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Shock tube and kinetic study of C₂H₆/H₂/O₂/Ar mixtures at elevated pressures



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ABSTRACT

Using a high-pressure shock tube facility, the ignition delay times of stoichiometric C₂H₆/H₂/O₂ diluted in argon were obtained behind reflected shock wave at elevated pressures ($p = 1.2, 4.0$ and 16.0 atm) with ethane blending ratios from 0 to 100%. The measured ignition delay times were compared to the previous correlations, and the results show that the ignition delay times of ethane from different studies exhibit an obvious difference. Meanwhile, numerical studies were conducted with three generally accepted kinetic mechanisms and the results show that only NUIG Aramco Mech 1.3 agrees well with the measurements under all test conditions. Sensitivity analysis was made to interpret the poor prediction of the other two mechanisms. Furthermore, the effect of ethane blending ratio on the ignition delay times of the mixtures was analyzed and the results show that ethane blending ratio gives a non-linear effect on the auto-ignition of hydrogen. Finally, chemical interpretations on this non-linear effect were made from the reaction pathway analysis and normalized H radical consumption analysis.

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1. Introduction

Increasing demand of energy and steady deterioration in atmospheric environment has accelerated endeavors to seek the renewable and clean energy sources and to develop high-efficiency combustion techniques. The so-called bio-hydrogen has attracted special attention [1,2], although numerous alternative sustainable energy sources have been proposed, such as alcohol, ether, hydrogen, diesel. Hydrogen is the most abundant element in the universe, and thus can be produced virtually unlimited quantities by various ways using renewable energy sources like solar, electric, geothermal and natural gas, etc. [2]. Fundamentally, hydrogen shows desirable

characteristics in combustion [3,4]. Carbon-neutral allows free combustion on carbon-related emissions such as CO₂, HC, soot and PAH. Wide flammability range permits a smooth engine operation under very lean mixture with low NO_x emission. High reactivity and flame speed of hydrogen make the real engine cycle closer to the thermodynamic ideal cycle with high thermal efficiency. Additionally, high diffusivity of hydrogen promotes the homogenous of fuel and air. These desirable natures have facilitated a number of studies on internal combustion engines [5–7] and gas turbine combustors [8,9]. Nevertheless, engines fueled with pure hydrogen are prone to abnormal burning such as knock, pre-ignition and backfire due to the extremely rapid combustion of hydrogen [4]. However, these drawbacks can be mitigated by mixing

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hydrogen with hydrocarbon, leading to the growing interests in the studies of hydrogen/hydrocarbon combustion.

Previous fundamental studies of hydrogen enriched methane or natural gas were reported in laminar flame speeds using the spherically expanding flame method [10–12], the stagnation flame method [13,14] and heat flux method [15], in ignition delay times using the shock tube [16–20] and rapid compression machines [21]. These experimental data are valuable for the validation of the kinetic mechanisms of methane and hydrogen, which is the foundation to build the mechanisms of large hydrocarbons because of its hierarchical structure. Furthermore, investigations on hydrogen enriched propane and butane were also reported. Laminar flame propagation characteristics of hydrogen enriched propane [22,23] were investigated using the spherically expanding flames and the studies showed that laminar flame speed experienced an initially gradual increase and then a steep increase with the increase of hydrogen blending ratio in the fuel mixtures. Additionally, hydrogen addition changes the diffusional–thermal property of the mixture, leading to an alternation on the flame front behavior. Using a hydrogen addition parameter, R_H , proposed by Yu et al. [13]. Tang et al. [24] investigated the laminar flame speed of hydrogen enriched butane and they found that laminar flame speed increases linearly with the increase of R_H . Recently, Man et al. [25] and Tang et al. [26] measured the ignition delay times of hydrogen enriched propane. They suggested that hydrogen addition yielded a non-linear effect on ignition delay time, which is similar to laminar flame behavior of hydrogen enriched propane. Rare investigations on hydrogen enriched hydrocarbons larger than butane are reported yet. Aggarwal et al. [27] numerically studied the effects of hydrogen on the ignition behavior of *n*-heptane/air mixtures using four widely used kinetic mechanisms. They found that hydrogen addition to *n*-heptane/air mixtures increased and decreased the ignition delay times at low and high temperatures, respectively, but this effect was relatively small even under 80% hydrogen in fuel blend. Later, Jain et al. [28] numerically studied the ignition characteristics of hydrogen addition to iso-octane/air mixtures. Small effect on ignition behavior of hydrogen addition iso-octane/air mixtures was found and this dependence was obviously generalized to propane, butane and heptane.

Although some studies have been reported on the ignition behavior of hydrocarbon/ H_2 mixtures, but no study on the ethane/ H_2 mixtures has been reported. Being an important constituent of natural gas, a well understanding of ignition behavior of hydrogen/natural gas requires a well understanding of ignition characteristic of hydrogen/ethane mixtures. Additionally, previous studies on ignition delay times of hydrogen enriched large hydrocarbons indicated that hydrocarbon addition exhibited small effect on the ignition of hydrogen, thus one objective of this study is to study the effect of ethane addition on hydrogen ignition characteristic. Meanwhile, a comparison of the measured ignition delay times with other previous data as well as predictions with some kinetic mechanisms was made and the performance of these mechanisms was evaluated. Finally, chemical kinetic analysis was performed to clarify the effect of ethane blending ratio on the ignition of hydrogen.

Table 1 – Main constituents in the test mixtures ($\phi = 1.0$ for all mixtures).

Mixture	Blend	$X_{C_2H_6}$ (%)	X_{H_2} (%)	X_{O_2} (%)	X_{Ar} (%)
1	100% C_2H_6	1.133	0.000	3.964	94.904
2	30% C_2H_6 /70% H_2	0.783	1.827	3.653	93.737
3	10% C_2H_6 /90% H_2	0.416	3.744	3.328	92.512
4	3% C_2H_6 /97% H_2	0.158	5.094	3.098	91.650
5	100% H_2	0.000	5.917	2.959	91.124

2. Experiment

The shock tube in this study was described in detail everywhere [17,29]. Only a brief description is given here. The shock tube with a diameter 11.5 cm has a whole length of 9.37 m which is divided into a 4 m driver section and 5.3 m driven section by a 0.07 m double-diaphragm section. The shock wave is generated by suddenly reducing the pressure in the double-membrane section. Before each experiment, a roots-mechanical pump was used to vacuum the whole shock to a pressure of 1 Pa. The stoichiometric fuel mixtures of ethane/ H_2 mixtures, as shown in Table 1, were prepared in a 128 L mixing tank by Dalton's Law of Partial Pressure. The partial pressure of each component was measured by a high-accuracy pressure transmitter (Rosemount 3051). Purities of ethane, hydrogen and oxygen are higher than 99.99%, and purity of helium and argon is 99.9999%.

Three time counters (FLUKE, PM6690) triggered by four pressure transducers (PCB 113B26) were used to obtain the time interval of adjacent transducers and the incident shock velocities are then correspondingly calculated. The incident shock velocities at the end-wall were obtained through extrapolating the shock velocity profile to the end-wall. The reflected temperature (T_5) and pressure (p_5) were calculated using a chemical equilibrium program Gaseq [30]. The ignition delay time was defined as the time interval between the pressure rise due to the arrival of incident shock wave at the end-wall and the steepest rise of excited OH^* emission, as shown in Fig. 1. The excited OH^* emission was detected by a

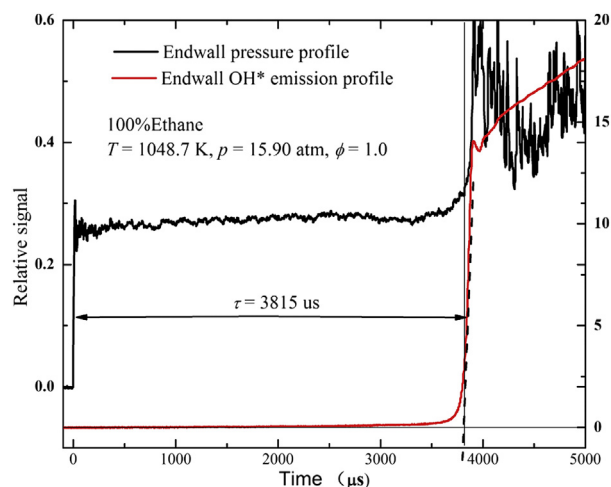


Fig. 1 – Definition of ignition delay time.

Table 2 – Summary of ethane correlations.

Sources	Parameters					Conditions range			
	A	a	b	c	E_a	p (atm)	T (K)	ϕ	Dilution (%)
Burcat et al. [34]	2.35E-14	0.46	-1.26	0	34.2	2–8	1235–1660	0.5–2	90.5–97.3
Cooke and Williams [35]	1.20E-15	0.4	-1.40	0	31.1	0.2–0.47	1400–2200	0.5–2	90–95
Hidaka et al. [37]	1.15E-13	1	-1.00	0	29.9	0.027–0.053	1300–2000	0.7–2	94.5–95.5
Shim et al. [39]	1.20E-14	0.71	-1.20	0	49.2	0.7–1.4	1227–1543	0.7–2	86.5–91
Lamoureux et al. [38]	2.46E-15	0.64	-1.05	0	55.2	2.9–14.2	1270–1520	0.5–2	94–98.6
de Vries et al. [36]	7.15E-19	0.79	-1.21	0.42	39.6	0.57–3.0	1218–1860	0.5–2	91–98

photomultiplier (Hamamatsu CR131) with a narrow filter centered at 307 ± 10 nm mounted in the end-wall.

Simulation works were made using SENKIN code [31] in the CHEMKIN II [32] package coupled with the VITM method developed by Chaos and Dryer [33] to consider non-ideal effect (dp/dt). Typical non-ideal effect (dp/dt) was measure to be 4% in our previous work [26]. The definition of calculated ignition delay time is similar to that in the experiment for direct comparison.

3. Results and discussion

3.1. Comparison with previous data

Ignition delay times of the stoichiometric $C_2H_6/H_2/O_2$ diluted with argon were measured behind reflected shock wave at pressures of 1.2, 4, 16 atm, temperatures from 900 to 1700 K, and hydrogen blending ratios from 0 to 100%. All measured ignition delay times are provided in [Supplementary material](#). Some of ignition data and correlations of ethane can be found in the previous studies [34–39], as summarized in [Table 2](#). Apparently, it needs caution in the comparison of these correlations from different authors because of their different applicability range.

[Fig. 2](#) gives the comparison between the measured ignition delay times and previous correlations for the stoichiometric ethane mixture. Considering the scope of each correlation, correlations of Shim et al. [39] and de Vries et al. [36] were used to compare with the measured data at 1.2 atm, while the correlations of Burcat et al. [34] and Lamoureux et al. [38] were used to compare with the measured data at 4 atm. At $p = 1.2$ atm, the measured ignition delay times fit fairly well to the correlation of de Vries et al. [36] with lower ignition activation energy. However, the measured data give lower and higher value than the correlation of Shim et al. [39] at higher and lower temperature respectively, indicating a lower global activation energy of the measurement. At $p = 4.0$ atm, the measurements agree well with the correlation of Burcat et al. [34] in both ignition delay times and global activation energy. However, the correlation of Lamoureux et al. [38] yields respectively lower and higher values at higher and lower temperature. Obviously, the ignition delay time of ethane measured by different authors exhibits the difference in global activation energy ranging from 30 to 50 kcal/mol, suggesting that further accurate measurements is required.

3.2. Calculated ignition delay time

In this study, three generally accepted mechanisms, NUIG Aramco Mech 1.3 [40], USC Mech 2.0 [41] and LLNL C4 Mech [42], are chosen to simulate the ignition delay times and conduct the kinetic analysis. NUIG Aramco Mech 1.3, proposed by the Combustion Chemistry Centre at NUI Galway in 2013, is the latest version by updating rate constant of reactions associated with methane, ethane, ethylene, acetylene and oxygenated hydrocarbon species, including formaldehyde, methanol, acetaldehyde, and ethanol. This mechanism consisting of 253 species and 1542 elementary reactions has

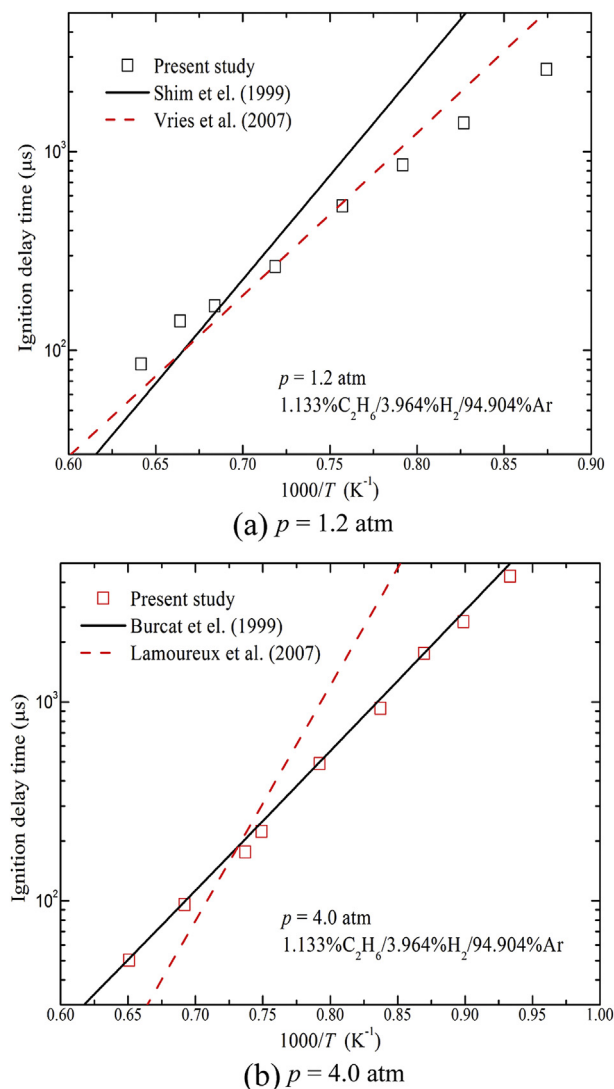
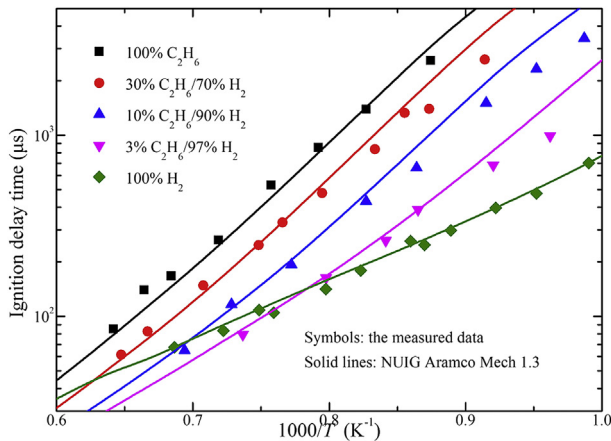


Fig. 2 – Comparison between measurements and previous correlations for stoichiometric ethane.

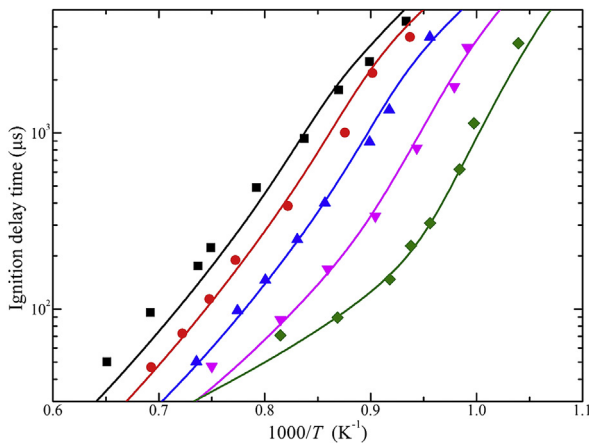
been widely validated against numerous of experimental measurements including the data from shock tubes, rapid compression machines, flames, jet-stirred and plug-flow reactors. USC Mech 2.0 consisting of 111 species and 784 reactions, developed by Wang's group in 2007, is found applicable to a wide variety of combustion scenarios. LLNL C4 Mech developed by Lawrence Livermore National Laboratory in 1998, involves 155 species and 689 elementary reactions.

This mechanism was also validated against large number of experimental targets.

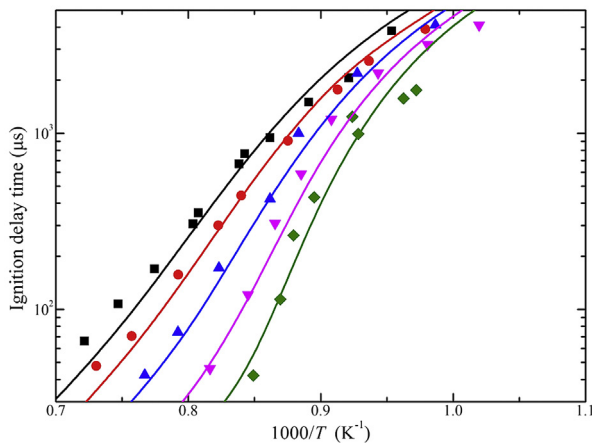
Figs. 3–5 give the comparison between the measured and calculated ignition delay times of the stoichiometric ethane/ H_2 mixtures at $p = 1.2, 4.0, 16.0$ atm using NUIG Aramco Mech 1.3, USC Mech 2.0 and LLNL C4 Mech, respectively. As shown in Fig. 3, NUIG Aramco Mech 1.3 not only well captures the



(a) $p = 1.2$ atm

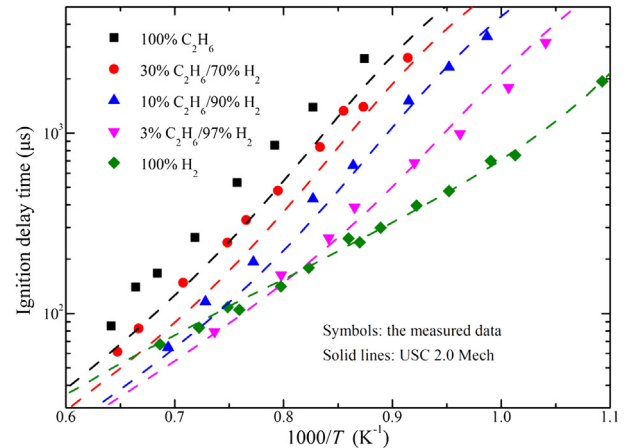


(b) $p = 4.0$ atm

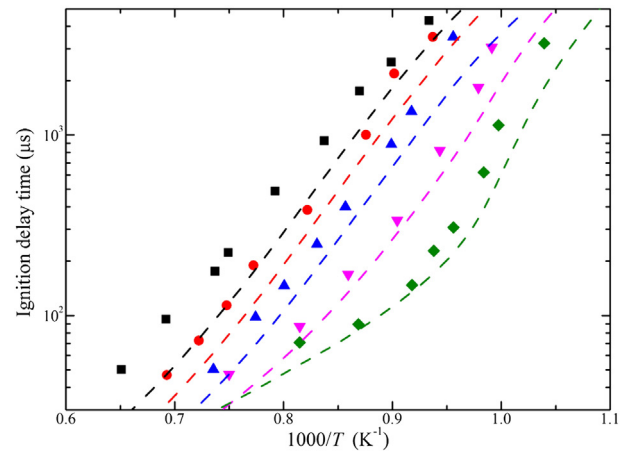


(c) $p = 16.0$ atm.

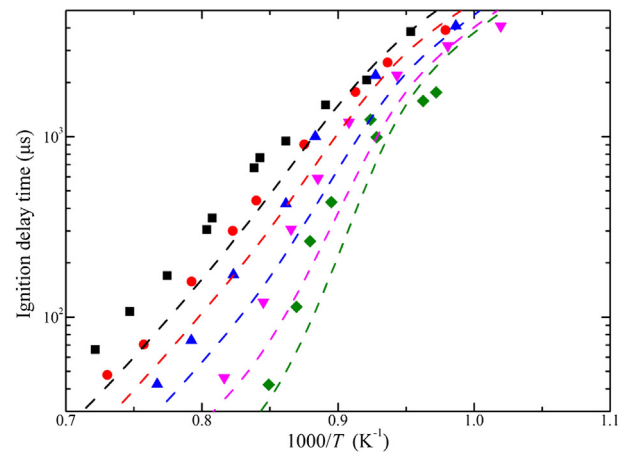
Fig. 3 – Comparison between measured and calculated by NUIG Aramco Mech 1.3 for ethane/hydrogen mixtures.



(a) $p = 1.2$ atm



(b) $p = 4.0$ atm



(c) $p = 16.0$ atm

Fig. 4 – Comparison between measured and calculated by USC Mech 2.0 for ethane/hydrogen mixtures.

ignition delay times of neat ethane and neat hydrogen, but also well reproduces the measured ignition delay times of the stoichiometric ethane/H₂ mixtures for mixtures 2, 3 and 4 under all test conditions. For USC 2.0 Mech, as shown in Fig. 4, it gives a reasonable agreement with the ignition delay times for the stoichiometric mixtures 2, 3 and 4 at $p = 1.2$ and 4.0 atm, while it gives under-prediction for the stoichiometric

mixtures 2, 3 and 4 at $p = 16.0$ atm. Additionally, USC 2.0 Mech predicts the faster ignition to the measurement for neat ethane at all pressures and for neat hydrogen at $p = 4.0$ and 16.0 atm. The poor prediction on the ignition delay times of

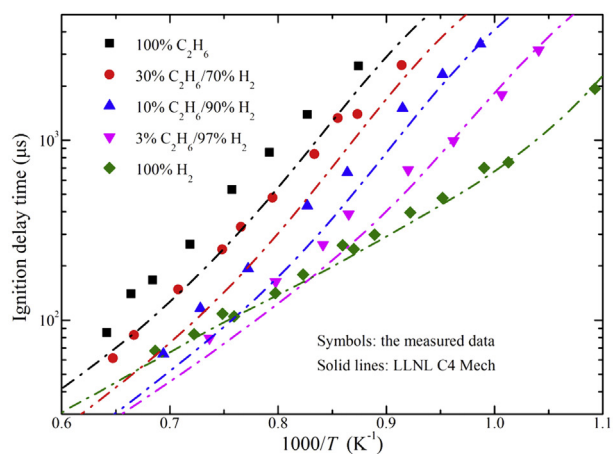
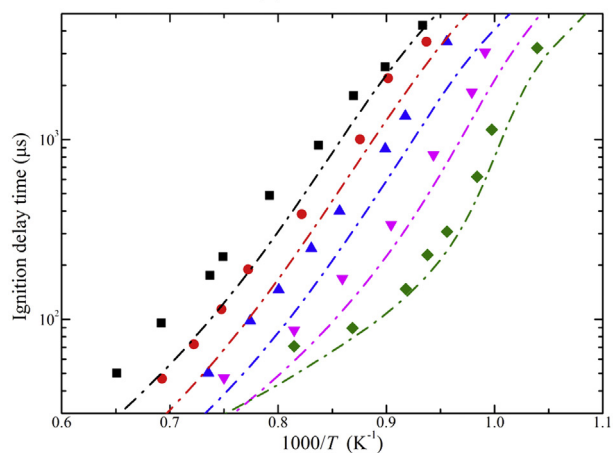
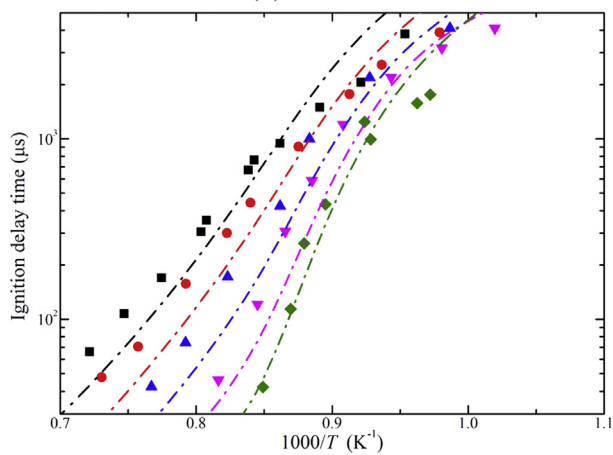
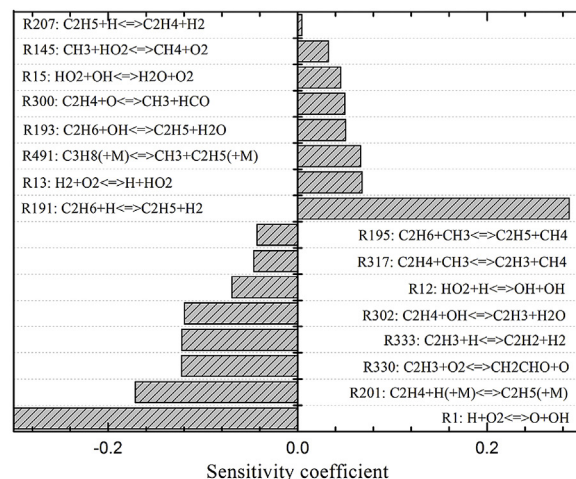
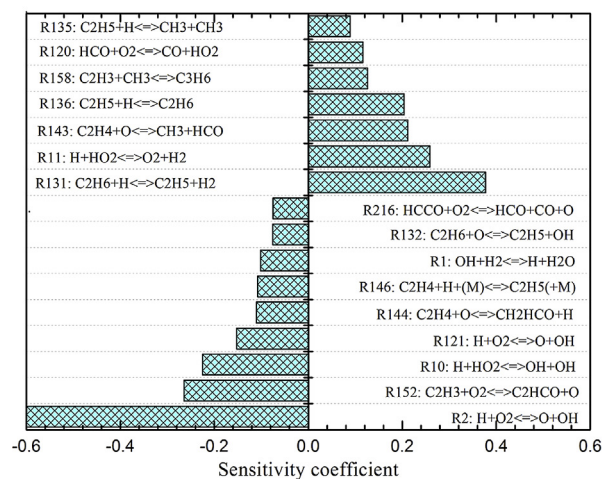
(a) $p = 1.2$ atm(b) $p = 4.0$ atm(c) $p = 16.0$ atm

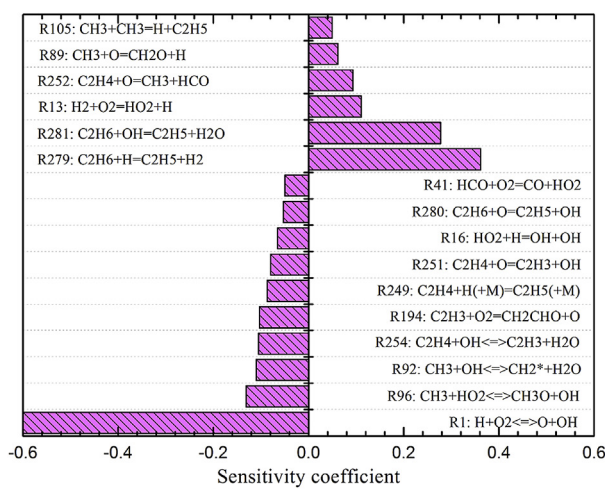
Fig. 5 – Comparison between measured and calculated by LLNL C4 Mech for ethane/hydrogen mixtures.



(a) NUIG Aramco Mech 1.3



(b) USC 2.0 Mech



(c) LLNL C4 Mech

Fig. 6 – Sensitivity analysis for neat ethane mixture at $T = 1250$ K and $p = 4.0$ atm.

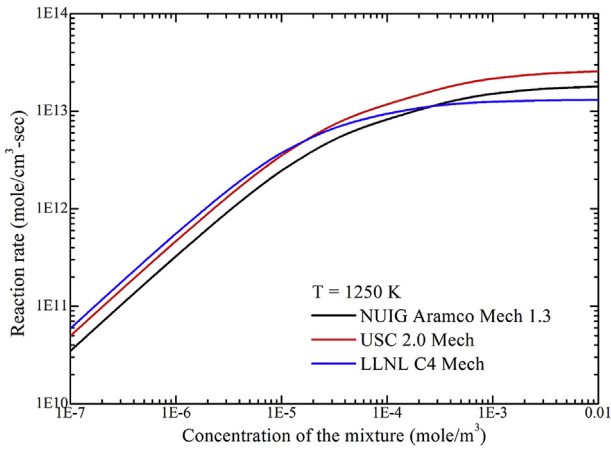


Fig. 7 – Rate constants of reaction: $C_2H_4 + H(+M) \rightleftharpoons C_2H_5(+M)$ in NUIG Aramco Mech 1.3, USC Mech 2.0 and LLNL C4 Mech.

ethane and hydrogen using USC 2.0 Mech is mainly resulted from its higher rate constant of reaction: $C_2H_4 + H(+M) = C_2H_5(+M)$ [43] and $H + O_2(+M) = HO_2(+M)$ [44], respectively. Regarding to LLNL C4 Mech, it well reproduces the ignition delay times of neat hydrogen at all pressures while gives under-prediction to the measurement for the stoichiometric ethane/ H_2 mixtures. The poor prediction on ignition delay times of the stoichiometric ethane/ H_2 mixtures by USC 2.0 Mech and LLNL C4 Mech suggests further optimization on the kinetic data of these mechanisms.

The above comparison shows that only NUIG Aramco Mech 1.3 can well predict the ignition delay times of ethane, hydrogen and their blends at all pressures. Thus, NUIG Aramco Mech 1.3 was chosen as the core mechanism to conduct chemical kinetic interpretations in the following section.

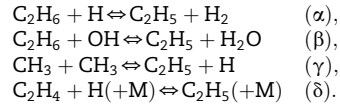
3.3. Chemical kinetic analysis

3.3.1. Sensitivity analysis

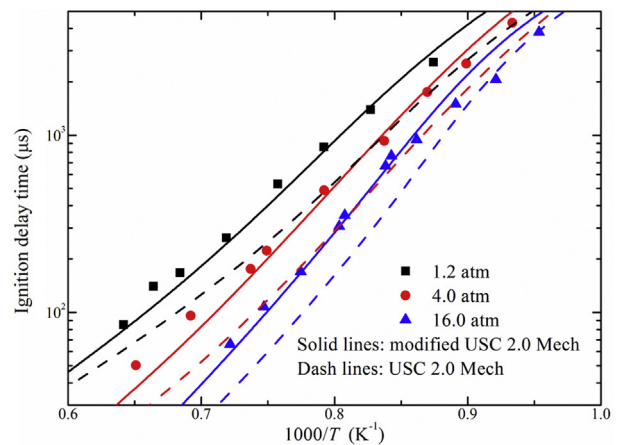
To clarify the reasons for the poor prediction on ethane ignition using USC 2.0 Mech and LLNL C4 Mech, sensitivity analysis was performed at $T = 1250$ K, $p = 1.2$ atm and $\phi = 1.0$ using the three mechanisms to identify the profound reactions in ethane ignition. The sensitivity coefficient is calculated by perturbing the reaction rate,

$$S_i = \frac{\tau(2.0 * k_i) - \tau(0.5 * k_i)}{1.5 * \tau(k_i)} \quad (1)$$

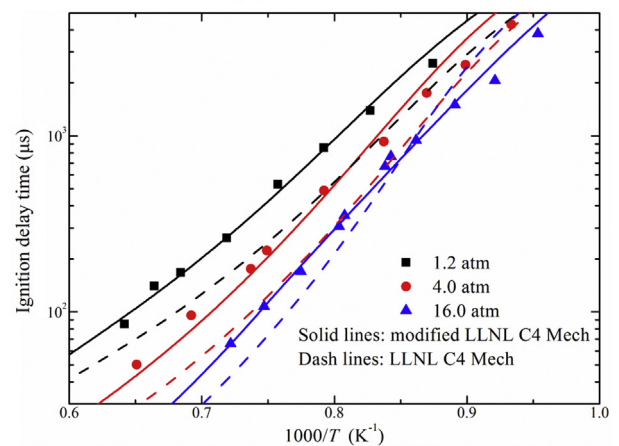
where τ is ignition delay time of combustible mixture, S_i and k_i are sensitivity coefficient and rate constant of the i th reaction, respectively. Negative sensitivity coefficient indicates the corresponding reaction is an ignition promoting reaction and vice versa. Fig. 6 lists 16 elementary reactions with the highest sensitivity coefficients. The poor prediction on the ignition of ethane by USC 2.0 Mech and LLNL C4 Mech is attributed mainly to the ethane-specific reactions since these models fit well with the experimental targets of hydrogen and methane [16]. There are four ethane-specific sensitive reactions in these three mechanisms:



It is observed that the absolute values of sensitivity coefficient for the reaction (δ) calculated by USC 2.0 Mech and LLNL C4 Mech are two times lower than that by NUIG Aramco Mech 1.3. Furthermore, the reaction (δ) as a pressure-dependent reaction is a critical reaction pathway in ethane oxidation. This rate constant in USC 2.0 Mech and NUIG Aramco Mech 1.3 was originally taken from Miller and Klippenstein [45], but high- and low-pressure limits are multiplied by a factor of 0.7 in NUIG Aramco Mech 1.3. In LLNL C4 model, it is originally derived from the values calculated by Feng et al. [46]. Comparison of the rates constants among these three mechanisms is presented in Fig. 7. It is found that the rate constants of reaction (δ) in USC 2.0 Mech and LLNL C4 Mech are about two or four times higher than that in NUIG Aramco Mech 1.3, likely leading to the under-prediction on ignition delay times of ethane mixture by USC 2.0 Mech and LLNL C4 Mech. To evaluate the effect of the reaction (δ) on the performance of mechanisms, their rate constants in USC 2.0 Mech and LLNL



(a) USC 2.0 Mech



(b) LLNL C4 Mech

Fig. 8 – Influence of rate constants of reaction: $C_2H_4 + H(+M) \rightleftharpoons C_2H_5(+M)$ on performance of USC Mech 2.0 and LLNL C4 Mech.

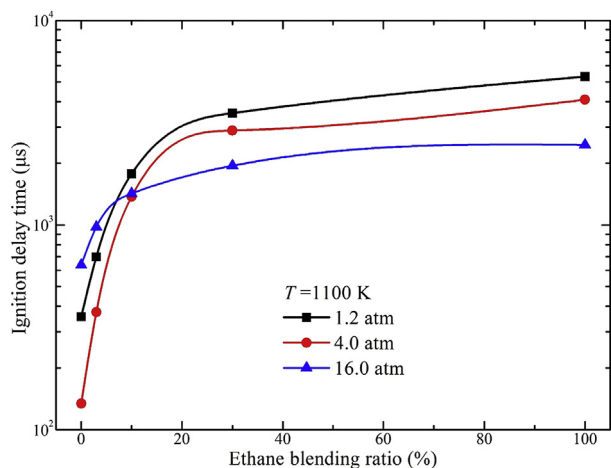


Fig. 9 – Effect of ethane blending ratio on ignition delay times for ethane/hydrogen mixtures using NUIG Aramco Mech 1.3.

C4 Mech were replaced by the corresponding one in NUIG Aramco Mech 1.3, as shown in Fig. 8. The simulation results show that the modified USC 2.0 Mech and LLNL C4 Mech well capture the ignition delay times of ethane. Additionally, the replacements of rate constants for other reactions were also made and negligible influences were observed. Therefore, it can be inferred that the large under-prediction on ignition delay time of ethane by USC 2.0 Mech and LLNL C4 Mech is primarily resulted from the higher rate constants of reaction (δ) in these two mechanisms. The reason for under-prediction on ignition delay times of ethane by USC 2.0 Mech was also proposed by Zhang et al. [43].

3.3.2. Chemical kinetic interpretations on the effect of ethane blending ratio

To investigate the effect of ethane addition on the auto-ignition of hydrogen, ignition delay times calculated by NUIG Aramco Mech 1.3 as a function of ethane blending ratio are presented in Fig. 9 at $p = 1.2, 4.0, 16.0$ atm and $T = 1100$ K. The NUIG Aramco Mech 1.3 is used in this study because it can well reproduce the ignition delay times of all ethane/ H_2 mixtures. It is observed that a small amount (3%) of ethane addition can significantly inhibit the ignition of hydrogen and this effect is weakened with further increasing ethane blending ratio. Obviously, ethane addition gives a non-linear effect on the ignition of hydrogen, which is generalized to propane, butane and heptane.

The non-linear effect of ethane blending ratio on the ignition delay time of ethane/hydrogen mixtures is attributed to the different ignition chemistry of the mixture. Generally, with the increase of ethane blending ratio, the ignition of the combustible mixture resembles more and more to that of neat ethane oxidation. To interpret the ignition delay time dependence on ethane blending ratio, reaction pathway analysis using NUIG Aramco Mech 1.3 for each mixture was made at $T = 1100$ K and $p = 4$ atm at the timing of 20% fuel consumption to identify the controlling steps in ignition, as shown in Fig. 10. The scheme shows that neat ethane is mainly consumed by H-abstraction reactions through free radicals including H (41.3%), OH (47.8%) and O (7.7%) to produce ethyl. Ethyl radicals undergo the H-abstraction reaction by oxygen molecular (O_2) (29%) and H radicals (1.1%) and unimolecular pyrolysis (55.7%) to produce ethylene which is consumed subsequently through several paths to form the final product. Compared to ethane, reaction pathways of neat hydrogen appear considerably clear. Hydrogen molecular is wholly attacked by OH (75.2%) radicals and O radicals (25.8%) and

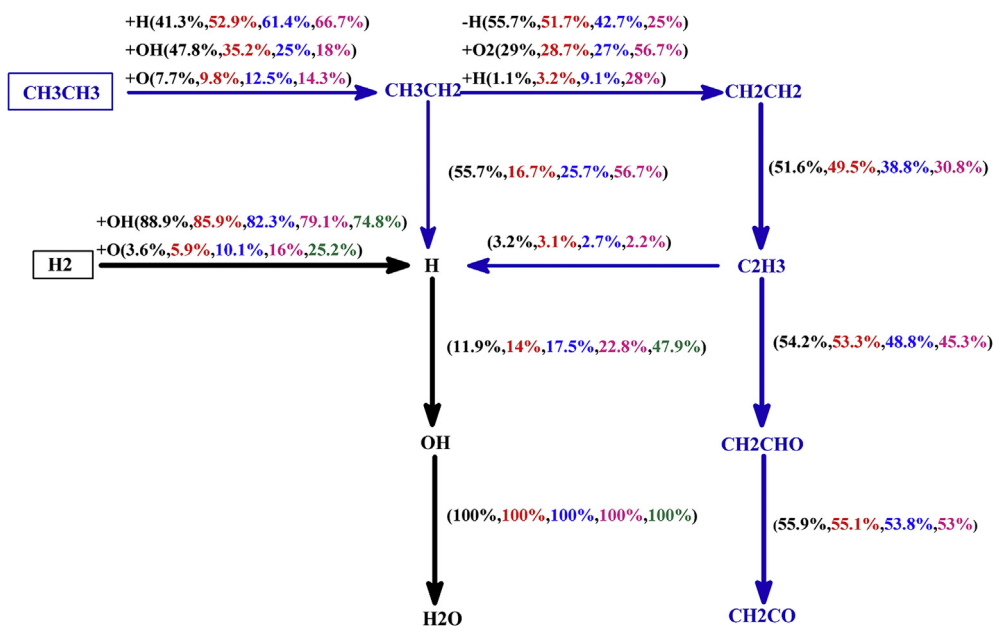


Fig. 10 – Reaction pathway diagram for stoichiometric ethane/hydrogen mixtures at $T = 1100$ K and $p = 4.0$ atm using NUIG Aramco Mech 1.3 (Black: 100% C_2H_6 ; Red: 30% C_2H_6 /70% H_2 ; Blue: 10% C_2H_6 /90% H_2 ; Magenta: 3% C_2H_6 /97% H_2 ; Olive: 100% H_2). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

produces H radicals. The H radicals are the chain promoters and then react with O_2 to produce O and OH radicals which are in turn to feed the hydrogen consuming ways, as discussed above. Actually, these pathways including reaction R1: $H + O_2 \rightleftharpoons O + OH$, R2: $OH + H_2 \rightleftharpoons H + H_2O$ and R3: $O + H_2 \rightleftharpoons H + OH$ evolve into the recycle reaction sequence that R2 and R3 produce H radicals to feed R1 which in turn produce OH and O radical to feed R2 and R3, respectively. As this recycle reaction sequence continues, a large amount of reactive free radicals are produced and promote the ignition. This is the main feature of the hydrogen ignition at high temperature.

As shown in Fig. 10, the main reaction steps of hydrogen/or ethane are changed by ethane/or hydrogen addition. Specifically, when the ethane is added to hydrogen, the H radical consumed through R1 exhibits the reduced tendency, and the hydrogen attacked by OH (R2) and O (R3) gives an opposite variation. However, when the hydrogen is added to ethane mixture, the ethane molecular consumed by H radicals is increased with hydrogen addition, while ethane molecular consumed by OH and O radicals is somehow decreased since hydrogen addition to hydrocarbon oxidation system increases the amount of OH and O radicals. Obviously, interaction between ethane and hydrogen ignition in C_2H_6/H_2 blends is manifested as the competition for H radicals between ethane (R191: $C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$) and oxygen molecular (R1). Reaction R1 and R191 are respectively the most important ignition promoting reaction and inhibiting reaction in C_2H_6/H_2 blends, as shown in Fig. 6.

To further understand the change of controlling reactions in the ignition chemistry and the effect of ethane blending ratio, the normalized consumption of H radicals by reactions R1 and R191 in the ignition induction period was presented at $T = 1150$ K and $p = 4.0$ atm at all ethane blending ratios, as shown in Fig. 11. H radicals are mainly consumed by R1 (57%) for the neat hydrogen and by R191 (79%) for the neat ethane in the induction period. As a result, neat hydrogen has faster ignition than neat ethane. When adding a small amount (3%) ethane, H radicals consumed by reaction R191 accounts for

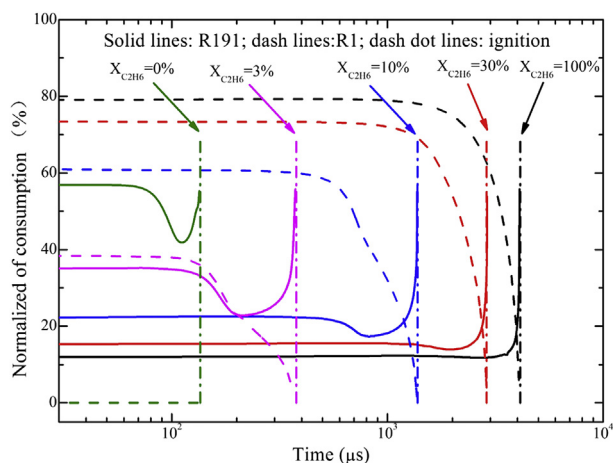


Fig. 11 – Reactions with highest H radical consumption rates of various ethane blending ratios at 1100 K and 4.0 atm.

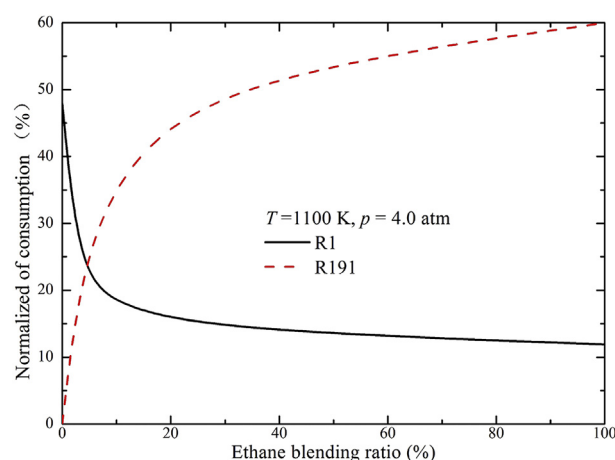


Fig. 12 – Competition of H radicals between reactions R1 and R191 at different ethane blending ratios at timing of 20% fuel consumption.

35% of total H radicals while the H radicals consumed by reaction R1 decrease by 23% compared to neat hydrogen. Consequently, reactions R2 and R3 are inhibited and result in an inhibition of H, O and OH productions and an increase of ignition delay time. However, this influence is weakened under higher ethane blending ratio, as shown in Figs. 11 and 12. Therefore, ignition delay times are more sensitive to small ethane blending ratio than higher ethane blending ratio, resulting in the non-linear effect in Fig. 9. The competition of H radicals by reactions R1 and R191 shows that H radicals react more readily with ethane than with oxygen. This is primary due to two aspects: 1) bond energy of C–H bond (~ 96.4 – 101.1 cal/mol) is much smaller than that of O=O bond (~ 118 cal/mol), leading to a lower activation energy for reaction R191; 2) There are six C–H bonds in an ethane molecular and only one O=O bond in an oxygen molecular, making the collision of H radicals with ethane molecular more efficient than that with oxygen molecular.

4. Concluding remarks

Ignition delay times of the stoichiometric C_2H_6/H_2 blends with emphasis on the effect of blending ratio were obtained at elevated pressures. The measured ignition delay times of ethane were compared to previous correlations and the ignition delay times obtained by different studies exhibited a significant difference in global activation energy. Simulations were made with three widely used mechanisms and the results show that NUIG Aramco Mech 1.3 agrees well with the measurements of all C_2H_6/H_2 blends, while USC 2.0 Mech and LLNL C4 Mech give under-prediction on the ignition delay time of neat ethane. Sensitivity analysis indicates that poor predictions by USC 2.0 Mech and LLNL C4 Mech are ascribed to the higher rate constant of reaction $C_2H_4 + H (+M) \rightleftharpoons C_2H_5 (+M)$. Ethane blending ratio exhibits the non-linear effect on the ignition delay time of C_2H_6/H_2 blends, which is generalized to propane and butane. This non-linear effect is mainly resulted

from the competition of H radicals between reaction $H + O_2 \rightleftharpoons O + OH$ and $C_2H_6 + H \rightleftharpoons C_2H_5 + H_2$.

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Appendix A. Supplementary material

Supplementary material related to this article can be found at <http://dx.doi.org/10.1016/j.ijhydene.2014.01.157>.

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