DETAILED CHEMICAL KINETIC MODELING; IS THERE LIFE AFTER GRI-MECH 3.0?

Henry J. Curran

National University of Ireland, Galway, Ireland

Introduction

Throughout the 1990s, the Gas Research Institute (GRI) sponsored a research program that focused on the development of an optimized detailed chemical reaction mechanism capable of the best representation of natural gas flames and ignition[1]. Altogether, there were three releases of the mechanism, GRI-Mech 1.1, 2.11, and GRI-Mech 3.0. This mechanism was optimized for methane and natural gas as fuel in the temperature range 1000—2500 K, in the pressure range 10 Torr to 10 atm, and at equivalence ratios from 0.1 to 5 for premixed systems.

GRI-Mech 3.0 includes all steps thought to be important for describing natural gas ignition and flame propagation (including NO formation and reduction) using rate parameters that reflect current understanding of elementary reaction rate theory. Some aspects of natural gas combustion chemistry are not described by GRI-Mech 3.0. These include soot formation and the chemistry involved in selective non-catalytic reduction of NO. The latter may be important in natural gas reburning at lower temperatures[1].

Even though GRI-Mech does include reactions for species pertinent to natural gas combustion (e.g. ethane, propane, methanol, ethylene and acetylene), GRI recommend that the mechanism should not be used to simulate these pure fuels since the optimization did not include targets relevant to them.

Despite, these drawbacks, the GRI program was very successful, being the first of its kind to make the mechanism readily available over the Internet. Unfortunately, in February 2000 support for this work was discontinued.

The purpose of the current study is to develop a detailed chemical kinetic mechanism in a similar manner to the methodology employed in the GRI study. To date, a mechanism has been developed to reproduce fuel oxidation over a wide range of conditions for hydrogen, carbon monoxide, methane, and associated oxygenated species such as methanol, formaldehyde and acetaldehyde. It is our aim to further extend the study to create a reliable chemical kinetic mechanism to describe the oxidation of fuels up to C_3 hydrocarbon species and larger.

Hydrogen

Since hydrogen is a major component of all hydrocarbon fuels, the hydrogen submechanism is an essential foundation mechanism. To that end we have developed and validated a detailed H_2 mechanism[2] in the temperature range 298 to 2700 K, in the pressure range 0.05 to 20 atm, and at equivalence ratios from 0.2 to 6. To present the full range of data validated is beyond the scope of this paper. Two sets of data are chosen to illustrate the mechanism performance.

Mueller et al[3] studied moderately lean to moderately rich H_2/O_2 mixtures diluted in nitrogen in the temperature range 880—935 K and in the pressure range 0.30—15.7 atm. Figure 1 illustrates experimental (points) versus model-predicted (lines) profiles for hydrogen oxidation at different reactor temperatures. Overall, excellent agreement is observed between the model and experiment.

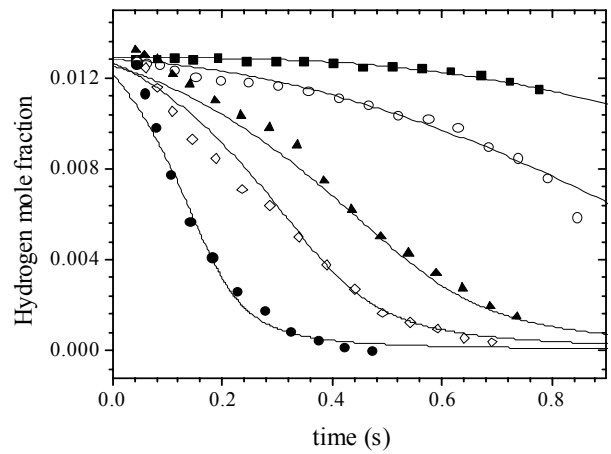

Figure 1. Comparison of experimental flow reactor[3] hydrogen concentration (points) and simulations (lines) versus residence time at 1.3% H_2, 2.2% O_2, P=6.5 atm. ■ 884 K, ○ 889 K, ▲ 906 K, ◊ 914 K, ● 934 K.

Moreover, Tse et al.[4] measured mass burning velocities for $H_2/O_2/He$ mixtures in the equivalence ratio range $0.5 \leq \phi \leq 3.5$, at 1, 5, 10, 15 and 20 atm, at an initial temperature of 298 K. It was reported that flames became increasingly unstable at elevated pressures, and thus true, stretch-free flame speeds became more difficult to measure. For the 10—20 atm data, the oxygen to fuel ratio was reduced to suppress diffusional-thermal instability and delay hydrodynamic instability. Using helium as the diluent also helped minimize instability up to 20 atm by reducing the Lewis number of the flame and retarding the formation of flame cells.

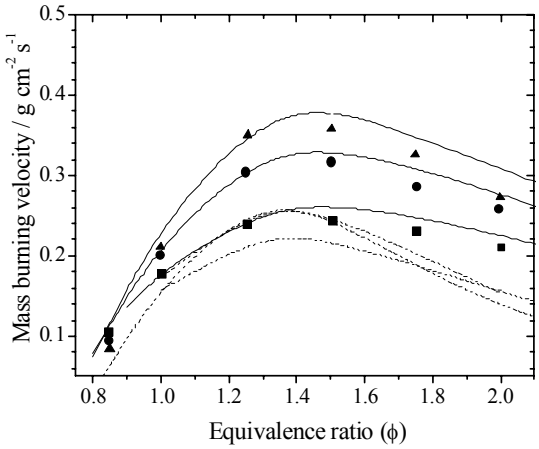

Figure 2. Comparison of experimental[4] (points) versus model predicted (lines) mass burning velocities for $H_2/O_2/He$ flames as a function of equivalence ratio. O2:He = 1:11.5, ■ 10 atm, ○ 15 atm, ▲ 20 atm. Solid lines are current mechanism prediction, dotted lines GRI-Mech 3.0.

[1] Smith, G. P., Golden, D. M., Frenklach, M., Moriarty, N. W., Eiteneer, B., Goldenberg, M., Bowman, T., Hanson, R. K., Song, S., Gardiner, Jr., W. C., Lissianski, V.V., and Qin, Z., http://www.me.berkeley.edu/gri_mech/

[2] O'Conaire, M., Curran, H. J., Simmie, J. M., Pitz, W. J., Westbrook, C. K., submitted to *Intl. J. Chem. Kin*et. Nov. 2003.

[3] Mueller, M. A.; Yetter, R. A.; Dryer, F. L.; *Intl. J. Chem. Kinet.* **31**:113--125 (1999).

[4] Tse, S. D., Zhu, D. L., Law, C.K., *Proc. Combust. Inst.***28**:1793—1800 (2000).

Methane

Methane is the main component of natural gas and being the simplest stable C_1 species, its oxidation mechanism forms the foundation for all other hydrocarbon mechanisms. Several experimental shock tube studies have been simulated over the temperature range $700 \leq T \leq 2400$ K, in the pressure range 0.3—260 atm and in the equivalence ratio range $0.4 \leq \phi \leq 6.0$. Flame speed measurements between 1 and 5 atm in the equivalence ratio range $0.4 \leq \phi \leq 1.8$ have also been simulated. Both of these data sets, particularly those recorded at high pressure, are of particular importance in validating a kinetic mechanism, as internal combustion engines operate at elevated pressures and temperatures and rates of fuel oxidation are critical to efficient system operation.

Petersen et al.[5] conducted an analytical study to supplement extreme shock tube measurements of CH_4/O_2 ignition at elevated pressures (4—26 MPa), high dilution (fuel plus oxidizer ≤ 30%), intermediate temperatures (1040—1500 K), and equivalence ratios as high as 6.

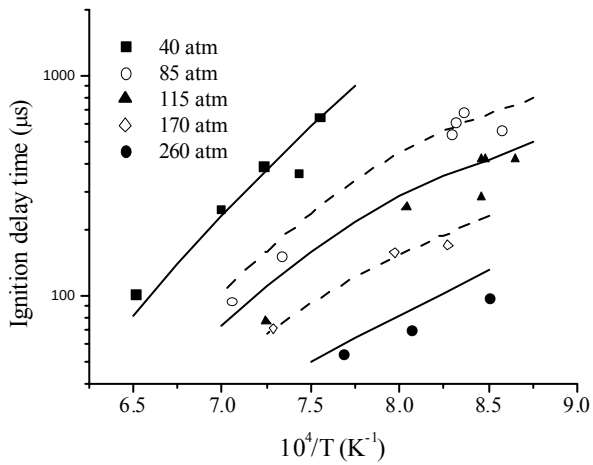

Figure 3. Comparison of experimental[5] (points) versus model predicted (lines) shock tube ignition delay times at 20% CH_4, 13.3% O_2, 66.7% Ar, ϕ = 3.0.

Figure 3 depicts experimental[5] and model predicted ignition delay times as a function of inverse temperature. It is observed that both the experimental data and the mechanism prediction show a decrease in activation energy at temperatures below approximately 1175 K. This is due to intermediate temperature chemistry where the $CH_3O_2 + CH_3 = CH_3O + CH_3O$ reaction is important. The Petersen study highlights the need to include the CH_3O_2 radical species and reactions in a reaction mechanism in order to correctly simulate methane oxidation chemistry under high-pressure, intermediate temperature conditions; conditions which prevail in high pressure natural gas combustors. The CH_3O_2 radical species and reactions are not included in GRI-Mech 3.0.

Methanol

Methanol is a component species in the natural gas submechanism, and has been validated using Princeton flow reactor data[6] in the temperature range 781—1043 K, in the equivalence ratio range $0.051 \leq \phi \leq 2.59$ and at pressures of 1, 2.5, 10, and 15 atm. Figure 4 depicts a comparison of the model-predicted intermediate profiles against the experimental data. Overall, the mechanism is able to reproduce the experimental data quite accurately.

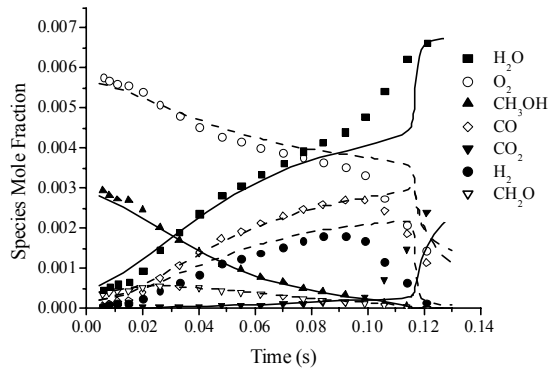

Figure 4. Comparison of experimental[6] (points) versus model predicted (lines) flow reactor species mole fractions for CH_3OH oxidation. 1010 ppm CH_3OH, ϕ = 0.86, P = 1.0 atm, T_i = 1043 K. τ_{offset} = -0.065 s.

In addition, experiments performed by Bowman[7] behind reflected shock waves in the temperature range 1545--2180~K, at reflected shock pressures of 1.5, 3, 3.5 and 4.5 bar and in the equivalence ratio range $0.75 \leq \phi \leq 6.0$, were also used to validate the mechanism. Figure 5 shows the influence of oxygen concentration on ignition delay time. Increasing the oxygen concentration from 1% to 4% results in a marked increase in the reaction rate—a positive shift in ignition delay time occurs as the oxygen content is increased at constant temperature. This trend is also well reproduced by the detailed mechanism.

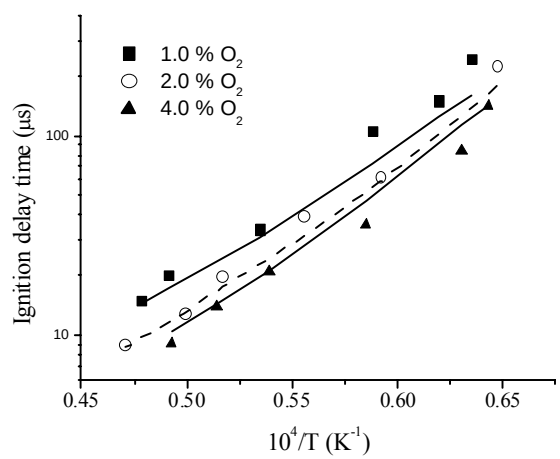

Figure 5. Comparison of experimental[7] (points) versus model predicted (lines) shock tube ignition delay times. 1.0% CH_3OH in Ar, P ≈ 3.0 bar.

[5] Petersen, E.L., Davidson, D.F., Hanson, R.K. *J. Prop. Power* (1999) **15**:82—91.

[6] Held,T.J., Dryer, F. L., *Int. J. Chem. Kinet.* **30**: 805—830 (1998).

[7] Bowman, C. T., *Combust. Flame* **25**: 343—354 (1975).