



# Studies of high pressure 1,3-butadiene flame speeds and high temperature kinetics using hydrogen and oxygen sensitization

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## ABSTRACT

The high pressure flame speeds and high temperature kinetics of 1,3-butadiene mixtures are studied by using spherical flames at fuel rich and lean conditions at 1–18 atm with H<sub>2</sub> and O<sub>2</sub> additions. H<sub>2</sub> and O<sub>2</sub> are added in the mixture to perturb concentrations of H/O radicals and the flame speed sensitivity to 1,3-butadiene + O/H reactions. The presently measured 1,3-butadiene/air flame speeds agree with previous studies at ambient pressure, but are lower at 5 atm. Comparison between the new experimental data and the prediction by the recently developed 1,3-butadiene model (Zhou et al., 2018) shows over-prediction of the flame speeds, especially at high pressure and fuel lean conditions. With H<sub>2</sub> and O<sub>2</sub> sensitization, the discrepancy between the model prediction and experiments becomes even larger. Sensitivity analysis shows that the flame speed is very sensitive to 1,3-butadiene + O/H reactions, especially to the branching and termination reaction ratio of 1,3-C<sub>4</sub>H<sub>6</sub> + O = C<sub>2</sub>H<sub>3</sub> + CH<sub>2</sub>CHO (R<sub>1</sub>) and 1,3-C<sub>4</sub>H<sub>6</sub> + O = CH<sub>2</sub>O + C<sub>3</sub>H<sub>4</sub>-a (R<sub>2</sub>). The sensitivity of the flame speed to the branching ratio of these two reactions increases with the increase of H<sub>2</sub> and O<sub>2</sub> enrichment. Due to the lack of accurate theoretical calculations of these two reaction rates, the new flame speed data and previously measured ignition delay time were used to assess the uncertainty of the branching ratio and reaction rates of R<sub>1</sub> and R<sub>2</sub>. It shows that the optimized branching ratio significantly improves the flame speed and ignition delay time predictions, especially at high pressure and fuel lean conditions. The present study reveals that H<sub>2</sub> and O<sub>2</sub> sensitization in flames provides an important way to identify the uncertainties of fuel + O/H reactions and to improve the model predictability for flames.

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## 1. Introduction

1,3-butadiene is listed as hazardous in air by the National Emission Standards and is a ubiquitous intermediate formed in the combustion of hydrocarbons from methane to practical fuels in gasoline, diesel, and aircraft engines. Moreover, it is a key precursor of poly-aromatic hydrocarbons (PAH) and soot formation through the benzene formation pathways [1,2]. Therefore, an accurate knowledge of 1,3-butadiene oxidation at high temperature is very important to the hierarchy development of kinetic mechanisms for combustion, PAH and soot formation, and emission control [3].

Different experimental methods, such as flow reactors [4,5], low pressure burner-stabilized flames [6], jet stirred reactors (JSR) [2], shock tubes [7–10], and laminar flames [11,12] have been used

to understand 1,3-butadiene chemistry in combustion. Brezinsky et al. [5] proposed that the oxidation of 1,3-butadiene started mainly through O atom addition to the double bond to form 3-butenal, while in Dagaut's JSR study [2], the attack of the O atom on 1,3-butadiene led primarily to the formation of vinyloxirane. These two proposed combustion pathways of the 1,3-butadiene reaction with O are somewhat contradictory as the former indicates a chain branching pathway and the latter causes a reaction termination. A recent study by Zhou et al. [12] showed that the O atom reaction with 1,3-butadiene had three different competing reaction pathways. However, despite the importance of these reactions, the reaction rates that were used are only analogous to those for propene + O<sub>2</sub> calculated by Cavallotti et al. [13]. Accurate theoretical calculations on the kinetics of these reaction rates are still not available.

Laminar flame speed measurements provide an important method to validate high temperature and high pressure combustion kinetics [14–17]. However, there is only one set of

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**Table 1**  
Experimental conditions.

Case	Equivalence ratio ( $\varphi$ )	C <sub>4</sub> H <sub>6</sub> (%)	O <sub>2</sub> (%)	N <sub>2</sub> (%)	He (%)	H <sub>2</sub> (%)	Pressure (atm)	T <sub>0</sub> (K)
Air condition	0.8–1.4	/	/	/	0	0	1	295
Air condition	0.7–1.4	/	/	/	0	0	5	295
Rich	1.4	4.00	15.71	66.91	13.38	0	1–18	295
Lean	0.8	2.54	17.46	72.72	7.27	0	1–18	295
H <sub>2</sub> addition	1.4–2.16	4.00	15.71	66.91–42.91	13.38	0.00–24.00	1–10	295
O <sub>2</sub> addition	1–0.35	2.54	14.08–40.00	76.22–50.19	7.27	0	1–10	295

1,3-butadiene flame speed data available up to 5 atm. No 1,3-butadiene flame speed data is available at higher pressures. Furthermore, due to uncertainties in linear extrapolation, flame instability, and flow compression [18–21], there is a large discrepancy in the 1,3-butadiene/air flame speed data of the literature [11,12]. Moreover, in these flame studies, no examinations of the uncertainties of 1,3-butadiene reactions with O and H radicals were emphasized, despite the fact that they play a critical role in fuel oxidation and flame speed.

Note that O<sub>2</sub> and H<sub>2</sub> addition in a flame can change the O/H radicals by orders of magnitude [14,15], especially at high pressure. Therefore, it would be interesting to use O<sub>2</sub> and H<sub>2</sub> sensitization in 1,3-butadiene flames to examine the high temperature kinetics of 1,3-butadiene combustion and the kinetic model uncertainties, especially for 1,3-butadiene reactions with O and H radicals.

Motivated by the above discussion, the goal of this work is to study the high pressure flame speeds of 1,3-butadiene mixtures up to 18 atm and to study the high temperature combustion kinetics of 1,3-butadiene oxidation by O/H radicals using O<sub>2</sub> and H<sub>2</sub> addition. First, 1,3-butadiene flame speeds in air mixtures are measured. Secondly, the uncertainty of 1,3-butadiene kinetic model [12] is examined by using the new high pressure flame speed data. Kinetic sensitivity analyses of flame speed are conducted to identify the key 1,3-butadiene reactions with O/H. Furthermore, 1,3-butadiene reactions with O and H are examined in the 1,3-butadiene flame speed measurement with different levels of O<sub>2</sub> and H<sub>2</sub> enrichments. Finally, based on the experimental data, Zhou's model is assessed by varying the branching ratio of the 1,3-butadiene reactions with O and H. An optimized model is derived from the experimental validation and examined by using both the present flame speed data and the shock tube ignition delay data from Zhou et al. [12].

## 2. Experimental methods and kinetic models

Experiments were conducted in a high-pressure constant-volume cylindrical chamber. Details of the apparatus and procedures were described elsewhere [14,15]. In brief, firstly, the chamber was evacuated and filled with a small amount of inert gas to avoid the trapping of fuel in crevices and pressure gauge lines. Then, the unburned gas reactant mixture was prepared by using the partial pressure method and centrally ignited. High pressure 1,3-butadiene flame speeds were then measured for different mixtures (Table 1). In order to adjust the O/H radical ratio to perturb the sensitivity of butadiene reactions with O and H radicals to flame speeds, the present experiments using O<sub>2</sub> and H<sub>2</sub> enrichment in 1,3-butadiene are conducted. He and N<sub>2</sub> were added to adjust the mixture Lewis number, suppress the hydrodynamic flame instability, and reduce the extrapolation uncertainty [18]. Moreover, the flow compression effect [19] was also considered in the flame speed extrapolation.

After the central ignition of the quiescent combustible mixture, the unsteady flame front time history was measured directly using the high-speed Schlieren imaging method at a frame rate of 10,000/s. The time-dependent flame front location data was

analyzed using an automated flame-edge detection and circle-fitting program in MATLAB. The un-stretched flame speed relative to the burned gas,  $S_b$ , was calculated using the linear extrapolation method with flow compression effect [18,19,22], and this extrapolated flame velocity was converted to the unstretched propagation speed relative to the unburned gas  $S_u$  using the density ratio of the adiabatic flame calculated by PREMIX [23]. The major source of the flame speed uncertainty at 1 atm is the fuel concentration at lean conditions due to the partial pressure method. At high pressures, the fuel concentration uncertainty becomes negligible and the main cause of the uncertainty is flame instability. The total uncertainty, calculated from the root-mean-square sum of the uncertainties from different sources, is within 5%.

A recently published 1,3-butadiene kinetic model by Zhou et al. [12] was used to predict the laminar flame speeds and compare with the experimental data. This model was developed with including the H<sub>2</sub>/O<sub>2</sub> sub-mechanism of Kéromnès et al. [24], the C<sub>1</sub>–C<sub>2</sub> sub-mechanism from Metcalfe et al. [25], the CH<sub>4</sub>/DME sub-mechanism from Burke et al. [26], the propene/allene/propyne sub-mechanism from Burke et al. [27,28], the 1- and 2-butene sub-mechanism developed by Li et al. [29,30], and the isobutene sub-mechanism from Zhou et al. [1]. Important reaction classes for 1,3-butadiene oxidation highlighted through sensitivity analyses at different temperatures and pressures include: (a) OH radical addition to the double bonds on 1,3-butadiene and their subsequent reactions (in analogy with OH radical additions to propene from Zádor et al. [31]). (b) HO<sub>2</sub> radical addition to the double bonds in 1,3-butadiene and their subsequent reactions (in analogy with HO<sub>2</sub> radical additions to butene from Villano et al. [32]). (c) O atom addition to the double bonds in 1,3-butadiene (in analogy with propene + O<sub>2</sub> from Cavallotti et al. [13]). (d) H atom addition to the double bonds in 1,3-butadiene (calculated using RRKM theory based on the potential energy surface obtained at the ROCCSD(T)/cc-pV $\infty$ Z//M062X/6-311++G(d,p) level of theory [33]). (e) Updates of C<sub>4</sub>H<sub>6</sub> unimolecular decomposition reactions and H-abstraction reactions. Zhou's model has been validated against a variety of experimental results of 1,3-butadiene ignition delay time and some laminar flame speeds below 5 atm.

## 3. Results and discussion

### 3.1. Laminar flame speeds of 1,3-butadiene in air

Figure 1(a) and (b) depict the measured and predicted 1,3-butadiene/air laminar flame speeds at 1 and 5 atm, respectively. Figure 1(a) shows that the present experimental flame speed agrees with the spherical flame results by Zhou et al. [12] well on both rich and lean sides. The flame speed measured in counter-flow flames by Davis and Law [11] is higher than the present and Zhou's data in a broad region. This is because in the counter-flow flame experiments, nonlinear extrapolation for flame speeds, which is especially important for counter-flow flames, was not considered, leading to a higher flame speed. It is seen that Zhou's model (the dashed line) agrees well with the experimental data on

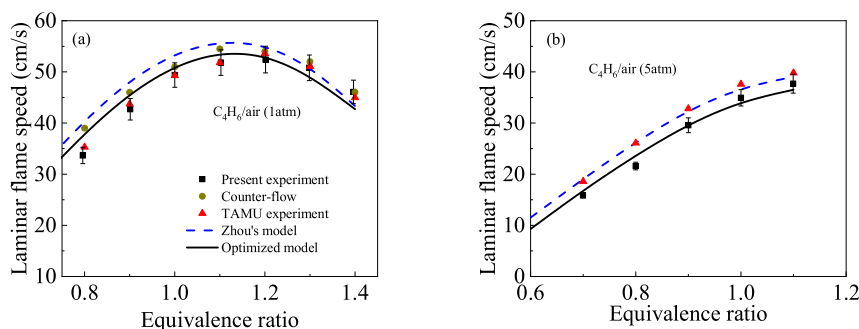


Fig. 1. Laminar flame speeds of 1,3-butadiene in air at 1 atm (a) and 5 atm (b).

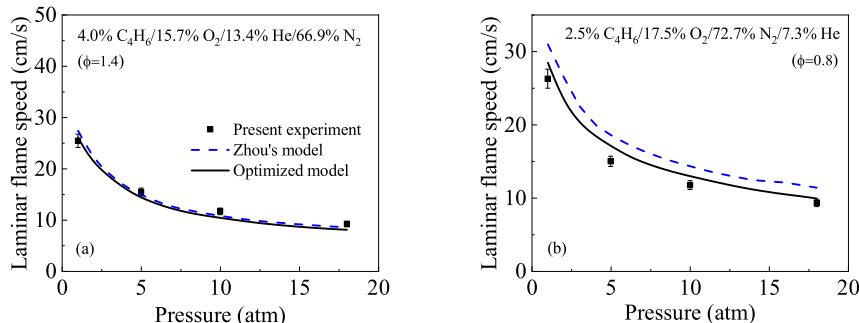


Fig. 2. Laminar flame speeds of 1,3-butadiene with pressure at fuel rich (a) and lean (b) conditions.

the fuel rich side but over-predicts the flame speeds on the lean side by more than 10% compared to the present and Zhou's data.

At 5 atm shown in Fig. 1(b), on the fuel lean side, consistent with the results in 1 atm, the present data is slightly below the model prediction by Zhou's model while the flame speed data from Zhou et al. [12] are in good agreement. Note that this difference may be caused by the flame instability. The high pressure flame instability tends to increase the flame speed if the ignition energy deposition or the mixture Lewis number is not well controlled. In fact, in our present experiment, flames at the equivalence ratios greater than 1.1 have serious instabilities at 5 atm, while the measured flame speed data is reliable below 1.1. In order to reduce the flame instability uncertainty at high pressure, it is necessary to conduct new high pressure experiments with mixture compositions not subject to hydrodynamic flame instability.

### 3.2. High pressure laminar flame speeds of 1,3-butadiene

In order to measure the flame speeds of 1,3-butadiene at high pressure without flame instability and to examine the validity of the kinetic model, He and N<sub>2</sub> dilution in the 1,3-butadiene/O<sub>2</sub> mixtures are employed for the new experiment between 1–18 atm. Therefore, the flame instability is successfully avoided in the present fuel rich and lean flame speed data. Figure 2(a) and (b) show a comparison of the pressure dependence of measured and predicted flame speeds, respectively, for fuel rich ( $\phi = 1.4$ ) and lean ( $\phi = 0.8$ ) conditions. With the increase of pressure, both the measured fuel rich and lean flame speeds decrease dramatically. It is seen that Zhou's model predicts the flame speed for fuel rich mixtures very well. However, it over-predicts the flame speeds for the fuel lean mixture between 1 and 18 atm. These results suggest that there are some uncertainties in the high temperature chemistry of 1,3-butadiene of Zhou's model at fuel lean conditions due to the change of the radical pool.

Flame speed sensitivity analyses are performed for both fuel rich ( $\phi = 1.4$ ) and lean ( $\phi = 0.8$ ) conditions at 5 atm and are shown in Fig. 3(a) and (b), respectively. As expected, only a few

key reactions in the C<sub>0</sub>–C<sub>2</sub> sub-mechanism involving H<sub>2</sub>/O<sub>2</sub> and CH<sub>2</sub>O/HCO/CH<sub>3</sub> reactions are sensitive. These reaction sets have been investigated extensively in literature [14,34–41] and thus are not our focus here. In both fuel rich and lean conditions, it is interesting to note that in addition to the high sensitivity of the C<sub>0</sub>–C<sub>2</sub> sub-mechanism, 1,3-butadiene reactions with O (e.g., reactions R<sub>1</sub> and R<sub>2</sub>) and H radicals (reaction R<sub>3</sub>)



are also important for the flame speed, while 1,3-butadiene reactions with OH are not irrelevant. More importantly, 1,3-butadiene reactions with O via R<sub>1</sub> and R<sub>2</sub> are, respectively, chain-termination and branching reactions. As such, the branching ratio of reactions R<sub>1</sub> over R<sub>2</sub> plays a key role in affecting the fuel-lean flame speed prediction. Unfortunately, the reaction rates of R<sub>1</sub> and R<sub>2</sub> in the Zhou's model were only taken by analogy with those for propene + O<sub>2</sub> calculated by Cavallotti et al. [13]. Therefore, there might be a large uncertainty in the branching ratio of R<sub>1</sub> and R<sub>2</sub>, which is the major cause contributing to the uncertainty of model prediction on lean mixtures (see Figs. 1(a), 2(b), and 3(b)). On the other hand, the rates of 1,3-butadiene reactions with H in Zhou's model were computed by using QRRK theory [33]. The uncertainty for these reaction rates should be much smaller than that of reactions R<sub>1</sub> and R<sub>2</sub>.

### 3.3. Laminar flame speeds of 1,3-butadiene with O<sub>2</sub> and H<sub>2</sub> enrichments

In order to sensitize reactions R<sub>1</sub>–R<sub>3</sub> in flames and study the model uncertainty in the flame speed prediction, we use O<sub>2</sub> and H<sub>2</sub> additions in 1,3-butadiene flames to vary the H/O radical ratios. The integrated H and O mole fractions over chamber radius with

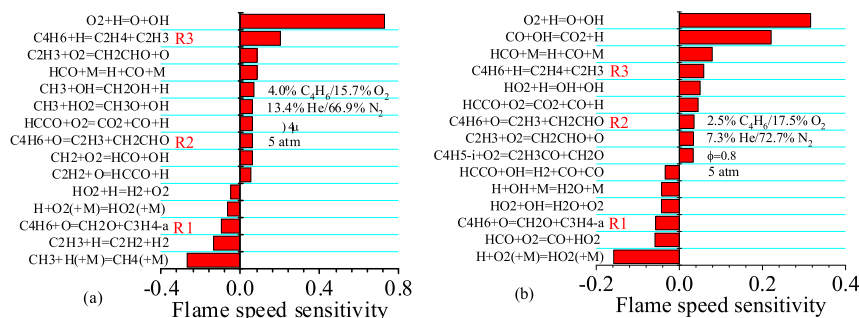


Fig. 3. Flame speed sensitivity analyses of 1,3-butadiene at 5 atm and at fuel rich (a) and lean (b) conditions by using Zhou's model.

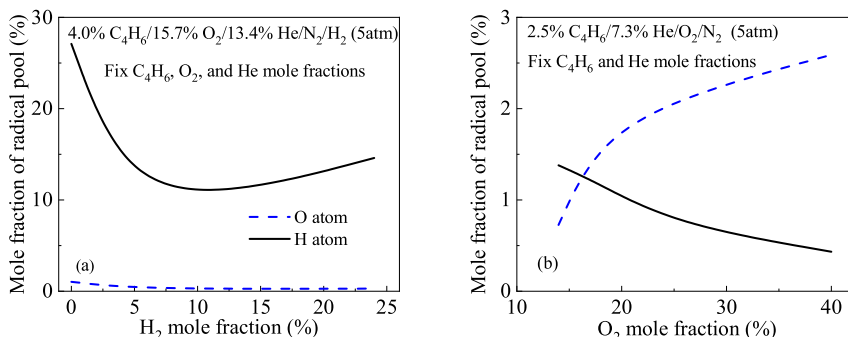


Fig. 4. Mole fractions of O and H in the laminar flame speed simulations with different H<sub>2</sub> additions (a) and O<sub>2</sub> enrichments (b), respectively, at fuel rich and lean conditions at 5 atm by using Zhou's model.

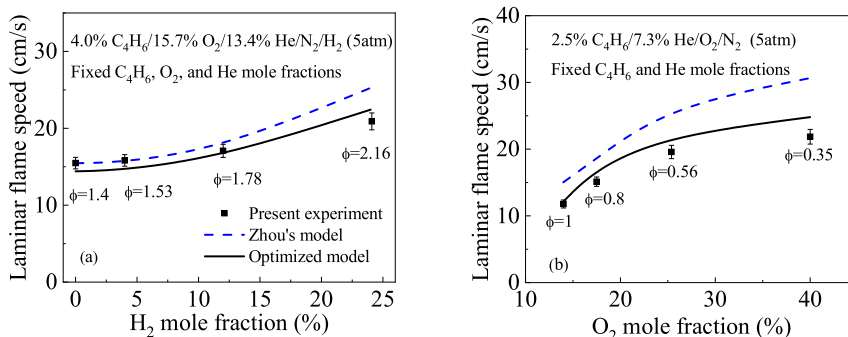


Fig. 5. Laminar flame speeds of 1,3-butadiene with different H<sub>2</sub> additions (a) and O<sub>2</sub> enrichments (b) at fuel rich and lean conditions, respectively, at 5 atm.

different H<sub>2</sub> and O<sub>2</sub> additions, respectively, at fuel rich and lean conditions at 5 atm are plotted in Fig. 4(a) and (b). It is seen that at the fuel rich condition with H<sub>2</sub> additions, the peak H/O ratio can be increased to greater than 10. And at the fuel lean condition with O<sub>2</sub> enrichments, the integrated O/H mole fraction ratio can be varied by more than a factor of 5. Therefore, O<sub>2</sub> and H<sub>2</sub> addition experiments can provide very useful information to examine the uncertainty of 1,3-butadiene reactions with O and H, respectively.

Figure 5(a) and (b) depict the laminar flame speeds of 1,3-butadiene with different H<sub>2</sub> additions and O<sub>2</sub> enrichments at fuel rich and lean conditions, respectively, at 5 atm by using Zhou's model. In Fig. 5(a), 1,3-butadiene, O<sub>2</sub>, and He mole fractions are fixed by varying H<sub>2</sub> (0–24%) and N<sub>2</sub> mole fractions. In Fig. 5(b), both 1,3-butadiene and He mole fractions are fixed by varying O<sub>2</sub> (14–40%) and N<sub>2</sub> mole fractions. It is seen in Fig. 5(a) and (b) that with H<sub>2</sub> addition and O<sub>2</sub> enrichment, the difference between measured flame speeds and Zhou's model predictions becomes larger. It implies that the uncertainty of 1,3-butadiene + O/H reactions is amplified with more H<sub>2</sub> addition and O<sub>2</sub> enrichment due to the change of the H/O mole fractions in the flames. Therefore, it suggests that the model uncertainty in the 1,3-butadiene flame speed

prediction in Figs. 1, 2, and 5 may mainly come from the 1,3-butadiene + O/H reactions.

Figure 6(a) shows the flame speed sensitivity on the fuel rich condition with 24% H<sub>2</sub> addition at 5 atm. It is seen that not only C<sub>4</sub>H<sub>6</sub> + H = C<sub>2</sub>H<sub>4</sub> + C<sub>2</sub>H<sub>3</sub> is sensitive, the other C<sub>4</sub>H<sub>6</sub> reactions with H atom, C<sub>4</sub>H<sub>6</sub> + H = C<sub>4</sub>H<sub>5-i</sub> + H<sub>2</sub>, also appears in the sensitivity analysis with more H<sub>2</sub> addition. Meanwhile, compared with Fig. 3(a), both the C<sub>4</sub>H<sub>6</sub> addition reactions with O atom (reactions R<sub>1</sub> and R<sub>2</sub>) in Fig. 6(a) are less sensitive in the high H<sub>2</sub> addition case. The sensitivity of R<sub>2</sub> even disappears from the top 15 sensitive reactions. Essentially, with more H<sub>2</sub> addition, C<sub>4</sub>H<sub>6</sub> + H reactions become more sensitive over C<sub>4</sub>H<sub>6</sub> + O reactions. In addition, 1,3-butadiene reactions with OH are still irrelevant with H<sub>2</sub> and O<sub>2</sub> additions. The good agreement on fuel rich side between Zhou's model and the present experiments (Figs. 1(a) and 2(a)) indicates that the uncertainty of C<sub>4</sub>H<sub>6</sub> + H reaction rates are small. On the other hand, for the fuel lean case, the sensitivity comparison between the mixtures with 17.5% and 40% O<sub>2</sub> mole fractions in Fig. 6(b) shows clearly that C<sub>4</sub>H<sub>6</sub> + O reactions (reactions R<sub>1</sub> and R<sub>2</sub>) are more sensitive with a higher O<sub>2</sub> content, while the sensitivity of C<sub>4</sub>H<sub>6</sub> + H reactions becomes very small. Due to the fact that

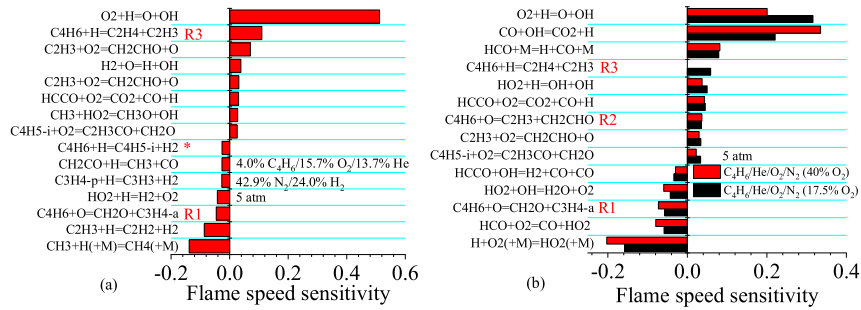


Fig. 6. Flame speed sensitivity analyses of 1,3-butadiene at 5 atm and at fuel rich condition with 24% H<sub>2</sub> addition (a) and fuel lean condition with 40% O<sub>2</sub> addition (b) by using Zhou's model.

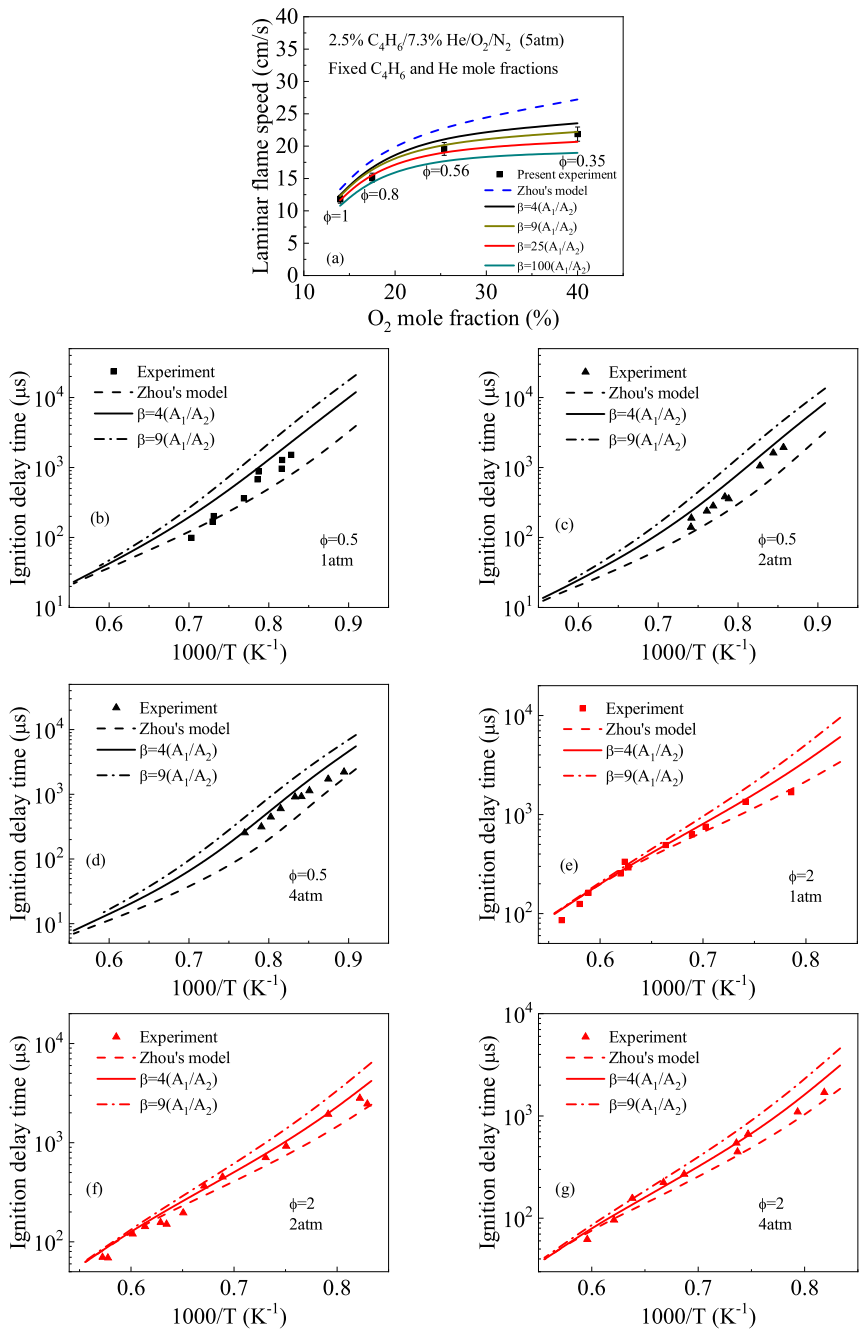
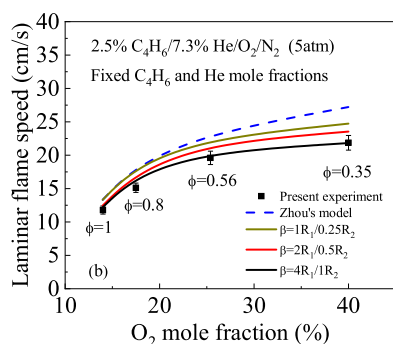


Fig. 7. Dependence of model prediction on the branching ratio ( $\beta$ ) of reactions  $R_1$  and  $R_2$  in the present 1,3-butadiene flame speed measurements with O<sub>2</sub> enrichments at 5 atm (a); in the ignition delay time measurements for  $\phi=0.5$  (b)–(d) and  $\phi=2$  (e)–(g), 1% C<sub>4</sub>H<sub>6</sub>/O<sub>2</sub>/Ar mixtures at 1–4 atm from Zhou et al. [12].

**Table 2**  
Modified rate coefficients in the optimized model.

Reaction	Pressure (atm)	A (cm <sup>3</sup> /mol/s)	n	Ea (cal/mol)	A factor modification	Reference
C <sub>4</sub> H <sub>6</sub> + O = CH <sub>2</sub> O + C <sub>3</sub> H <sub>4</sub> -a	0.1	3.112E+11	0.809	1857	x4	
	1	2.904E+11	0.819	1829	x4	[12]
	10	8.960E+11	0.679	2149	x4	
C <sub>4</sub> H <sub>6</sub> + O = C <sub>2</sub> H <sub>3</sub> + CH <sub>2</sub> CHO	0.1	2.290E+10	0.570	1189	Not changed	
	1	1.620E+9	1.253	539	Not changed	[12]
	10	2.460E+11	0.562	1220	Not changed	
C <sub>4</sub> H <sub>6</sub> + H = C <sub>2</sub> H <sub>4</sub> + C <sub>2</sub> H <sub>3</sub>	0.1	1.123 E+34	-5.38	23264	x1.3	
	1	8.424E+32	-4.91	26478	x1.3	[12]
	10	1.521E+20	-1.14	23027	x1.3	



**Fig. 8.** Optimizations of absolute values of reactions R<sub>1</sub> and R<sub>2</sub> in the present 1,3-butadiene flame speed measurements with O<sub>2</sub> enrichments at 5 atm.

the increase in the discrepancy of the flame speed prediction coincides with the increase of the sensitivity of C<sub>4</sub>H<sub>6</sub> + O reactions and the increase of the O radical mole fraction with O<sub>2</sub> enrichment, we can conclude that the C<sub>4</sub>H<sub>6</sub> + O reaction rates derived from the analogy to propene + O<sub>2</sub> [13] in Zhou's model are not accurate and need further validation from experimental data, especially for lean flames.

#### 3.4. Branching ratio of reactions R<sub>1</sub> and R<sub>2</sub>

Based on the present flame speed data, Zhou's model is further optimized by changing reactions rates of R<sub>1</sub>–R<sub>3</sub> with the focus on the branching ratio between R<sub>1</sub> and R<sub>2</sub>. Specifically, optimizations of branching ratio of reactions R<sub>1</sub> and R<sub>2</sub> are made by using the present measurement of 1,3-butadiene flame speeds with O<sub>2</sub> enrichments at 5 atm (Fig. 7(a)) and the 1,3-butadiene ignition delay time measurements at 1–4 atm ( $\phi = 0.5$ , Fig. 7(b)–(d);  $\phi = 2$ , Fig. 7(e)–(g)) from Zhou et al. [12]. In the sensitivity tests of reactions R<sub>1</sub> and R<sub>2</sub>, the branching ratio of these two reactions,  $\beta = A_1/A_2$ , is simply defined as the ratio of pre-exponential coefficients A<sub>1</sub> and A<sub>2</sub> of R<sub>1</sub> and R<sub>2</sub>, respectively. It is seen that both ignition delay times at lean (Fig. 7(b)–(d)) and rich conditions (Fig. 7(e)–(g)) are under-predicted by Zhou's model, which is corresponding with the over-prediction of the laminar flame speeds in Figs. 1(a), 2(b), and 7(a). The increase of  $\beta$  leads to a decrease of oxidation reactivity, and as a result, 1,3-butadiene flame speed reduces while the ignition delay time increases. It is seen that  $\beta = 4(A_1/A_2)$  is the best fitting for both the flame speed and the ignition delay time between experiments and modeling as shown in Fig. 7(a–g).

Furthermore, at fixed  $\beta = 4(A_1/A_2)$ , the reaction rates of A<sub>1</sub> and A<sub>2</sub> ( $\beta = 4A_1/1A_2$ ,  $2A_1/0.5A_2$ , and  $1A_1/0.25A_2$ ) are varied and predictions are compared with the 1,3-butadiene flame speed with O<sub>2</sub> enrichments in Fig. 8. It is seen that the optimized model with  $\beta = 4A_1/1A_2$  gives the best prediction of the 1,3-butadiene flame speed. In addition, based on experimental data in Fig. 5(a) and (b), reaction R<sub>3</sub> is optimized by increasing the pre-exponential

coefficient by 30%, which is within the uncertainty of this reaction rate. The changes of the reaction rates in the optimized model are listed in Table 2.

It is seen that the flame speed predictions at fuel lean conditions are improved by the optimized model in Figs. 1(a) and (b) and 2(b), especially at fuel lean condition and high pressures. At 5 atm with H<sub>2</sub> addition and O<sub>2</sub> enrichment, Fig. 5(a) and (b) show that the optimized model significantly improves the flame speed predictions, particularly at high H<sub>2</sub> addition and O<sub>2</sub> enrichment. And the predictions of the previously measured ignition delay time at both rich and lean are improved by using the optimized model. The improvement of model predictions confirms that the C<sub>4</sub>H<sub>6</sub> + O/H reactions, especially for the branching ratio of reactions R<sub>1</sub> and R<sub>2</sub> in the reference [12], need to be re-assessed. Note that both ignition delay time and flame speed are global combustion parameters. To accurately determine the reaction rates of R<sub>1</sub>–R<sub>3</sub>, high accuracy quantum chemistry calculations are needed.

#### 4. Conclusion

This paper studied the high pressure flame speeds of 1,3-butadiene mixtures at fuel rich and lean conditions up to 18 atm and the high temperature combustion kinetics of 1,3-butadiene oxidation by O/H radicals using O<sub>2</sub> and H<sub>2</sub> enrichments.

- (1) The presently measured 1,3-butadiene/air flame speeds agree well with the recently developed 1,3-butadiene model [12] prediction at 1 atm, but are slightly lower than the prediction at 5 atm. With a further increase of pressure, a significant model over-prediction of the flame speeds was observed, especially at fuel lean conditions. Moreover, with H<sub>2</sub> and O<sub>2</sub> enrichment, the increase of H and O mole fractions results in increased discrepancy between experimental data and model predictions.
- (2) Sensitivity analysis shows that the flame speed is very sensitive to 1,3-butadiene + O/H reactions, especially to the branching and termination reaction ratios of 1,3-butadiene reactions with O. The results show that H<sub>2</sub> and O<sub>2</sub> enrichment further increases the sensitivity of flame speeds to this branching ratio. It is found that the increase in the discrepancy of the flame speed prediction coincides with the increase of the sensitivity of C<sub>4</sub>H<sub>6</sub> + O/H reactions and the increase of the O and H radical pool.
- (3) Based on the new flame speed data and the previous ignition delay time measurement, the branching ratio and absolute values of reactions R<sub>1</sub> and R<sub>2</sub> are assessed. A recommended branching ratio of 4 for 1,3-butadiene reactions with O is derived. The results show that the optimized 1,3-butadiene model significantly improves the flame speed and ignition delay time predictions, especially at high pressure and fuel lean conditions. The present study also indicates that H<sub>2</sub> and O<sub>2</sub> additions in flames provide an important platform to identify the uncertainties of fuel + O/H reactions and to improve the model predictability for flames.

- (4) Note that both ignition delay time and flame speed are global combustion parameters. To accurately determine the reaction rates of  $R_1$ – $R_3$ , high accuracy quantum chemistry calculations are needed.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.combustflame.2018.11.018.

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