Preprint
UCRL-JC-141541

Kinetic Modeling of Hydrocarbon Autoignition at Low and Intermediate Temperatures in a Rapid Compression Machine

H. J. Curran, W. J. Pitz, C. K. Westbrook, J. F. Griffiths, C. Mohamed

This article was submitted to
3rd Workshop on Modeling of Chemical Reaction Systems,
Heidelberg, Germany, July 24-26, 1996

November 1, 2000

DISCLAIMER

This document was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor the University of California nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or the University of California, and shall not be used for advertising or product endorsement purposes.

This is a preprint of a paper intended for publication in a journal or proceedings. Since changes may be made before publication, this preprint is made available with the understanding that it will not be cited or reproduced without the permission of the author.

This work was performed under the auspices of the United States Department of Energy by the University of California, Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48.

This report has been reproduced directly from the best available copy.

Available electronically at http://www.doc.gov/bridge

Available for a processing fee to U.S. Department of Energy
And its contractors in paper from
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
Telephone: (865) 576-8401
Facsimile: (865) 576-5728
E-mail: reports@adonis.osti.gov

Available for the sale to the public from
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
Telephone: (800) 553-6847
Facsimile: (703) 605-6900
E-mail: orders@ntis.fedworld.gov
Online ordering: http://www.ntis.gov/ordering.htm

OR

Lawrence Livermore National Laboratory
Technical Information Department's Digital Library
http://www.llnl.gov/tid/Library.html

Kinetic Modeling of Hydrocarbon Autoignition at Low and Intermediate Temperatures in a Rapid Compression Machine

H. J. Curran, W. J. Pitz, C. K. Westbrook
Lawrence Livermore National Laboratory
P. O. Box 808, Livermore, CA 94550 USA
email: westbrook1@llnl.gov

and

J. F. Griffiths, and C. Mohamed
Chemistry Department, The University of Leeds
Leeds, LS2 9JT England
email: johng@chem.leeds.ac.uk

ABSTRACT

A computer model is used to examine oxidation of hydrocarbon fuels in a rapid compresson machine. For one of the fuels studied, n-heptane, significant fuel consumption is computed to take place during the compression stroke under some operating conditions, while for the less reactive n-pentane, no appreciable fuel consumption occurs until after the end of compression. The third fuel studied, a 60 PRF mixture of iso-octane and n-heptane, exhibits behavior that is intermediate between that of n-heptane and n-pentane. The model results indicate that computational studies of rapid compression machine ignition must consider fuel reaction during compression in order to achieve satisfactory agreement between computed and experimental results.

1. INTRODUCTION

Kinetic modeling of hydrocarbon ignition has been a very useful tool in many combustion chemistry studies. At high temperatures, coupled experimental and kinetic modeling of shock tube ignition of fuel/oxidizer mixtures have long been particularly productive. The special advantage of the shock tube is that it is an experiment where onset of high temperature and pressure is very rapid, compared to the time required for reaction of the fuel and oxidizer. Therefore, models can assume that no reaction has occurred until the arrival of the shock wave, and both the experiment and the model effectively have the same initial time. This absence of ambiguity in timing and the virtually instantaneous jump to the initial reactive condition are quite important in this area of combustion modeling.

Kinetic models are often developed on the basis of experiments carried out for a rather narrow range of experimental conditions. Shock tube experiments and models are a good example of this narrow focus, emphasizing the high temperature regime. However, extrapolation of kinetic models from one experimental regime to another regime is difficult and often inaccurate. For example, shock tube models are incorrect when applied to low temperature hydrocarbon oxidation, since the chain branching reactions and many of the reaction paths are different in the two regimes. The best solution for this problem is to find experimental tests that are closer to the conditions desired. In the past, we have emphasized [1,2] the value of so-called "comprehensive reaction mechanisms" which include reaction submechanisms to describe combustion in each range of conditions to be studied, and comprehensive mechanisms have been developed for many practical hydrocarbon fuels [3-6].

Important practical combustion problems can occur at temperatures in the range from 600 - 1000 K. For example, many problems associated with diesel and spark ignition engines take place in this range, and kinetic modeling has provided basic understanding of the chemistry in this regime [7-10]. For many years, the rapid compression machine (rcm) has been used to provide experimental data under carefully controlled conditions to develop and test these lower temperature kinetic mechanisms [11-15]. Typically, compression time scales in rcm experiments are assumed to take place on a time scale which is short compared with the time scales of the fuel ignition and oxidation. Like in the shock tube, it is commonly assumed that reaction begins at the time where the compression is complete, so the reaction time for the reactive gases is equivalent to the time subsequent to the end of the compression stage.

The present work addresses the point that rates of compression in most rapid compression machine experiments are slow enough that, under certain operating conditions, considerable amounts of reaction may occur prior to the end of the compression stage, and chemical models should include reactions taking place during the compression phase.

2. RCM EXPERIMENTS

In any rcm experiment, a reactive mixture of fuel, oxygen, and diluent is placed in a combustion chamber. This mixture is then rapidly compressed by a single piston stroke to its "initial condition" for reaction. In a typical case with a hydrocarbon fuel, this compressed mixture will experience an ignition delay of some milliseconds duration, followed by rapid reaction or ignition. Depending on the temperature, pressure, and fuel/oxidizer ratio, and on the specific structure and size of the fuel molecule, this ignition process can be quite complex and consist of multiple stages, while under other operating conditions a single-stage ignition is observed. Most often, the rate of reaction and the ignition delay time in the combustion chamber are observed by measuring the pressure in the reactor. Further diagnostics can be used to determine fuel consumption and species concentrations during the ignition process, and these concentrations can then be used to provide additional tests of a proposed chemical reaction mechanism.

Kinetic models can then be used to interpret the measured pressure-time histories and other data, including any complex features that were observed. It is usually convenient to assume that, as in the shock tube, no reaction has occurred until the end of the compression stroke. The temperature at the end of compression can be computed from the experimental pressure measurements, assuming an adiabatic compression. This of course assumes that the compression is sufficiently rapid that no heat is lost to the combustion chamber walls and that no exothermic reactions occur during compression.

Recent rcm experiments carried out at Leeds University have indicated that these assumptions are incorrect under some operating conditions, and a careful analysis of this issue was undertaken. The rcm at Leeds University has been described previously in considerable detail [15-19], and only a few details will be presented here. The compression ratio used in this study was 11:1 and the compression stroke duration is 22 ms. Stoichiometric mixtures of fuel and "air" were used, and fuels included n-heptane, n-pentane, and a mixture of 60% iso-octane with 40% n-heptane, chosen for reasons described below. The "air" used in the experiments consisted of 21% oxygen and 79% diluent. The diluent consisted of mixtures of nitrogen and argon, but the total concentration of diluent was always equal to 79% of the "air". Because of the differences in specific heat between nitrogen and argon, the compressed gas temperature could be varied by selecting different ratios of nitrogen to argon in the diluent; the highest temperatures were obtained when the diluent consisted entirely of argon, and the lowest temperatures with nitrogen.

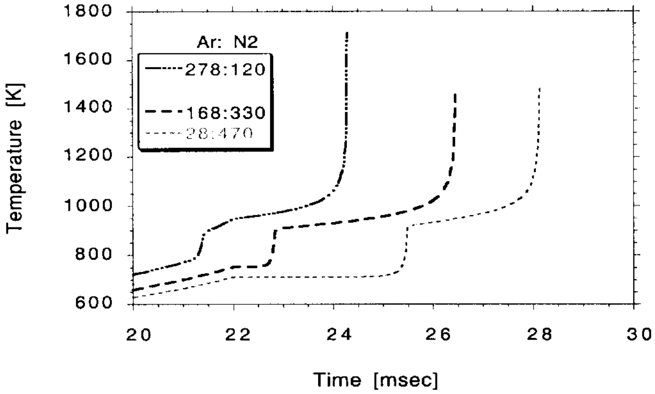

Figure 1. Computed temperature histories for four n-heptane/O_2/Ar/N_2 mixtures. Temperatures at end of compression are 711, 753, 798 and 949 K in order of increasing Ar concentration.

A typical example of the modeling results is shown as the bottom curve in Figure 1, where the diluent mixture consisted of Ar:N_2 = 28:470 (partial pressures measured in mm Hg). The initial temperature at the end of compression (22 ms in Fig. 1) was 711 K. This mixture ignited in two distinct stages, the first stage occurring at about 25.5 ms (3.5 ms after the end of compression), and the second stage slightly after 28 ms (6 ms after the end of compression).

As the ratio of argon/nitrogen is increased, the post compression temperature increases and the overall ignition delay time becomes shorter, as shown by the second curve (Ar:N_2 = 168:330) in Fig. 1, and both first and second stages occur earlier. As the Ar:N_2 ratio is further increased, onset of a negative temperature coefficient (ntc) region is observed, and the total ignition delay time actually increases with increasing temperature. At this point, the first stage ignition occurs immediately at the end of the compression stroke, and the increase in total ignition delay is clearly equivalent to an increase in the second stage of ignition. The results in Figure 1 actually represent computed results based on the kinetic model described below, but these results have been shown [20] to agree well with the experimental results, both with respect to the two-stage nature of the ignition for these mixtures as well as reproducing the absolute delay times for both stages.

The final curve in Fig. 1 demonstrates behavior that is quite different; the rapid temperature rise that is associated with the first stage ignition can be seen to occur at a time of approximately 21.3 ms, about 0.7 ms prior to the end of the compression stroke. The resulting mixture temperature at the end of the compression is thus 949 K. As discussed below, the entire first stage of ignition has occurred prior to the end of the compression stroke.

The same type of behavior was observed experimentally and reported previously [15,20] and was apparent from three different types of phenomena. First, some of the more reactive mixtures were found to have pressures and temperatures at the end of the compression stroke that were significantly greater than could be achieved by adiabatic compression alone. Second, direct measurements of reactant concentrations in the reaction chamber during the compression stroke found that fuel consumption prior to the end of compression for some cases was as great as 40%. Even in some cases where no observable heat release occurred during the compression stroke, n-heptane consumption was predicted computationally to be 5-10% of the total fuel present initially.

The final point is somewhat more subtle. It was found experimentally [15] that when n-heptane was the fuel, temperatures at the end of compression below about 750 K could be attained and temperatures above 850 K could be attained, but there was an interval between 750 and 850 K which was essentially inaccessible, regardless of argon/nitrogen content. The implication is that the onset of the first stage of ignition is very rapid once the mixture temperature reaches 750 K, so that any mixture that reaches this level during compression will react and the resulting temperature will quickly increase to 850 K. The "inaccessible" temperature range in the model simulations was found to be 800 - 900 K, slightly higher than the corresponding experimental values, but the same phenomenon is responsible for the existence of that interval.

3. DETAILED KINETIC REACTION MECHANISM

The kinetic model used to simulate this system has been developed over a number of years, primarily intended to study fuel chemistry issues related to engine knock in internal combustion engines. The mechanism combines a well-tested high temperature oxidation mechanism with a very detailed treatment of low and intermediate temperature oxidation, including alkylperoxy radical formation and isomerization, degenerate chain branching, and many other steps that distinguish among isomeric forms of different hydrocarbons. While early versions of the reaction mechanism were fairly primitive and used a large number of approximations, refinements in the details of its low temperature portions have steadily improved its abilities to describe engine combustion and knock. The present rcm modeling was undertaken to provide further refinements. The reaction mechanism used in the PRF fuel calculations included 965 chemical species and 4004 elementary reactions, and we believe that further refinement will be necessary to describe oxidation of iso-octane with sufficient accuracy.

Specifically, most addition-decomposition reactions are now implemented by specifying the reaction rate in the addition direction, and careful thermochemical methods using bond-additivity [21] are used to determine the decomposition rates. New reaction paths have been added to account for processes that are possible only for species with certain structural features. For example, all hydroperoxyalkyl radicals, denoted as QOOH, produced by isomerization of alkylperoxy radicals, can decompose by breaking the O - O bond, followed by cyclization to produce a cyclic ether. However, in cases where the unbonded electron is located at the α site relative to the COOH group, the hydroperoxyalkyl radical can decompose by breaking the C - O bond and producing HO2 radicals and a large olefin. Similarly, only when the unbonded electron is located β to the COOH group is it possible for the species to break the O - O bond and then proceed through β-scission to produce OH, a smaller olefin and a carbonyl species. Inclusion of these distinctions can have important consequences for some hydrocarbon species and little effect on other fuels.

Another recent refinement especially important in the present rcm simulations has been the inclusion of the stable ketohydroperoxide produced by addition of molecular oxygen to the hydroperoxyalkyl radicals, followed by internal H atom transfer and O - O bond scission. These species do not immediately decompose at most of the temperatures of the present study but accumulate until the temperature reaches a level where they become unstable. The activation energies for decomposition of these compounds are 43 kcal/mole in the model. Inclusion of this step provides an intermediate induction time during ignition that is observed experimentally in many engine and other situations that cannot otherwise be explained by a kinetic model.

4. COMPUTED RESULTS

The model was used to compute the overall progress of reaction, beginning at the start of the compression stroke. As in the experiments, the initial mixture temperature was 327 K, and the diluent concentrations were selected to vary the compression temperature. For each fuel, two sets of compression histories were computed, both neglecting heat losses to the combustion chamber walls. The first consisted of a full kinetic calculation, following all reactions and heat release during the compression stroke, followed by a constant volume calculation throughout the ignition period. Results such as those shown in Fig. 1 were the result. The second class of problems considered the compression as an adiabatic process during which no chemical reaction was permitted, followed by a constant volume calculation which included all reactions and heat release.

In the case of n-heptane as the fuel, the results of these paired calculations can be summarized by plotting the total ignition delay time as a function of the mixture temperature at the end of compression. These results for the two sets of calculations are shown in Fig. 2. Below 750 K, the two sets of calculations show the same ignition delay time. The computed results show that essentially no fuel consumption or other reaction takes place during the compression phase, so both treatments result in the same computed ignition delay times. As the mixture composition is adjusted further to increase the temperature during compression, the model shows that the extent of reaction during compression begins to increase. In particular, the concentrations of ketohydroperoxide species increase. At a temperature of about 800 K, these species start to decompose, leading to rapid chain branching and rapid heat release.

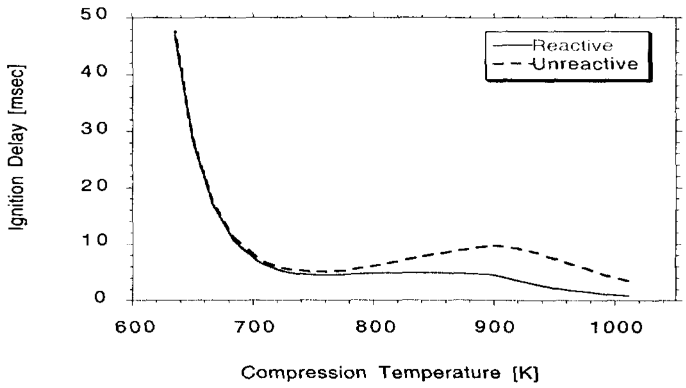

Figure 2. Ignition delay time for n-heptane/"air" mixtures, showing the difference between cases with and without reaction considered during compression stroke.

At this point, a second factor becomes important, the equilibrium of the addition reaction between alkyl radicals and molecular oxygen. This reaction represents the transition between the high and low temperature reaction regimes; at temperatures above some limiting value, the equilibrium of this reaction lies on the side of the alkyl radical and molecular oxygen, while at lower temperatures the alkylperoxy radical is formed and the low temperature regime is important. It is interesting to note that, regardless of the ratio of argon to nitrogen, for all of the mixtures in Fig. 2 that show a two-stage ignition, the first stage ends when the gas temperature reaches 940 ± 10 K (Fig. 1). For each mixture with n-heptane as the fuel, the first ignition stage is largely associated with ketohydroperoxide species decomposition at a temperature between 800 and 850 K, and the end of the first stage occurs when the temperature reaches a level where the equilibrium of the R+O2 = RO2 reactions begins to shift towards dissociation at about 950K, thereby shutting off the low temperature branching reaction paths.

An important conclusion of the present modeling study is that reaction during the compression phase for reactive fuels like n-heptane leads to a dependence of ignition delay time on compression temperature as shown in the Reactive curve in Figure 2. The long flat region from 750 - 850 K is due to fuel consumption and heat release during the final portions of the compression stroke. However, if a modeling study assumes that no reaction occurs during the compression and that the initial temperature for computation is that reached at the end of compression, the computed ignition delay times would appear to be like the Unreactive curve in Fig. 2. This familiar s-shaped curve would be expected on the basis of many theoretical studies, but it bears little resemblance to actual experimental results over the temperature range from 800 - 1000 K. Again, it is the result reached if one neglects reaction during the compression stroke when n-heptane is the fuel.

Two other fuels were considered in the present modeling study, n-pentane with a research octane number (RON) of 62, and a mixture consisting of 60% iso-octane and 40% n-heptane, which has by definition a RON of 60. Both fuels have the same resistance to ignition and knocking in spark-ignition internal combustion engines by virtue of having the same octane number, so one might assume that they would exhibit much the same ignition rate under conditions relating to engine knock, such as encountered in the rcm. Computations were carried out for both of these fuels, including reactions during the compression stroke as noted above for n-heptane, and the results are summarized in Figure 3, together with the comparable results for n-heptane. In the case of n-pentane, a strongly s-shaped curve is the result. The negative temperature coefficient regime is very distinct, indicating several facts. First, n-pentane is much less reactive than n-heptane, and even at the highest compression temperatures little or no fuel consumption occurs during the compression stroke. This conclusion is confirmed by the detailed kinetics calculations. The ntc behavior is dependent on the equilibrium of the addition reaction of pentyl radicals with molecular oxygen, as expected with alkane fuels.

In the case of the mixture of iso-octane and n-heptane, there are several interesting results. First, the ntc and s-shaped behavior of the the curve is not as distinct as for n-pentane. The computational results show that this is a result of the very reactive fuel component, n-heptane, reacting rapidly and producing an overall behavior similar to that for pure n-heptane. The presence of the much less reactive iso-octane slows the overall rate of ignition, but the presence of nearly half n-heptane gives this fuel mixture many of the properties of n-heptane, including the feature of having the extended region where the computed ignition delay time does not depend on compressed gas temperature.

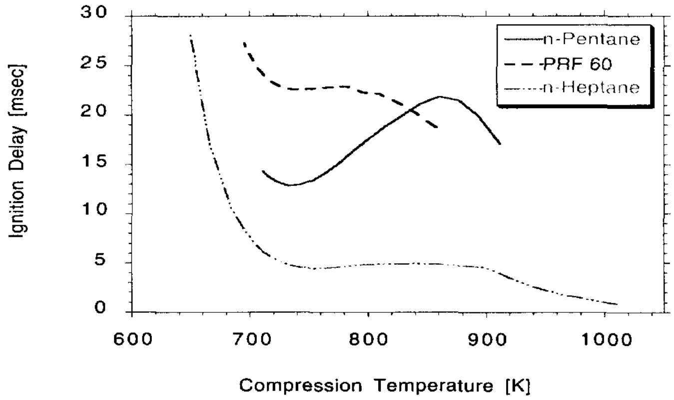

Figure 3. Computed ignition delay times, including reaction during compression stroke, for n-heptane, n-pentane, and PRF 60 mixture.

The model shows that, over this range of compressed gas temperatures from 750 - 800 K, reaction of the n-heptane can occur during the compression stroke and increase the gas temperature by about 50 K. It is interesting to note that when n-heptane is the fuel, the heat release of the n-heptane in this low temperature regime produces an increase in gas temperature of about 100 K, as shown in both Fig. 2 and Fig. 3. This is the length of the flat region for the n-heptane curve in Figs. 2 and 3. In the case of the fuel mixture where n-heptane is approximately half of the fuel, the flat region extends for about half the temperature range, about 50 K in Fig. 3.

These computations show that the two fuels with nearly the same octane ratings show very different variations in ignition delay time with compressed gas temperature. Although their overall ignition delay times are both in the range of 15 - 25 ms, the variation with compressed gas temperature is quite different, and in the rcm it is unrealistic to treat the two fuels as being virtually equivalent. Chemical simulations of ignition both in the rcm and for end gas knock in IC engines represent integrated tests, and it should not be unexpected for the two to give somewhat different results. In the engine, residual gases from past cycles contribute to the chemical evolution in ways not reflected in the rcm, and other smaller differences could also be identified. Therefore, although the compositions, temperatures, pressures, and reactive time scales are quite similar in the two combustion ignition environments, these reactive systems are extremely sensitive to a great many parameters, and careful attention to detail is necessary to connect experiments and modeling results from the rcm to engine environments. The same limitation is true even when comparing results between motored and fired engine cycles [8-10]. However, the rcm offers the closest possible combustion environment to conditions found in engine end gases close to knocking operation, and the present work points out the strengths and limitations of rcm results, as well as factors which must be included in analysis of rcm experiments.

5. CONCLUSIONS

The chemical kinetic model was used to examine the question of whether or not fuel consumption and heat release occur to any appreciable extent during the compression stroke in a rapid compression machine. Computed results show that for very reactive fuels such as n-heptane, at some temperatures and reactant concentrations, considerable fuel reaction and heat release can occur during compression. In some cases, the entire first stage of ignition can be completed prior to the end of the compression stroke. For less reactive fuels such as n-pentane, no appreciable reaction is computed during compression, and the entire negative temperature coefficient regime is observed. An important result of this study is the realization that computer models used to simulate oxidation in rapid compression machine experiments have previously neglected reaction in the compression stroke, assuming that the entire reaction sequence begins at the end of the compression stroke, analogous to the common assumption used in shock tube simulations. This type of modeling study must consider reaction during the compression stroke in order to achieve an accurate simulation of the overall rate of oxidation under these conditions.

6. ACKNOWLEDGMENTS

The authors are pleased to thank Dr. Paolo Gaffuri of the Politecnico di Milano and Dr. William Leppard of General Motors Research Laboratories for many valuable contributions in the development of this reaction mechanism. The computational portions of this study were performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract No. W-7405-ENG-48.

7. REFERENCES

1. Westbrook, C. K., and Dryer, F. L., Eighteenth Symposium (International) on Combustion, p. 749, The Combustion Institute, Pittsburgh, 1981.
2. Westbrook, C. K., and Dryer, F. L., Prog. Energy Comb. Sci. **10**, 1 (1984).
3. Westbrook, C.K., and Dryer, F. L., Combust. Sci. Technol. **20**, 125 (1979).
4. Miller, J. A., Mitchell, R.E., Smooke, M.D., and Kee, R.J., Nineteenth Symposium (International) on Combustion, p. 181, The Combustion Institute, Pittsburgh, 1982.
5. Pitz, W. J., and Westbrook, C. K., Combust. Sci. Technol. **37**, 117 (1984).
6. Pitz, W.J., Westbrook, C.K., Proscia, W.M., and Dryer, F.L., Twentieth Symposium (International) on Combustion, p. 831, The Combustion Institute, Pittsburgh, 1984.
7. Westbrook, C.K., Warnatz, J., and Pitz, W.J., Twenty-Second Symposium (International) on Combustion, p. 893, The Combustion Institute, Pittsburgh, 1988.
8. Cernansky, N. P., Green, R. M., Pitz, W.J., and Westbrook, C. K., Combust. Sci. Technol. **50**, 3 (1986).
9. Westbrook, C.K., Pitz, W.J., and Leppard, W.R., Society of Automotive Engineers paper SAE-912314 (1991).
10. Curran, H.J., Gaffuri, P., Pitz, W.J., Westbrook, C.K., and Leppard, W.R., Society of Automotive Engineers paper SAE-952406 (1995).
11. Ohta, Y., Hayashi, A. K., Fujiwara, T., and Takahashi, H., Prog. Astro. Aero. **113**, 225 (1988).
12. Halstead, M. P., Kirsch, L. J., Prothero, A., and Quinn, C. P., Proc. Roy. Soc. London **A346**, 515 (1975).
13. Minetti, R., Ribaucour, M., Carlier, M., Fittschen, C., and Sochet, L. R., Combust. Flame **96**, 201 (1994).
14. Minetti, R., Carlier, M., Ribaucour, M., Therssen, E., and Sochet, L. R., Combust. Flame **102**, 298 (1995).
15. Griffiths, J. F., Halford-Maw, P. A., and Rose, D. J., Combust. Flame **95**, 291 (1993).
16. Beeley, P., Gray, P., and Griffiths, J. F., Combust. Flame **39**, 269 (1980).
17. Griffiths, J.F., and Hasko, S.M., Proc. Roy. Soc. Lond. **A393**, 371 (1984).
18. Griffiths, J.F., and Perche, A., Eighteenth Symposium (International) on Combustion, p. 893, The Combustion Institute, Pittsburgh, 1981.
19. Griffiths, J. F., Jiao, Q., Schreiber, M., Meyer, J., and Knoche, K.F., Combust. Flame **91**, 209 (1992).
20. Cox, A., Griffiths, J. F., Mohamed, C., Curran, H., Pitz, W. J., and Westbrook, C. K., Twenty-Sixth Symposium (International) on Combustion, in press (1996).
21. Ritter, E., and Bozzelli, J., Int. J. Chem. Kinet. **23**, 767 (1991).

**This work was performed under
the auspices of the U. S. Department
of Energy by Lawrence Livermore
National Laboratory under Contract
No. W-7405-Eng-48.**