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A Detailed Modeling Study of Propane Oxidation

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Abstract

A detailed chemical kinetic mechanism has been used to simulate ignition delay times recorded by a number of experimental shock tube studies over the temperature range $900 \leq T \leq 1800$ K, in the pressure range 0.75– 40 atm and in the equivalence ratio range $0.5 \leq \phi \leq 2.0$. Flame speed measurements at 1 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.

Experiments in which reactant, intermediate and product species were quantitatively recorded, versus temperature in a jet-stirred reactor (JSR) and versus time in a flow reactor are also simulated. This data provide a stringent test of the kinetic mechanism as it must reproduce accurate quantitative profiles for all reactant, intermediate and product species. The JSR experiments were performed in the temperature range 1000–1110 K, in the equivalence ratio range $0.5 \leq \phi \leq 4.0$, at a pressure of 5 atm. These experiments are complemented by those carried out in a flow reactor in the temperature range 660–820 K, at 10 atm and at an equivalence ratio of 0.4. In addition, burner stabilized flames were simulated, where chemical species profiles were measured at atmospheric pressure for two propane–air flat flames. Overall, reasonably good agreement is observed between the model simulations and the experimental results.

Introduction

Propane is the simplest hydrocarbon that is employed as a practical hydrocarbon jet fuel; its thermochemcial and combustion properties more closely reflect those of larger hydrocarbon fuels than either methane or ethane. The development of detailed chemical kinetic mechanisms are needed to obtain accurate models of fuel oxidation rates in practical combustion devices such as internal combustion engines and gas turbines. Thus, a chemical kinetic mechanism which accurately describes the oxidation behaviour of propane over a wide range of conditions (temperature, pressure and equivalence ratio) in a broad range of sampling systems (a jet-stirred reactor [1], flow reactors [2], shock tubes [3–17], counterflow diffusion flames [18], and burner-stabilized flames— [19]) is extremely important to the combustion community. To this end, there have been a number of detailed chemical modeling studies carried out on propane oxidation [1, 20–24] all more than ten years ago, with the most recent modeling study being performed at high pressures and in the low to intermediate temperature range by Koert et al. [2] in 1996. It is the aim of this work to validate a new chemical kinetic mechanism using flow reactor data [2], and shock tube ignition delay measurements at low temperatures (900–1100 K) [13], and at high temperatures (1350–1800 K) [14]. The mechanism has also been used to calculate laminar burning velocities measured for C_3H_8/air mixtures in counterflow diffusion flames [18] at 1 atm pressure and in the equivalence ratio range $0.6 \leq \phi \leq 1.6$. These experiments are complemented by those performed in a burner stabilized flame in which chemical species profiles have been measured for two propane–air mixtures [19]. Overall, the mechanism reproduces the data quite well.

Computer Modelling

The chemical kinetic mechanism was developed and simulations performed using the HCT (Hydrodynamics, Chemistry and Transport) program [25]. Initially, the jet-stirred reactor experiments of Dagaut et al. [1], the flow reactor experiments of Koert et al. [2] and the ignition delay times measured by Cadman et al. [13] and Kim and Shin [14] were simulated with good agreement observed between experiment and model. The mechanism was then converted into the Reaction Design CHEMKIN 3.6 [26] format and the simulations repeated in order to compare results from both codes, which were in excellent agreement. The Chemkin Premix code [27] was then used to compute flame velocities measured in the freely propagating flames [18] and the species profiles for the burner-stabilized flames [19].

The detailed chemical kinetic mechanism employed here is based on the methane mechanism described in a previous report. This also contains C_2 chemistry and C_3 chemistry including propane.

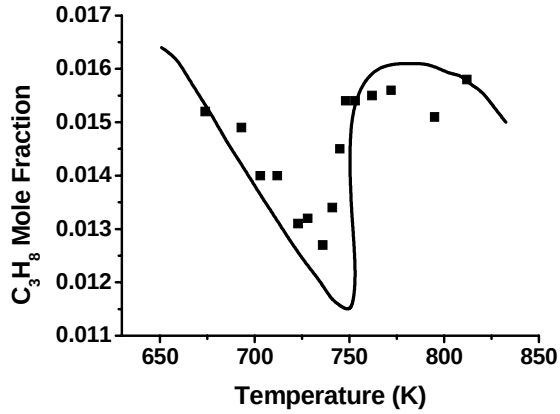

Figure 1: C_3H_8 oxidation, τ = 198 ms, P = 10 atm. Propane mole fraction ¥ and model simulation (line).

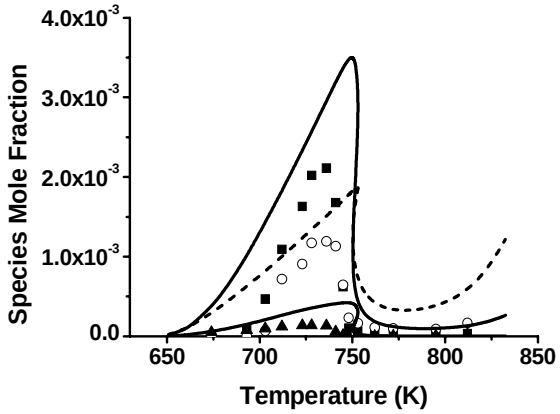

Figure 2: C_3H_8 oxidation, τ = 198 ms, P = 10 atm. Experimental mole fraction (symbols) ¥ CO, ○ C_3H_6, N CO_2 and model simulations (lines).

Flow-Reactor

Koert et al. [2] studied propane oxidation in a high pressure flow reactor. Experimental conditions ranged from 10–15 atm and 650–800 K and have a residence time of 198 ms for propane-air mixtures at an equivalence ratio of 0.4. The experimentals results clearly indicated a negative temperature coefficient (NTC) behavior. Intermediate species concentration profiles were measured quantitatively and recorded versus temperature. The current detailed chemical kinetic mechanism was used to simulate these experiments and the results of this analysis are depicted in Figs. 1– 2.

The overall reactivity of the system is well reproduced by the mechanism. The simulated fuel profile agrees well with the experimental profile up to 720 K. However, from 720–760 K fuel consumption is overpredicted by the model. Moreover, the classical NTC behavior is well reproduced in that from 640–740 K, there is an increase in reactivity with temperature. Above approximately 740 K, the reactivity of the system slows down, less fuel is consumed as the temperature increases.

Figure 2 depicts the experimental and model predicted profiles for carbon monoxide, propene and carbon dioxide. These species are well reproduced by the model, but are all overpredicted at 740 K, consistent with the over-consumption of the fuel. In addition, although not presented, the experimental- and model-predicted profiles for acetaldehyde, ethylene, methanol and propanal are also well reproduced by the kinetic mechanism with the exception of acetaldehyde, which is overpredicted by almost a factor of four.

Shock Tube

Cadman et al. [13] measured auto-ignition delay times in mainly lean (ϕ = 0.5) propane–air mixtures at intermediate temperatures in the range 850 K upwards and in the pressure range 5–40 bar. Comparisons of model-predicted ignition delay times versus those measured experimentally are depicted in Figs. 3–4. Under dilute conditions (ϕ = 0.5, 0.8% C_3H_8) the experimental data of Cadman et al. coincides with that of Burcat et al. [6] studied under similar conditions, Fig. 3. The model-predicted ignition delay times agree quite well with the high temperature data of Burcat et al. but at low temperatures, in the range of the Cadman data, the model predicts a longer than measured ignition delay time. This behavior is also observed for the more concentrated mixtures (ϕ = 0.5, 2.1% C_3H_8) where the simulated ignition delay times are always longer than those measured experimentally, Fig. 4. It should also be noted that the experiments of Cadman et al. at 2.1% C_3H_8, ϕ = 0.5, have also been repeated by Herzler et al. [15] at 10 and 30 bar reflected shock pressure, and their results are in very good agreement with those of Cadman et al.

Kim and Shin [14] investigated propane oxidation behind reflected shock waves in the pressure range 0.75–1.57 bar, and in the high temperature regime (1350–1800 K). Fig. 5 depicts experimental and simulated ignition delay times versus inverse temperature for mixtures containing 2.0% C_3H_8 diluted in argon at reflected shock pressures of approximately 1 atm. As the mixtures become more lean, i.e. as the oxygen content increases, the ignition delay time decreases and the system is more reactive. Overall, very good agreement is observed between simulation and experiment.

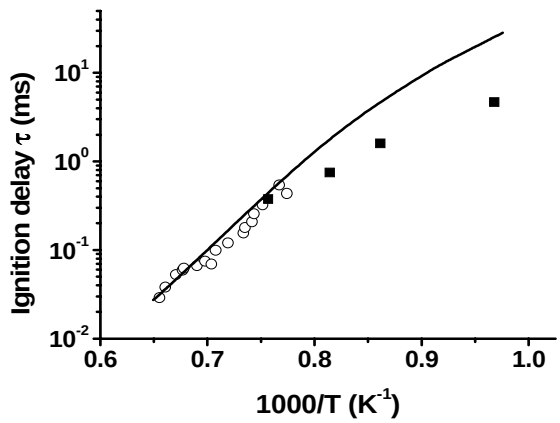

Figure 3: Experimental shock tube results ¥ [13] and ○ [6] versus model predictions (lines) at 0.8% C_3H_8, $\phi = 0.5$ in Ar, $P_5 \approx 5$ bar.

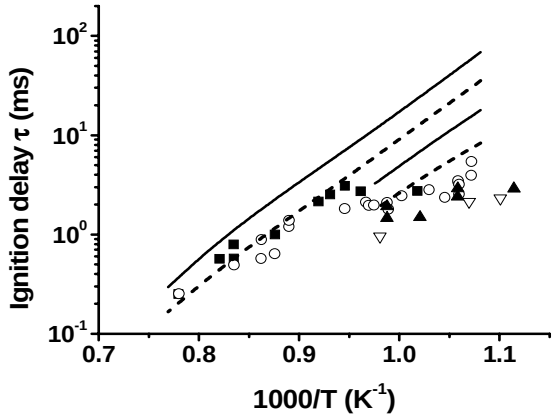

Figure 4: Experimental shock tube results (symbols) [13] versus model predictions (lines) at 2.1% C_3H_8, $\phi = 0.5$ in Ar. ¥ 5 bar, ○ 10 bar, N 20 bar, O 40 bar.

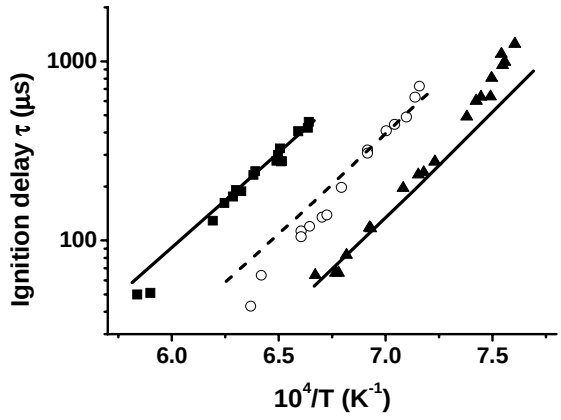

Figure 5: Influence of equivalence ratio for propane oxidation at 2.0% C_3H_8, $P_5 \approx 1$ atm. ¥ $\phi = 2.0$, ○ $\phi = 1.0$, N $\phi = 0.5$, experimental results (symbols) [14] versus model predictions (lines).

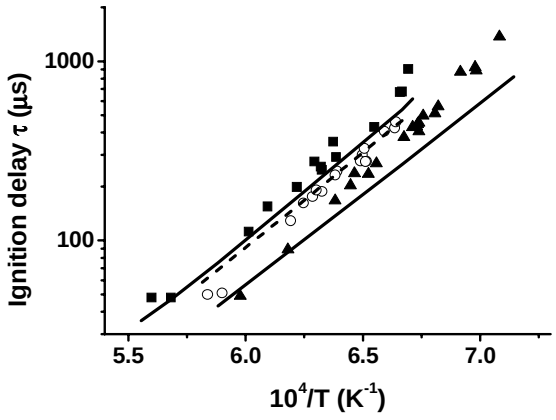

Figure 6: Influence of dilution for propane oxidation at $\phi = 2.0$, $P_5 \approx 1$ atm. ¥ 1.6% C_3H_8, ○ 2.0% C_3H_8, N 4.0% C_3H_8, experimental results (symbols) [14] versus model predictions (lines).

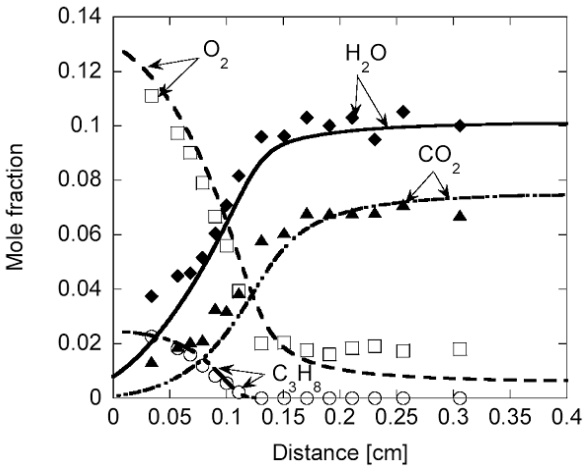

Figure 7: Spatial variations of stable species in the lean ($\phi = 0.9$) propane flame. Symbols show experimental data, curves are computed results.

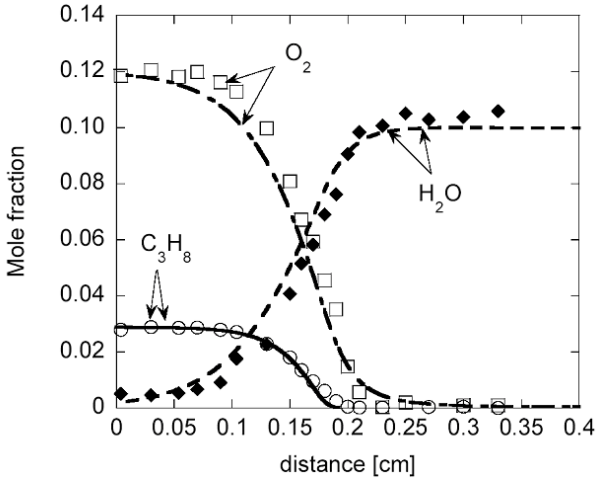

Figure 8: Spatial variations of stable species in the rich ($\phi = 1.2$) propane flame. Symbols show experimental data, curves are computed results.

Figure 6 depicts experimental and model predicted ignition delay times versus inverse temperature for mixtures containing differing fuel concentrations; Fig. 6 shows the influence of dilution at $\phi = 2.0$, As the mixtures become more concentrated, i.e. as the fuel content increases, the ignition delay time decreases and the system is more reactive. Overall, very good agreement is observed between simulation and experiment.

Burner-Stabilized Flame

Combustible $C_3H_8/O_2/Ar$ mixtures (lean, 0.025/0.136/0.839, $\phi \approx 0.9$, and rich, 0.029/0.121/0.85, $\phi \approx 1.2$) have been studied in stabilized premixed laminar flames, at atmospheric pressure and at slightly elevated unburned gas temperatures of about 380 K [19]. Chemical species profiles were measured and are plotted together with the model predicted profiles for the lean flames, Fig. 7 and the rich flame, 8. The Chemkin Premix code [27] was used to compute the species profiles for these burner-stabilized flames. Experimentally measured temperatures were used as input for the burner-stabilized flames.

Counterflow Twin-Flame

Laminar flame speeds were measured by Vagelopolous et al. [18] using a counterflow twin flame for propane/air mixtures in the equivalence ratio range $0.6 \leq \phi \leq 1.6$ at 1 atm pressure and at an unburned gas temperature of 298 K. A comparison of the model-predicted flame speeds together with those measured experimentally is provided in Fig. 9. The mechanism was used to simulate flame speeds in the equivalence ratio range 0.8–1.3, and in this range the predictions agree very well with the experimental results. However, due to time constraints it was not possible to simulate all equivalence ratios and therefore the predictions show an extrapolation to lower and higher equivalence ratio (dashed line) than those actually calculated.

Conclusions

The present study has developed a detailed chemical kinetic reaction mechanism using the low temperature flow-reactor data of Koert et al. [2] in the temperature range 600–800 K, at a pressure of 10 atm and at residence times of 198 ms. In addition, the low–intermediate temperature ignition delay time data of Cadman et al. [13] were used to validate the mechanism. It was found that, although the flow reactor data were quite well reproduced by the kinetic mechanism, the shock tube ignition delay times predicted by the mechanism were significantly longer than those measured experimentally. Thus, the low–intermediate temperature portion of the kinetic mechanism needs to be refined further in order to rectify this disagreement. However, simulations of the high temperature ignition delay data of Kim and Shin [14] and Burcat et al. [6] were in very good agreement with the experimental data and suggests strongly that the high temperature portion of the mechanism is reasonably accurate over the range of physical conditions studied. This mechanism has been employed to simulate laminar burning velocities of C_3H_8/air mixtures recorded by Vagelopolous et al. [18], with the mechanism in very good agreement with the experimental results. Finally, experiments performed in lean and rich tabilized premixed laminar flames by Korobeinichev et al. [19] in which species

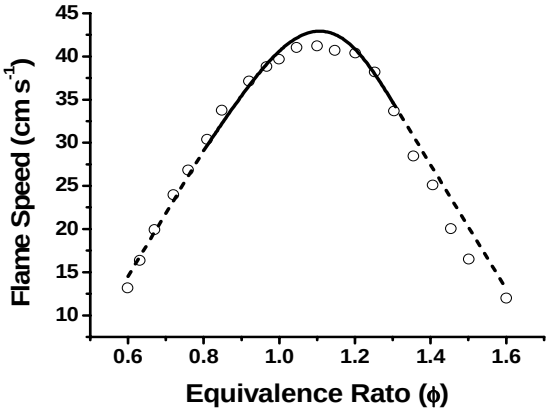

Figure 9: Experimental [18] (symbol) and model predicted (line) laminar flame speeds as a function of equivalence ratio, ϕ, for atmospheric propane/air mixtures. Dashed line is an extrapolation of the predicted result.

concentrations were recorded at various positions above the burner surface. Again, very good agreement was observed between experiment and model.

Acknowledgements

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