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# DEVELOPMENT AND OPTIMIZATION OF A COMPREHENSIVE KINETIC MODEL OF HYDROCARBON FUEL COMBUSTION

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## SUMMARY/OVERVIEW

The objective of the present research program is to develop a comprehensive, predictive, and detailed kinetic model of hydrocarbon combustion for aer propulsion simulations. During the reporting period progress has been made in the following projects: (1) a comparative study of the influence of reaction rate constant and binary diffusion coefficient on laminar flame speed predictions and close coupled scattering calculations for the binary diffusion coefficients of H-He and H-Ar, (2) a study on the mechanisms for the initiation of radical chain reactions during homogeneous oxidation of unsaturated hydrocarbons, and (3) development of a comprehensive mechanism for C<sub>1</sub>-C<sub>4</sub> fuel combustion. These three projects represent the two key ingredients that are necessary to the success of the overall research program. These are, (1) the formulation of physico-chemical properties that are relevant to kinetic model development and validation, and (2) further development of a unified and optimized kinetic model for higher hydrocarbon combustion.

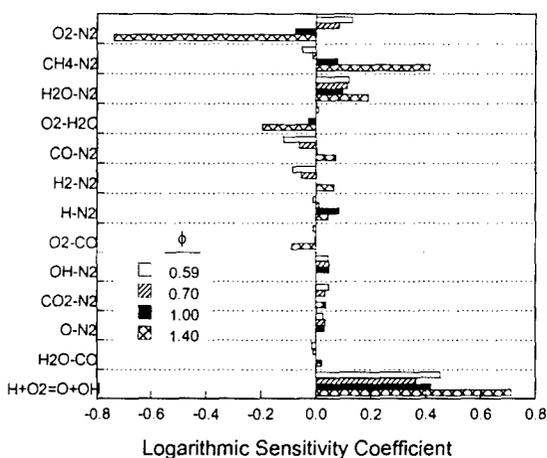
## TECHNICAL DISCUSSION

### 1. Influences of Binary Diffusion Coefficients on Laminar Flame Speed Predictions

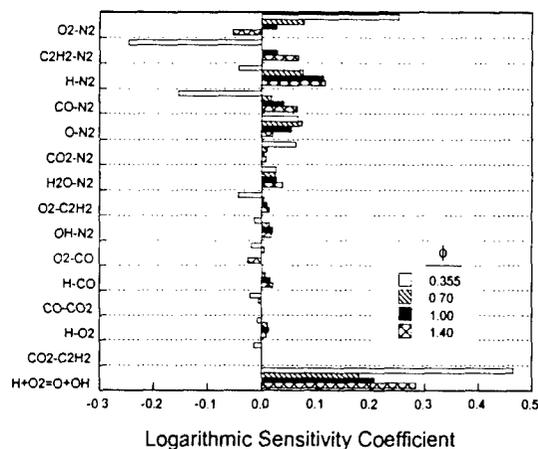
Numerical simulation of complex combustion flows requires a valid chemical reaction model as well as a satisfactory transport model. Much of the research emphasis in the past has been placed on the chemical reaction model. This emphasis was completely valid, because thirty years ago the uncertainty in reaction kinetics was substantially larger than that of the transport model and parameters. While we had enjoyed a fruitful advance of knowledge in reaction kinetics, little to no advance was made in transport processes and notably in the theory of diffusion of gaseous free radical species.

The uncertainties of the transport parameters stem mainly from the difficulties to measure the viscosity, conductivity, and diffusivity of a free radical species. In general, the transport parameters of free radicals other than the H atom were approximated by those of their parent molecules. In the case of the H atom, the binary diffusion coefficients have only been measured at the room temperature and with inert gases such as He, Ar, and N<sub>2</sub>. In addition, it is suspected on the basis of theoretical considerations that the Chapman-Enskog theory is inadequate when used for prediction of free radical diffusion. Our recent study [1] suggested that the diffusion coefficients of free radical species may be highly uncertain because of the formation of a transiently bound complex upon molecular collision. This type of collision applies to binary pairs H-N<sub>2</sub>, H-CO, O-CO, H-CO<sub>2</sub>, H-C<sub>2</sub>H<sub>2</sub> etc, and may enhance the binary diffusion coefficient of a free radical species by as much as 50% at the temperature of 1500 K.

While transport uncertainties are apparent, it is not clear to what extent these uncertainties affect the predictions of laminar flame properties like the laminar flame speed. The objective of the present study is to determine the sensitivity of flame speed predictions with respect to binary diffusion coefficients for hydrogen-, methane-, acetylene-, and propane-air flames under fuel-lean, stoichiometric, and fuel-rich conditions, and near the lean flammability limits of these flames. The Sandia PREMIX program was modified to determine the sensitivity coefficient for binary diffusion coefficients. The sensitivity coefficient was obtained by solving the linear system of equations  $(\partial F/\partial \phi)(\partial \phi/\partial D) + (\partial F/\partial D) = 0$ , where  $F$  is the residual vector of the discretized governing equations,  $\phi$  the solution vector (mass flux, temperature, and species mass fractions), and  $D$  is the binary diffusion coefficient. Here,  $\partial F/\partial \phi$  is the Jacobian of the residue vector. The normalized sensitivity coefficient of laminar flame speed,  $s_u$ , is defined by  $S_{ij} = \partial \ln s_u / \partial \ln D_{ij}$



**Figure 1.** Ranked logarithmic sensitivity coefficients of the laminar flame speeds of methane-air mixtures with respect to binary diffusion coefficients, compared to that for the rate constant of chain-branching reaction  $H + O_2 \rightarrow O + OH$ .



**Figure 2.** Ranked logarithmic sensitivity coefficients of the laminar flame speeds of acetylene-air mixtures with respect to binary diffusion coefficients, compared to that for the rate constant of chain-branching reaction  $H + O_2 \rightarrow O + OH$ .

Figures 1 and 2 present representative results of the logarithmic sensitivity coefficients computed for methane and acetylene flame speeds with respect to binary diffusion coefficients. For comparison, the respective sensitivity coefficients computed for the rate constant of  $H + O_2 \rightarrow O + OH$  are also shown in the same figures. These and additional results obtained for the hydrogen and propane flames indicate that (a) the flame speed is markedly influenced by the diffusion coefficients of binary pairs involving the major combustion reactants and products and the major flame free radicals, e.g., H and O, with molecular nitrogen, and (b) depending on the nature of the fuel, these influences could be as significant as that of key elementary reactions, e.g., the  $H + O_2$  chain branching reaction. Considering the uncertainties in these coefficients and comparing them to the uncertainties in reaction kinetics, we conclude that the transport model and coefficients deserve as much attention as the reaction kinetics in the development of predictable reaction models for hydrocarbon fuel combustion. At the present time, close coupled scattering and molecular dynamics calculations are underway to determine the binary diffusion coefficients, with the aim of reconciling the molecular beam scattering data with the binary diffusion coefficients of simple pairs like H-He and H-Ar. These computational methods will then be used to determine the diffusion coefficients of H-N<sub>2</sub>, H-O<sub>2</sub>, and H-CO in the next step of research.

The above results are reported in the Second Joint Meeting of the U.S. Sections of The Combustion Institute [2].

## 2. Initiation of Free-Radical Chain Reactions in Oxidation of Unsaturated Hydrocarbons

The initiation of free-radical chain reactions during homogeneous oxidation and ignition of hydrocarbon compounds is traditionally described by two types of reactions. The first is the C-H fission in the fuel molecule. The second is the hydrogen abstraction of fuel molecules by molecular oxygen. In most cases initiation reactions are overtaken by chain branching reactions at the very onset of reaction. For this reason they usually do not exhibit as large an influence as chain branching processes. On the other hand, an accurate prediction of the characteristics of fuel oxidation such as the shock-tube ignition delay cannot be made without adequately considering the nature and rates of initiation reactions.

A good example is the homogeneous oxidation of acetylene in shock tubes. It is well established that the initial radicals are produced from the reaction of acetylene and molecular oxygen, yet the nature of this reaction became known only until recently. Following the pioneering work of Kiefer and coworkers, we proposed that the initiation reactions during acetylene oxidation start with acetylene isomerization to vinylidene followed by the reaction of vinylidene with molecular oxygen. We showed that a detailed kinetic model of acetylene oxidation featuring this chain-initiation mechanism describes very well a variety of shock-tube ignition delay data reported for acetylene.

The conclusion of that study also opens up the possibility that there is a third type of initiation reactions for the oxidation of unsaturated fuels, namely, the isomerization or decomposition of the fuel molecule to a singlet carbene species followed by the reaction of carbene with molecular oxygen. In fact, many unsaturated hydrocarbons (e.g., acetylene, ethylene, propyne, and allene) can isomerize via 1,2-H shift to form singlet carbene species with threshold energy much smaller than that of C-H fission. If these carbene species are capable of reacting with molecular oxygen within their lifetime, they may provide a source of initial radicals to initiate chain reactions. In this work, we examine the viability of a chain initiation mechanism involving single carbene species in the homogeneous oxidation of representative unsaturated hydrocarbon compounds including ethylene, allene, propyne, and 1,3-butadiene. The work is of critical importance to a generalized understanding of the nature of radical-chain reactions during hydrocarbon combustion, and to the development of a comprehensive kinetic mechanism of hydrocarbon combustion.

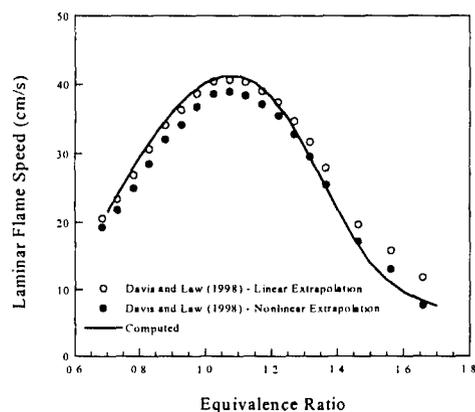
We propose that the initial radicals in the homogeneous oxidation of ethylene, propyne, allene, and 1,3-butadiene are produced from two types of singlet species, vinylidene ( $\text{H}_2\text{CC}:$ ) and propenylidene ( $\text{CH}_3\text{CHC}:$ ), as the intermediates of the initial decomposition or isomerization of the fuel molecules, i.e.,  $\text{C}_2\text{H}_4 \rightarrow \text{H}_2\text{CC} + \text{H}_2$ ,  $a\text{C}_3\text{H}_4$  and  $p\text{C}_3\text{H}_4 \rightarrow \text{CH}_3\text{CHC}:$ , and  $1,3\text{-C}_4\text{H}_6 \rightarrow \text{H}_2\text{CC} + \text{C}_2\text{H}_4$ , followed by  $\text{H}_2\text{CC} + \text{O}_2 \rightarrow$  free radicals and  $\text{CH}_3\text{CHC} + \text{O}_2 \rightarrow$  free radicals. Quantum chemistry calculations were carried out to estimate the thermochemistry of species that participate in these reactions and to explore the potential energy surfaces of selected reactions. The reaction steps were then included in a detailed kinetic model of  $\text{C}_2\text{-C}_4$  fuel combustion [e.g., 3]. The validity of the initiation mechanism was verified by kinetic modeling of shock-tube ignition delay of ethylene, propyne, and allene, with and without the carbene chemistry. For every unsaturated fuels tested carbene reactions were found to produce initial free radicals at significantly faster rates than C-H fission and H-abstraction by molecular oxygen.

Thus we conclude that the initial radical pool during high-temperature, homogeneous oxidation of ethylene, propyne, allene, and 1,3-butadiene is produced by singlet carbene intermediates of initial fuel decomposition, followed by the rapid reaction of the carbene species with molecular oxygen. Combined with the findings of previous studies on the chain initiation mechanisms of acetylene, we conclude that the singlet carbene species plays a short-lived, yet significant role in the homogeneous oxidation of unsaturated hydrocarbons.

The above results are reported in the Second Joint Meeting of the U.S. Sections of The Combustion Institute [4].

### 3. Development of a Comprehensive Reaction Mechanism of C<sub>1</sub>-C<sub>4</sub> Fuel Combustion

In this work we extended the previously developed and validated reaction model of 1,3-butadiene combustion [3] to *n*-butane, *i*-butane, 1-butene and 2-butene. In addition to mechanism development, there are two additional objectives in this study. First, we intend to address the question concerning the critical size of a well-optimized, small-hydrocarbon kinetic subset that can be used as secure foundations for extension to larger-hydrocarbon oxidation models. This question is motivated by our previous study which showed that a well-optimized C<sub>1</sub>-C<sub>2</sub> kinetic subset cannot be used as a base set for the C<sub>3</sub> combustion model without reoptimizing the subset. Yet it is not clear whether there exists a critical kinetic subset larger than which a sequential optimization process can be conducted without having to re-optimize the critical subset when the combustion of a new hydrocarbon fuel is included in the comprehensive



reaction model. Second, in collaboration with Professors C. K. Law (Princeton) and C. J. Sung (Case Western Reserve), we have initiated a study of the laminar flame speed of fuel blends with a specific objective to examine the influence of kinetic coupling of fuel mixtures on laminar flame propagation [5]. The initial fuel blend used in the investigation was the *n*-butane and ethylene mixture, which is representative of an alkane-alkene fuel blend.

**Figure 3.** Experimental and computed flame speeds of *n*-butane-air mixtures at the atmospheric pressure.

A detailed reaction model was compiled, which consists of 81 species and 570 elementary reactions. Figure 3 presents the preliminary comparison between the experimental flame speeds and computational results of *n*-butane-air mixtures. The reaction model used in the computation was not optimized. Preliminary comparisons of the experimental data and modeling results for ethylene, 2-to-1, 1-to-1, and 1-to-2 mixtures of ethylene and butane, and butane flame speeds were also carried out. The results are found in the progress report of the Princeton group (Professor C. K. Law).

#### **PUBLICATIONS AND CONFERENCE PRESENTATIONS (May 2000 – April 2001)**

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2. Yang, Z., Yang, B., and Wang, H. "The influence of H-atom diffusion coefficient on laminar flame simulation." *Proceedings of the Second Joint Meeting of the U.S. Sections of The Combustion Institute*, March, 2001, Berkeley, CA, Paper 237.
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4. Wang, H. "Chain reaction initiation in homogeneous oxidation of ethylene, propyne, and 1,3-butadiene." *Proceedings of the Second Joint Meeting of the U.S. Sections of The Combustion Institute*, March, 2001, Berkeley, CA, Paper 151.
5. Hirasawa, T., Sung, C. J., Yang, Z., Wang, H., and Law, C. K. "Determination of laminar flame speeds using digital particle image velocimetry." *Proceedings of the Second Joint Meeting of the U.S. Sections of The Combustion Institute*, March, 2001, Berkeley, CA, Paper 138.