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Comparative Study on Ignition Delay Times of C1−C4 Alkanes

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ABSTRACT: Ignition delay times of C1−C4 alkanes (methane, ethane, propane, and n-butane) diluted with argon were respectively measured behind reflected shock waves at the same equivalence ratio (ϕ = 1.0) and different pressures (1.2 and 5.3 atm) and temperatures (1100−2100 K). A same argon-dilution ratio was employed to obtain a reasonable comparison. First, attention was paid on the specific experimental conditions when compared to previous data. Subsequently, two widely used models, USC 2.0 and NUI C4, were used and validated against the experimental data. It was observed that methane and ethane respectively have the longest and the shortest ignition delay times while propane and n-butane show the intermediate values. Both models yield fairly good agreement with the ignition data of C1−C4 alkanes, except the poor prediction of ethane by the USC 2.0 model. Finally, reaction pathway and sensitivity analysis were performed to ascertain the controlling steps during the ignition of ethane in the USC 2.0 model.

1. INTRODUCTION

Due to the increasing demand for energy and greenhouse gas reduction, the research on low-carbon fuels has been attracting more attention in the combustion and engine communities. So far some low-carbon fuels have been used in practical combustion devices, such as natural gas, liquefied petroleum gas, methanol, ethanol, butanol, dimethyl ether, etc.[1−6] Compared to the investigation in the practical application, fundamental studies on the combustion of low-carbon fuels are also of great significance. It is well-known that mechanisms of high-carbon fuels are usually constructed based on the hierarchical nature of the hydrocarbon−oxygen system.[7,8] Therefore, the chemistry of low-carbon fuels exerts influence not only on low-carbon fuels themselves but also on high-carbon fuels. In this study, a comparative research study was conducted to give us an insight into the high-temperature ignition reactivity of C1−C4 alkanes.

High-temperature ignition delay times of C1−C4 alkanes have been measured by many researchers[9−24] in the past decades. However, only three studies conducted a comparison for C1−C4 alkanes. Burcat et al.[15] studied the ignition delay times of C1−C5 alkanes with a fixed argon-dilution ratio. It was found that methane has the longest ignition delay times while ethane has the shortest ones. Propane, n-butane, and n-pentane have intermediate reactivity. They attributed the longest ignition of methane to the strong C−H bonds. However, no convictive explanation was given for the anomalously short ignition delay times of ethane. Lamoureux et al.[23] measured the ignition delay times of methane, ethane, and propane using ultraviolet emission spectrometry behind reflected shock waves. Ignition correlations of the three alkanes were also proposed. Nevertheless, no comparison of the three alkanes was conducted in their study. Horning et al.[24] studied the ignition delay times of propane, n-butane, n-heptane, and n-decane by using the endwall CH emission diagnostic over the temperature range 1300−1600 K and pressure range 1−6 atm. An ignition correlation covering four test fuels was proposed and yields fairly good agreement with their experimental data.

Although numerous studies have been conducted on the ignition measurements of C1−C4 alkanes, experimental data obtained by different researchers still show some disagreements. Consequently, more accurate data are needed to validate the chemical kinetic models for C1−C4 alkanes. In this study, ignition delay times of stoichiometric C1−C4 alkanes/oxygen/argon mixtures were measured behind reflected shock waves over the temperature range 1100−2100 K and at the pressures 1.2 and 5.3 atm. Furthermore, the present data were compared to previous values and validated against two models involving C1−C4 chemistry.

2. EXPERIMENTAL SECTION

The ignition measurement was conducted in a shock tube, which has been described in detail in previous literature.[25] The shock tube with a diameter of 11.5 cm is separated into a 4.0 m long driver section and a 5.3 m long driven section by two polyester terephthalate (PET) diaphragms.

In this study, test fuels (methane, ethane, propane and n-butane) are of the same purity of 99.9%, and purities of oxygen, argon, and helium are 99.999%. Fuel mixtures were prepared manometrically in a 128 L stainless steel tank and allowed to mix for at least 12 h by molecular diffusion. The ignition delay time is defined as the time interval between the arrival of the incident shock wave at the endwall and the extrapolation of the steepest rise in the endwall CH* chemiluminescence signal to the zero baseline, as shown in Figure 1. The incident shock velocity is determined by four pressure transducers (PCB, 113B26) located along the shock tube with the same length interval of 30 cm. The three time intervals are recorded by three time counters (FLUKE, PM6690). The incident shock velocity at the endwall is obtained by linear extrapolation of the three incident shock velocities calculated using the three time intervals. The CH* emission selected by a narrow filter centered at 430 ± 10 nm is measured by a photomultiplier (HAMAMATSU, CR131) located at the endwall. All data acquisition is carried out using a digital recorder (YOKOGAVA, scopecorder-DL750). The temperature behind reflected shock waves is
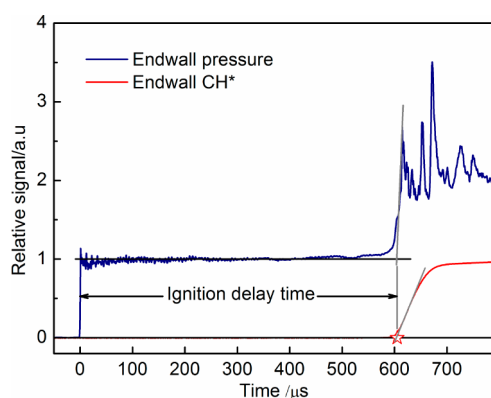
Figure 1. Definition of the ignition delay time.

calculated using the reflected shock module in the software Gaseq.[26] The uncertainty of the temperature is about ±25 K.

The stoichiometric fuel mixtures of C1−C4 alkanes were tested at 1.2 and 5.3 atm, and their composition is tabulated in Table 1. In this

Table 1. Composition of the Fuel Mixtures

mixture	fuel	X_{Fuel} (%)	X_{O_2} (%)	X_{Ar} (%)
1	CH_4	3.03	6.06	90.91
2	C_2H_6	1.75	6.14	92.11
3	C_3H_8	1.23	6.17	92.59
4	n-C_4H_{10}	0.95	6.19	92.86

study, the argon-to-oxygen dilution ratio was fixed at 15, which is similar to that of Burcat et al.[15] Consequently, all the mixtures were prepared at a dilution level of 90%. Table 2 presents all the measured ignition data.

Simulations were performed using the Senkin[27] code in Chemkin II package.[28] The computed ignition delay time is defined as the time interval between the beginning of the simulation and the maximum rate of temperature rise (max dT/dt).

3. RESULTS AND DISCUSSION

3.1. Comparison with Previous Data. Many measurements for ignition delay times of C1−C4 n-alkanes have been conducted behind reflected shock waves. Table 3 summarizes previous ignition correlations for C1−C4 alkanes.[9−24] It is observed that experiments by different authors were performed under specific conditions. Therefore, special attention should be paid to match as closely as possible the range of experimental conditions for fair comparison. Only the correlations roughly covering the current condition will be employed.

For methane, there have been seven correlations developed under different experimental conditions. However, the correlation of Tsuboi and Wagner[10] has a too wide range of pressures, and that of Hidaka et al.[11] has a too low pressure range. Therefore, theirs will not be employed for comparison. Figure 2 shows the comparison between the measured data and previous correlations for methane under the test condition. At p = 1.2 atm, it can be seen that the present data agrees fairly well with that of Lifshitz et al.[9] with a slight lower ignition activation energy. Nevertheless, the correlation of Cheng and Oppenheim[13] presents approximately three times higher values, and all the other three correlations present approximately 50−80% lower values compared to the present data. Among these correlations, the correlations by Cheng and Oppenheim[13] and Krishnan and Ravikumar[14] show comparative ignition activation energy with that of present data. At p = 5.3 atm, the present data agrees well with those of Lifshitz et al.[9] and Cheng and Oppenheim[13] in both absolute values and ignition activation energy. Again, all the other three present lower results. In addition, the correlation of Krishnan and Ravikumar[14] also shows fairly good agreement in ignition activation energy with the present data.

Figure 3 shows the present data and previous correlations for ethane under the test conditions. The correlations of Cooke and Williams[17] and Hidaka et al.[18] were not employed here for their quite lower pressure ranges. The present data match

Table 2. Measured Ignition Delay Times of C1−C4 Alkanes

	CH_4			C_2H_6			C_3H_8			n-C_4H_{10}	
p(atm)	T(K)	$\tau(\mu s)$	p(atm)	T(K)	τ (μs)	p(atm)	T(K)	τ (μs)	p(atm)	T(K)	τ (μs)
1.31	1461	3106	1.22	1232	966	1.27	1453	276	1.25	1253	1791
1.30	1526	1685	1.24	1307	508	1.33	1415	416	1.39	1332	797
1.29	1601	1128	1.25	1384	279	1.27	1333	977	1.49	1386	485
1.25	1642	838	1.22	1426	194	1.29	1280	1899	1.24	1450	267
1.31	1744	439	1.18	1467	183	1.28	1229	2780	1.23	1511	155
1.28	1800	397	1.21	1172	1835	1.27	1570	97	1.24	1585	70
1.26	1865	204	1.20	1573	69	1.29	1606	71	1.24	1250	1898
1.32	1935	129	1.23	1545	80	1.31	1689	44	1.23	1276	1432
1.29	2025	91	5.50	1290	287	1.33	1769	26	5.46	1281	814
5.31	1417	2098	5.45	1352	148	1.33	1841	19	5.50	1355	322
5.40	1513	969	5.44	1422	77	5.37	1271	1001	5.30	1400	199
5.19	1533	751	5.39	1203	774	5.23	1220	1976	5.32	1477	93
5.27	1636	355	5.41	1133	1988	5.27	1166	4105	5.42	1543	46
5.29	1616	288	5.37	1234	484	5.27	1357	396	5.44	1230	1457
5.09	1704	187	5.30	1165	1213	5.15	1409	217			
5.37	1816	79				5.20	1456	106			
5.27	1831	74				5.47	1580	41			
5.18	1876	61				5.25	1680	16			
5.68	2082	16									
5.08	1983	31									

Table 3. Summary of the Correlation Parameters Given by Different Authors for C1−C4 Alkanes[a]

author	dilution	ϕ	T (K)	P (atm)	A	E_a (kcal/mol)	a	b	c
				CH₄					
Lifshitz et al. (1971)	87−97%	0.5−2	1500−2500	3−10	3.62×10^{-14}	46.4	0.33	−1.03	0
Tsuboi and Wagner (1975)	78−99.88%	0.2−2	1200−2100	3−30	4.00×10^{-15}	53.0	0.32	−1.02	0
Hidaka et al. (1978)	96−97%	0.67−2	1800−2500	0.47−0.75	4.53×10^{-10}	35.6	0.37	−0.64	0
Eubank et al. (1978)	76.8−79.2%	0.1−0.4	1350−1850	3.35−4.60	1.80×10^{-14}	51.6	0.4	−1	0
Cheng and Oppenheim (1984)	90.0%	0.5−1	1700−2160	1.5−3	1.88×10^{-18}	46.3	0.48	−1.94	0
Krishnan and Ravikumar (1981)	95.0%	0.2−5	1600−2100	1−6	2.21×10^{-14}	44.7	0.33	−1.05	0
Lamoureux et al. (2002)	89−97%	0.5−2	1520−2000	3.65−18.2	2.73×10^{-15}	54.1	0.36	−1.04	0
				C₂H₆					
Burcat et al. (1972)	90.5−97.3%	0.5−2	1235−1600	2−8	2.35×10^{-14}	34.2	0.46	−1.26	0
Cooke and Williams (1975)	90−95%	0.7−2	1400−2200	0.2−0.47	1.20×10^{-15}	31.1	0.4	−1.4	0
Hidaka et al. (1981)	94.5−95.5%	0.7−2	1300−2000	0.027−0.053	1.15×10^{-13}	29.9	1	−1	0
Shim et al. (1999)	86.5−91%	0.7−2	1227−1543	0.7−1.4	1.20×10^{-14}	49.2	0.71	−1.2	0
Lamoureux et al. (2002)	94−98.6%	0.5−2	1270−1520	2.9−14.2	2.46×10^{-15}	55.2	0.64	−1.05	0
de Vries et al. (2006)	91−98%	0.5−2	1218−1860	0.57−3	7.15×10^{-19}	39.6	0.79	−1.21	−0.42
				C₃H₈					
Burcat et al. (1971)	77−99.5%	0.125−2	1250−1600	2−10	1.40×10^{-14}	42.1	0.57	−1.22	0
Hidaka et al. (1983)	92−96%	0.7−2	1300−1800	0.33−0.60	5.70×10^{-13}	35.9	0.7	−1.3	0
Kim et al. (2001)	79−94.8%	0.5−2.0	1350−1800	0.75−1.57	4.50×10^{-14}	61.9	1.22	−1.61	0
Lamoureux et al. (2002)	97−99%	0.5−1.5	1375−1580	3.5−9.7	5.06×10^{-15}	56.5	0.85	−1.3	0
				n-C₄H₁₀					
Horning et al. (2002)	85−96.3%	0.5−2.0	1385−1666	1.0−3.80	7.63×10^{-14}	42.8	0.99	−1.61	0

[a] $\tau_{ign} = A \exp(E_a/RT)[\text{fuel}]^a[O_2]^b[\text{Ar}]^c$. τ_{ign} is in seconds; concentrations are in mol/cm³.
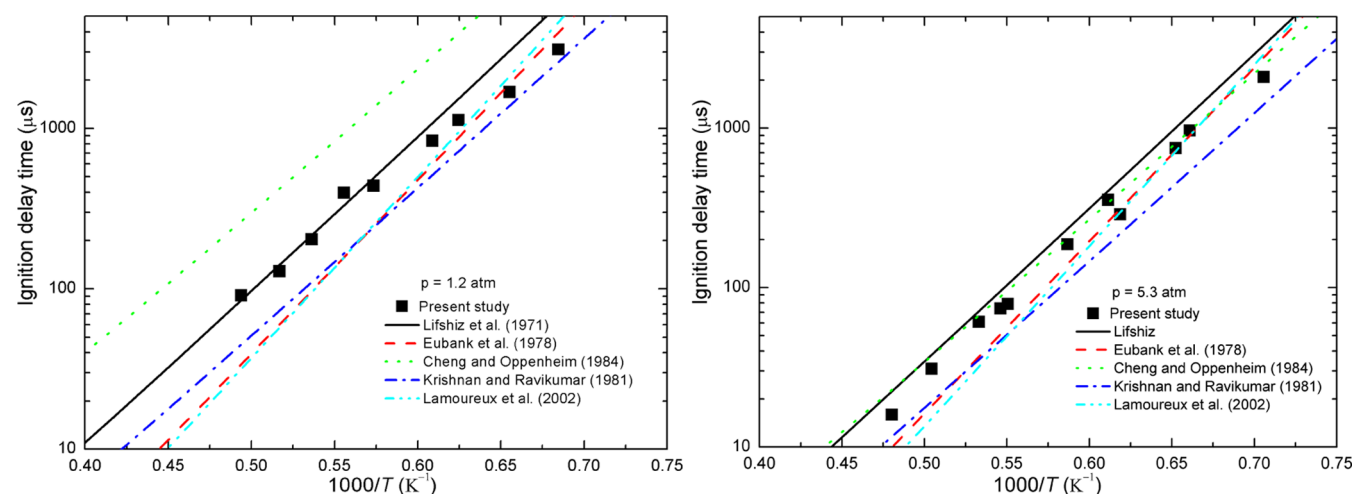

Figure 2. Comparison between the measured data and previous correlations for stoichiometric methane mixture.

relatively well with the correlations of Burcat et al.[16] and de Vries et al.[20] at p = 1.2 atm but show about 20% higher values at p = 5.3 atm. However, the correlations by Shim et al.[19] and Lamoureux et al.[23] present higher ignition activation energy as well as remarkably quantitative deviation.

For propane, the correlation of Hidaka et al.[21] was also not employed for its quite lower pressure range. The comparison between the present data and previous correlations is shown in Figure 4. It is observed that the comparisons at p = 1.2 and 5.3 atm present the similar tendency. The correlation of Lamoureux et al.[23] matches relatively well with the present data, but it shows a higher ignition activation energy. Although the present data agree well with the correlation of Burcat et al.[15] in ignition activation energy, the former shows about two times higher values than the latter. For the correlation of Kim et al.,[22]

it shows quite large disagreement with the present data in both ignition activation energy and quantitative values.

Finally, the present n-butane data is compared to the correlation of Horning et al.,[24] as shown in Figure 5. Although the ignition measurement for n-butane was also conducted by Burcat et al.,[15] the ignition correlation was not provided in their study since only one test mixture was utilized in their experiments. So, it is difficult to perform direct comparison with Burcat's results on a quantitative basis. In this study, the correlation of Horning et al.[24] agrees fairly well with the present data in both ignition activation energy and absolute values.

3.2. Measured and Calculated Ignition Delay Times. Two models, USC 2.0 Mech[29] and NUI C4Mech,[30] were used in this study for simulation. Both of them contain C1−C4 chemistry and have been validated against various experimental
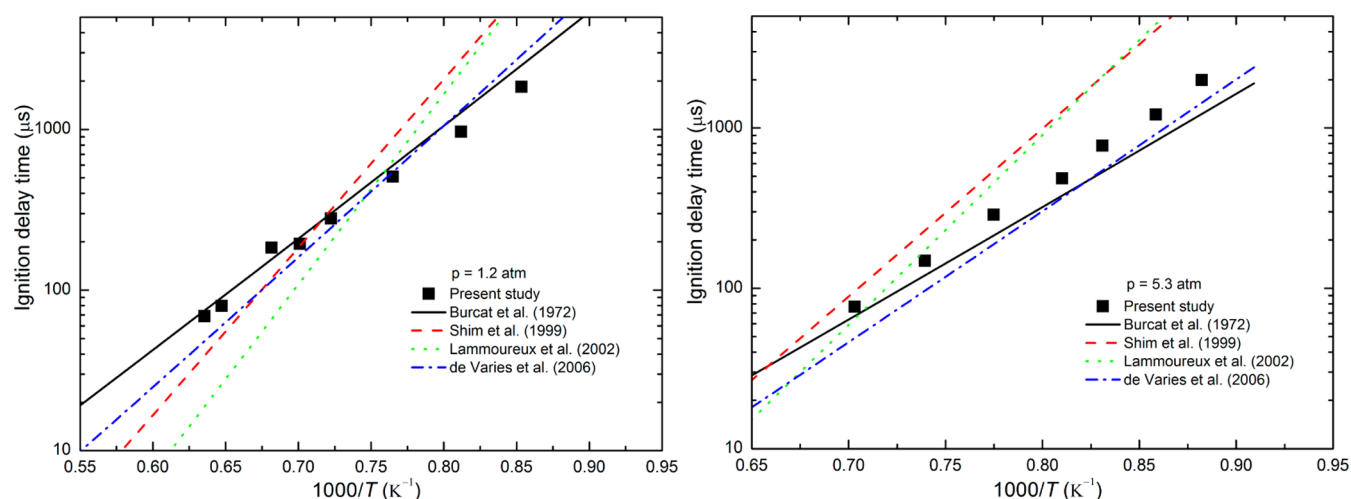
Figure 3. Comparison between the measured data and previous correlations for stoichiometric ethane mixture.
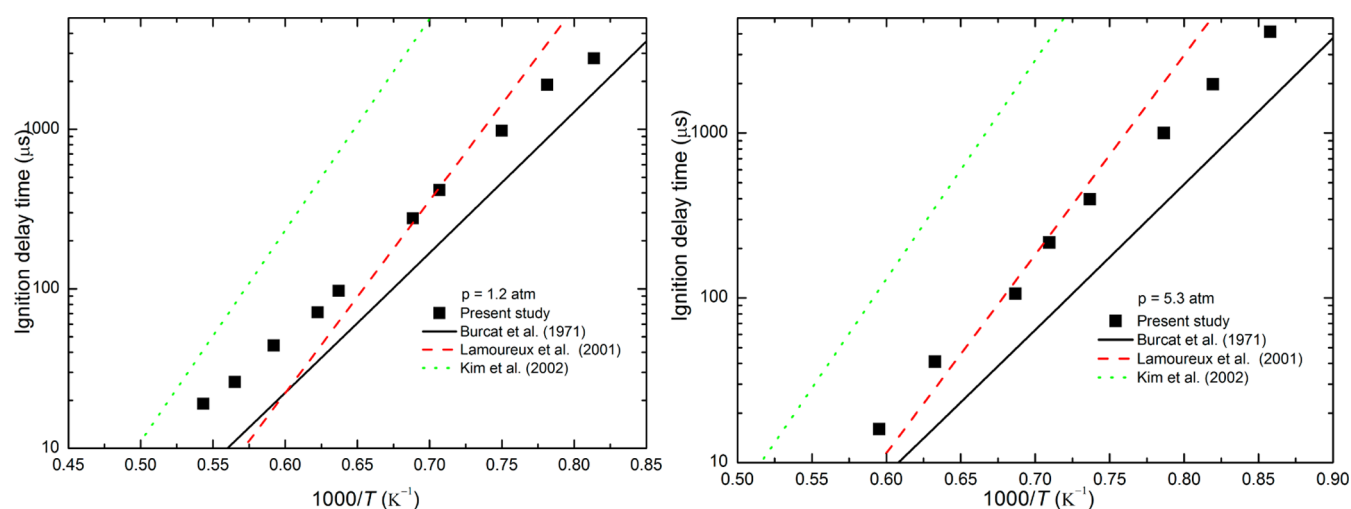

Figure 4. Comparison between the measured data and previous correlations for stoichiometric propane mixture.
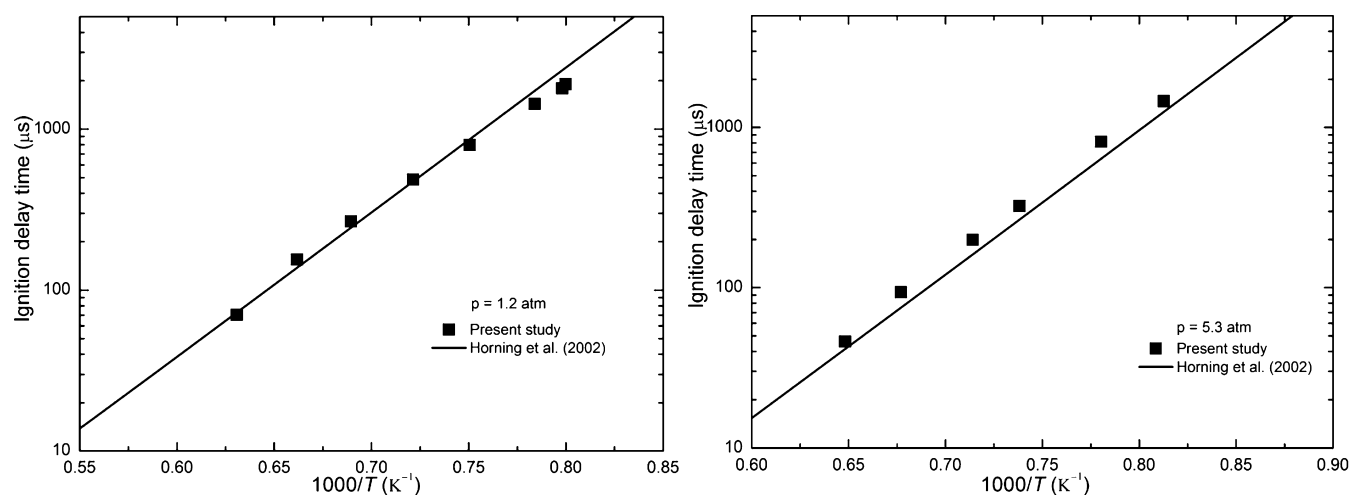

**Figure 5.** Comparison between the measured data and previous correlations for stoichiometric *n*-butane mixture.

targets. As studied by Chaos et al.,[31] the pressure rise exerts considerable effect on ignition delay times longer than 1 ms. Due to the relatively long ignition delay time (up to 3 ms) in this study, a pressure rise of 4%/ms was considered in the simulation by using the variable volume approach suggested by

Chaos et al.[31] The pressure rise in our shock tube has been demonstrated by experimental measurements in a previous study.[32]

Figures 6 and 7 respectively show the experimental and modeling results by using two different models. It can be seen
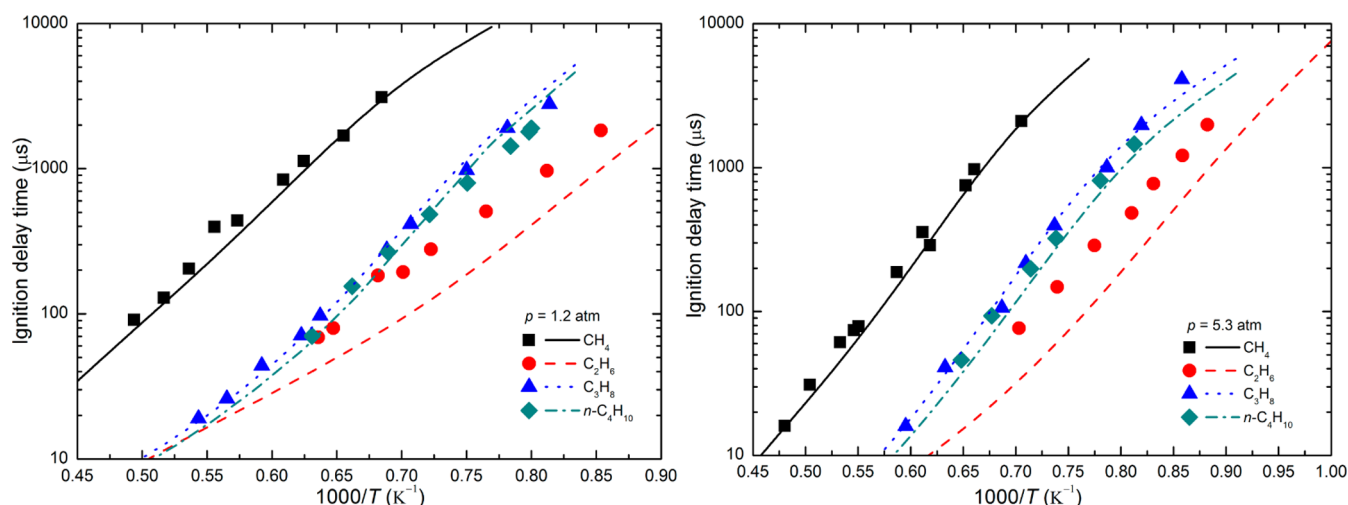
Figure 6. Experimental and calculated ignition delay time of C1−C4 alkanes at p = 1.2 and 5.3 atm (Symbols: measurements. Lines: simulations using USC 2.0 Mech). A pressure rise of 4%/ms was employed in the simulation.
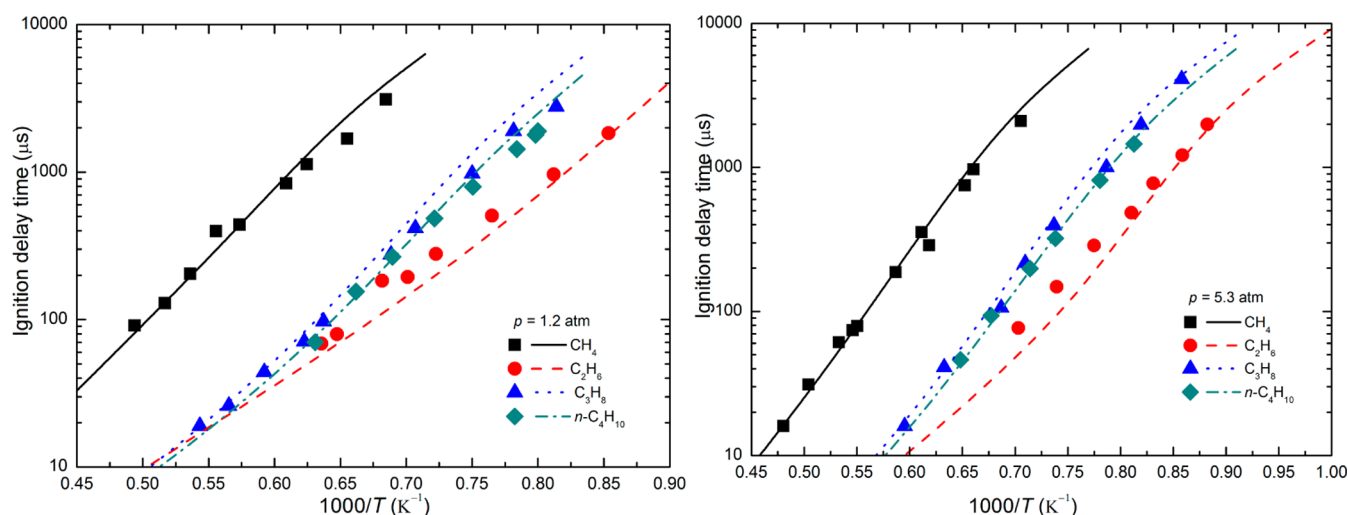
Figure 7. Experimental and calculated ignition delay time of C1−C4 alkanes at p = 1.2 and 5.3 atm (Symbols: measurements. Lines: simulations using NUI C4Mech). A pressure rise of 4%/ms was employed in the simulation.

that methane shows the longest ignition delay times, while ethane shows the shortest ones. The ignition delay times of propane and *n*-butane are comparative and located between those of methane and ethane. A similar phenomenon for the ignition of C1−C4 alkanes was also observed by Burcat et al.[15] As analyzed by Westbrook et al.[33] and Ranzi et al.,[34] for the high-temperature ignition of *n*-alkanes, the production of methyl radicals inhibits the overall ignition rate by the chain termination reaction $CH_3 + CH_3(+M) = C_2H_6(+M)$, while the production of ethyl radicals accelerates the ignition process by the subsequent chain branching reaction $C_2H_5(+M) = C_2H_4 + H(+M)$. The initial reactions of methane only produce methyl radicals and those of ethane only produce ethyl radicals, leading to the longest and shortest ignition delay times, respectively. For *n*-alkanes larger than ethane, their initial reactions produce both methyl and ethyl radicals. As a result, they have intermediate ignition values compared to methane and ethane.

As shown in Figures 6 and 7, both models yield fairly good agreement with the experimental data of four alkanes at two pressures except a remarkable under-prediction by the USC 2.0 Mech for ethane. To further validate the performance of the models on the prediction of ethane, Figure 8 shows the
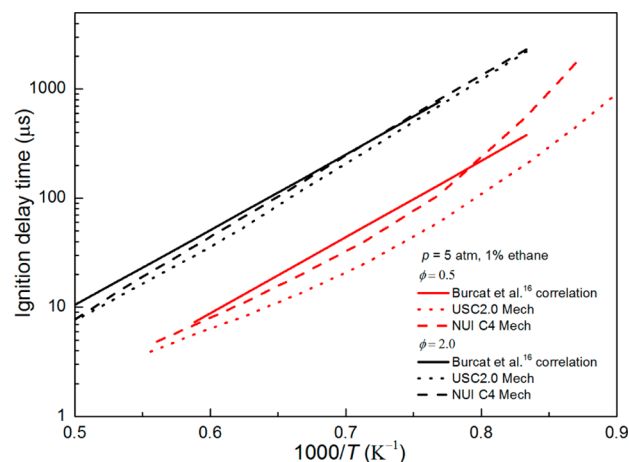
Figure 8. Comparison between two models and experimental data by Burcat et al.[16]

validation of the two models against the experimental data by Burcat et al.[16] under fuel-lean and fuel-rich conditions. The data
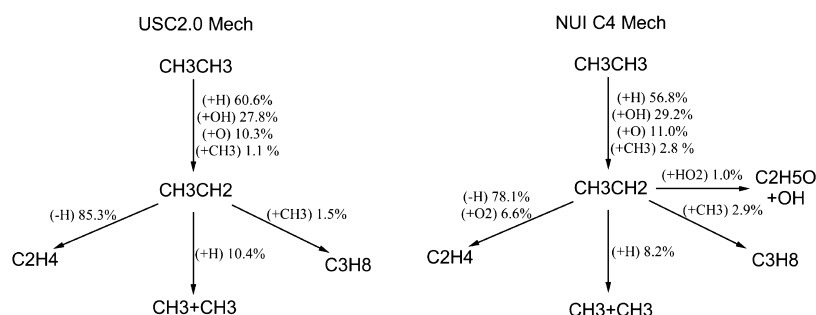
Figure 9. Reaction pathways for stoichiometric ethane mixture at T = 1300 K and p = 1.2 atm using USC 2.0 Mech and NUI C4Mech.
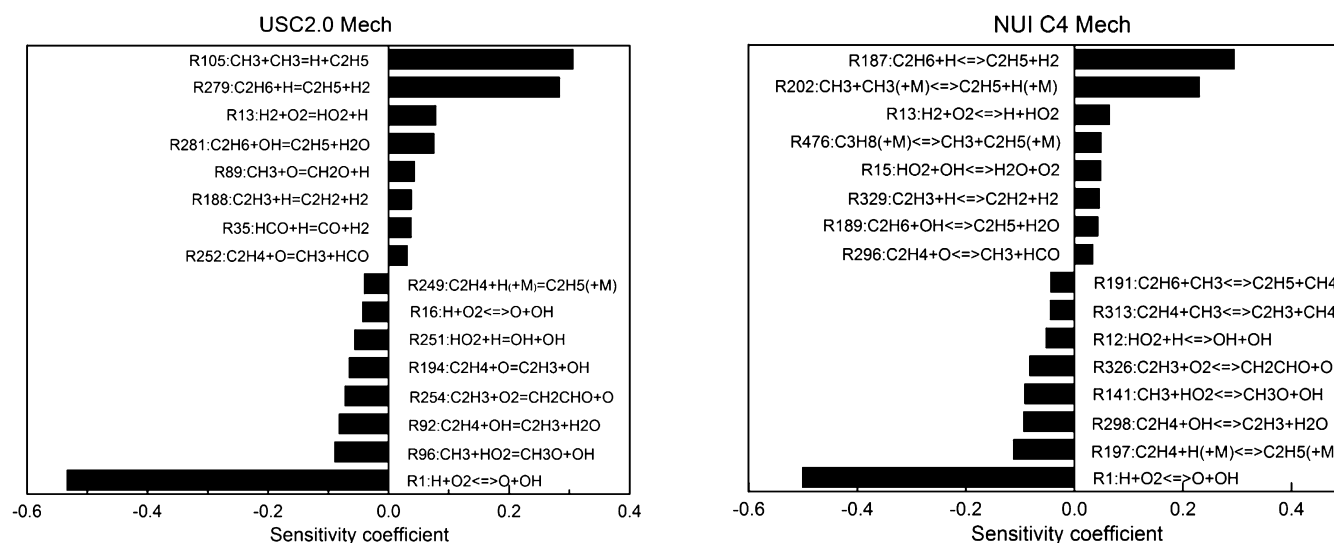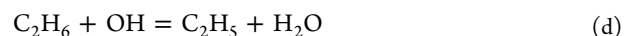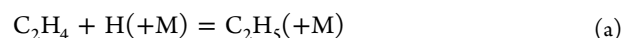

Figure 10. Sensitivity analysis for stoichiometric ethane mixture at T = 1300 K and p = 1.2 atm using USC 2.0 Mech and NUI C4Mech.

from Burcat et al.[16] were chosen for their relatively good agreement with the present study, as discussed. At ϕ = 0.5, the USC 2.0 Mech also greatly under-predicts the experimental data, while the NUI C4Mech predicts it well. Both models yield fairly good agreement with experimental data at ϕ = 2.0 except the slight under-prediction by the USC 2.0 Mech at high temperatures. To find out the reason for the relatively poor prediction on ethane by the USC 2.0 Mech, reaction pathway and sensitivity analysis were performed in the following section.

3.3. Reaction Pathway and Sensitivity Analysis. Both USC 2.0 Mech and NUI C4Mech were employed for reaction pathway and sensitivity analysis of ethane to give fair comparison. Figure 9 shows the reaction pathway of ethane at p = 1.2 atm, T = 1300 K, and ϕ = 1.0. The timing at 20% fuel consumption was chosen, which is the same as in previous literature.[25,35] It is observed that ethane is almost exclusively consumed by H-abstraction reactions to form ethyl radicals. Particularly, H-abstraction by H atom plays a dominant role among these reactions. Most of the produced ethyl radicals then decompose to form ethylene and hydrogen atoms. Subsequently, the hydrogen atoms feed the most important chain branching reaction at high temperature, H + O$_2$ = OH + O, and the H-abstraction reaction consuming ethane. Therefore, the ethyl radicals exert positive effect on the overall ignition process, leading to the shortest ignition delay times among the four n-alkanes.

As shown in Figures 6 and 7, the NUI C4Mech gives more accurate prediction on ethane compared to the USC 2.0 Mech. Furthermore, both models yield fairly good agreements with

the measured data of methane, propane, and n-butane. Therefore, it can be inferred that the relatively poor prediction on ethane by the USC 2.0 Mech is likely to be caused by ethane-specific reactions. Figure 10 presents the sensitivity analysis using two models. There are four sensitive ethane-specific reactions presented in both models among the most sensitive 16 reactions.

$$C_2H_4 + H(+M) = C_2H_5(+M) \qquad (a)$$

$$CH_3 + CH_3 = C_2H_5 + H \qquad (b)$$

$$C_2H_6 + H = C_2H_5 + H_2 \qquad (c)$$

$$C_2H_6 + OH = C_2H_5 + H_2O \qquad (d)$$

It is noted the sensitivity analysis was performed by perturbing each reaction rate by a factor of 2. The detailed definition was described in a previous study.[25] The negative coefficient indicates an accelerating effect on the overall reactivity and vice versa. Among these four reactions, it is found that reaction a exerts an accelerating effect and has quite different rate constants in two models. In addition, this reaction is also a critical pathway, as discussed. As a pressure-dependent reaction, the rate constants of this reaction in two models are treated in a TROE form. The rate constant in the USC 2.0 Mech is originally derived from the calculation by Miller et al.,[36] while it is a new fit by the Curran group in the NUI C4Mech. The rate constants of this reaction in two models are compared in Figure 11. It can be observed that the rate constant from the USC 2.0 Mech is approximately three or four times higher than
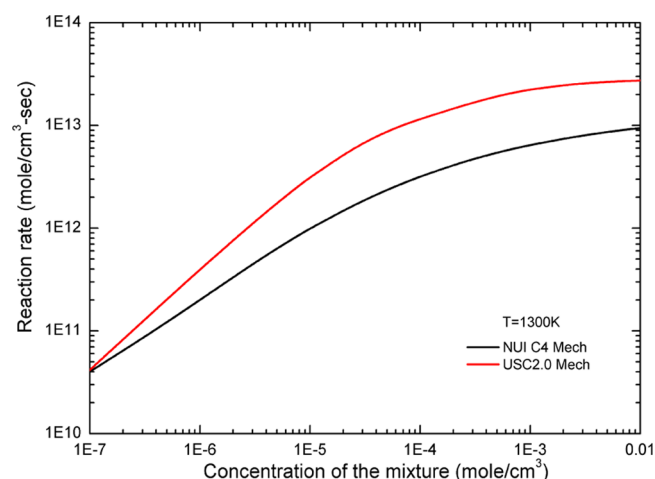
Figure 11. Rate constants for reaction a $C_2H_4 + H$ (+M) $\rightleftarrows$ C_2H_5 (+M) in USC 2.0 Mech and NUI C4Mech.

that from the NUI C4Mech. To examine the influence of this reaction, its rate constant in the USC 2.0 Mech was replaced by the corresponding one in the NUI C4Mech, as shown in Figure 12. It is found that the modified USC 2.0 Mech yields better
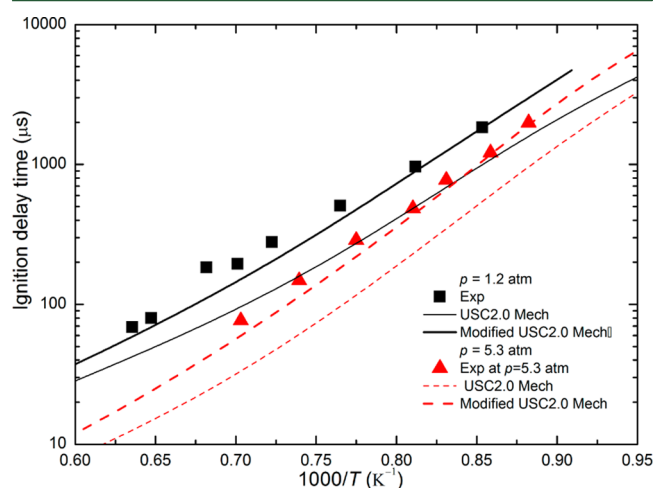
Figure 12. Effect of the rate constant of reaction a $C_2H_4 + H(+M) = C_2H_5(+M)$ on the USC 2.0 Mech.

agreement with experimental data. Additionally, the replacement of this reaction brings negligible effect on the ignition simulation for methane, propane, and *n*-butane, as shown in Figure 13. Although the rate constant of reaction b is treated as a pressure dependent reaction in a SRI form in the NUI C4Mech, its low-pressure limit, $4.99 \times 10^{12} \times T^{0.1} \exp(-10.6$ kcal mol$^{-1}/RT$) cm^3 mol^{-1} s^{-1} is identical to the rate constant of reaction b in the USC 2.0 Mech. Reaction c in the two models has the same rate constant, $1.15 \times 10^8 \times T^{1.90} \exp(-7.53$ kcal mol$^{-1}/RT$) cm^3 mol^{-1} s^{-1}, which is originally derived from the GRI 3.0 mechanism.[37] The rate constant of reaction d in the USC 2.0 Mech, $3.54 \times 10^6 \times T^{2.12} \exp(-0.87$ kcal mol$^{-1}/RT$) cm^3 mol^{-1} s^{-1}, is only approximately 20% higher than that in the NUI C4Mech, $1.48 \times 10^7 \times T^{1.9} \exp(-0.95$ kcal mol$^{-1}/RT$) cm^3 mol^{-1} s^{-1}. Reactions b and d were also tested by replacing them in the USC 2.0 Mech with those in the NUI C4Mech. It is found that their influence on the ignition of ethane is very limited. Consequently, it is the
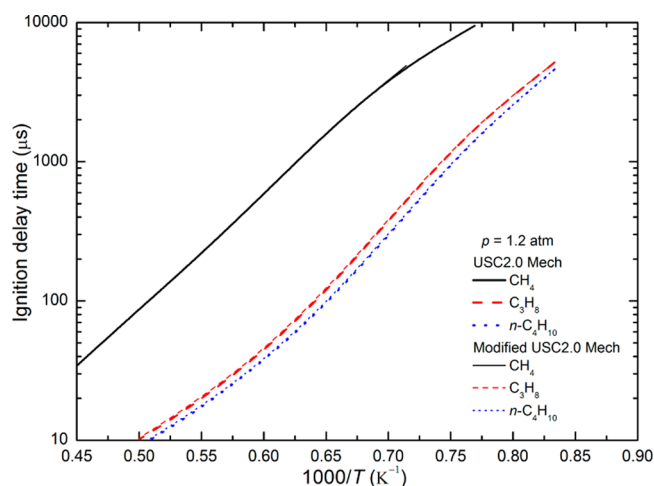
Figure 13. Simulation for ignition delay times of methane, propane, and *n*-butane using the modified USC 2.0 Mech.

higher rate constant of reaction a in the USC 2.0 Mech that leads to the remarkable under-prediction on ethane. Nevertheless, it may be arbitrary to conclude that the rate constant of this reaction in the NUI C4Mech is definitely more accurate. In view of its great effect on the ignition, further theoretical studies on this rate constant by employing high-level calculation method are recommended. In addition, the validation of this reaction against other experimental targets (e.g., JSR) is also recommended.

4. CONCLUSIONS

Experimental measurements on ignition delay times of C1−C4 alkanes were conducted behind reflected shock waves. Ignition simulations were also performed using Chemkin package with USC 2.0 Mech and NUI C4Mech models. Main conclusions are as follows:

(1) Attention was paid to the specific experimental conditions by different researchers when compared to previous data. The present data shows fairly good agreement with the previous data and can be used with confidence for further mechanism optimization.

(2) Methane shows the longest ignition delay times, while ethane shows the shortest ones. Propane and *n*-butane have comparative ignition values and locate between methane and ethane. The production of methyl and/or ethyl radicals during the ignition chemically contributes to the different reactivity of C1−C4 alkanes.

(3) Both USC 2.0 Mech and NUI C4Mech models yield fairly good agreement with experimental data except the notable under-prediction by the USC 2.0 Mech for ethane. Reaction pathway and sensitivity analysis were performed to ascertain the dominant ethane-specific reactions. After replacing the rate constant of the reaction $C_2H_4 + H(+M) = C_2H_5(+M)$ with the one in the NUI C4Mech, the modified USC 2.0 Mech yields significant improvement on the prediction for ethane

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