

Simulation of Chemical Mechanisms Using Computational Methods

Michael J. Manka, *Alchemy Software, Wesley Chapel, FL 33543-5759*

Keywords: Computer simulation, reaction modeling software, chemical mechanisms

Abstract

The use of computational methods for the simulation of chemical mechanisms is discussed. A computer program, *REACT for Windows*, is presented which implements the basic functions for simulating chemical mechanisms. Strategies for modeling experimental data and complex chemical mechanisms are discussed including methods for estimating kinetic rate data.

Introduction

With the proliferation and advancement of powerful desktop computers, the ability to simulate complex chemical mechanisms is readily available to even the most casual users of computational tools. An important factor in simulating chemical mechanisms is the availability of software which performs the necessary integration calculations and provides an easy to use interface for the entry of mechanistic and reaction time data, and contains the ability to present the calculated results in tables and plots for the user to view and print. Until recently software with these features has not been available in a single program running in a Microsoft Windows environment. A computer program, which provides all these features and many more, is now available. This program is called *REACT for Windows* and runs on desktop personal computers with any of the Microsoft Windows operating system. In this paper, I would like to review the important features involved in simulating chemical mechanisms and how they are implemented in a computer program such as *REACT for Windows*.

The three basic features of a functional program which performs computational simulations of chemical mechanisms are the input of mechanistic and reaction time data, the differential equation integration algorithm, and the output of the calculated results in useable formats. We will discuss each of these three areas and how they are implemented in the *REACT for Windows* program. Using specific mechanistic examples, we will also present results calculated using the *REACT* program. We will also suggest strategies for the modeling of experimental data based on a hypothetical mechanism and the simulation of a chemical mechanism where, perhaps, not all the reaction rate coefficients are known. While it may be straightforward to hypothesize individual reactions in a chemical mechanism, it can be a much more difficult matter to provide reasonable kinetic rate data for those reactions if none are available. Thus, methods for the estimation of kinetic rate coefficients will be discussed in some detail.

React for Windows Program

General Description. The *REACT for Windows* program evolved from previous programs^{1,2} developed at the National Institute of Standards and Technology (NIST) and used to solve chemical mechanisms by experimental chemical kineticists. Unlike its predecessors, *REACT* has been written to execute on personal computers (PC) running any of the popular Microsoft Window operating system environments, including Windows 3.1/3.11, Windows 95/98 and Windows NT. The program requires as a minimum an Intel 80486 microprocessor with math coprocessor and a clock speed of 66 MHz or its equivalent. The program also recommends a graphics accelerator card capable of supporting a monitor resolution of 1024 × 768 and 256 colors or better. The program was designed for a 17 inch monitor and this size monitor or larger is recommended for optimal use with the recommended monitor resolution. While a mouse is required, there is an equivalent keystroke combination for most mouse initiated actions. The program supports the printing of reports with tabulated results as well as printing plots of results. The program is composed of three integral parts: the chemical mechanism editor, differential equation integration algorithm, and calculated results tabulation and plotting function. Each of these three parts will now be discussed.

Chemical Mechanism Editor. The chemical mechanism editor facilitates the entry and editing of the mechanistic and reaction time data. This data includes the title of the mechanism and any ancillary information about the mechanism, the chemical reactions in the mechanism and their respective forward and reverse rate coefficients, the initial concentrations of each species involved in the mechanism, and the reaction times where the concentration data and its time derivative are reported for each species. The mechanism title identifies the mechanism under simulation and any additional information, such as the reaction temperature, can be entered as ancillary information and saved with the mechanistic data. The reaction equations are entered into the program with the limitation that each species name cannot exceed twelve characters. There is provision for including the charge of ions and the spectroscopic state of the species

within the species name. Like its predecessor programs, the *REACT* program does not permit the entry of reactions with orders higher than two. If higher order reactions, such as third-order reactions are involved in the mechanism, they can be simulated by using consecutive, second-order reactions. The program does allow the introduction and removal of species using zeroth-order reactions, as well as the more familiar first- and second-order reactions. If the rate coefficients are known, they can be entered directly after the entry of the reaction equation. If they are not known, but kinetic rate parameters for the reaction are available from the literature or a kinetic rate database like the NIST Chemical Kinetics Database⁵, a reaction rate calculator is provided to facilitate the calculation and entry of rate coefficient data. The mechanism editor provides the ability to add a reaction to the mechanism, insert a reaction into the mechanism, reposition a reaction within the mechanism, delete and hide a reaction from the mechanism, and edit a reaction within the mechanism. Once a reaction is added to the mechanism, it appears in the mechanism list of reactions where it can be accessed for editing or deletion. These features provide abundant flexibility in manipulating the reaction mechanism.

The mechanism editor monitors all entries for reasonableness and prevents illegal entries. It also automatically performs all the necessary bookkeeping regarding species in the mechanism as reactions are entered, deleted or edited. The species are arranged alphabetically by length of name in a list of components. Initial concentrations of species having non-zero values are easily entered using this list of components. The initial concentration of all newly added species are initialized to zero and may need to be changed prior to performing a calculation.

There is considerable flexibility available in selecting the reaction times. The reaction times can be any combination of as many as 1000 linearly or geometrically spaced values and any number of other specific values. Once all the pertinent mechanistic data has been entered, the integration algorithm can be called to perform the calculations. The mechanism can have no more than 85 species in the current version of the program, but the number of reactions allowed is quite large (>2000) and is mainly limited by the memory available in the computer. The program uses dynamic memory allocation to accommodate the array size requirements of the mechanism. Mechanistic data are easily saved to memory for future retrieval and use.

Integration Algorithm. The integration calculation simulates homogeneous reactions occurring in a fixed volume at a constant temperature. The differential equation integration algorithm is an implementation of an adaptive step size fifth-order implicit Runge-Kutta method with fourth-order error control^{2,4}. Similar differential equation integration algorithms have been presented previously⁵⁻¹⁰. To perform the integration in a reliable and efficient manner, the integration algorithm uses variable order, variable step methods of the linear multi-value type. This means that the integration algorithm adapts its integration step size, as well as the integration formula order, so as to progress from the initial end of the time range to the other with the least amount of work. The step size selection is completely automatic, including the initial step size. The relative integration error value, which is set by the user, controls the integration step size. A smaller value results in greater overall integration accuracy, at the expense of longer execution time. Solution values at the user's reaction time are rarely exact integration end points. Normally, integration proceeds beyond a reaction time value and then the solution is obtained by an appropriate backward interpolation. The integration method is implicit and requires the use of a Jacobian matrix, which is calculated exactly by the algorithm. The relative integration error value governs the error control mechanism, which in turn controls the step size strategy as previously mentioned. Errors are measured with each individual step. Thus, there is no guarantee that cumulative errors will not be significantly larger, but experience has shown that for stable systems this very rarely occurs. The integration process can be halted and its progress monitored. The integration algorithm automatically reports its status every 5000 integration steps if the final end point of the time range is not achieved or when an error occurs. The results of the integration process include not only concentration data but also the time derivative of the concentration data for each time point including zero time. The latter data are important in the simulation of photon emission in spectroscopic measurements.

Displaying Results. Once the integration has been successfully completed, the program displays the concentration results for all the species in a tabular format. The program provides considerable flexibility in the presentation and viewing of both the concentration data and time derivative of the concentration data of each species. The data for any number of species can be presented in any desired order for an enhanced focus and comparison of pertinent results. Any desired set of results can also be printed in a report format together with optional mechanistic information. Specific sets of data can be exported to an ASCII file for importing into other software applications such as Microsoft Excel for further analysis. Finally, any data set type, concentration or time derivative of concentration data, can be plotted for a graphical summary view of trends in the data for that species. In an effort to limit the complexity of an individual plot, no more than five such data sets can be plotted at one time. A printed copy of the plot can

also be readily obtained using either laser or inkjet type printers. Customized plots intended for presentation or publication can be obtained using graphics programs and data exported as mentioned above. Reports containing calculated results can also be generated. Again, like the ability to display data, any combination of selected data can be included in the report. The amount of mechanistic information included in the report can be controlled as well.

Program Interface. As a Windows compatible program REACT has many features common to Windows programs. The menu bar contains menu items familiar to most users as well as menu items specific to REACT. It contains an extensive online Help function to aid the user in using the program efficiently and answering questions about the program. A tool bar is included to provide access to icons, which activate the most frequently used commands. A status bar at the bottom of the program window provides information about the status of the program and instructions about what to do next. The interface of the program is composed of four tabbed pages which can be selected using the mouse. The first page is titled, Mechanistic Data, and is used to enter and edit all the mechanistic data. The second page is the Reaction Times page and is used to enter and edit the reaction times and adjust the Relative Error Value for the integration process. The command button to begin the integration calculation is also located on this page as well as in the tool bar. The Tabulated Data page, which is used to present the calculated results in a tabular format, is automatically exposed after an integration calculation has been successfully completed. Once exposed, one can view the calculated results and access the display options for selecting data items for display. The Plot of Results page, which is used to display plots of selected results, also becomes accessible after an integration calculation has been successfully completed and is exposed to access the plot options for the selection of data items to be presented in a plot.

Modeling of Experimental Data

The modeling of experimental data provides a straightforward example of the application of the REACT program. Under ideal circumstances, experimental data is obtained under conditions where a single rate coefficient is determined from the rate of appearance or disappearance of a single reaction component. In this case a straightforward mathematical analysis of the data may be sufficient. However, modeling the complete mechanism may reveal insights into discrepancies in the fit of the data due to unanticipated reactions. The strategy used in making experimental measurements of kinetic rate parameters is to reduce the kinetic importance of all reactions except the one under investigation. This is usually done by judiciously adjusting the initial concentrations of the reactants and the reaction temperature. However, by modeling the mechanism in sufficient detail one can obtain a better appreciation for the influence each reaction may have on the one under investigation and anticipate difficulties in making kinetic rate measurements under various reaction conditions, i.e. as the initial component concentrations or reaction temperature are changed. Under simulation, any prior assumptions about reaction species, such as steady-state conditions, are not only not required but are totally unnecessary.

The recommended approach to modeling experimental data is as follows. First, it requires entering the chemical mechanism under investigation in as much detail as possible into the REACT or similar program. Consider the mechanism shown below which is operative for many mechanisms involving fuel-related reactions where radical chemistry is predominant. The mechanism includes thermally initiated bond homolysis, hydrogen transfer and radical recombination and disproportionation reactions. The available rate coefficients for the reactions at the temperature of interest and the initial species concentrations are also entered into the program. Reasonable estimates of the upper or lower limit for some of the rate coefficients may



Fuel-Related Thermal Mechanism

suffice if actual values are not available. The rate coefficient under investigation is then adjusted to provide the best fit with experimental results. Simulated results may be exported for use in a spreadsheet program like Microsoft Excel where statistical analyses of the experimentally measured results and the calculated results can be performed.

Dissociation Reaction. Let us first consider the modeling of experimental data from the measurement of the dissociation reaction of AA. Once the relevant mechanistic information, including available kinetic rate data, and initial species concentrations have been entered into the program, reaction times corresponding to experimental times are entered using the specific reaction times program feature. An initial choice for the value of k_1 can be made based on the first reliable experimental measurement of the disappearance of AA using the following equation.

$$k_1 = \frac{1}{t} \ln \frac{[AA]_0}{[AA]_t}$$

where t is the experimental time at which the measurement of the disappearance of AA was made. The simulation calculation is repeated, while adjusting the value of k_1 in the program mechanism, until an acceptable fit of the experimental data and the calculated results are obtained. Statistical analyses can be applied to obtain the goodness of fit using external programs. A typical plot of the result of modeling k_1 using the above mechanism is shown below in Figure 1. Alternatively, each experimental data point could be fit exactly under simulation and the resultant rate coefficient values would then be averaged. This method is effective when there are only a few data points. The ratio of the rate coefficients for the radical recombination and disproportionation reactions of D• radicals may also be obtained from experimental data if these reactions are operative in the above mechanism. The rate of hydrogen transfer may also be obtained, but more suitable initial reaction conditions will provide more reliable experimental data which we will address next.

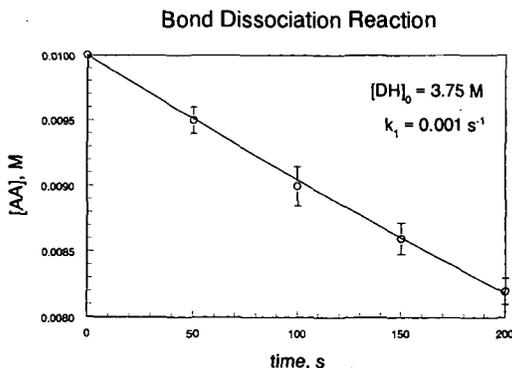


Figure 1. Plot of bond dissociation reaction experimental measurements and its reaction simulation results.

Hydrogen Transfer Reaction. The rate of hydrogen transfer from the hydrogen donor DH to the radical A• is governed by the rate coefficient k_2 in the above mechanism. This rate coefficient can be determined by again experimentally measuring the disappearance of AA and DH and the appearance of AH, but with the relative initial amounts of AA and DH changed. In this reaction the initial reactant concentrations of AA and DH are adjusted so that the rate of recombination of A• becomes competitive with its rate of hydrogen abstraction from DH. An initial choice for k_2 is given by the following equations¹¹.

$$k_2 = \frac{1}{t} \frac{[AH]}{[DH][A^{\bullet}]}$$

where

$$[\text{DH}] = [\text{DH}]_0 - [\text{DD}] - \frac{[\text{AD}]}{2}$$

and

$$[\text{A}^*] = \frac{\sqrt{k_1 [\text{AA}]^2}}{1 + 2 \frac{[\text{DD}]}{[\text{AD}]}}$$

The time average concentration of AA is given by

$$[\overline{\text{AA}}] = \sqrt{(1 - \xi_{\text{AA}}) [\text{AA}]_0^2}$$

where ξ_{AA} is the extent of reaction based on the disappearance of AA. The simulation calculation is repeated, while adjusting the value of k_2 in the program mechanism, until an acceptable fit of the experimental data and the calculated results is obtained. A typical plot of the result of modeling k_2 using the above mechanism is shown in Figure 2. Using additional experimental measurements of the concentrations of AA, DH and the various combination products, the rate coefficients for reactions affecting these species can also be adjusted to improve the overall fit of all the experimental data to the calculated results.

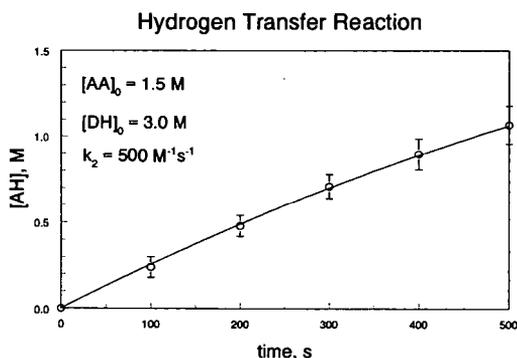


Figure 2. Plot of hydrogen transfer reaction experimental measurements and its reaction simulation results.

The strategy for adjusting any rate coefficient in a mechanism under simulation is to focus on the reactions having the most kinetic importance. This can be accomplished by determining the time derivative of each species concentration at initial reaction times where the reactant concentrations are known. Using estimated rate coefficients if necessary, a crude reaction analysis can be performed to provide an ordering of reaction importance. If the rate coefficient for a reaction is adequately known, it can be removed from the group of reactions with uncertain rate coefficients. If two reactions are contributing prominently to the change in the concentration of the species being measured, the only recourse may be to adjust the reactant concentrations of these reactions in order to discriminate their contributions. Once the final rate coefficients of interest are determined, the agreement between calculated results and experimental data should remain good for a wide range of initial species concentrations.

Simulation of Complex Chemical Mechanisms

The ability to simulate a complex chemical mechanism depends not only on providing a sufficiently complete reaction mechanism, but also requires providing rate coefficients for these reactions with adequate accuracy. As chemists, it should not be particularly difficult to hypothesize the important reactions in a mechanism, but the determination or estimation of

unknown rate coefficients can be quite challenging. The first step in the preparation for the simulation of any mechanism is to obtain as much information about it as possible from the literature. This information should provide the basic framework for developing a model of the mechanism. Once this information has been gathered, the task of assigning forward and reverse rate coefficients to each reaction begins. As information on the mechanism is researched in the literature, information on reaction rates should also be obtained. Kinetic rate parameters found in the literature can be used to calculate rate coefficients appropriate for the reaction temperature used in any simulation, even if the kinetic data must be extended to apply to the reaction conditions of interest. An excellent source for the compilation of gas phase rate data is the NIST Chemical Kinetics Database³ which is available for searching on personal computers. The NIST kinetics database primarily contains kinetic rate measurements of hydrocarbon reactions in the gas phase and provides kinetic rate parameters and references to the literature on these measurements. Some of the references provide critical evaluations of the available rate data for a reaction and these evaluations should be used as part of the evaluation of the kinetic rate parameters for the reactions in the mechanism being modeled. Often, however, an evaluation of the available kinetic rate data is left to the user. While this analysis may not be straightforward, it should provide a set of kinetic rate parameters which can be used to initially calculate rate coefficients. These initial values can be adjusted later to agree with whatever experimental data is available on the process. A similar compilation of gas phase reactions to consider is *Bimolecular and Termolecular Gas Reactions*¹², although these reactions should be included in the NIST database. Another excellent source of kinetic rate data is the *International Journal of Chemical Kinetics* where rate measurements for hydrocarbon reactions occurring in the liquid phase are also reported. *Chemical Abstracts* can also be searched to find additional literature references in other journals like the *Journal of Physical Chemistry* and engineering oriented journals on process chemistry. Despite the availability of these resources, it is often necessary to estimate the rate of a reaction where little or no data exists.

Estimation of Kinetic Rate Data

The ability to calculate kinetic rate data from first principles has made important progress. The calculation of energy barriers for hydrogen transfer reactions involving small hydrocarbon radicals and various hydrocarbons using *ab initio* methods and transition state theory has yielded results in good agreement with reliable experimental data¹³. But before we resort to this type of high-level calculation, let us explore simpler and more straightforward approaches to estimating rate parameters for a reaction. The relationship between kinetics and thermodynamics lies in the equilibrium constant. For a given reaction in the gas phase, the equilibrium constant for the reaction is given by the ratio of the forward and reverse rate coefficients as shown in the following equation.

$$K_{eq}(T) = \frac{k_f(T)}{k_r(T)} \quad (7)$$

where each variable is a function of the temperature T . But the equilibrium constant can be calculated directly from thermodynamic properties of the reactants and products involved in the reaction yielding the Gibbs energy of the reaction, $\Delta G(T)$. This relationship is represented by the following equation.

$$K_{eq}(T) = \exp\left(\frac{-\Delta G(T)}{RT}\right) \quad (8)$$

where R is the universal gas constant and

$$\Delta G(T) = \Delta H(T) - T\Delta S(T)$$

The enthalpy and entropy changes of a reaction, $\Delta H(T)$ and $\Delta S(T)$, respectively, are determined from the individual reactant and product enthalpies and entropies.

$$\Delta H(T) = \sum_{\text{products}} H_p(T) - \sum_{\text{reactants}} H_r(T)$$

and

$$\Delta S(T) = \sum_{\text{products}} S_p(T) - \sum_{\text{reactants}} S_r(T)$$

The problem is now reduced to determining the enthalpy and entropy change of the reaction over the temperature range of interest. This subject has been covered in detail in *Thermochemical Kinetics*¹⁴ by S. Benson. Benson eloquently discusses in his book how thermodynamic data are used to calculate kinetic rate parameters. However, the problem often arises that there are insufficient thermodynamic data to perform the calculation. Benson solves this problem in his book by introducing a group additivity method for calculating the enthalpy and entropy of a species based on group enthalpy and entropy values for molecular fragments of chemical species. Group values have been used to estimate thermodynamic properties of hydrocarbon molecules and radicals for over ten years^{15, 16} and new group values continue to be added although there does not seem to be a common compilation of currently accepted values.

Once the thermodynamic data is assembled and ΔH and ΔS are calculated, we can begin to address the problem of calculating the individual rate coefficients. If one of the rate coefficients is known, the other can be obtained directly using equations 7 and 8. If neither rate coefficient is known then one of them must be calculated. Benson addresses this calculation in his book as well for a number of common reaction types. He relates the above thermodynamic properties with the kinetic rate parameters, Arrhenius A factor and activation energy, E , for the forward and reverse reactions.

$$\frac{A_f}{A_r} = \exp\{T\Delta S\}$$

and

$$E_f - E_r = \Delta H$$

where the subscripts f and r refer to the forward and reverse reactions, respectively. In each of the equations above, one of the rate parameters for the forward or reverse reaction must be known in order to solve for the other parameter,

The rate coefficient for a reaction may also be obtained by analogy with a similar reaction whose rate coefficient is known or can be more easily estimated. Adjustment in the activation energy and A factor may be made to account for differences in the enthalpy and entropy change differences in the two reactions. Since the enthalpy change for a bond dissociation reaction can be equated with the bond dissociation energy, these values can be used directly as the activation energy when calculating these rate coefficients.

As an example, let us consider the initial stages of the pyrolysis mechanism of tetralin (1,2,3,4-tetrahydronaphthalene). Briefly, the mechanism initiation involves the bond homolysis reaction of a carbon-carbon bond in the saturated ring producing a diradical with benzylic and alkyl carbon-centered radicals. The alkyl carbon-centered radical portion in turn abstracts a hydrogen atom from other tetralin molecules forming a resonance stabilized radical, 1-tetra-yl and reducing the diradical to a single resonance-stabilized carbon-centered radical, 3-propylbenzyl radical. Hydrogen transfer and structural rearrangements occur to form the major products, 1-methylindan, naphthalene and butylbenzene. The mechanism includes 20 reactions and 20 species. These reactions and their rate coefficients were obtained from the literature¹⁷⁻²⁸ or estimated for a reaction temperature of 478°C. Simulation calculations were performed in an effort to model experimental data. Comparisons of the calculated results and experimental data for the concentrations of tetralin and the major products are shown in Figures 3 and 4. The result of modeling this mechanism provides an affirmation of the important reactions involved and a framework by which evaluate extensions to this mechanism.

In conclusion, it can be stated that the simulation of chemical mechanisms is an important computational tool for understanding and modeling chemical reactions. Hypothetical mechanisms can be tested by comparison with experimental data and once verified predictive calculations can be performed with confidence. The simulation of chemical mechanisms is applicable to all areas of chemistry which involve chemical reactions and with the availability of

powerful desktop computers and suitable software, like *REACT for Windows*, its application is well within the capabilities of most researchers.

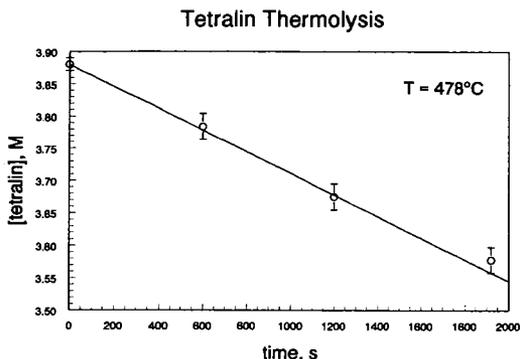


Figure 3. Simulation of tetralin concentration as a function of time during its thermolysis at a temperature of 478°C . Experimental data is indicated by the open circles and associated error bars.

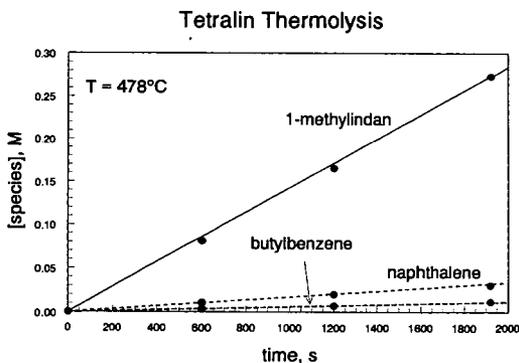


Figure 4. Simulation of species concentrations as a function of time during tetralin thermolysis at a temperature of 478°C . Experimental data is indicated by the closed circles.

References

1. Brown, R. L. *HICHM: A Fortran Code for Homogeneous Isothermal Chemical Kinetics Systems*, NBSIR 81-2281; National Bureau of Standards: Gaithersburg, MD, 1981.
2. Braun, W.; Herron, J. T.; Kahaner, D. K. *Int. J. Chem. Kinet.* **1988**, *20*, 51.
3. Mallard, W. G.; Westley, F.; Herron, J. T.; Hampson, R. F.; Frizzell, D. H. *NIST Chemical Kinetics Database: Version 5.0*; National Institute of Standards and Technology: Gaithersburg, MD, 1993.
4. Boisvert, R. F.; Howe, S. E.; Kahaner, D. K. *The Guide to Available Mathematical Software (GAMS)*, PB 84-17135; National Technical Information Service (NTIS): Springfield, VA 12161, 1984.
5. Gear, C. W. *Numerical Initial Value Problems in Ordinary Differential Equations*; Prentice Hall: Englewood Cliffs, NJ, 1971.
6. Vernier, J. H. *SIAM J. Numer. Anal.* **1978**, *15*.

7. Norris, A. C. *Computational Chemistry: An Introduction to Numerical Methods*; John Wiley & Sons: New York, 1981.
8. Cash, R.; Karp, A. H. *ACM Transactions on Mathematical Software* **1990**, *16*, 201.
9. Press, W. H.; Teulosky, S. A.; Vetterling, W. T.; Flannery, B. F. *Numerical Recipes in C*, 2nd ed.; Cambridge University: Cambridge, UK, 1992.
10. Conway, D. J. *Dr. Dobbs's J.* **1995**, *20*(12), 52.
11. Manka, M. J.; Brown, R. L.; Stein, S. E. *Int. J. Chem. Kinet.* **1987**, *19*, 943.
12. Kerr, J. A.; Moss, S. J. *Bimolecular and Termolecular Gas Reactions*, Vol. 1; CRC Press: Boca Raton, FL, 1981.
13. Litwinowicz, J. A.; Ewing, D. W.; Jurisevic, S.; Manka, M. J. *J. Phys. Chem.* **1995**, *99*, 9709.
14. Benson, S. W. *Thermochemical Kinetics*, 2nd ed.; John Wiley & Sons: New York, 1981.
15. O'Neil, H. E.; Benson, S. W. *Int. J. Chem. Kinet.* **1969**, *1*, 221.
16. McMillen, D. F.; Golden, D. M. *Annu. Rev. Phys. Chem.* **1988**, *33*, 493.
17. Hooper, R. J.; Battaerd, H. A. J.; Evans, D. G. *Fuel*, **1979**, *58*, 132.
18. Benjamin, B. M.; Hagaman, E. W.; Raaen, V. F.; Collins, C. J. *Fuel*, **1979**, *58*, 386.
19. Collins, C. J.; Raaen, V. F.; Benjamin, B. M.; Maupin, P. H.; Raork, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 5009.
20. Franz, J. A.; Camaioni, D. M. *J. Org. Chem.* **1980**, *45*, 5247.
21. Franz, J. A.; Camaioni, D. M. *Fuel* **1980**, *59*, 803.
22. Pennington, J. M. L. *Int. J. Chem. Kinet.* **1982**, *14*, 761.
23. Brower, K. R.; Pajak, J. *J. Org. Chem.* **1984**, *49*, 3970.
24. Franz, J. A.; Barrows, R. D.; Camaioni, D. M. *J. Am. Chem. Soc.* **1984**, *106*, 3964.
25. McPherson, W. P.; Foster, N. R.; Hastings, D. W.; Kalman, J. r.; Gilbert, T. D. *Fuel* **1985**, *64*, 457.
26. King, H.; Stock, L. M. *Fuel* **1981**, *60*, 748.
27. Allen, D. T.; Gavalas, G. R. *Int. J. Chem. Kinet.* **1983**, *15*, 219.
28. Franz, J. A.; Camaioni, D. M.; Beishline, R. R.; Dalling, D. K. *J. Org. Chem.* **1984**, *49*, 3563.