Burning Velocities and a High Temperature Skeletal Kinetic Model for n-Decane

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Laminar flame speeds of n-decane/air mixtures were determined experimentally over an extensive range of equivalence ratios at 500 K and at atmospheric pressure. The effect of N_2 dilution on the laminar flame speed was also studied at these same conditions. The experiments employed the stagnation jet-wall flame configuration with the flow velocity field determined by Particle Image Velocimetry (PIV). Reference laminar flame speeds were obtained using linear extrapolation from low to zero stretch rate. The determined flame speeds are significantly different that those predicted using existing published kinetic models, including a model validated previously (Zeppieri et al., 2000a) against high temperature data from flow reactor, jet-stirred reactor, shock tube ignition delay, and burner stabilized flame experiments. A significant update of this model is described which continues to predict the earlier validation experiments as well as the newly acquired laminar flame speed data and other recently published shock tube ignition delay measurements.

Key words: skeletal reduced kinetic model, n-decane, burning velocity, premixed flame, dilution.

INTRODUCTION

Improving internal combustion engine efficiency (to control CO_2 production) while continuing to minimize combustion pollutant emissions is requiring increased emphasis on more accurate numerical design tools for internal combustion engine development. Robust chemical kinetic models are needed to predict the complex physical and chemical processes that occur in advanced engine designs utilizing distillate-type fuels, for example, direct injection diesel and homogeneous charge compression ignition operation. Since practical diesel fuels are complex mixtures of very large numbers of different hydrocarbon species, extensive efforts have been focused on understanding and numerically modeling single components and simple mixtures of components that emulate diesel fuel autoignition and combustion properties. In multidimensional engine simulations, it is not currently possible to use detailed hydrocarbon models involving large numbers of reactions and species. Recognizing the problem of mechanistic complexity versus predictive robustness, our laboratory previously developed a partially reduced skeletal mechanism approach for high temperature, large n-alkane oxidation and pyrolysis by applying the methodology to n-decane (Zeppieri et al., 2000a). In the kinetic model, the number of required species was significantly reduced by using a novel method of assumption that each of the n-alkyl radicals with more than three carbon atoms is in isomeric partial equilibrium. Constructs with carbon number of three or less were simulated using detailed elementary kinetics. The resulting n-decane kinetic model was shown to reproduce high temperature atmospheric pressure flow reactor pyrolysis and oxidation (Zeppieri et al., 2000a), jet-stirred reactor oxidation (Balesgueret et al., 1992)

and shock tube ignition delay data (Pfahl et al., 1996). In presenting the published paper (Zeppieri et al., 2000b), predictions were also shown to compare favorably with the burner stabilized flame data of Douté et al. (1995). However, no comparisons were made with laminar flame speed data, primarily because only two data points from high temperature Bunsen burner experiments were available in the literature (Wagner and Dugger, 1955). Furthermore, only one point obtained by extrapolation of these data to room temperature and atmospheric pressure has typically been used for comparison. More recently, Bikas and Peters (2001) published a kinetic model for n-decane oxidation and compared predictions with this single extrapolated measurement. The most recent n-decane laminar speed data were reported by Skjøth-Rasmussen et al. (2003). As in the early experiments, Skjøth-Rasmussen et al. utilized the Bunsen burner approach for determining the flame speed, and no stretch corrections were applied to the measurements.

The laminar flame speed, i.e. the propagation speed of a one-dimensional, adiabatic, planar, laminar flame in a doubly infinite domain, embodies the fundamental properties of diffusivity, reactivity, and exothermicity for a given mixture and is commonly used to partially validate kinetic models. As noted above, the literature is sparse for accurate laminar flame speed data for n-decane, and this is also more generally true for all higher molecular weight species characteristic of gas turbine and diesel fuel components. Thus, additional experimental laminar flame speed data are important to advancing comprehensive kinetic models for large carbon number species that can be utilized in developing smaller dimensional models for design applications involving diesel as well as gas turbine energy conversion systems.

The specific objective of the present work was to experimentally determine laminar flame speeds of n-decane/air mixtures over a range of equivalence ratio at 500K, with particular interest near lean flammability and sooting limit conditions. Since applications frequently involve exhaust gas recirculation, the dilution effect on the laminar flame speed was also studied for a range of equivalence ratios with of N_2 dilution volume percentages up to 20%. The generated data were then compared with the predictions using kinetic models appearing in the literature (Zeppieri et al., 2000a; Bikas and Peters, 2001). In collaboration with the authors of (Bikas and Peters, 2001), we were unable to reproduce the calculations shown in the original paper. Disparity was also found in comparison to predictions utilizing the model reported in (Zeppieri et al., 2000a). Here, we update the latter model with modifications in sub-mechanisms, elementary rate parameters, and thermochemistry and compare the updated mechanism with the new laminar flame speed data, and well as other data appearing in the literature.

EXPERIMENTAL METHODOLOGY

The single jet-wall stagnation flame experimental configuration for determining laminar flame speeds was first introduced by Egolfopoulos et al. (1997), and the basic single jet-wall stagnation flame technique and the modified procedural methodologies we use in our laboratory are discussed in more detail elsewhere (Zhao, 2002). A premixed reactant flow emerges vertically upward from the 14 mm converging nozzle situated at the center of a water/N_2-cooled burner surface and impinges vertically onto an 8 cm diameter thin ceramic, flat, stagnation plate (Fig. 1). When the strain rate is low, the flame front is far away from the (nearly) adiabatic stagnation plate; therefore, the small downstream heat

loss has minimal effect on the flame propagation speed. The burner flow is shrouded by a 2 mm annular flow of nitrogen to stabilize the core flame.

A metered airflow is first seeded with 0.3-0.7 micron Boron Nitride particles to apply Particle Image Velocity (PIV), and then the particle-laden flow is preheated using an inline heater. The flow is then mixed with preheated, prevaporized fuel in a turbulent mixer. The residence time of fully mixed components upstream of the burner are restricted to preheat temperatures that do not lead to two-stage ignition/flash back conditions.

The flow of particle laden, premixed mixture is then separated into two parts by pressure drop across two high-temperature needle valves. By varying the relative pressure drop of the two flow channels, the core flow rate to the burner and that purged directly to exhaust can be varied to change the burner flow velocity without manipulating the individual flow rates of each component (which can be a source of uncertainty in maintaining experimental equivalence ratio). The N_2 shroud co-flow is independently heated and temperature controlled to match the temperature of the entering burner flow, and all of the gas heaters, mixer, and needle flow splitters are installed in an insulated container to maintain near isothermal conditions. The burner body itself is also heated and independently temperature controlled. Several 1.6 mm exposed-junction fast-response thermocouples are used to monitor local temperatures. The final temperature of the burner flow, which is measured 3.8 mm upstream of and prior to a screen at the burner nozzle exit plane, is used as the control temperature. The location of the temperature sensor was selected to minimize flame radiation effects, flow disturbance, and achieve close proximity to the flame location itself.

A Continuum® Minilite PIV Nd:Yag laser is used as the PIV light source and the light beam is shaped into a thin light sheet using cylindrical and spherical lenses. The images at two different times are recorded by double exposure using a Kodak DCS 460 digital camera with resolution of 3060×2036 pixels. The recorded images, in appropriate digital form, are subsequently analyzed using an in-house auto-correlation code. The PIV code utilizes self-optimizing FFT algorithms, variable interrogation window size, and sub-pixel peak detection techniques. In addition, customized filtering algorithms implemented in the code facilitate auto-detection of the flow centerline and the flame edge, allowing the processing of large data sets (reducing statistical experimental errors) with minimal user interaction. Additional features include algorithms for automatic interrogation peak selection/rejection as well as stretch rate/reference flame speed determination. The use of this software package eliminates human bias in determining the stretch rate manually, which is a technique commonly reported for the LDV/PIV-related flame speed studies appearing in the literature.

PIV was employed to velocity-map the entire two-dimensional flow field for each set of experimental conditions. The particle density and displacement between two exposures were chosen for the optimal application of the auto-correlation technique. Because of thermal expansion and flow acceleration upstream of the flame front, the particle density becomes too low to obtain reliable vectors using auto-correlation at the flame front itself. However, the rapid particle acceleration and loss of correlation results in a very well defined flame front location (Hirasawa et al., 2002; Zhao et al., 2002). The minimum velocity location in the axial velocity profile was defined as the reference flame speed, while the stretch rate for each measurement was determined from the quasi-

linear part of the axial velocity profile upstream. Linear extrapolation was used to determine the zero-stretched laminar flame speed from a plot of the reference flame speed versus the stretch rate. The direction of the velocity in a stagnation flow is well defined, thus avoiding a directional ambiguity issue characteristic of the auto-correlation approach.

RESULTS AND DISCUSSION

The vapor pressure temperature dependence of n-decane is such that at atmospheric pressure, no flammable vapor/air ratios can be formed at room temperature. To perform flame speed measurements over a wide range of stoichiometry, the present experiments (Fig. 2) were performed at atmospheric pressure and with the mixtures preheated to the initial temperature of 500 K. Experiments were conducted with and without additional N_2 dilution of the mixture in order to simulate the effects of exhaust gas recirculation on laminar flame speed. The dilution ratio is defined here as the mole fraction of the diluent in the total mixture (diluent + air + fuel), expressed as a percentage.

The statistical averaging of the raw experimental data can reduce the uncertainties in the measured flame velocities and stretch rates. Uncertainties in stretch rate are one of the largest sources of error determining laminar flame speeds using the stagnation flame method (Zhao et al., 2002). While the automatic determination of the stretch rate used in the present work is more systematic, it may result in an apparent greater degree of scatter, which would otherwise appear smaller as a result of human bias present in manual data reduction. In the present work, the uncertainty in the equivalence ratio is about ±0.01.

The uncertainty in the determined flame speed evaluated using conventional regression analysis is less than about 5% (Zhao et al., 2004).

The laminar flame speed data obtained in the present work are also consistent with the experimental data of Wagner and Dugger (1955). Using their temperature extrapolation correlation, $U_f = cT_0^a$, where T_0 is the initial temperature, c and a are empirical constants (for n-decane at φ =1.05, c = 1.67, a = 2.97×10^{-3}), we obtain the value of 95.5 cm/s at 500 K. Our experimental measurements at φ =1.05 for the case without dilution yield 94.0 cm/s, and the difference is well within the accuracy of the experiments and the correlation itself.

Laminar flame speed predictions were obtained using PREMIX (Kee et al., 1985) and CHEMKIN II packages (Kee et al., 1989a). Transport parameters were taken from the Sandia database (Kee et al., 1989b), and unknown Lennard-Jones parameters were estimated from the species critical properties using techniques described in Wang and Frenklach (1994). Critical properties (T_c and P_c) were also estimated using the group contribution approach of Joback (Reid et al., 1987), as implemented in the NIST software package (Stein, 1994).

Predictions using the kinetic models of Zeppieri et al. (2000) and Bikas and Peters (2001) were compared with the experimental results. Figure 2 shows the comparison of predictions using the Zeppieri et al. model with the single experimental point at 300 K used previously by Bikas and Peters and with our new experimental data at 500 K. The Zeppieri et al. model significantly under-predicts the experimentally determined peak flame speeds. Calculations using the Bikas and Peters model from the thesis of Bikas (2001) or the publication underpredict the experimental results by similar magnitudes.

However, the Bikas and Peters model also predicts flame speeds that differ substantially from those reported in the original paper. Prof. Peters and colleagues have collaborated with us in an attempt to resolve these discrepancies (Honnet and Peters, 2003). While it has been mutually concluded that our implementation of the kinetics and calculations are indeed correct, the source of the discrepancy from the published results remains unresolved.

Since the development of the original Zeppieri et al. model, significant advances in fundamentals (mechanistic issues, thermochemical and kinetic parameters) have occurred particularly for H_2/O_2 and C_1-C_3 kinetics. As a result, we investigated and updated the small molecule and radical kinetics and thermochemistry utilized in the Zeppieri et al. model to evaluate recent updates on the predicted laminar flame speeds. In particular, we revised the model by substituting our recent update of the H_2/O_2 kinetic model (Li et al, 2003). The key updates included new expressions for the $H+O_2=OH+O$ (Hessler, 1998) and $H+O_2+M=HO_2+M$ (Michael et al., 2002) reactions, a revision in the heat of formation of OH radical (Ruscic et al., 2002) and a modification of the rate expression utilized for H + OH + M (Li et al, 2003) (which appears to contribute primarily to achieving good agreement with high pressure laminar flame speed data).

The C_1-C_3 kinetics in the model were replaced with those recently published by Qin et al. (2000), with the following modifications:

1) $aC_3H_5 + HO_2 \rightarrow OH + C_2H_3 + CH_2O$ Similar to the recent work of Zheng et al. (2003), this global reaction was first replaced with the corresponding elementary step, $aC_3H_5 + HO_2 = OH + C_3H_5O$ (R_1). The new intermediate species, C_3H_5O, was introduced into the mechanism and the associated thermochemical data were

estimated using THERM package (Ritter and Bozzelli, 1991). The reaction rate was taken the same as the global reaction. Also, the decomposition reactions of C_3H_5O, $C_3H_5O = C_2H_3 + CH_2O$ (R_2) and $C_3H_5O = C_2H_3CHO + H$ (R_3), were added to the mechanism. Rate coefficient of reactions (R_2) and (R_3) were estimated using kinetic information for similar reactions available in the literature (Wang et al., 1999; Baulch et al., 1994).

2) The rate coefficient of $CH_3 + X$ reactions were replaced by those reported in Scire et al. (Scire et al., 2001).

The complete mechanism used in this study may be obtained electronically by contacting the corresponding author.

The predictions utilizing the updated model (Fig. 2) agree well with the newly-obtained flame speed data, especially for the fuel lean and stoichiometric results. A small discrepancy still remains on the fuel rich side. The prediction for diluted flame speed conditions also agree reasonably well with the experimental data. While it is possible to further improve the agreement between the model predictions and the present data by adjusting less established rate coefficients or thermochemistry within known uncertainties, uncertainty contributions may also come from other sources, such as the transport model (Kee et al., 1989b). Figure 2 also shows the n-decane flame speeds at initial temperature of 473 K reported by Skjøth-Rasmussen et al., 2003. The data essentially overlap the present experimental data obtained at a higher initial temperature of 500 K. Moreover, the present model predicts well the present and other published data obtained at both higher and lower initial temperatures than that of the Skjøth-Rasmussen et al. data. The sources of the discrepancy of the Skjoth-Rasmussen et al.

with our data certainly include the fact that the reported results were not corrected for stretch, but may include other unknown sources.

To illustrate the influence of individual reaction rates on predicted flame speeds, a sensitivity analysis was performed for three selected cases of lean, stoichiometric, and rich mixture compositions at 500 K without N_2 dilution using the Zeppieri et al. model. The sensitivity spectrums at the same conditions with N_2 dilution are very similar to that without dilution, and only those without dilution are presented in Fig. 3.

The sensitivity spectrum for n-decane/air flames exhibits features typically observed previously and well documented for flames of small (e.g., see Qin et al., 2000; Smith, et al., 1999) as well as larger molecular weight (e.g., see Held et al., 1997)) alkanes. The sensitivity spectrum is dominated by the main chain branching reaction, $H + O_2 = OH + O$, CO oxidation, $CO + OH = CO_2 + H$, the reactions of formyl radical, particularly $HCO + M = CO + H + M$ and $HCO + O_2 = CO + HO_2$ and of several C_2 and C_3 reactions. Reactions involving the fuel itself or species larger than C_4 produced during the oxidation make no significant contribution to the predicted flame speed. The latter observation points to the lack of utility of using flame speed values to validate large molecule (and high molecular weight fragments) kinetic chemistry. All of the above factors, as well as the literature suggest that the inadequacy in predicting flame speeds of large carbon number fuels is related to the inadequacies of the small species kinetics.

We further investigated the ability of the revised model to reproduce the data compared against the original Zeppieri et al. model as well as with other data. The agreement of the revised model with the pyrolysis data presented in (Zeppieri et al., 2000b) is essentially of similar quality as that achieved with the Zeppieri et al. model for

major species and intermediates (e.g., n-decane, ethane, ethene, methane, and propene) and remains less satisfactory for trace intermediates (e.g., 1,3-butadiene, pentene). Comparisons with the n-decane oxidation data appearing in Zeppieri et al. (2000a) are similarly in good agreement with earlier results, with the some disparities still remaining for CO and 1,3-butadiene (Fig. 4). The sensitivity analysis performed for the flow reactor conditions suggest the need for further model refinement for reactions involving both pentene and 1,3-butadiene, such as $C_5H_{10} + OH = H_2O + C_4H_6 + CH_3$, as well as in the sub-mechanism at the C_3 level.

Model predictions were also compared with the published burner-stabilized flame data of Douté et al. (1995). The model reproduces very well the observed fuel/O_2 decay and the major species evolution (e.g., H_2O, CO_2, C_3H_6), with some slight discrepancies for minor species such as CO and 1,3-butadiene.

Finally, the present was also validated against shock tube ignition delay data that recently appeared in the literature (Horning et al., 2002) (Fig. 7). Constant volume, zero-dimensional adiabatic conditions were used in these simulations, and the computed ignition delay time was determined from CH radical peak or pressure rise, consistent with the experimental measurement methods. The predicted ignition delays are in excellent agreement with 1.2 atm, high temperature cases (Horning et al., 2002).

Comparisons with the high pressure ignition delay data (Pfahl et al., 1996) are also very good at high temperatures, but discrepancies become substantial below 1100 K. This disagreement is expected since the high temperature mechanism utilized here does not include radical-oxygen addition reactions characteristic of low and intermediate temperature oxidation of large carbon number species.

CONCLUSIONS

Laminar flame speeds for n-decane/air mixtures at atmospheric pressure and initial temperature of 500 K were determined on a stagnation flame burner using PIV. Predictions of the experimental data based on the partially reduced skeletal mechanism for n-decane pyrolysis and oxidation of Zeppieri et al. (2000a) were found to be in poor agreement. The analyses of these results further support that laminar flame speed data for large carbon number alkanes primarily constrains the kinetic sub-mechanisms for hydrogen/carbon monoxide oxidation and small carbon containing species with carbon number generally less than 3. Revision of the Zeppieri et al. model by updating the hydrogen/oxygen and small carbon number C_1-C_3 sub mechanisms, thermochemistry and elementary rates results in acceptable prediction of the experimental results. Predictions using the revised model were found to reproduce data used in validating the original model in (Zeppieri et al., 2000a) including high temperature, atmospheric pressure flow reactor pyrolysis and oxidation, high pressure shock tube ignition delay, and stirred reactor species measurements. The revised model predictions also agree well with atmospheric pressure, burner stabilized flame data and recently published shock tube ignition delay measurements at both low and high pressure.

As noted above, the present mechanism is developed for high temperature applications where the reactions of radicals with oxygen that are of significance to two-stage ignition phenomena are not of importance. Recent work on in our laboratory on kinetic modeling of two-stage large alkane oxidation suggests that without first developing robust high temperature mechanistic features, the resulting coupling precludes

construction of predictive models for low and intermediate temperature kinetics. Addition of low and intermediate temperature submechanisms to the present high temperature mechanism is the subject of current work in our laboratory and will result in a wide range mechanism for n-decane oxidation for applications involving two-stage ignition as well as high temperature oxidation phenomena.

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Figure 1: Schematics of the experimental setup.

Figure 2: Atmospheric pressure laminar flame speeds for *n*-decane/air mixtures. Symbols: 500 K and 500 K with 20% N_2 dilution – present experimental data; 300 K – Wagner and Dugger (1955) (extrapolated based on two higher temperature measurements); 473 K – Skjøth-Rasmussen et al. (2003); lines: model predictions (dashed line- Zeppieri et al. (2000a), solid line - present *n*-decane model).

Figure 3: Normalized sensitivity coefficients of *n*-decane flame speeds at 500 K calculated using the present kinetic model.

Figure 4: Fig. 4 Comparison of experimental (Zeppieri et al., 2000a) (symbols) and computed (lines) species profiles during *n*-decane pyrolysis in a flow reactor (P = 1 atm, T_i = 1060 K, initial *n*-decane concentration 1456 ppm in N_2). Model predictions are shifted by 46 ms.

Figure 5: Comparison of experimental (Zeppieri et al., 2000a) (symbols) and computed (lines) species profiles during n-decane oxidation in a flow reactor (P = 1 atm, T_i = 1019 K, $\phi \approx 1.0$, initial *n*-decane concentration 1452 ppm in N_2). Model predictions are shifted by 11.6 ms.

Figure 6: Comparison of experimental (Doute et al., 1995) (symbols) and computed (lines) species profiles in *n*-decane-O_2-N_2 burner stabilized flame (P = 1 atm, ϕ = 1.7).

Figure 7: Comparison of experimental (symbols) and computed (lines) ignition delay times for *n*-decane. Mixture compositions used in the experiments: 0.2% *n*-decane-O_2-Ar (Horning et al., 2002) and *n*-decane/air (Pfahl et al., 1996).

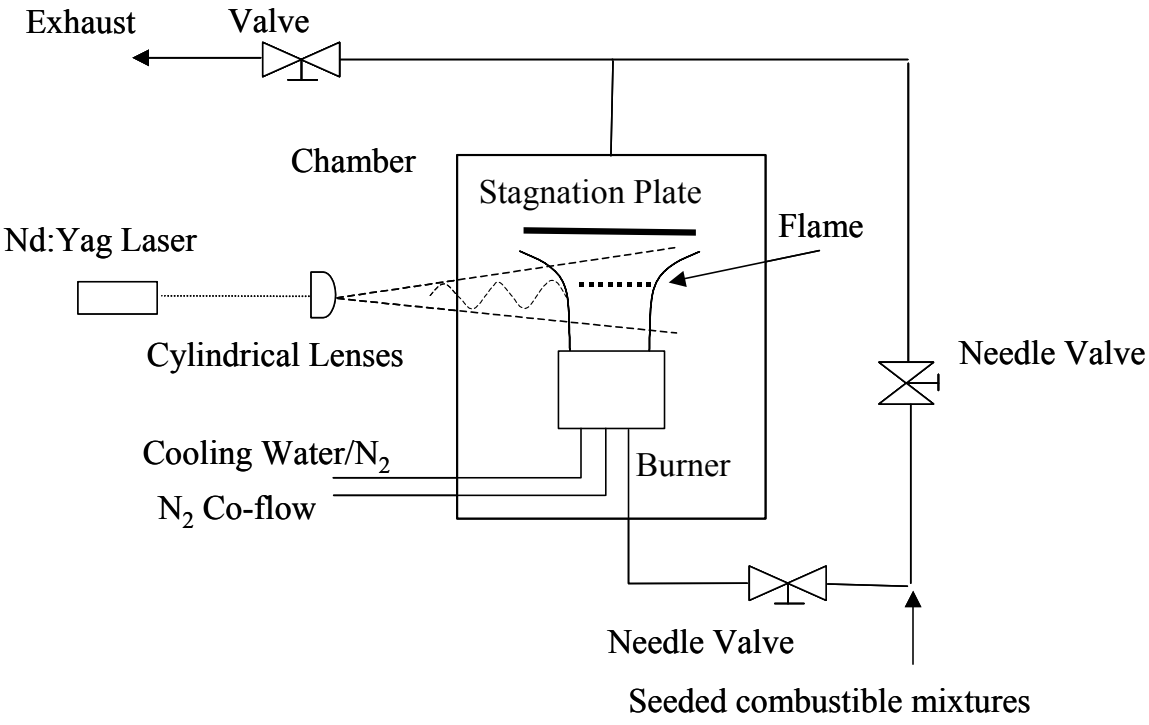

Fig. 1 Schematics of the experimental setup.

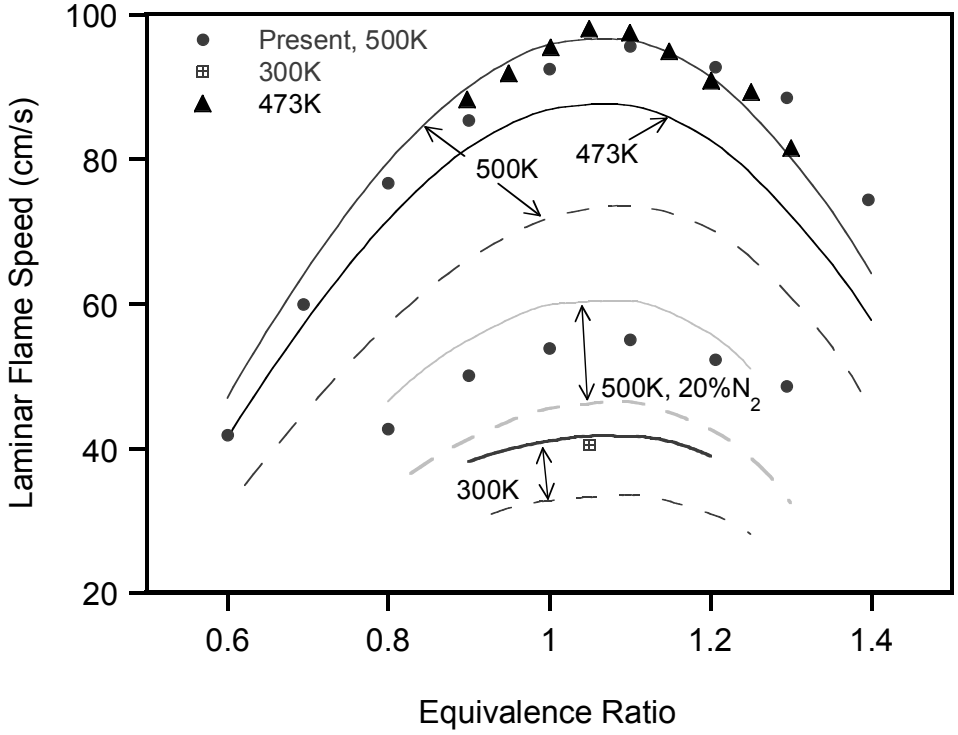

Fig.2 Atmospheric pressure laminar flame speeds for *n*-decane/air mixtures. Symbols: 500 K and 500 K with 20% N_2 dilution - present experimental data; 300 K – Wagner and Dugger (1955) (extrapolated based on two higher temperature measurements); 473 K – Skjøth-Rasmussen et al. (2003); lines: model predictions (dashed line- Zeppieri et al. (2000a), solid line - present *n*-decane model).

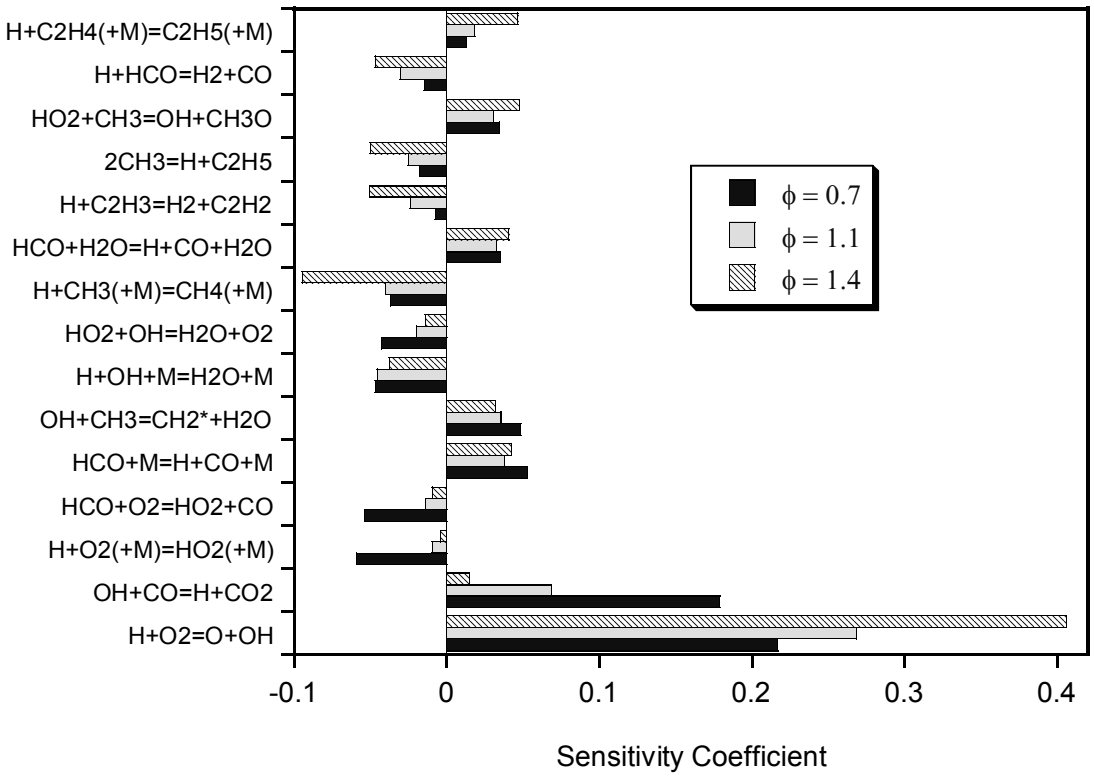

Fig. 3 Normalized sensitivity coefficients of *n*-decane flame speeds at 500 K calculated using the present kinetic model.

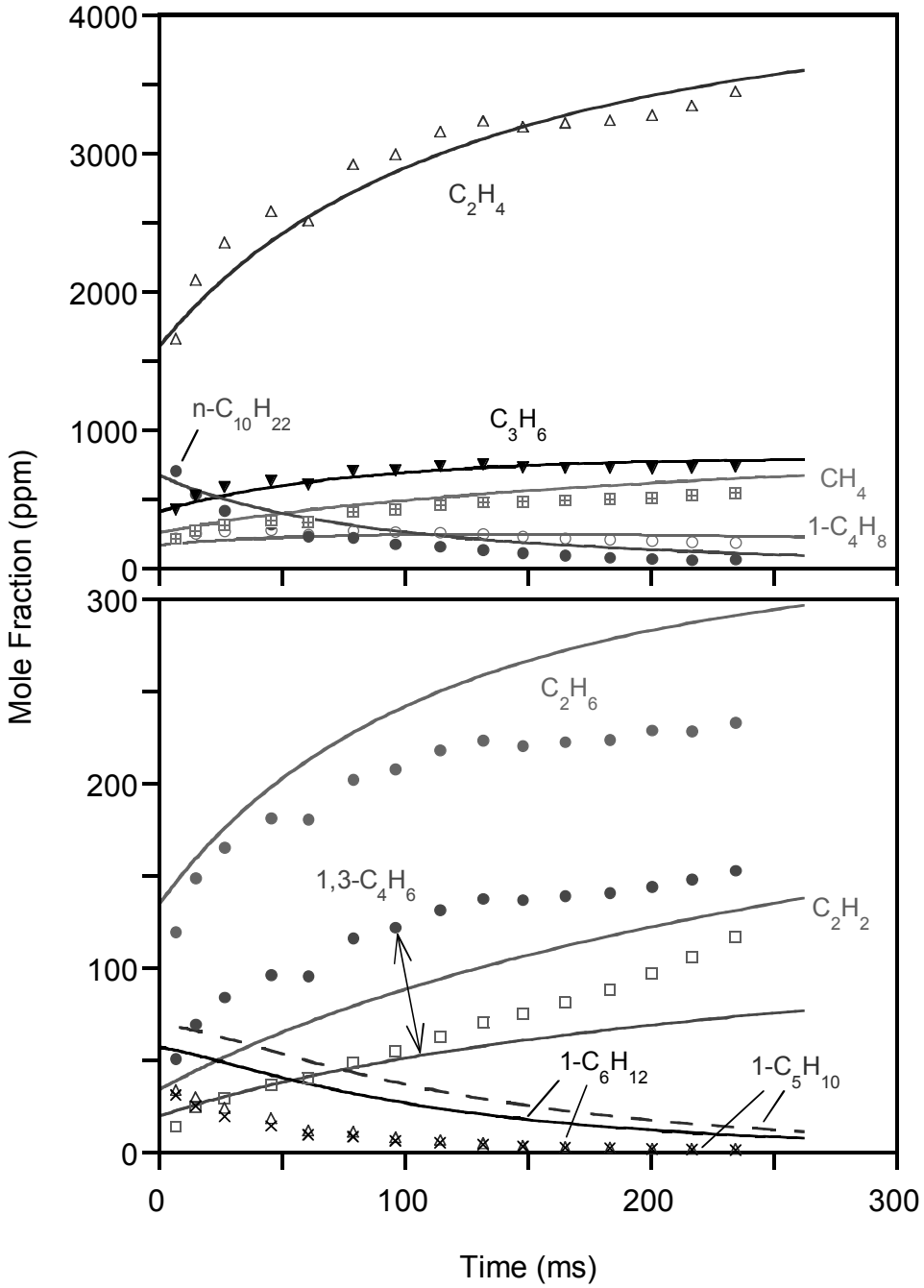

Fig. 4 Comparison of experimental (Zeppieri et al., 2000a) (symbols) and computed (lines) species profiles during *n*-decane pyrolysis in a flow reactor (P = 1 atm, T_i = 1060 K, initial *n*-decane concentration 1456 ppm in N_2). Model predictions are shifted by 46 ms.

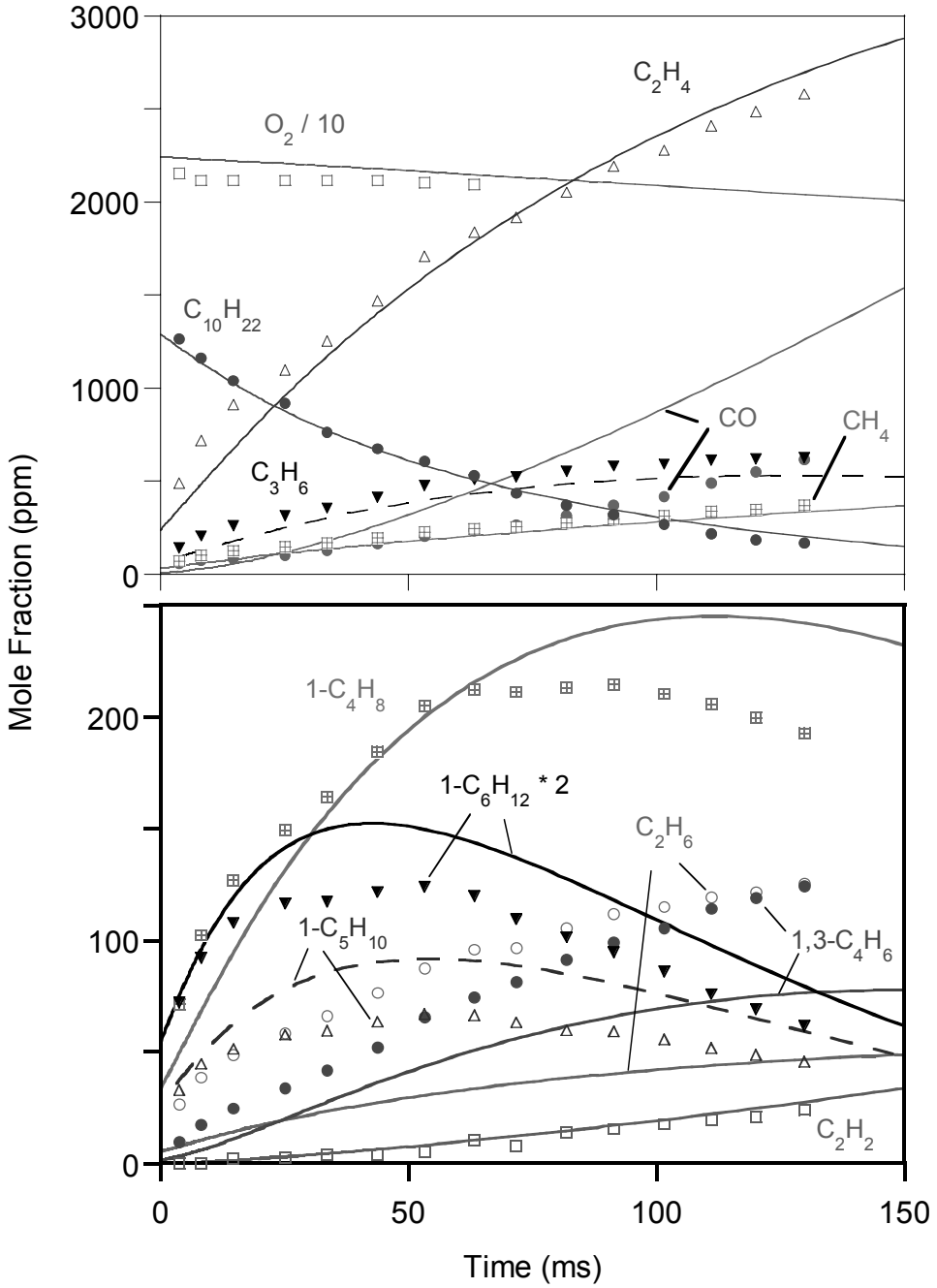

Fig. 5 Comparison of experimental (Zeppieri et al., 2000a) (symbols) and computed (lines) species profiles during n-decane oxidation in a flow reactor (P = 1 atm, T_i = 1019 K, $\phi \approx 1.0$, initial *n*-decane concentration 1452 ppm in N_2). Model predictions are shifted by 11.6 ms.

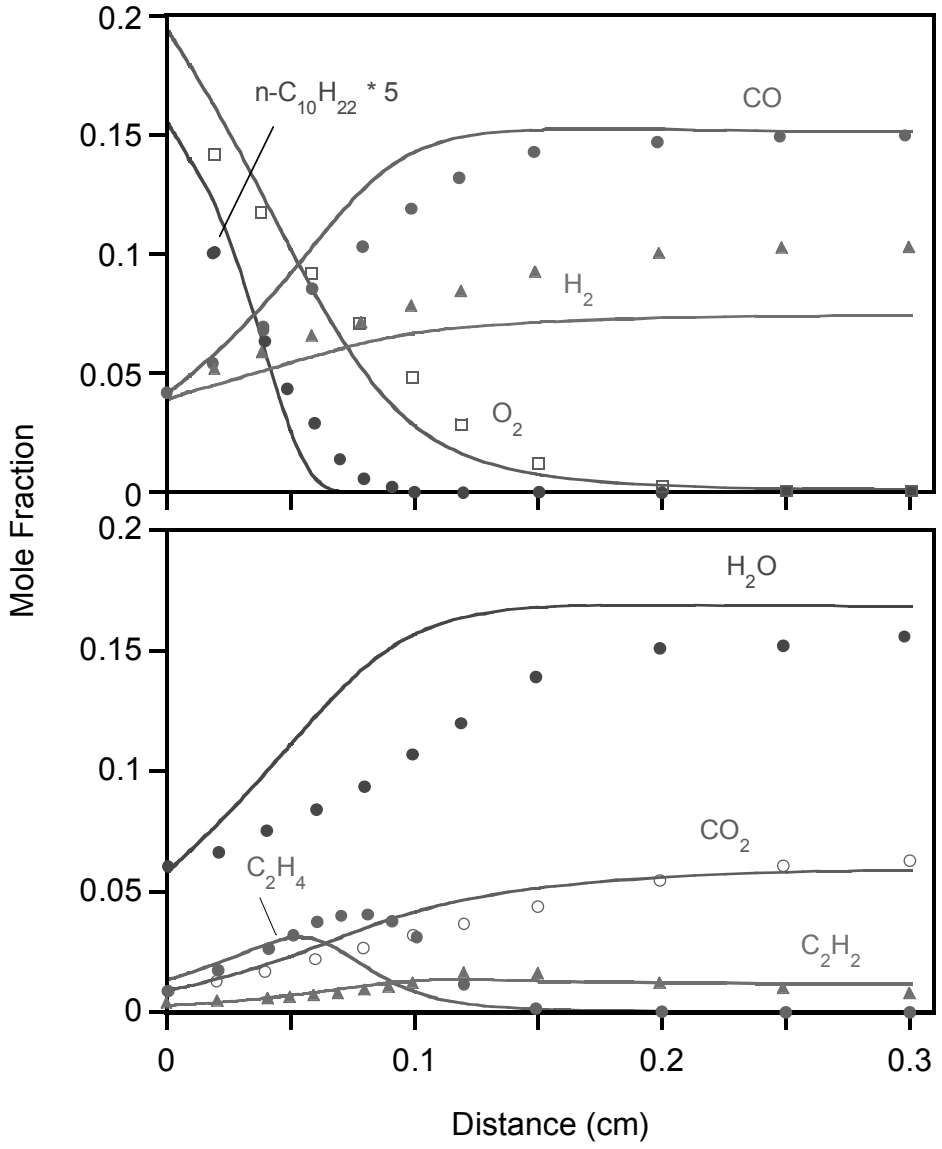

Fig. 6 Comparison of experimental (Doute et al., 1995) (symbols) and computed (lines) species profiles in *n*-decane-O_2-N_2 burner stabilized flame (P = 1 atm, ϕ = 1.7).

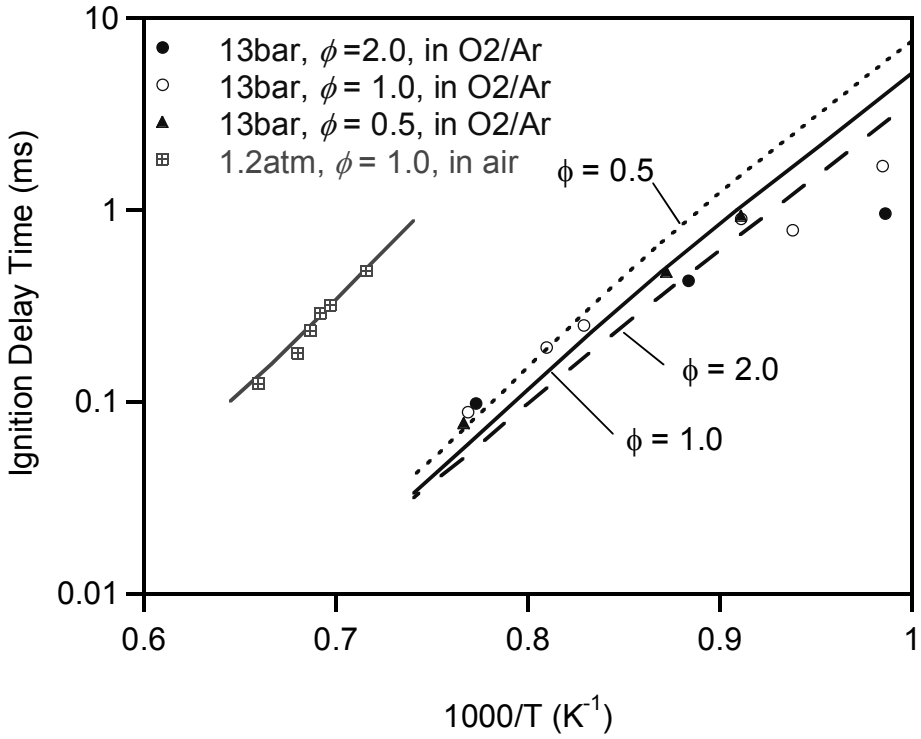

Fig. 7 Comparison of experimental (symbols) and computed (lines) ignition delay times for *n*-decane. Mixture compositions used in the experiments: 0.2% *n*-decane-O_2-Ar (Horning et al., 2002) and *n*-decane/air (Pfahl et al., 1996).