Experimental and modeling study of styrene oxidation in spherical reactor and shock tube

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ABSTRACT

The oxidation of styrene, one of the main stable intermediates from the oxidation of large alkylated aromatic hydrocarbons, has been investigated in the present work both experimentally and numerically. Experiments were performed using two complementary techniques, spherical bomb for laminar flame speed studies and shock tube for ignition delay time measurements. In particular, the laminar flame speeds of styrene/air mixtures were measured at three different initial temperatures (342 K, 373 K, and 405 K), over a wide range of equivalence ratios (0.75–1.45), for an initial pressure of 100 kPa. In addition, the autoignition of styrene/O_2 mixtures in argon bath gas ($\phi = 0.5$, 1.0, and 1.5) was investigated over a wide range of temperatures (1390–1990 K), at highly diluted conditions (94.3%–99% argon), and for pressures between 110 and 200 kPa. A detailed chemical kinetic model, based on the toluene chemistry by Metcalfe et al. (2011), was developed and validated against the newly obtained experimental results and the flow reactor data available in the literature (Litzinger et al., 1986). Sensitivity and rate of production analyses were performed and showed that, at the conditions studied herein for the flame speed investigation, the main fuel consumption pathways include the reaction of the fuel with H atoms to form phenyl radical and ethylene or benzene and vinyl radical, with O to form benzyl radical + HCO, and the H-abstraction reactions on both the vinyl moiety and the ring. On the other hand, the analyses performed at the high-temperature, highly-diluted conditions encountered in the shock tube study highlighted the importance of the fuel thermal decomposition steps for the simulation of the ignition delay time measurements. The model was also tested against the low-pressure flame and jet stirred reactor data by Yuan et al. (2015). The results highlight the need for future modifications in the benzene chemistry by Metcalfe et al. and inclusion of pressure dependent rate parameters in order to improve the prediction capabilities of the model.

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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 ($\phi = 0.56$), 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], suggested 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 a high-pressure shock tube by Gudiyella and Brezinsky [8]. Indeed, the accuracy in the description of the chemistry involved in the styrene oxidation does not only influence the ability to predict the oxidation of large aromatics and fuel mixtures, but also the formation of polycyclic aromatic hydrocarbons and finally soot. In fact, the oxidation of styrene leads to the formation of several intermediates, such as phenylacetylene, 2-phenylvinyl (C_6H_5CHCH), and 2-vinylphenyl ($C_6H_4C_2H_3$), which constitute essential building blocks for the growth to the second-ring structure [9–11].

Despite 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 in-

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termediates and products of the styrene oxidation. In a recent investigation, Yuan et al. [12] measured species profiles both in laminar premixed flames of styrene at low pressure (0.0395 atm, ϕ = 0.75, 1.00, and 1.70) using synchrotron vacuum ultraviolet photoionization mass spectrometry and in a jet-stirred reactor for styrene/benzene mixtures at atmospheric pressure using gas chromatography. The authors also developed a detailed chemical kinetic model to simulate the species profiles previously obtained. Other studies on styrene include the works by Müller-Markgraf and Troe [13] and by Grela et al. [14] which performed kinetic experiments to derive the reaction rate constant of the styrene dissociation to benzene and vinylidene. In the present investigation, new experimental results on the laminar flame speeds of styrene/air mixtures have been obtained using a heated spherical reactor. Ignition delay time measurements in a glass shock tube were also performed as a complement to the flame speed study. Finally, a chemical kinetic model was developed to simulate the newly obtained experimental results as a base for the development of kinetic models for larger alkylated compounds and fuel surrogates.

2. Experimental and modeling techniques

2.1. Spherical bomb

Details of the experimental apparatus have been reported in a recent publication [15] and only the main features are described below. The spherical bomb consists of a spherical stainless steel vessel of 56-L equipped with 4 quartz windows (100 mm optical diameter) and homogeneously heated with a maximum uncertainty of ±1 K. In the present study, the initial temperature was varied (342 ±1 K, 373 ±1 K, and 405 ±1 K) while the initial pressure in the spherical bomb was fixed to 100 kPa for all the experimental sets presented. The liquid fuels and the gases were introduced directly in the vessel using the partial pressure method. The pressures were measured using capacitive manometers (MKS Baratron, Type 631) of different full scales according to the desired pressure range (100 and 1000 Torr). Based on the precision of the capacitive manometers (0.5% of the reading), the partial pressure of each component could be estimated with an accuracy of ~0.5%, thus the maximum error on the equivalence ratio is around 1%. This value is a conservative estimate of the real error since the manometers are periodically calibrated against a reference capacitive manometer (for the 0–100 Torr) or against a mercury manometer (0–1000 Torr) with small deviations between the measurements corrected by the calibration curve and the reference values (lower than 0.5%).

The combustion process, initiated at the center of the sphere by an electric spark obtained using tungsten electrodes, was monitored using two 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 25,000 i/s. An average increase of around 0.75% was observed in the pressure traces between the TTL signal (produced by a digital delay/pulse generator (Stanford Research System INC) at the spark and used for the synchronization of the camera and the oscilloscope) and the time corresponding to the last image which could be observed and measured. Examples of flame images and pressure trace are presented in Fig. 1.

2.2. Laminar flame speed determination and related uncertainties

Automated software was used to analyze the images (i.e., in Fig. 1) and 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 [16], as subsequently modified by Kelley and Law [17], 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,

$$\left(\frac{S_b}{S_b^0}\right)^2 \cdot \ln \left(\frac{S_b}{S_b^0}\right)^2 = -\frac{2L_b \cdot \kappa}{S_b^0} \tag{1}$$

where κ is the stretch rate. The value S_b^0 and L_b are determined using the following steps: (i) a couple of values of S_b^0 and L_b are chosen to initialize the optimization process, (ii) the non-linear equation is solved to get the radii predicted by the equation based on the values of the chosen S_b^0 and L_b, (iii) these radii are compared to the experimental ones, and if they differ, a new set of S_b^0 and L_b is chosen. A minimization process is then applied in order to obtain the best correspondence between the experimental radii and the ones derived from the nonlinear equation. A Matlab processing is used to perform these optimization steps. The minimum radius used in the data processing was around 10 mm, while the maximum radius between 30 and 35 mm. This range was chosen to guarantee the optimal quality of the flame images and accuracy of the consequent experimental profiles.

The unstretched laminar flame speed of the unburned gases, S_u^0, was derived from the continuity equation. For a flame propagating at constant pressure conditions, as in the present experiments, $S_u^0 = S_b^0/\sigma$, where $\sigma = \rho_u/\rho_b$ and ρ_u, ρ_b are the unburned and burned densities of the mixture, respectively. The densities of unburned and burned gases, ρ_u and ρ_b, were calculated using COSILAB [18] with the Equilibrium code. The maximum estimated error in the derivation of the laminar flame speed is around ±1 cm/s which derives from the estimated uncertainty in the determination of the radii (±1 pixel).

Examples of unstretched spatial laminar burning speed extractions using the non-linear method (NQ based on the notation in Ref. [19]) are shown in Fig. 2. The solution of the linear relation between burning speed and stretch rate ($S_b = S_b^0 - L_b \cdot \kappa$, [20,21], named LS) is also reported for comparison. The symbols in Fig. 2 correspond to the spatial laminar burning speed derived from the measured radius versus time: $S_b(R_i) = \frac{R_{i+1} - R_{i-1}}{t_{i+1} - t_{i-1}}$. The radius is not fitted using an expression of dR_f/dt and the plotted symbols corresponding to S_b are presented for display purposes only. The solid line corresponds to the non-linear solution and the dashed line to the linear solution. While at fuel rich conditions the two unstretched laminar burning speeds appear to be nearly identical, the solutions diverge moving toward lean mixtures. These results highlight the influence of the extrapolation method based on the current (R_f, t) datasets, and they do not provide any information on the global uncertainty in the laminar flame speed measurements. Nevertheless, in order to better assess such influence, additional methods were implemented including the two models investigated by Chen [22] (NM-I and NM-II) and the non-linear model in expansion form (NE based on the notation in Ref. [19]). The comparison between the results is reported in Fig. 3 for the case of initial temperature equal to 342±1 K, although similar results were obtained for the other datasets.

Excluding the linear model which is not a realistic model to describe correctly the propagation of expanding flames over the entire range of equivalence ratios studied herein, the use of NM-I (solid line), NM-II (dash-dot line), and NE (dash line) leads to results which are within the experimental uncertainties of the measurements obtained solving Eq. 1, represented by the symbols in Fig. 3. In particular, all the methods converge at fuel rich conditions, including the linear model as already mentioned concerning Fig. 2, while they diverge at lean conditions. In particular, the