Experimental and modeling investigation of laminar flame speeds of styrene

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1 Introduction

Styrene is a fundamental intermediate in the high-temperature oxidation of alkylated aromatic compounds and consequently of commercial fuels which contain a substantial portion of aromatic components. For example, in their study on the oxidation of ethylbenzene performed using the Princeton atmospheric flow reactor, Litzinger et al. [1] measured large amounts of styrene produced from the dehydrogenization of the fuel. In order to facilitate the kinetic analysis, an experimental set was also conducted with styrene as the fuel molecule, at fuel-lean conditions (ϕ = 0.56), and at an initial temperature of around 1060 K. Subsequent studies performed by the same research group on larger alkylated single-ring aromatics, such as n-propylbenzene [2,3] and n-butylbenzene [4], suggest once again the importance of the pathways to styrene. Other experimental investigations on these large alkylated compounds highlighted styrene as one of the key aromatic intermediates, including the species measurements in jet-stirred reactors by Dagaut et al. [5], by Diévart and Dagaut [6], and by Husson et al. [7], and in the UIC high-pressure shock tube by Gudiyella and Brezinsky [8].

Although the central role of styrene in the oxidation of aromatic compounds, few investigations have been specifically focused on its chemistry. As mentioned above, the flow reactor study by Litzinger et al. [1] provides species profiles for the main intermediates and products of the styrene oxidation. In addition, Müller-Markgraf and Troe [9] and Grela et al. [10] performed kinetic experiments to derive the reaction rate constant of the styrene dissociation to form benzene and acetylene. In the present investigation, new experimental results on laminar flame speeds of styrene have been obtained using a heated spherical reactor. Such data are fundamental for the validation of chemical kinetic models of large alkylated aromatic hydrocarbons. In addition, a chemical kinetic model was developed to simulate the newly obtained experimental results.

2 Experimental and modeling techniques

Spherical Bomb

The spherical bomb consists of a spherical stainless steel vessel of 56-L (i.d. 48 cm) equipped with 4 quartz windows (100 mm optical diameter, 50 mm thickness). Thermal insulation ensures a homogeneous temperature throughout the entire apparatus with a maximum divergence from the desired value of ±1 K. Two tungsten electrodes are located along a diameter of the sphere and used to ignite the mixtures. They are linked to a controlled high voltage discharge device (primary voltage of about 10 kV) that produces a spark at the center of the spherical reactor. The voltage and intensity

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discharge were measured via a high voltage and a current probe, thus the energy provided to the mixture could be estimated. The adjustable gap between the electrodes was usually fixed around 1 mm but was larger near the flammability limits.

The liquid fuels and the gases were introduced directly in the vessel using the partial pressure method. In order to minimize the uncertainties in the mixture preparation, the pressures were measured using capacitive manometers (MKS Baratron, Type 631) of different full scales according to the desired pressure range (100 Torrs and 1000 Torrs). Based on the precision of the capacitive manometers, the mixtures were prepared with an accuracy of 0.5%. The initial pressure in the spherical bomb was fixed to 1 bar for all the experimental sets presented herein, while the initial temperature was varied (343.2±0.5 K, 373.2±0.5 K, and 403.2±0.5 K).

The combustion process was monitored using 2 different diagnostics: pressure measurements using a piezo-electric pressure transducer (Kistler 601A coupled to a Kistler Type 5011B Charge Amplifier) and recording of the flame. The visualization of the flame was obtained via a Schlieren diagnostic coupled with a high speed camera (Phantom v1610). The frame rate was fixed to 25000 i/s. The 2 diagnostics were synchronized using a TTL signal generated at the onset of the spark between the electrodes. This synchronization was mandatory in order to correlate the pressure increase with the observations obtained by the fast imaging. An average increase of around 0.75% was observed in the pressure traces between the TTL signal and the time corresponding to the last image considered for deriving the flame speed.

An automated software was subsequently used to obtain the radius of the flame (Canny method) as a function of time from which the unstretched laminar flame speed of the unburned gases is derived. In particular, the following relation by Ronney and Sivashinsky [11] was solved iteratively to obtain both the adiabatic unstretched gas speed of the burned gases relative to the flame, S_b^0, and the Markstein length, L_b,

$$\left(\frac{S_b}{S_b^0}\right)^2 \cdot \ln\left(\frac{S_b}{S_b^0}\right)^2 = -\frac{2L_b \cdot k}{S_b^0},$$

where k is the stretch rate. The unstretched laminar flame speed of the unburned gases, S_u^0, can be derived from the continuity equation. The maximum estimated error in the final flame speed measurement is around ±0.5 cm/s.

Reagents

Commercial styrene contains a certain amount of stabilizer (p-tert-butylcatechol in the present case) which is added to the fuel in order to minimize the polymerization process during storage. Two different styrene samples were considered in the present study in order to assess the influence of the impurities and stabilizer mole fractions on the experimental results. The first styrene sample by Sigma Aldrich (ReagentPlus, >99% purity) contains relatively high amounts of the stabilizer (50 ppm), while the second one by Acros Organics (>99.5% purity) only 10 to 20 ppm of p-tert-butylcatechol. The comparison between the two fuels has been conducted based on the flame speeds measured at an initial temperature of 403.2±0.5 K (Fig. 1). The two experimental sets show a slight shift with the styrene from Acros Organics, characterized by higher purity and lower stabilizer concentration, having higher flame speeds over almost the entire equivalence ratio range. The polynomial fits presented in Fig. 1 can be used in order to further estimate the difference between the experimental sets. In fact, the discrepancy between fits and measurements is always less than 0.5 cm/s, specifically less than 0.2 cm/s for around 90% of the data. On average the two polynomial fits differ by around 0.6 cm/s in the equivalence ratio range between 0.75 and 1.40, thus slightly higher than the experimental uncertainty on the single measurement. We can thus conclude that the difference in the amounts of impurities and inhibitor plays a minor role on the flame speed results, although a small variance was observed. For the remaining experiments conducted at different temperatures the Acros Organics styrene was used, being the purest compound, while laboratory dry air consisted of 0.209 O_2 + 0.791 N_2.

As mentioned above, styrene isomerizes quite rapidly, with a rate of 0.1% per hour at 60 °C and 2% per hour at 100 °C (purified styrene, [12]). In order to reduce the experimental uncertainties, the time employed to run the experiments was minimized and the experimental procedure was maintained consistent during the entire study. Of course, the measurements performed at 343.2 K will be almost unaffected by the polymerization process, while at higher temperatures a larger uncertainty in the absolute flame speed value should be considered. On the other hand, no evident sign of the polymerization process, such as for example condensation of solid particles on the glass windows, could be observed even at 403.2 K.

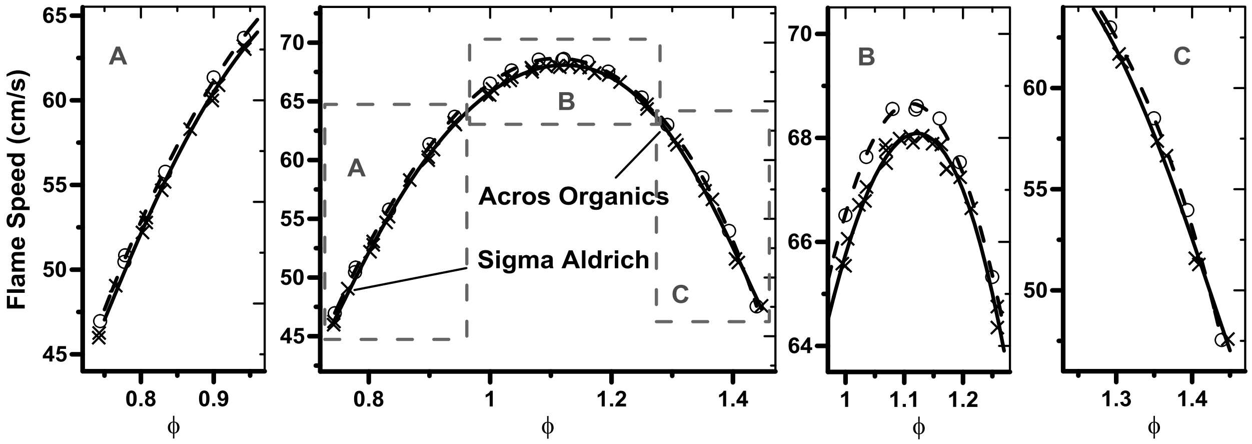

Figure 1. Flame speed measurements. T_{in} = 403.2 K; P_{in} = 1 bar. Styrene by: × Sigma Aldrich; ○ Acros Organics. Solid lines (Sigma Aldrich) and dashed lines (Alfa Aesar) represent the polynomial fits.

Chemical kinetic modeling

The chemical kinetic model developed herein is based on the work by Metcalfe et al. [13]. The authors extensively studied the pyrolysis and oxidation of toluene and validated their comprehensive kinetic model against various experimental results including flame speed measurements for both benzene and toluene. No modifications were made on the aromatic chemistry up to toluene and on the C0-C4 base mechanism. The model proposed by Metcalfe et al. [13] also contains a sub-set of reactions for styrene and ethylbenzene which was replaced to better fit the new experimental data. In particular, the H-abstraction reactions by radicals on the vinyl moiety were estimated based on the corresponding reactions for ethylene (terminal carbon) and propene, while the H-abstraction reactions on the ring based on the parameters for benzene and toluene. The thermal decomposition of the primary radicals of the oxidation of styrene (C_6H_5CHCH and $C_6H_5CCH_2$) were taken from the work by Tokmakov and Lin [14], while the oxidation steps were estimated based on the reactions of the vinyl radical.

All the simulations have been performed using Cosilab software, version 3.3.2 [15]. For the flame speed calculations the one-dimensional freely-propagating flame system was solved, with GRAD and CURV values equal to 10^{-5} and a spatial domain from -1 to 5 cm. All the flame calculations were performed using multi-component transport properties and including the Soret effects.

3 Results and discussions

The experimental results are reported in Fig. 2a for the three initial temperatures considered (343.2 K, 373.2 K, and 403.2 K). The equivalence ratio was varied between 0.75 and 1.45, while the initial pressure was maintained constant during the entire study (1 bar). The increment in the flame speed due to the variation in the initial temperature is similar for a similar increase in temperature from 343.2 K to 373.2 K and from 373.2 K to 403.2 K. In particular, the profiles at around the maximum differ by around 8 cm/s, while they slightly converge at fuel rich and lean conditions.

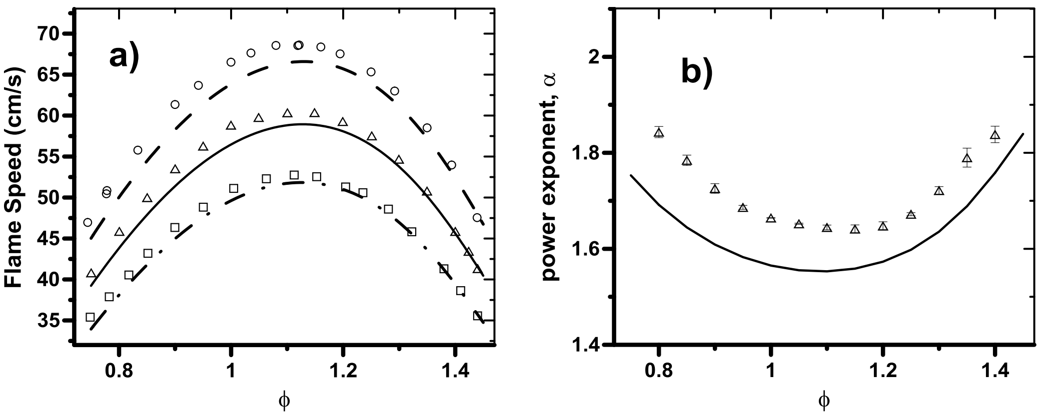

Figure 2. a) Laminar flame speed of styrene; b) power exponent α. Symbols represent experimental results at 1 bar and initial temperature equal to: ○ 403.2 K, △ 373.2 K, □ 343.2 K; lines represent modeling results.

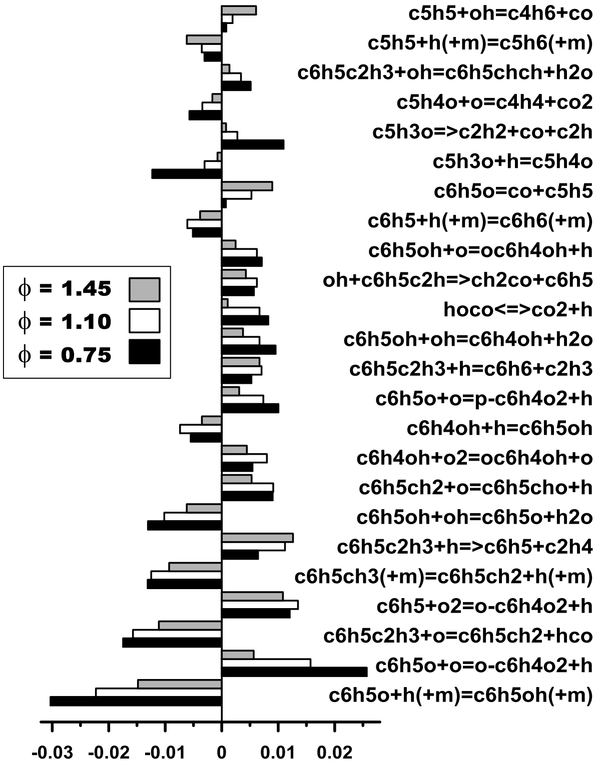

Figure 3. Sensitivity analysis of the flame speed with respect to the reaction rate coefficients, T_{in} = 343.2 K.

Fig. 2a also contains the simulation profiles. Overall the experimental trends are well reproduced by the model, especially with regard to the position of the maximum flame speed. In particular, the experimental results obtained at 343.2 K are in excellent agreement with the simulations over the entire equivalence ratio range, while at higher temperatures the measured flame speeds are slightly underestimated around stoichiometric and fuel lean conditions. The discrepancy for the maximum flame speeds is around 0.85 cm/s, 1.57 cm/s, and 2.04 cm/s for the data obtained at 343.2 K, 373.2 K, and 403.2 K respectively, which correspond to 1.6%, 2.6%, and 3.0% of the experimental values.

The results presented in Fig. 2a can be used to estimate the influence of the initial temperature on the adiabatic laminar burning velocity based on the relationship $S_L/S_{L0} = (T/T_0)^{\alpha}$, where the reference temperature T_0 is, in this case, equal to 343.2 K. The experimental and modeling results are presented in Fig. 2b. The mild dependence of the experimental power exponents α on the equivalence ratio is well reproduced by the model although the simulations profiles are slightly shifted compared to the experimental ones with a discrepancy lower than 10%. This result is in agreement with the underprediction of the flame speed measurements at 373.2 K and 403.2 K as in Fig. 2a.

The chemical kinetic model simulates quite accurately the flame speed measurements (Fig. 2a), thus it can be used to further analyze the styrene oxidation at the present conditions. In particular, Fig. 3 contains the sensitivity analysis of the flame speed with respect to the reaction rate coefficients for an equivalence ratio of 1.1 and an initial temperature equal to 343.2 K (white bars). In order to simplify the analysis, only the reactions specific to the aromatic chemistry are reported. The results clearly indicate how the flame speed of styrene is strongly influenced by the chemistry of the single ring radicals with competition between the oxidation steps and the recombination reactions to form stable intermediate. For example, the reaction of the phenoxy radical (C_6H_5O) with hydrogen to form phenol (C_6H_5OH) has the greatest coefficient, opposite in sign to the coefficients for the displacement reactions with molecular oxygen to form the benzoquinones (p-c6h4o2 and o-c6h4o2) and for the decomposition step to CO and cyclopentadienyl radical (C_5H_5). Similarly, the oxidation steps of the phenyl radical (C_6H_5) and the benzyl radical ($C_6H_5CH_2$) are in competition with the recombination steps to benzene (C_6H_6) and toluene ($C_6H_5CH_3$), respectively.

Among the reactions specific to the fuel molecule, three main reactions of styrene with radicals appear to be important. In particular, the formation of benzyl radical ($C_6H_5CH_2$) + HCO from the reaction between styrene and molecular oxygen reduces the flame speed mainly due to the formation of the very stable benzyl radical which acts as H-atom scavenger. On the other hand, the reactions of the fuel with hydrogen atoms to form the phenyl radical + ethylene (C_6H_5+C_2H_4) and benzene + vinyl radical (C_6H_6+C_2H_3) lead to the formation of very reactive C2 compounds, thus they contribute to an increase in the flame speed.

The sensitivity analysis was also performed at different temperatures and equivalence ratios. In particular, no substantial differences were observed between the results obtained at 373.2 K or 403.2 K ($\phi = 1.1$) and the ones presented in Fig. 3 for the same equivalence ratio condition. On the other hand, as show in Fig. 3, the change in equivalence ratio affects the relative importance of the different reactions. At lean conditions (black bars in Fig. 3), the flame speed is strongly influenced by the phenoxy radical reactions (reaction with atomic oxygen and recombination with H) as well as by the reactions involving the c5h3o intermediate (produced from the oxidation of the ring) which do not play a relevant role at fuel rich conditions. This result suggests a prominent role of the oxidation steps at these conditions. On the contrary, at $\phi = 1.45$ the sensitivity coefficients of the two main phenoxy radical (C_6H_5O) reactions become smaller in absolute value, while the one of the thermal decomposition step to cyclopentadienyl radical C_5H_5 and CO becomes larger. As a consequence, the chemistry of the cyclopentadienyl radical influences the flame speed, with the competition between the oxidation step (c5h5+oh = c4h6+co) and the recombination with H to form cyclopentadiene (C_5H_6).

The model was also validated against the flow reactor data by Litzinger et al. [1] (data not shown). Both the fuel decomposition and the formation of the main intermediate compounds are well reproduced by the model, with the exception of the underpredition for the benzene profile. This may suggest a more pronounced role of the vinyl group displacement reaction by atomic hydrogen, although additional analyses have to be performed to confirm this hypothesis.

4 Conclusions

Laminar flame speeds of styrene were measured in a spherical bomb heated to 343.2 K, 373.2 K, and 403.2 K at an initial pressure of 1 bar and over a wide range of equivalence ratios. The experimental results were used to develop a chemical kinetic model which is able to simulate quite accurately the measured flame speeds as well as the temperature dependence observed in the results, in addition to the data available in literature. Sensitivity analyses of the flame speed were also performed in order to understand the influence of the various aromatic reactions on the simulation results at the different conditions considered herein.

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