jk} R_k(\mathbf{Z}_{\text{big}}) \quad & \mathbf{Z}_{\text{big}}(t_0) = \mathbf{Z}_0 \\ & \forall j = 1, \dots, N_{\text{species}} \\ d\mathbf{Z}_{\text{small},j}/dt = \sum \eta_{jk} y_k R_k(\mathbf{Z}_{\text{small}}) \quad & \mathbf{Z}_{\text{small}}(t_0) = \mathbf{Z}_0 \\ y_k \in \{0,1\} \quad & \forall k = 1, \dots, N_{\text{reactions}} \end{aligned} \quad (3)$$

where $\mathbf{Z}_{\text{big}}(t)$ represents the concentrations of all of the species in the original large model, $\mathbf{Z}_{\text{small}}(t)$ represents these concentrations in the smaller reduced model, \mathbf{y} is an array of binary variables that switches various reactions off in the reduced model, \mathbf{R} represents the reaction rates, η represents the stoichiometries, and the integral runs from t_0 to some user-specified t_{final} . Note that the $\mathbf{Z}(t)$ values generally have to be obtained by numerically solving stiff nonlinear systems of differential equations, and a different system must be solved for each realization \mathbf{y} .

There are several practical and conceptual problems with this formulation. The main practical problem is that the constraints are not convex in \mathbf{y} (in fact, this is an example of a nonconvex integer dynamic optimization), and there is no known method that is guaranteed to find the optimal \mathbf{y} (except for exhaustive search over all possible \mathbf{y} 's, which is impractical for realistic problems). Several methods have been developed^{34,36,37} that are rather successful at finding good reduced models, although one would not expect them to necessarily find the globally optimal reduction, and in unfortunate cases, they can find reduced models that are considerably larger than the optimal model.

Conceptually, the standard formulation forces the reduced model to be accurate only at a single initial condition and time scale (and the large “full” model is



20. $\text{H}_2\text{O}_2 + \text{OH} = \text{H}_2\text{O} + \text{HO}_2$
19. $\text{H}_2\text{O}_2 + \text{H} = \text{HO}_2 + \text{H}_2$
18. $\text{H}_2\text{O}_2 + \text{M} = \text{OH} + \text{OH} + \text{M}$
16. $\text{H} + \text{HO}_2 = \text{H}_2 + \text{O}_2$
13. $\text{H} + \text{OH} + \text{M} = \text{H}_2\text{O} + \text{M}$
10. $\text{H} + \text{H} + \text{M} = \text{H}_2 + \text{M}$
9. $2\text{OH} = \text{O} + \text{H}_2\text{O}$
8. $\text{O} + \text{HO}_2 = \text{O}_2 + \text{OH}$
7. $\text{H} + \text{HO}_2 = 2\text{OH}$
6. $\text{OH} + \text{HO}_2 = \text{H}_2\text{O} + \text{O}_2$
5. $\text{H} + \text{O}_2 + \text{M} = \text{HO}_2 + \text{M}$
4. $\text{O} + \text{H}_2 = \text{OH} + \text{H}$
3. $\text{O} + \text{OH} = \text{H}_2\text{O} + \text{H}$
2. $\text{OH} + \text{H}_2 = \text{H}_2\text{O} + \text{H}$

Figure 3. Variation with time of the important reactions during premixed H_2/O_2 combustion as determined using the optimal dynamic model reduction approach described in section IV.A. Different reduced models can be used at different times; none require more than 13 of the 20 reactions in the complete model, and some are much smaller.

likely to be accurate only close to that reaction condition and time scale). The choice of time scale is sometimes problematic; in some cases, it would be better to use two different reduced models and to switch models at some intermediate time, rather than trying to find a single reduced model that works through the whole time interval.

We are currently pursuing an alternative time-local formulation of the problem represented by

$$\min \sum y_k \quad k = 1, \dots, N_{\text{reactions}}$$

$$|\mathbf{Z}_{\text{small},j}'(t) - d\mathbf{Z}_{\text{big},j}/dt| < \text{rtol} \times |d\mathbf{Z}_{\text{big},j}/dt| + \text{atol} \quad \forall t \in \{t_i\} \quad \forall j = 1, \dots, N_{\text{species}}$$

$$d\mathbf{Z}_{\text{big},j}/dt = \sum \eta_{jk} R_k(\mathbf{Z}_{\text{big}}) \quad \mathbf{Z}_{\text{big}}(t_0) = \mathbf{Z}_0 \quad (4)$$

$$\mathbf{Z}_{\text{small},j}'(t) = \sum \eta_{jk} y_k R_k(\mathbf{Z}_{\text{big}}(t))$$

$$y_k \in \{0,1\} \quad \forall k = 1, \dots, N_{\text{reactions}}$$

This new formulation has two huge practical advantages over the conventional formulation: (1) it is linear (and so convex) in \mathbf{y} , so that it can be solved efficiently for the globally optimal \mathbf{y} using branch and cut techniques; and (2) $\mathbf{Z}_{\text{small},j}'(t)$ is just an algebraic function of the state variables $\mathbf{Z}_{\text{big}}(t)$ and \mathbf{y} , so there is no need to solve a new system of ODEs for each choice of \mathbf{y} . (One still must solve an initial value problem for $\mathbf{Z}_{\text{big}}(t)$ as before, but this need only be done once and the results stored.)

We solve this linear optimization problem repeatedly for different reaction conditions in order to confirm the robustness of the reduced model. If a separate optimization problem is solved for each t_i , the reduced model changes dynamically to follow the chemistry. If a static model (i.e., fixed \mathbf{y}) is desired over a specified time interval $t_0 - t_i$, a single optimization problem can be

solved using multiple constraints evaluated at several t_i in the range $t_f \geq t_i \geq t_0$. If one wants the very best possible reduced model, one can instead perform different optimizations using only constraints evaluated at that time t_i ; this leads to a set of reduced models that dynamically follow the changes in the chemistry. As an example, in Figure 3, we show how the reduced models computed using eqs 4 vary with time during adiabatic isobaric ignition of a 12 vol % mixture of H_2 in O_2 . The H_2/O_2 mechanism used is the standard CHEMKIN¹⁴ test case with 20 reactions; the reaction was held at 1 atm, and the initial temperature was 1000 K. For the calculation presented in Figure 3, the tolerances on the discrepancy between the reduced models and the full model were set at $\text{rtol} = 0.7$ and $\text{atol} = 50 \text{ mol}/(\text{cm}^3 \text{ s})$.

B. Range of Validity of Reduced Kinetic Models.

As mentioned above, a major problem of the model-reduction approach is that one must first produce a large model that is known to include all of the important reactions and species under all possible reaction conditions of interest. The model completeness criteria in eq 1 provides a method of confirming that a given large model is indeed complete and, so, a criterion to use when assessing the range of validity of a model.

Our approach is to feed the kinetic model into XMG and to have XMG generate the edge species that can be formed in a single elementary step from the species in the model. One can then apply the test

$$d\mathbf{Z}_{\text{edge},m}/dt = \sum \eta_{mn} R_n(\mathbf{Z}_{\text{big}}(t; \mathbf{Z}_0)) < \text{tol} \times R_{\text{char}}(\mathbf{Z}_{\text{big}}(t; \mathbf{Z}_0)) \quad (5)$$

over a range of initial conditions \mathbf{Z}_0 to confirm that the structure of the model is robust. Note that one never needs to solve the very large system of differential equations involving \mathbf{Z}_{edge} , but at present, this approach still requires that a large number of initial value problems be solved to determine $\mathbf{Z}_{\text{big}}(t; \mathbf{Z}_0)$ if the dimen-

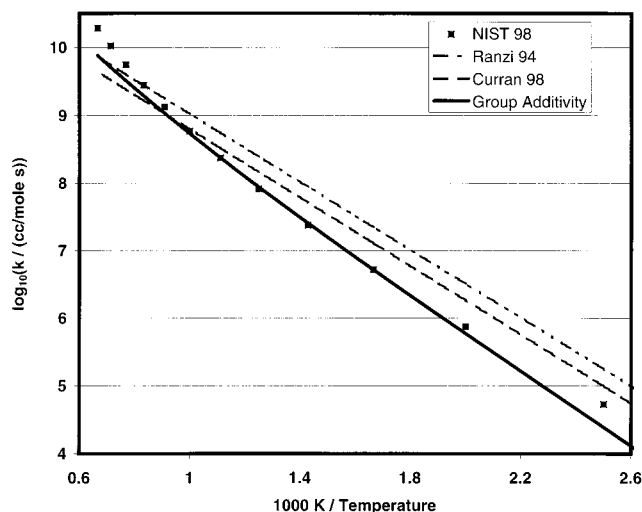


Figure 4. Our “group additivity” rate estimates based on quantum calculations compared with prior, primarily empirical, rate-estimation rules for H abstractions from methyl groups by H atoms. Our rate estimates agree well with the empirical NIST⁵¹ estimates in the middle temperature range where good experimental data are available. We predict sharper Arrhenius plot curvature at high temperatures than Ranzi et al.⁴² or Curran et al.⁴³

sion of the space of variations in \mathbf{Z}_0 is large. Fortunately, in many problems, most of the chemical intermediates are “partially equilibrated”, and the trajectory lies on an intrinsic lower-dimensional manifold (ILDM),³¹ so the effective dimension of this space is much smaller than the number of species in the model. We are currently developing practical methods to determine the range of validity of large kinetic models using this approach. We expect to use these methods to also establish the range of validity of each of the reduced models in the library used by the adaptive-chemistry procedure.

V. Calculating the Kinetic Parameters

A. TST/Group Additivity. In many situations, the accuracy of the simulation is constrained primarily by the accuracy of the reaction rate parameters employed. The number of reactions in these models can be very large, so it is not feasible to measure each reaction’s rate experimentally, much less to thoroughly characterize each rate at all temperatures and pressures of interest. Quantum-chemistry-based transition state calculations are now accurate enough to supplant experimental rates in many situations. Although such calculations are generally much faster and cheaper than experimental measurements, it is not yet computationally feasible to perform quantum calculations for each reaction in a complex kinetic model. Instead, we generalize from a limited number of quantum calculations and experimental data, using a scheme based on the organic chemistry idea of functional groups. Group additivity schemes very accurately describe thermochemical properties for stable species; we are extending this approach to predict the transition state properties (e.g., the free-energy of activation needed to compute reaction rates). We have tested the group additivity idea and have been able to identify “supergroups” characteristic of each type of transition state.³⁸ One advantage of this approach over the more conventional linear free-energy relationship (LFER) approach is that we naturally predict the

Arrhenius plot curvature; for example, see Figure 4. These calculations require correct handling of hindered internal rotors, including the fact that several bond lengths and angles often depend significantly on the torsional coordinate. Using this group additivity approach and other methods, we and others are making rapid progress at developing the set of reaction rate rules required for modeling the pyrolysis, combustion, and oxidation of organics.^{38–43}

B. Pressure Dependence. Pressure-dependent fall-off and chemical activation effects are major complications in the development of accurate reaction rate estimates for gas-phase reactions. It is not unusual for more than half of the reactions in a large kinetic model to be significantly pressure-dependent, and these rates can be orders of magnitude different from their high-pressure-limit values. Most detailed rate measurements and model validation experiments are performed at low pressures, whereas most practical reactors and engines are operated at pressures above 10 atm, so accurate pressure extrapolations are critical. Although it is frequently overlooked, even large-molecule reactions are often significantly pressure-dependent at high temperatures.⁴⁴ As a general rule, pressure dependence should be computed whenever

$$A > k_s[M] \quad (6)$$

and

$$T > (E_a/R)\{(\ln(2A/k_s[M]))^{-1} - (6N - 14)^{-1}\} \quad (7)$$

where A and E_a are the Arrhenius parameters for the lowest-energy reaction channel of the complex, k_s is the hard-sphere collision rate constant, $[M]$ is the concentration of the bath gas, and N is the number of atoms in the activated complex. These general rules come from using the strong-collision (Langmuir–Hinshelwood) approximation for the P dependence, using the inverse Laplace transform⁴⁶ expression for the microcanonical rate

$$k(E) = A\rho(E - E_a)/\rho(E) \quad (8)$$

and making the semiclassical approximation for the energy dependence of the density of states (treating all of the internal modes as vibrations)

$$\rho(E) \approx (E + \text{zero-point energy})^{3N-7} \quad (9)$$

The pressure dependence can be important at even lower temperatures for strongly chemically activated systems where the input channel is much higher in energy than the lowest-energy output channel.

A key aspect of pressure dependence is that many systems have numerous accessible wells (isomers). For example, there are more than 200 C_8H_{15} isomers accessible in the low-pressure addition of isopropyl radical to isoprene.⁴⁵ Only very recently^{47–50} have general pressure-dependence codes capable of handling arbitrarily large multiple-well problems been developed. No cases involving hundreds of isomers have yet been reported in the literature, in part because of the difficulty of preparing the input decks for such complex situations.

We have recently adapted the automatic reaction-generation code XMG to prepare the input decks for

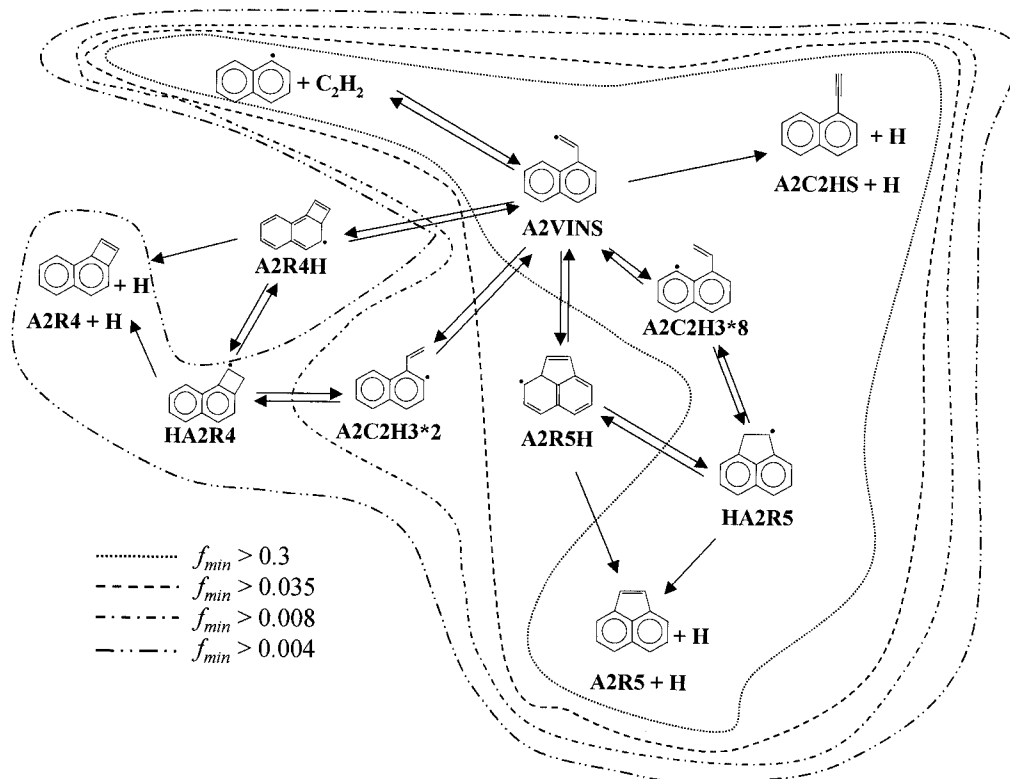


Figure 5. Truncated isomerization networks needed to predict $k(T,P)$ to various specified tolerances, f_{\min} , for the chemically activated 1-naphthyl + acetylene reaction at 1500 K and 10 atm. Each dashed line represents a pressure-dependent network "screened" so that unimportant pathways are not included. Each f_{\min} can be associated with a maximum error bound between the truncated network and full network predictions of the pressure-dependent rate constant; the lower the f_{\min} value, the lower the error bound.⁴⁵

these cases, comprehensively including all possible isomers, making these calculations much more feasible and avoiding the mistakes common with hand-construction of these models.^{13,20} We have also recently developed an algorithm that numerically screens out the isomers that are kinetically insignificant, making it feasible to address cases where the comprehensive enumeration of all of the isomers becomes impractical. This "ASA" algorithm is based on equations similar to eq 1 above, although because the unimolecular reactions important in pressure dependence have linear kinetics, it is possible to prove rigorous bounds on the truncation errors introduced by the screening.⁴⁵ The isomerization networks necessary to guarantee specified accuracies in the pressure-dependent rate predictions for the reaction of 1-naphthyl radical ($C_{10}H_7$) plus acetylene (C_2H_2) are shown in Figure 5.

VI. Conclusions

Soon, fairly accurate detailed kinetic models for high-temperature gas-phase free-radical chemistry (e.g., pyrolysis, combustion) will be easily and rapidly constructed and solved using computers. We have devised suitable criteria for including species and reactions and reliable methods for computing thermochemical parameters and enforcing microscopic reversibility. However, all existing methods for constructing and analyzing kinetic models are "local", i.e., they deal with only one reaction condition at a time. We are currently attempting to adapt these techniques to generate models that are valid over a range of conditions. Considerable work remains to be done on this range-of-validity issue, and numerous user interface tools must be developed before

constructing and working with very large kinetic models can become a routine part of practical reaction engineering.

The problem of coupling heat/mass transport, fluid dynamics, and complex chemical reaction models in an efficient and accurate way has challenged reaction engineering for decades. It has long been thought that kinetic model reduction must be part of the ultimate solution, but this subproblem has itself proved very challenging. Both problems have gradually yielded to hardware and software/algorithmic advances, but we are still a very long way from the goal of being able to simulate a realistic reactor or engine dynamically in three dimensions including all of the kinetically significant species and reactions (even for nonturbulent cases). Here, we present two new approaches that we believe are important advances toward that ultimate goal: the "adaptive-chemistry" approach to reacting flow simulation and a reformulation of the model-reduction problem that allows for an efficient solution to the global optimum. Although these methods both look very promising from the limited number of examples we have presented so far, we still need to develop efficient software implementations and to conclusively demonstrate their accuracy and effectiveness.

Although the fundamentals of reaction rate theory and quantum chemistry are now well-established, calculations can rarely compete with the accuracy of direct experimental rate measurements. Rate computations are likely to be the largest source of uncertainty in many kinetic models for many years to come, and there is still a lot of experimental chemistry that is not understood. Nonetheless, the methodology for computing reaction-family rate estimates based on detailed transition state

theory calculations is improving rapidly and will soon lead to a very significant improvement in accuracy over the currently used LFER relationships.

We are the first to implement $k(T,P)$ calculations in a general way that is suitable for use in an automatic reaction-generation algorithm. This advance will significantly improve the accuracy of the kinetic models for light hydrocarbon chemistry and for high-temperature gas-phase chemistry in general.

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