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A Rapid Compression Machine Study of 2-Phenylethanol Autoignition at Low-To-Intermediate Temperatures

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Abstract: To meet the increasing anti-knocking quality demand of boosted spark-ignition engines, fuel additives are considered an effective approach to tailor fuel properties for satisfying the performance requirements. Thus, screening/developing bio-derived fuel additives that are best-suited for advanced spark-ignition engines has become a significant task. 2-Phenylethanol (2-PE) is an attractive candidate that features high research octane number, high octane sensitivity, low vapor pressure, and high energy density. Recognizing that the low temperature autoignition chemistry of 2-PE is not well understood and the need for fundamental experimental data at engine-relevant conditions, rapid compression machine (RCM) experiments are therefore conducted herein to measure ignition delay times (IDTs) of 2-PE in air over a wide range of conditions to fill this fundamental void. These newly acquired IDT data at low-to-intermediated temperatures, equivalence ratios of 0.35–1.5, and compressed pressures of 10–40 bar are then used to validate the 2-PE model developed by Shankar et al. (2017). It is found that this literature model greatly overpredicts the current RCM data. The comparison of experimental and simulated results also provides insights into 2-PE autoignition behaviors at varying conditions. Further chemical kinetic analyses demonstrate that the absence of the O_2-addition pathway of β-$\dot{R}$ radical in the 2-PE model of Shankar et al. (2017) could account for the model discrepancies observed at low-to-intermediated temperatures.

Keywords: 2-phenylethanol; autoignition; low temperature chemistry; rapid compression machine

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1. Introduction

The anti-knocking quality of a fuel is essential to spark-ignition (SI) engines for achieving higher compression ratios and thus higher thermodynamic efficiency. Fuels with high octane rating are desired for advanced SI engines because they not only can meet the increasing requirement on fuel's anti-knocking quality but also exhibit reduced CO_2 emissions [1]. As conventional gasoline will still be the fuel for running most of the SI engines, fuel additives become a viable way to tailor fuel properties for meeting those anti-knocking performance requirements. Moreover, with escalating global concerns about energy security and environmental sustainability, whether the candidate fuel additives can be derived from domestic biomass should be taken into consideration. Therefore, it is imperative to identify top bio-derived fuel additives that are suitable for further development and have the potential to enable more efficient engine design and operation.

2-Phenylethanol (2-PE) is an alcoholic compound from the aromatics family with high research octane number (RON = 110) and high octane sensitivity (S = 20) [2], which well suits the role of an anti-knocking additive especially at high engine load conditions [3]. 2-PE not only exhibits other desirable features such as low vapor pressure [4] and high energy density [2], but also has the potential to be produced via a low-cost feedstock known as lignocellulose [5,6]. As such, 2-PE has drawn researchers' attention in recent years, both as alternate fuel and anti-knocking additive. Ratcliff et al. [7] blended several bio-derived oxygenates, including 2-PE, with gasoline and evaluated the knocking resistance and particle emissions of each candidate. It was found in [7] that 2-PE exhibits excellent anti-knocking performance. Pan et al. [8] investigated the effects of 2-PE addition on engine performance and emissions using a downsized gasoline SI engine. Compared with a gasoline reference fuel, 2-PE addition resulted in decreased in-cylinder pressure and heat release rates [8]. The combustion phasing was also affected as the crank angle at 50% burn (CA50) location was retarded with 2-PE addition, which reduced engine torque output and combustion efficiency under optimal SI timing [8]. Furthermore, it was reported in [8] that 2-PE addition affected engine emissions, with increased unburned hydrocarbon/CO and reduced nitric oxide in the exhaust gas. Those literature engine studies revealed both the great potential of 2-PE as an anti-knocking additive and the challenge of using 2-PE, namely the altered combustion phasing.

A key to resolving the combustion phasing issue is our fundamental understanding of the 2-PE autoignition characteristics under engine-relevant conditions and the underlying chemical kinetics, which however is very limited. Only a few fundamental works investigated the chemical kinetics of 2-PE. Sakai et al. [9] studied thermal decomposition of 2-PE using quantum mechanical calculations at the CBS-QB3 level. Shanker et al. [10] experimentally explored 2-PE autoignition via cooperative fuel research engine and shock tube (ST) measurements. In addition, a detailed chemical kinetic model describing the high temperature chemistry of 2-PE autoignition was developed in [10] and validated against their experimental data. Otten et al. [11] determined the oxidation reaction products of 2-PE via synchrotron photoionization and deduced the key oxidation pathways of 2-PE. Apart from the above-mentioned fundamental studies, both fundamental experimental data and chemical kinetic model at low-to-intermediate temperatures (<1000 K) are still lacking.

In view of this fundamental void, rapid compression machine (RCM) experiments are conducted over a wide range of engine-like conditions. A set of ignition delay time (IDT) data of neat 2-PE in air is acquired at low-to-intermediate temperatures, which provides the much-needed autoignition data for model validation. In addition, the high temperature 2-PE model developed by Shanker et al. [10] is used to simulate the newly acquired RCM data. Based on the current RCM IDT data, the model performance is evaluated, and the major discrepancy sources are analyzed and identified to provide guidance to future 2-PE model refinement and development.

2. Experimental and Computational Methodologies

2.1. Experimental Specifications

The RCM facility used for IDT measurements of 2-PE/air mixtures consists of a heated reaction chamber, a piston assembly, a hydraulic cylinder, a pneumatic cylinder, and a driving air tank, as shown in Figure 1. As the detailed descriptions of the RCM used in this work have been documented in [12,13], a brief overview is given here. This RCM simulates a single compression stroke of an internal combustion engine, and the fuel–oxidizer mixture in the reaction chamber is rapidly compressed by the piston assembly to reach the desired temperature and pressure at the end of compression (EOC). The piston assembly is driven by compressed air and stopped by hydraulic forces. At the EOC, the piston assembly is held in place which creates a constant volume reactor enclosed by the piston and the reaction chamber walls. To ensure homogeneity of the reactant mixture during and after the compression stroke, the piston is machined with a crevice to suppress the roll-up vortex as well as to contain the cold boundary layer gas. As such, the present RCM provides an idealized engine-relevant environment for investigating fuel autoignition behaviors. In-cylinder pressure histories are considered as the primary diagnostic of the RCM and are measured by a piezo-electrical thermal-shock resistant pressure transducer (Kistler 6125C-C20) along with a charge amplifier (Kistler 5010B). The EOC temperature and pressure (T_C and P_C, respectively) can be adjusted independently by varying the overall compression ratio, initial pressure (P_0), and initial temperature (T_0). The fuel–oxidizer mixtures are prepared in a pre-vacuumed mixing tank which is connected to the RCM reaction chamber by a heated manifold.

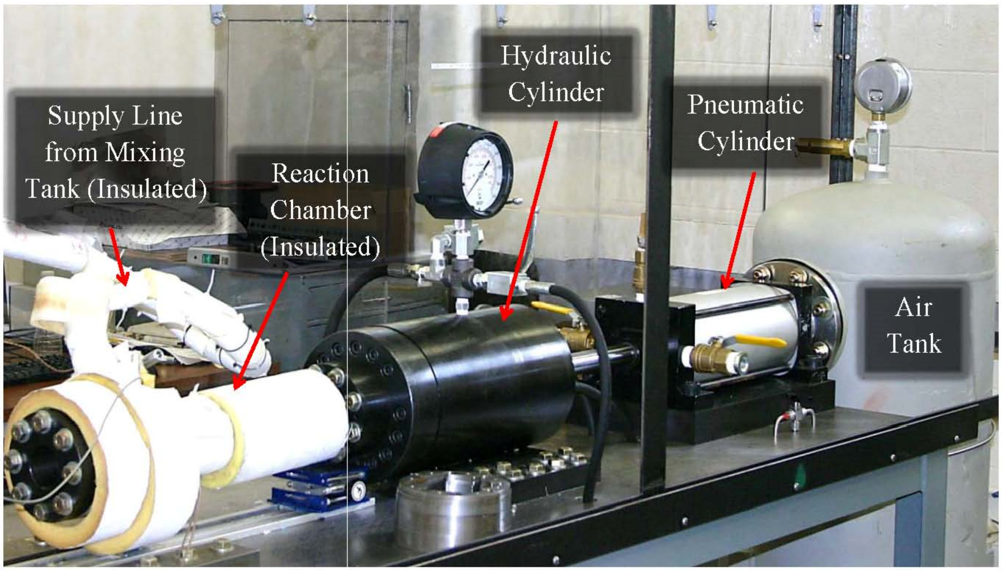
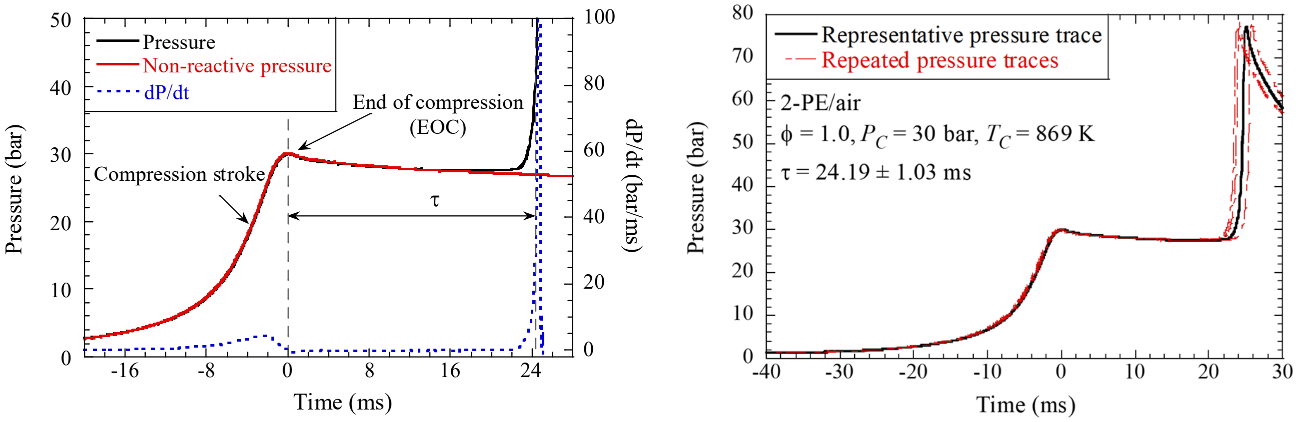


Figure 1. Rapid compression machine facility at the University of Connecticut.

The raw experimental pressure traces are processed using a Python package called UConnRCMPy [14] to determine the resulting T_C, P_C, and IDT. Specifically, T_C can be computed from the pressure profile obtained in the compression stroke by applying the "adiabatic core hypothesis" [15] via $\int_{T_0}^{T_C} \frac{\gamma}{\gamma-1}\frac{dT}{T} = \ln\frac{P_c}{P_0}$, where γ is the temperature-dependent specific heat ratio. This process is carried out through the Python interface of Cantera 2.3.0 [16], from which T_C is generated following the procedure detailed in Section 2.2.1. Figure 2a presents the representative experimental pressure trace obtained by the current RCM, as well as the definition of the total ignition delay time (τ). Namely, τ is defined as the time from the EOC to the maximum of the first-order time derivative of pressure (dP/dt). At least four consecutive runs are taken for each experimental condition to ensure repeatability, as shown in Figure 2b. Among repeated experiments, the one with τ closest to the average is selected as the representative pressure trace. The associated parameters (such as P_0, T_0) and outputs (such as P_C, T_C, and τ) of each representative experiment are reported instead of reporting all repeated experiments. The normal scatter of τ for repeated experiments is less than 15% of the reported value (while the standard deviations of repeated experiments are typically less than 6% of the reported values) and are plotted as error bars in the Arrhenius plots in the subsequent sections. To determine the machine-specified effect (i.e., the heat transfer effect [15]) on the reactive experiment as well as to confirm that there is no exothermicity during the compression stroke, the corresponding non-reactive experiment is conducted by replacing O_2 in the reactive mixture with N_2. Due to the similar specific heat values of O_2 and N_2, the change in the specific heat of the mixture is thus deemed negligible. Figure 2a demonstrates that the reactive pressure trace prior to the hot ignition is well-captured by its non-reactive counterpart.



(**a**) (**b**)

Figure 2. (**a**) Pressure trace of reactive experiment with stoichiometric 2-PE/air at P_C = 30 bar and T_C = 869 K, demonstrating the definition of the total IDT (τ). The non-reactive pressure trace by replacing O_2 with N_2 is also shown as a reference. (**b**) Representative and repeated experimental pressure traces with stoichiometric 2-PE/air at P_C = 30 bar and T_C = 869 K.

High-purity (99.8%) 2-phenylethanol from Sigma-Aldrich, as well as high-purity (>99.99%) O_2 and N_2 from Airgas, are used to prepare the test mixtures in a pre-vacuumed stainless-steel mixing tank at room temperature. The liquid fuel (2-PE) is first injected into the mixing tank using a glass syringe. Subsequently, O_2 and N_2 are filled into the mixing tank consecutively based on barometric measurements. Adequate time interval is necessary between the fillings of two consecutive gases to minimize the temperature change (~5 K) in the mixing tank caused by filling the preceding gas. For "air", the molar ratio of N_2/O_2 is kept at 3.76. A magnetic stirrer is placed at the bottom of the mixing tank to enhance mixing of the constituents. After filling the reactants, the heaters and magnetic stirrer are switched on and 4 h are allowed to completely vaporize the liquid fuel as well as stabilize the preheat temperature and ensure homogeneity of the reactant mixture. The preheat temperature used in this study is 420 K to prevent 2-PE condensation during experiments. The test conditions of this study, including equivalence ratio (ϕ), P_C, T_C, and mixture composition, are summarized in Table 1. The temperature regimes covered by the current RCM experiments are based on the consideration of avoiding excessively long τ and the constraints of machine setting capability.

Table 1. Summary of test conditions for 2-PE/air mixtures in the current RCM experiments.

ϕ	**P_C (bar)**	**T_C (K)**	**Molar Percent (%)**		
			2-PE	**O_2**	**N_2**
0.35	20, 30, 40	886–992	0.7299	20.8551	78.4150
0.5	20, 30, 40	838–970	1.0395	20.7900	78.1705
1.0	10, 20, 30, 40	813–937	2.0576	20.5761	77.3663
1.5	20, 30	829–893	3.0550	20.3666	76.5784

2.2. Computational Specifications

2.2.1. Ignition Delay Time Simulations and T_C Determination

Two types of IDT simulations are performed in this study. The first type is 'RCM simulation' which accounts for machine-specific effect by modeling it as change in reactor volume [17]. After confirming there is no exothermicity during the compression stroke by comparing the reactive pressure trace with its non-reactive counterpart, a combined pressure trace is then constructed and used to deduce the reactor volume history. The combined pressure trace uses the pressure profile during the compression stroke (before the EOC) from the reactive experiment, while the pressure profile after the EOC is taken from the corresponding non-reactive run. This is to ensure that the combined pressure trace faithfully captures the reactor condition during and after the compression stroke. Cantera [16] is used to convert the combined pressure trace to a volume trace by assuming that the mixture undergoes an isentropic compression during the compression stroke and an isentropic expansion after the EOC. With the generated volume trace as an input, the IdealGasReactor in Cantera [16] is used to yield the simulated reactive pressure trace, from which the IDT of RCM simulation is obtained following the same procedure of determining experimental τ described in Section 2.1. Moreover, by disabling the reactions (i.e., assigning the reaction multiplier to zero in Cantera) during RCM simulation, the temperature at the EOC is recorded as T_C. More details about the RCM simulation and T_C determination can be found in [14,18].

The second type of simulation is 'CONV simulation' that uses the IdealGasReactor in Cantera [16] assuming constant reactor volume. The CONV-simulated τ value is defined as the time required for the simulated temperature to increase by 400 K over the initial temperature, which is found to be close to that determined using the time derivative of pressure. The CONV simulations in this study are mainly used to simulate shock tube IDTs as well as perform model-based analyses.

2.2.2. Sensitivity Analyses

Besides IDT simulations, brute force sensitivity analyses of IDTs to the reaction rate coefficient of each reaction are carried out using CONV simulation in Cantera [16]. By perturbing the pre-exponential factor of the target reaction by a factor of 2 (0.5), the corresponding τ^+ (τ^-) is obtained with the perturbed rate coefficient of $k^+ = 2k$ $(k^- = 0.5k)$, where k is the unperturbed reaction rate coefficient. The sensitivity coefficient for τ with respect to k is then defined as $S_\tau = \ln(\tau^+/\tau^-)/\ln(k^+/k^-)$. Thus, the reaction with a negative (positive) value of sensitivity coefficient promotes (retards) the overall reactivity.

3. Results and Discussion

3.1. Comparison with Literature Data

Figure 3 first compares the experimental τ of stoichiometric mixtures at 10 bar and 20 bar obtained from the current RCM experiments (2-PE/air) and the ST experiments (2-PE/Ar/O_2) of Shankar et al. [10]. It is seen that the τ trends of the two studies in different temperature regimes have different slopes on the Arrhenius plot, with the RCM data at lower temperatures exhibiting steeper slopes than those of Shankar et al. [10] at higher temperatures. These slope differences can be attributed to two possible reasons: (1) different oxidizer compositions (i.e., air in RCM and highly diluted Ar/O_2 in ST) and (2) different controlling autoignition chemistry in different temperature regimes. In addition, the pressure effects demonstrated by the two studies show different trends. While the highly-diluted ST data of Shankar et al. [10] display insignificant pressure effect on τ at high temperatures, a clear pressure effect is observed in the current RCM study as τ decreases noticeably with increasing pressure at low temperatures.

Figure 3 also shows that the CONV-simulated τ using the 2-PE model developed by Shankar et al. [10] agrees well with the ST data at high temperatures (>1000 K). However, comparing the RCM-simulated τ with the experimental results obtained in this work at lower temperatures (below 1000 K), the model of [10] significantly overpredicts τ up to a factor of 5. This suggests the change in controlling chemistry of 2-PE autoignition at different temperature regimes.

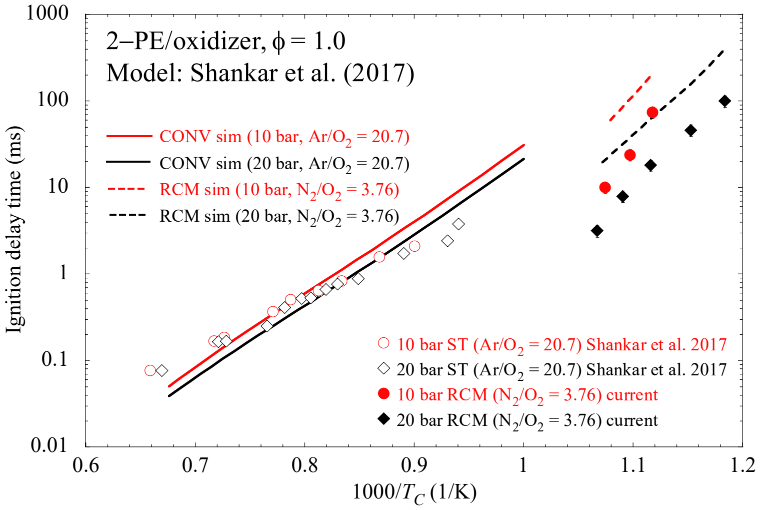


Figure 3. Experimental τ comparison of stoichiometric mixtures between the current RCM study (solid symbols) and the literature ST data of Shankar et al. 2017 [10] (hollow symbols). The simulated τ using the model of [10] are displayed as lines. Solid lines: CONV simulation. Dashed lines: RCM simulation.

3.2. Reaction Pathway Analyses

As the 2-PE model of [10] displays significant overprediction against the RCM data at low-to-intermediated temperatures, the overall reaction pathways of this literature model are analyzed to identify the possible reasons causing such discrepancies. Figure 4 depicts the key reaction pathways/species included in the original model of [10] (marked in black). Note that the model of [10] did not include the O_2-addition pathway on the β site. Consequently, the β-$\dot{R}$ radicals mostly go through the styrene pathways, as shown in Figure 4. As the O_2-addition pathways are generally insignificant at high temperatures, including or excluding those O_2-addition pathways in the 2-PE model is not expected to affect the model performance at high temperatures. At low-to-intermediate temperatures, however, the O_2-addition pathways become critical in the autoignition chemistry of hydrocarbon fuels due to their subsequent chain branching channels. Thus, the inclusion of the β site O_2-addition pathway of 2-PE has the potential to improve the performance of the original model of [10] at low temperatures.

In view of the above, the original model in [10] is modified by adding four additional reactions: O_2-addition on β-$\dot{R}$ radicals, intramolecular H-abstraction ($\beta\text{-}RO\dot{O} \rightleftarrows \beta\text{-}\dot{Q}OOH$), and two unimolecular decomposition reactions of β-$\dot{Q}OOH$. In Figure 4, the newly added reactions and species are marked with green arrows and shadows, respectively. These newly added pathways were proposed by Otten et al. [11] based on the experimentally identified reaction products of 2-PE oxidation. Due to the lack of theoretical calculations of those reaction rate parameters, they are determined herein via analogies to similar reactions of n-propylbenzene [19] and iso-octane [20]. Further, the thermodynamic properties of the two newly added species are acquired from the RMG database [21], which are estimated by using the group additivity method. This modified 2-PE model will be used to simulate the RCM/ST data and its performance will be compared with that of the original model of [10] in the following to illustrate the impact of the β site O_2-addition pathway on the autoignition of 2-PE, especially at low-to-intermediate temperatures. The detailed information of the newly added species and reactions are provided in the Supplementary Material.

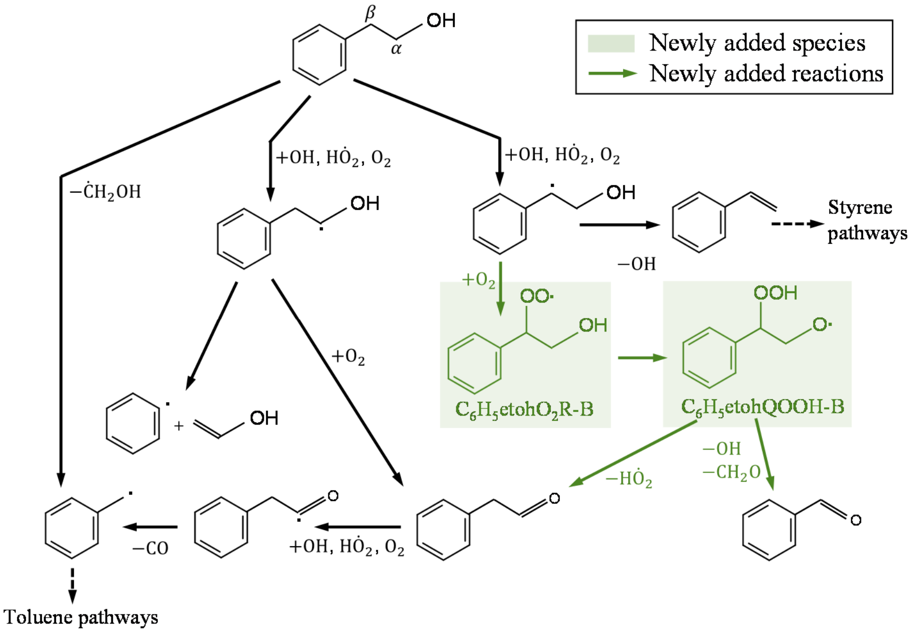
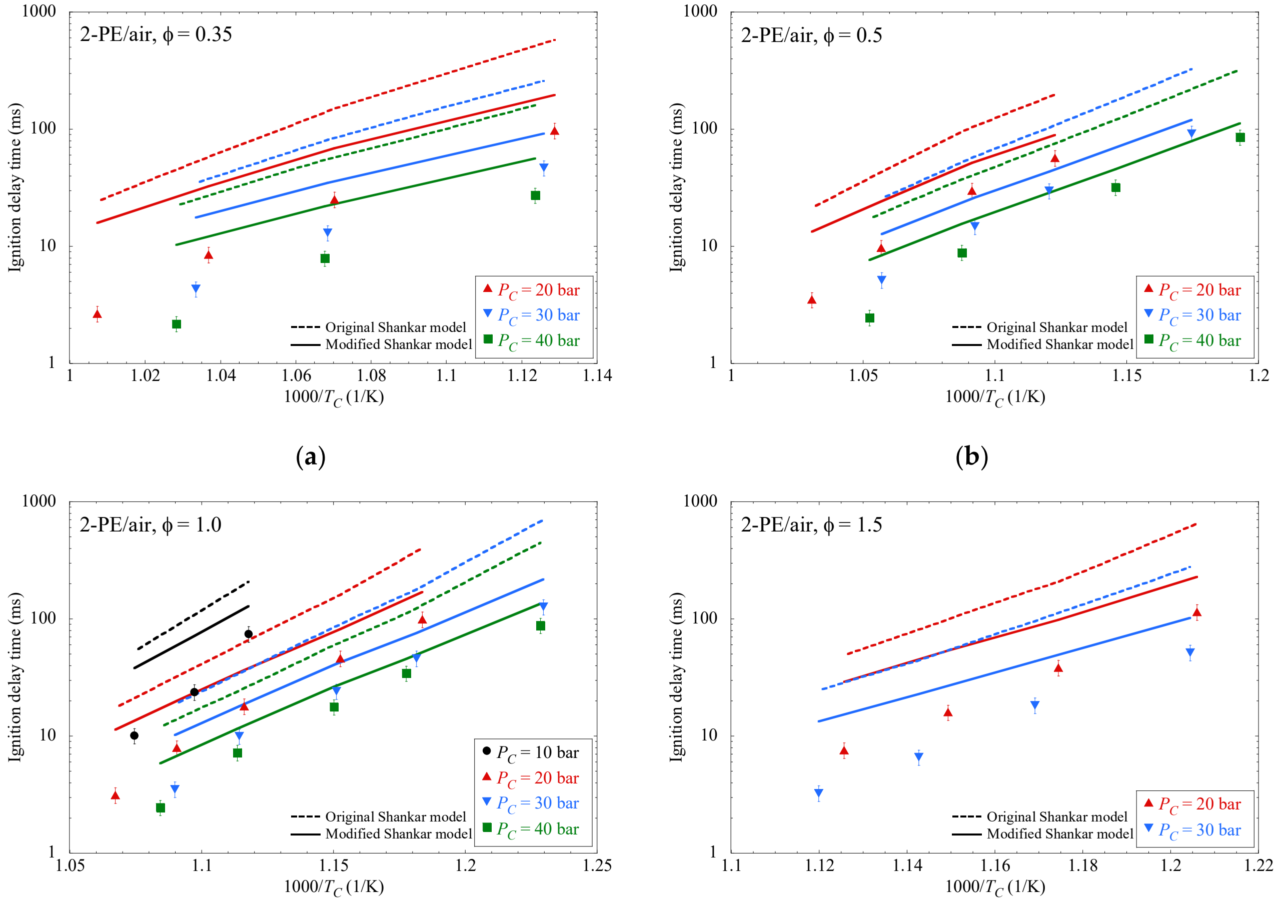


Figure 4. Reaction schematic of 2-PE autoignition proposed by Shankar et al. [10] (black arrow) and the newly added reactions (species) considered in the current investigation that are marked with green arrows (shadows).

3.3. RCM Ignition Delay Times of 2-PE/Air Mixtures

Figure 5 compares the experimental τ obtained in this study at varying T_C, P_C, and ϕ. It is seen that τ monotonically decreases with increasing T_C at all test conditions. Meanwhile, no negative temperature coefficient response is observed in the experiments and 2-PE only exhibits single-stage ignition behavior at all test conditions. The pressure effect on 2-PE autoignition is demonstrated in Figure 5 by varying P_C at a given equivalence ratio, showing that increasing pressure monotonically reduces τ at all equivalence ratios investigated. For the stoichiometric condition shown in Figure 5c, although increasing P_C from 10 bar to 20 bar leads to a large τ reduction, increasing P_C from 30 bar to 40 bar only exhibits a very small τ reduction. At the fuel-lean conditions, while the ϕ = 0.5 case (Figure 5b) shows a somewhat similar pressure effect as the stoichiometric case, the extent of the pressure effect for the ϕ = 0.35 case is seen to remain unchanged with increasing P_C. For the two pressures tested at the fuel-rich condition (ϕ = 1.5), Figure 5d illustrates that the τ variation with T_C between P_C = 20 bar and 30 bar changes minimally over the temperature range investigated here.

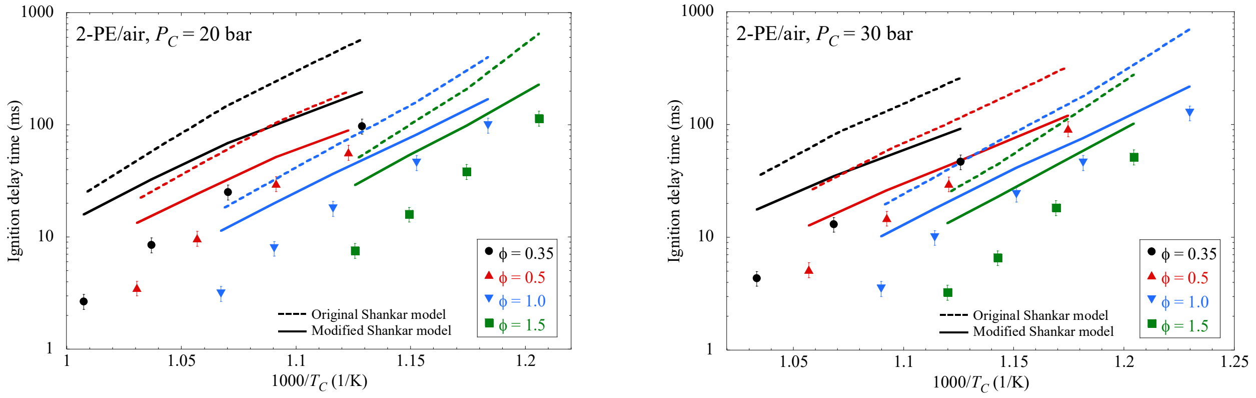
In addition to the pressure effect, the equivalence ratio effect is evaluated by varying ϕ at a given P_C. As shown in Table 1, the mole fraction of O_2 in the reactive mixture remains similar when varying ϕ from 0.35 to 1.5. Therefore, the present equivalence ratio effect represents the effect of fuel loading. In Figure 6, the experimental results show that increasing ϕ monotonically reduces τ at all P_C investigated. It is also seen from Figure 6 that the extent of the equivalence ratio effect seems to be insensitive to the T_C variation for a given P_C.



(**a**) (**b**)

(**c**) (**d**)

Figure 5. Experimental and simulated τ comparison for 2-PE/air mixtures at varying P_C and (**a**) ϕ = 0.35, (**b**) ϕ = 0.5, (**c**) ϕ = 1.0, and (**d**) ϕ = 1.5. Experimental results are shown as symbols. Simulated results are displayed as lines. Solid lines: modified Shankar model. Dashed lines: original Shankar model [10].



(**a**) (**b**)

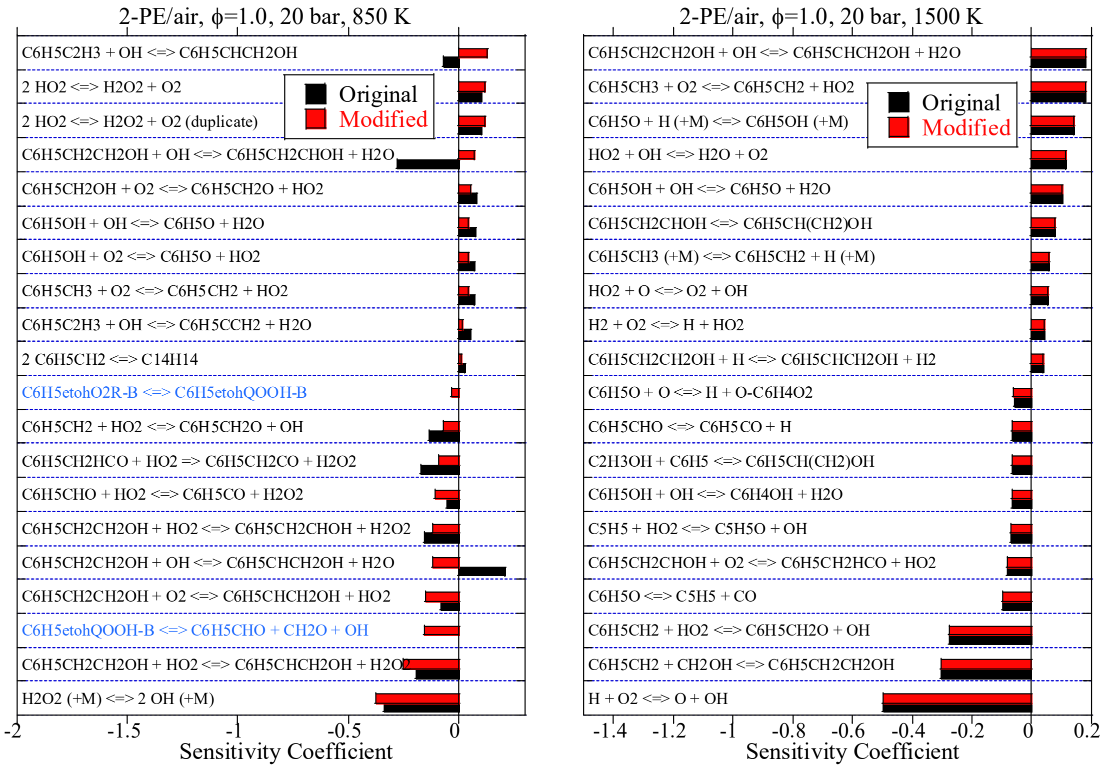
Figure 6. Experimental and simulated τ comparison for 2-PE/air mixtures at varying ϕ and (**a**) P_C = 20 bar and (**b**) P_C = 30 bar. Experimental results are shown as symbols. Simulated results are displayed as lines. Solid lines: modified Shankar model. Dashed lines: original Shankar model [10].

Using RCM simulations, the performance of both the original model of [10] and the modified model is assessed by comparing the simulated τ with RCM data. It is seen from Figures 5 and 6 that the original model (dashed lines) significantly overpredicts τ at all conditions typically in a factor of ~5, while the modified model (solid lines) agrees better with experimental results than the original model does at all tested conditions, with overprediction of τ typically in a factor of ~2. This suggests that adding the β site O_2-addition pathway alone in the 2-PE model of [10] greatly improves the model performance at low-to-intermediate temperatures as expected. Furthermore, both the original and modified models well capture the τ dependences on pressure and ϕ. Furthermore, note that both the original and modified models show gentler slopes on the Arrhenius plots than the experimental trends, especially at fuel-lean conditions as shown in Figure 5a,b. This is an important aspect to be improved in the future modeling effort of 2-PE autoignition by including all other pathways that are essential under low-temperature combustion conditions. In addition, although the modified model demonstrates better agreement with the RCM data compared to the original model, the discrepancies between the modified model and experiments are still large (a factor of 2), and hence further experimental and chemical kinetic modeling investigations are warranted.

3.4. Chemical Kinetic Analyses

To investigate the controlling chemistry of the original and modified models, brute force sensitivity analyses are further conducted for the stoichiometric 2-PE/air mixture to identify and compare the key reactions at two different initial temperatures of 850 K and 1500 K. As shown in Figure 7 for an initial pressure of 20 bar, the top ten promoting and retarding reactions in each model are listed. The original model of [10] is examined first. At 850 K, Figure 7a shows that the fuel H-abstraction reaction via $\dot{O}H$ radical forming an α-$\dot{R}$ radical exhibits a promoting effect while its β site counterpart displays an inhibiting effect. This is because the β-$\dot{R}$ radicals in the original model mostly produce styrene, which is a “stable” species and will accumulate during the induction period. As the major destruction of styrene only occurs near hot ignition, the styrene produced during the induction period has no contribution to the growth of the radical pool, thereby leading to an inhibiting effect. By contrast, the α site pathway can route to the formation of $C_6H_5\dot{C}H_2$, which can facilitate its subsequent chain-branching pathways in the toluene sub-model. Thus, the α site H-abstraction reaction via $\dot{O}H$ radical in the original model exhibits a promoting effect.

In the modified model, however, the trend is reversed as seen in Figure 7a. The fuel H-abstraction reaction via $\dot{O}H$ radical that forms an α-$\dot{R}$ radical exhibits an inhibiting effect while its β site counterpart displays a promoting effect. This is because the newly added β site O_2-addition pathway not only can bypass the styrene formation but also can link to the $C_6H_5\dot{C}H_2$ chemistry, as shown in Figure 4. The inclusion of the O_2-addition pathway of β-$\dot{R}$ radical shifts the overall effect of the β-$\dot{R}$ radical formation reaction to promoting. As a result of the competition over fuel molecules, the overall effect of the α-$\dot{R}$ radical formation reaction shifts towards inhibiting. In addition, the two newly added reactions mark in blue in Figure 7a demonstrate their high impact on 2-PE autoignition at 850 K. The unimolecular decomposition reaction of C_6H_5etohQOOH-B $\rightleftarrows$ $C_6H_5CHO + CH_2O + OH$ exhibits a strong promotion effect due to its ability to produces $\dot{O}H$. The intramolecular H-abstraction reaction of C_6H_5etohO_2R-B $\rightleftarrows$ C_6H_5etohQOOH-B also displays a promoting effect. Due to the high activation energy of this intramolecular H-abstraction reaction, it is the controlling reaction in this channel.

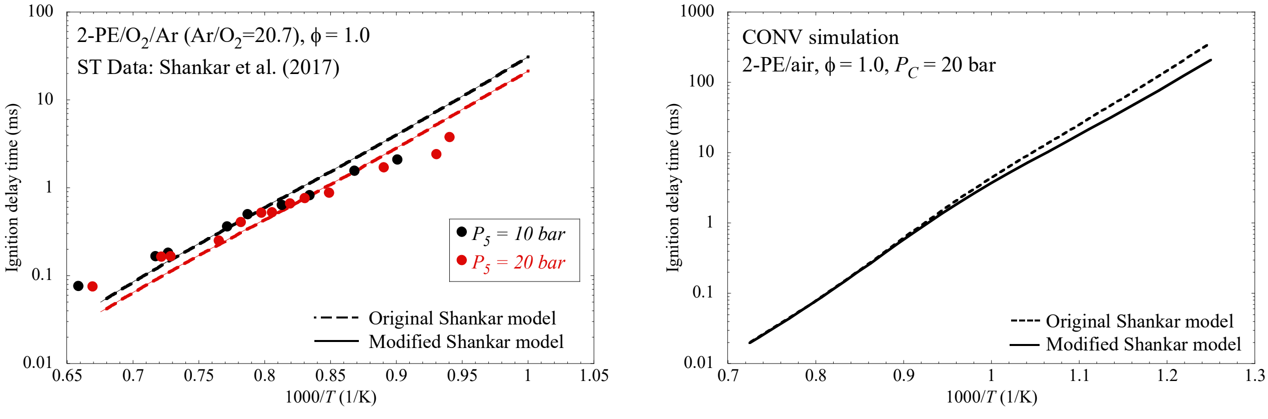


(**a**) (**b**)

Figure 7. Brute force sensitivity coefficients of τ in the original and modified models for stoichiometric 2-PE in air based on CONV simulations at initial pressure of 20 bar and initial temperatures of (**a**) 850 K and (**b**) 1500 K. In panel (**a**), the newly added reactions in the modified model are marked in blue.

At 1500 K, it is seen from Figure 7b that both the original and modified models show identical sensitivity coefficient trends, indicating the diminishing role of the newly added O_2-addition pathway of β-$\dot{R}$ radical at high temperatures. This is because the rate coefficient of the O_2-addition reaction reduces as temperature increases while those of the competing high temperature pathways (high activation energy) increase rapidly with increasing temperature. As such, the branching percent of 2-PE that enters the O_2-addition pathway on both α and β sites becomes negligible at 1500 K, thereby minimizing the impact of the O_2-addition pathways on the overall reactivity. This is also reflected in the sensitivity analysis shown in Figure 7b, as the O_2-addition reactions on the α and β sites are not in the top-10 list.

Figure 8a further compares the simulated results using the original and modified models with the ST data of [10]. It is found that the CONV-simulated τ values using the two models are identical and agree well with the experimental IDT data, showing that the inclusion of the O_2-addition pathway of β-$\dot{R}$ radical does not affect the model performance at high temperatures. Figure 8b presents the CONV-simulated τ using the original and modified models across different temperature regimes. The modified model is seen to be faster than the original model on the low temperature side. As temperature increases, the difference between the two models gradually reduces. Beyond 1100 K, the two models essentially yield the same results, which is consistent with the findings from the sensitivity analyses illustrated in Figure 7b. As the model-based analyses reasonably explain the discrepancies when validating the original and modified models against the RCM/ST IDT data, it is concluded that the inclusion of the β site O_2-addition pathway is needed to improve the comprehensiveness of the model of [10] for predicting the autoignition of 2-PE under low-temperature combustion conditions. It must be pointed out that although the inclusion of the β site O_2-addition pathway greatly improves the model performance at low-to-intermediate temperatures, a systematic construction of detailed low temperature reaction sets is required for rigorous model refinement and development. Obviously, low-temperature chemistry of 2-PE merits further experimental and computational investigations.



(**a**) (**b**)

Figure 8. (**a**) Comparison of experimental and CONV-simulated τ for stoichiometric 2-PE/O_2/Ar mixture at P_5 = 10 and 20 bar per the test conditions of [10]. (**b**) Comparison of CONV-simulated τ between the original and modified models over a wide range of temperatures. Experimental results are shown as symbols. Simulated results are displayed as lines. Solid lines: modified Shankar model. Dashed lines: original Shankar model [10].

4. Conclusions

The autoignition experiments of 2-phenylethanol (2-PE) in air are performed in this study using a rapid compression machine (RCM) at varying compressed temperatures (T_C), compressed pressures (P_C), and equivalence ratios (ϕ). Experimental results show that the total ignition delay time (τ) of 2-PE monotonically decreases with increasing T_C, P_C, and ϕ. Moreover, only single-stage ignition behavior is exhibited for the conditions investigated and there is no negative temperature coefficient response observed in the experiments. While the literature ST study [10] showed an insignificant pressure effect on τ at high temperatures, the present RCM results demonstrate stronger influences of pressure on τ at lower temperatures. Comparison of the RCM data acquired in this work and the literature shock tube (ST) data in [10] with the simulated results using the 2-PE model in [10] shows that the model in [10] well predicts the high-temperature ST data of [10], but greatly overpredicts the current RCM results at low-to-intermediate temperatures. This suggests the change in controlling chemistry of 2-PE autoignition at different temperature regimes.

To examine the discrepancy sources of the 2-PE model in [10] at low-to-intermediate temperatures, a modified 2-PE model is compiled by adding the β site O_2-addition pathway to the original model. While the modified model still overpredicts the current RCM data, it presents better agreement against experimental results than the original model does. This indicates that the inclusion of the β site O_2-addition pathway can potentially account for the discrepancies of the original model. Additionally, the modified model still well predicts the ST data of [10] and demonstrates identical performance at high temperatures compared to the original model. Sensitivity analyses using the original and modified models illustrate that the inclusion of the β site O_2-addition pathway shifts the overall effect of the β-$\dot{R}$ radical formation reaction from inhibiting to promoting. As the importance of the O_2-addition reactions greatly reduces with increasing temperature, the impact of the β site O_2-addition pathway diminishes at high temperatures. Therefore, the discrepancies between the model in [10] and the current RCM data can be partially attributed to the absence of the O_2-addition pathway of β-$\dot{R}$ radical in the original 2-PE model.

This RCM study provides validation datasets for model development/refinement and insights into the 2-PE autoignition chemistry at low-to-intermediate temperatures. The potential issues in the 2-PE model in [10] are also investigated and identified to offer guidance for future development of a comprehensive 2-PE kinetic model that includes detailed low temperature reactions for 2-PE autoignition.

Supplementary Materials: The following are available online at https://www.mdpi.com/article/10.3390/en14227708/s1, (1) Information of the added species/reactions in the modified 2-PE model (Added species_reactions.txt). (2) RCM experimental pressure traces and deduced time-volume histories for RCM simulations.

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Data Availability Statement: RCM experimental pressure traces and deduced time-volume histories for RCM simulations are available from the website of the Combustion Diagnostics Laboratory at the University of Connecticut https://combdiaglab.engr.uconn.edu/database/rcm-database (accessed on 15 November 2021).

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Nomenclature

2-PE	2-phenylethanol
CA50	crank angle at 50% burn
CONV	constant volume
EOC	end of compression
IDT	ignition delay time
k	reaction rate coefficient
P_C	pressure at the end of compression
P_0	initial pressure
RCM	rapid compression machine
RON	research octane number
S	octane sensitivity
SI	spark ignition
ST	shock tube
S_τ	sensitivity coefficient for total ignition delay time
T_C	temperature at the end of compression
T_0	initial temperature
ϕ	equivalence ratio
γ	specific heat ratio
τ	total ignition delay time

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