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2 **at Elevated Pressures and Low-to-Intermediate Temperatures**

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4 Goutham Kukkadapu, Bryan W. Weber, Chih-Jen Sung

5
6 Department of Mechanical Engineering
7 University of Connecticut, Storrs, CT 06269

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16 Corresponding Author:
17 Chih-Jen Sung
18 Department of Mechanical Engineering
19 University of Connecticut
20 191 Auditorium Road
21 Storrs, CT 06269-3139, USA
22 E-Mail: cjsung@engr.uconn.edu
23 Phone: (860) 486-3679
24 Fax: (860) 486-5088

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31 **Autoignition Study of Tetralin in a Rapid Compression Machine**
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34 Department of Mechanical Engineering, University of Connecticut, Storrs, CT, 06269
35

36 **Abstract**

37 Tetralin (1,2,3,4-tetrahydronaphthalene) is a naphtheno-aromatic compound found in diesel fuels
38 and a candidate component widely used in diesel surrogates. The fundamental understanding of
39 the autoignition characteristics of tetralin is meager due to the lack of experimental and
40 computational studies in the literature. Considering this, an experimental study using a rapid
41 compression machine (RCM) has been conducted to investigate the ignition characteristics of
42 tetralin at varying pressures from 15 bar to 50 bar, temperatures between 763 K and 950 K, and
43 equivalence ratios of $\phi=0.5$ and 1. The effect of dilution on ignition delay times was also studied
44 by varying the initial concentrations of oxygen and tetralin independently. Furthermore, the test
45 conditions investigated in the current study were designed to provide ignition delay
46 measurements complementary to the literature data. A comparison of the ignition delays
47 measured from the current study with those existing in the literature demonstrated consistent
48 trends and good agreement. Examination of the RCM pressure histories showed that while
49 tetralin does not exhibit two-stage ignition behavior, some evidence of pre-ignition heat release
50 was noticed at the low temperature conditions investigated in the study. Further comparison with
51 experimentally measured ignition delays of *n*-butylbenzene was conducted to demonstrate the
52 effect of molecular structure on the autoignition properties. Chemical kinetic simulations carried
53 out to assess the performance of an available kinetic model showed this model to be significantly
54 less reactive than the experiments. Brute force sensitivity analyses and reaction path analyses
55 were further conducted at varying pressures, temperatures, and equivalence ratios to identify the
56 controlling chemistry. Possible reasons for the poor performance of this chemical kinetic model
57 in predicting the experimental ignition delays have been discussed based on experimental results
58 and chemical kinetic analyses from the current study.

1. Introduction

1,2,3,4-tetrahydronaphthalene, commonly known as tetralin, is a naphtheno-aromatic hydrocarbon found in diesel fuels. As such, tetralin has been proposed as a constituent in simplified fuel blends, known as surrogate fuels [1], designed to emulate the properties of real diesel fuel. Typically, a model describing the chemical kinetics of a real fuel is generated by hierarchically merging the chemical kinetic models of each of the constituents of the surrogate for the target real fuel. Therefore, it is necessary to develop high fidelity chemical kinetic models for each of the surrogate constituents. The chemical kinetic models developed to describe the combustion chemistry of the surrogates need to be validated against fundamental experimental data such as ignition delays from rapid compression machines (RCMs) and shock tubes, species measurements from jet stirred reactors (JSRs) and flow reactors, and laminar flame speed measurements. To date, very few studies [2–4] have focused on studying the fundamental combustion characteristics of tetralin. Yang and Boehman [2] studied ignition characteristics of tetralin in a CFR engine and compared the ignition propensity of tetralin with those of methylcyclopentane and decalin. Yang and Boehman [2] also conducted a detailed product analysis to understand the important reaction pathways of tetralin oxidation. From the product analysis, Yang and Boehman [2] concluded that tetralin does not exhibit low temperature chemistry and that the oxidation of tetralin is dominated by dehydrogenation reactions leading to formation of dialin and naphthalene. Wang *et al.* [3] measured ignition delays of tetralin/air mixtures using a shock tube at equivalence ratios of $\phi=0.5$ and 1, and at pressures of 13 bar and near 38 bar for temperatures between 978 K and 1277 K. Dagaut *et al.* [4] studied the oxidation characteristics of diluted tetralin/oxidizer mixtures in a JSR, with the initial concentration of

tetralin at 1000 ppm, in the temperature range of 800 K to 1400 K, at varying pressures between 1 atm and 10 atm, and over a range of equivalence ratios between 0.5 and 1.5.

In addition to the oxidation studies, the pyrolysis of tetralin has been studied by several researchers [5–9]. Tsang and Cui [5] studied pyrolysis of tetralin in a shock tube in the temperature range of 1000 K to 1400 K by measuring concentrations of products formed due to unimolecular decomposition and hydrogen atom induced decomposition. Using the concentrations of the pyrolysis products, Tsang and Cui [5] determined rate constants of several decomposition reactions and reactions of tetralin with hydrogen radical. Yu and Eser [6] studied the pyrolysis chemistry of tetralin and decalin at near-critical and supercritical conditions. For the conditions investigated in their study, Yu and Eser [6] found 1-methylindan and naphthalene to be the dominant products with the yield of the former being always greater than the latter. Stewart *et al.* [7] studied supercritical pyrolysis of tetralin in a specially constructed flow reactor at varying pressures between 0.2 MPa and 10 MPa and varying temperatures between 700 K and 810 K. Stewart *et al.* [7] observed 1-methylindan, naphthalene, and *n*-butylbenzene to be the major products of supercritical pyrolysis of tetralin. Li *et al.* [8] studied pyrolysis of tetralin using a flow reactor at low pressures of 30 Torr and at varying temperatures from 850 K to 1500 K. Pyrolysis products were identified using synchrotron vacuum ultraviolet photoionization mass spectrometry, and Li *et al.* [8] concluded that tetralin pyrolysis is dominated by unimolecular decomposition and H-abstraction reactions at low pressures. Li *et al.* [8] also developed a kinetic model consisting of 149 species and 554 reactions that describes the pyrolysis chemistry of tetralin. Zámotný *et al.* [9] studied pyrolysis of tetralin along with fifty-five other hydrocarbon molecules at a temperature of 810 °C, pressure of 400 kPa, and residence times of 0.2 s to 0.4 s.

Napthalene was found to be the major product from pyrolysis of tetralin for the conditions investigated by Zámotný *et al.* [9].

Only one model describing the oxidation kinetics of tetralin has been presented in the literature to our knowledge. In the work of Dagaut *et al.* [4], their chemical kinetic model was found to predict the ignition delays from the shock tube work of Wang *et al.* [3], the speciation measurements from the JSR work of Dagaut *et al.* [4], and the pyrolysis data of Li *et al.* [8] and Zámotný *et al.* [9] to a reasonable agreement.

The objective of the current study is to investigate the autoignition characteristics of tetralin at low-to-intermediate temperatures and elevated pressures using an RCM. These engine-relevant conditions have not been extensively studied in the literature. Further, the high quality experimental data from the RCM will be compared with the simulated results using the chemical kinetic model from the work of Dagaut *et al.* [4]. In addition, several chemical kinetic analyses of the model will be conducted to elucidate the underlying mechanics of the autoignition delay predictions under the conditions of the present experiments. In the following, we will sequentially detail the experimental specification, test conditions, experimental results, model performance assessment, and chemical kinetic analyses and discussion.

2. Experimental facility

2.1 Experimental procedure

The RCM at the University of Connecticut has been described extensively by Das *et al.* [10]. It employs a creviced piston to compress test mixtures to elevated pressures and temperatures. The creviced piston was specially designed following the work of Mittal and Sung [11] to effectively suppress the effects of roll-up vortex and ensure that an adiabatic core region of gas is maintained throughout the experimental duration. Moreover, Das *et al.* [12] and Uddi *et al.* [13]

have shown that the temperature distribution of the core region is adequately homogeneous prior to hot ignition. The piston is driven pneumatically and brought to rest by a hydraulic pin-groove mechanism towards the end of the compression stroke. While the typical compression times are around 30 ms to 45 ms, the majority (> 50 %) of pressure/temperature rise occurs in the last 6 ms of compression, as shown in Fig. 1. A trigger from LabView[®] initiates the compression event and starts data acquisition. Dynamic pressure in the reaction cylinder is measured using a thermal-shock resistant Kistler 6125C transducer in conjunction with a 5010B charge amplifier. A test gas mixture can be compressed to the desired test condition at the end of compression, represented by compressed pressure (P_C) and compressed temperature (T_C), by independently varying the geometric compression ratio, intake pressure (P_0), and intake temperature (T_0). Geometric compression ratios varying between 7 and 17 can be attained by varying the piston stroke length and/or the end of compression (EOC) clearance length. Moreover, the compressed temperature is deduced from the measured pressure trace by applying the adiabatic core hypothesis and the assumption of isentropic compression: $\int_{T_0}^{T_C} \frac{\gamma}{\gamma-1} \frac{dT}{T} = \ln \left(\frac{P_C}{P_0} \right)$, where γ is the specific heat ratio of the test mixture and is a function of temperature.

Prior to the start of an experiment, the reaction chamber is filled to the desired intake pressure with a homogenous fuel/oxidizer mixture prepared in a separate stainless steel mixing chamber. The mixing chamber, the RCM reaction chamber, and all connecting manifolds are equipped with heaters to preheat the mixture uniformly to the desired intake temperature. In the current study, tetralin (99% purity), supplied by Sigma Aldrich, and ultra-high purity (>99.99%) O₂ and N₂ from Airgas were used to prepare homogenous tetralin/oxidizer mixtures in the mixing chamber. Tetralin was injected into the mixing chamber on a gravimetric basis using a syringe. The mass of tetralin injected into the mixing chamber was measured using an electronic

mass balance with a least count of 0.01 gm. The oxidizer used in these experiments was a mixture of O_2 and N_2 in varying proportions. Oxidizer mixtures were prepared by filling the mixing chamber with constituent gases to the corresponding partial pressures manometrically. The mixing chamber, intake manifold, and reaction cylinder were heated to the desired preheat temperature for about four hours before starting the experiments. Additionally, the mixing chamber is equipped with a magnetic stirrer that aids in preparation of homogeneous mixtures.

Figure 1 shows the definition of ignition delay used for reporting the present data. The ignition delay is defined as the time difference between the EOC and the maximum of the time derivative of the pressure trace after EOC. Figure 2 demonstrates the typical experimental repeatability of the data reported in the current study. A minimum of five consecutive runs are conducted at each condition and the value closest to the mean of the measured ignition delays is reported as the representative value. The scatter in ignition delays is less than 10% of the representative value for all the cases investigated. Furthermore, to ensure repeatability, ignition delay data obtained from each fresh mixture is checked against that from an earlier mixture.

After the EOC, the piston is locked in place and the reactions proceed in a constant volume chamber. Examination of the pressure traces in Figs. 1 and 2 shows that the pressure after the EOC decreases due to energy transferred from the hot reactant gases to the colder reactor walls. In order to estimate the effect of this heat loss on ignition delay, nonreactive experiments corresponding to each reactive run need to be conducted. In these nonreactive experiments, tetralin/ N_2 mixtures were prepared by replacing O_2 with N_2 in the corresponding reactive mixtures while maintaining the same fuel concentrations. This ensures that a similar specific heat ratio of the mixture is maintained and similar heat transfer conditions exist between the reactive case and the nonreactive counterpart. The measured pressure traces from the nonreactive experiments were further used to generate volume time histories during and after compression in

conjunction with the adiabatic core hypothesis and the assumption of isentropic compression/expansion. These volume histories were then imposed on autoignition simulations to characterize the effects of the compression stroke and the heat loss over the experimental duration prior to ignition. The measured pressure traces from the reactive experiments and the corresponding volume histories needed for RCM simulations are available on our website at <http://combdialab.engr.uconn.edu/database/rcm-database>.

2.2 Test conditions

Table 1 summarizes the test conditions investigated in the current study. The test conditions were designed to study the effects of pressure, equivalence ratio, fuel loading, and dilution on the autoignition of tetralin. In addition, experiments conducted in “air” ($O_2:N_2=1:3.76$ by mole) were designed to provide ignition delay data that will complement the existing shock tube data of Wang *et al.* [3].

Further, the initial temperatures used to conduct experiments were chosen to ensure that the fuel injected into the mixture preparation chamber is completely vaporized. The saturated vapor pressures of tetralin at preheat temperatures of $T_0=380$ K, 400 K, and 420 K are 35 Torr, 73 Torr, and 145 Torr, respectively. As such, the maximum partial pressures of vaporized tetralin in the mixtures were kept at 22 Torr for $T_0=380$ K and 400 K and 45 Torr for $T_0=420$ K. The margin of safety between the partial pressure of tetralin and its saturation pressure ensures that no fuel condensation occurs in any of the experiments.

3. Experimental results

3.1 Pressure measurements

Examination of the pressure traces from the experiments shows that tetralin does not exhibit two-stage ignition behavior for any of the conditions investigated in this study. This is depicted for three representative conditions in Fig. 3. In addition, Fig. 4 shows a comparison between selected

cases from Fig. 3a, and includes the nonreactive pressure traces corresponding to the two reactive experiments shown. Note that the pressure trace corresponding to the compressed temperature $T_C=802$ K (the red lines) has been offset by +5 bar for clarity in Fig. 4. Comparison of the reactive and nonreactive pressure traces illustrates some evidence of pre-ignition heat release. Since tetralin does not undergo two-stage ignition under the conditions investigated in this study, the term “pre-ignition heat release” is used. It can also be seen from Fig. 4 that the extent of pre-ignition heat release is higher at lower temperature, as indicated by the larger deviation of the reactive pressure trace from the nonreactive pressure trace at $T_C=763$ K.

The larger extent of pre-ignition heat release at low temperatures as shown in Fig. 4 could be because of weak low temperature reactivity of tetralin. Earlier experiments in a CFR engine conducted by Yang and Boehman [2] found that tetralin did not exhibit any pre-ignition heat release in the temperature range of 800–1000 K. In addition to different temperature ranges, this discrepancy in observations could be because the equivalence ratios, compressed pressures, and chemical induction times investigated in the current study are considerably higher than those from Yang and Boehman [2]. It is noted that Yang and Boehman [2] used lean tetralin/air mixtures at a fixed equivalence ratio of $\phi=0.25$ for their investigation and the compressed pressures tested therein were less than 25 bar. On the other hand, the current study considers conditions up to 50 bar and the stoichiometric equivalence ratio (c.f., Table 1), as well as includes temperatures lower than 800 K.

3.2 Ignition delay measurements

Figure 5 shows Arrhenius plots of the ignition delays measured in this study. Also shown on Fig. 5 are error bars for the ignition delay and the compressed temperature. The error bars for the ignition delay represent an uncertainty of $\pm 10\%$ of the ignition delay, corresponding to the

maximum variation in the various experiments at a given condition. The error bars for the compressed temperature were estimated using the detailed uncertainty analysis method of Weber *et al.* [14]. In this study, we used the Monte Carlo method detailed by Weber *et al.* [14] and considered the uncertainty in measurements of the initial pressure, compressed pressure, initial temperature, ambient temperature, mixing tank volume, injected fuel mass, and proportions of oxygen and nitrogen. From this analysis, the error in T_C was estimated to be less than $\pm 0.5\%$ of the deduced compressed temperature of a given experiment, and hence error bars of $\pm 0.5\%$ are drawn for the inverse temperatures ($1000/T_C$) in Fig. 5. For clarity, only the first and last points have error bars; error bars for the other points have substantially similar sizes.

In Fig. 5, it can be observed that the ignition delays decrease monotonically with compressed temperature and compressed pressure for all of the conditions in this study. The monotonic decrease of ignition delay with compressed temperature indicates that there is no negative temperature coefficient (NTC) region of the ignition delays in the present experiments. This is another reason why we prefer the term “pre-ignition heat release” for the behavior discussed in conjunction with Fig. 4. It appears that the low temperature chemistry of tetralin is not strong enough to generate a two-stage ignition response or an NTC behavior, although it does generate noticeable heat release prior to hot ignition. The weak low temperature reactivity of tetralin could be because of its structural characteristics, particularly the presence of an alkyl ring and an aromatic ring. The chain initiation reactions on the cycloalkyl ring lead to the formation of conjugated alkenes, reducing the importance of the typical low temperature pathways [2,4]. However, it should be noted that the dominant reactions leading to the formation of conjugated alkenes does not necessarily eliminate the propagation of the reactants through the low temperature pathways during the oxidation of tetralin. In particular, at high pressures and low

temperatures, such as those investigated in the current study, the low temperature pathways may compete with reactions generating conjugated alkenes, leading to the weak low temperature reactivity observed in the present experiments. Thus, the radical pool generated by the low temperature pathways can accelerate ignition, even for conditions at which only weak exothermicity is observed.

In addition, in Figs. 5a and 5b it can be observed that the ignition delay decreases monotonically with increase in equivalence ratio for tetralin/oxidizer mixtures under the conditions studied in the present work. Figure 5a shows mixtures of tetralin in air, for which the initial fuel mole fraction changes by -50% from $\phi=1.0$ to $\phi=0.5$, while the initial oxygen mole fraction changes by only $+1\%$ for the same conditions. In Fig. 5b, the initial oxygen molar percentage is fixed at 10.42% , while the initial fuel mole fraction changes by -50% from $\phi=1.0$ to $\phi=0.5$. Thus, Figs. 5a and 5b indicate the effect of changing initial fuel mole fraction on the ignition delay and in both cases, increasing the initial fuel concentration (i.e., increasing the equivalence ratio) decreases the ignition delay. Figure 5c shows the effect of varying initial oxygen mole fraction at a fixed initial fuel mole fraction. In this case, lower equivalence ratios with higher initial oxygen mole fraction by keeping initial fuel mole fraction constant result in shorter ignition delays. This result is consistent with other works in the RCM, including studies on *n*-decane [15], jet fuels [16], and *n*-butanol [17].

3.3 Comparison of ignition delays of tetralin and *n*-butylbenzene

Figure 6 shows the comparison of ignition delays of tetralin obtained from the current study and *n*-butylbenzene available in the literature [18,19]. This comparison of the ignition delays provides insights into the understanding of fuel structure effect on ignition propensities and fuel chemistry, as tetralin and *n*-butylbenzene have the same number of carbon atoms. *n*-

Butylbenzene has an aliphatic C₄ chain attached to a phenyl ring while the C₄ chain in tetralin forms the bulk of the second ring attached to the phenyl. The structures of *n*-butylbenzene and tetralin are shown and compared in Fig. 7.

It is observed in Fig. 6 that tetralin is less reactive than *n*-butylbenzene. The differences in reactivity could be explained by the relative importance of low-temperature chain-branching reactions over the chain-propagating or chain-terminating reactions. In particular, the C₄ aliphatic chain in *n*-butylbenzene facilitates low-temperature chain-branching reactions while the cyclic structure in tetralin favors formation of conjugated alkenes. These reactions are shown schematically in Fig. 7 for each of the two fuels. The conjugated olefin producing pathways dominate for tetralin, and hence the low-temperature reactivity of tetralin is reduced as compared to that of *n*-butylbenzene. As further evidence of this point, Husson *et al.* [19] noted first-stage ignition in their $\phi=0.5$ experiments for *n*-butylbenzene, while no first-stage ignition occurred for tetralin in the present experiments. Regarding the reaction pathways of *n*-butylbenzene, the interested reader is referred to the study of Husson *et al.* [19].

4. Chemical kinetic analyses

4.1 Ignition delay simulations

To the best of our knowledge, the semi-detailed chemical kinetic model developed by Dagaut *et al.* [4] is the only reaction mechanism which describes the oxidation of tetralin. This reaction mechanism has been made on a hierarchical model and the oxidation of tetralin involves 30 major reaction types [4]. As mentioned previously, this mechanism has been shown to have good performance in predicting the speciation data from a JSR [4] and ignition delays from a shock tube [3].

Two types of simulations were conducted using the mechanism of Dagaut *et al.* [4]. The first is a simulation that reproduces the compression stroke and post compression heat transfer processes inherent to RCM experiments. These are known as VPRO simulations, after the CHEMKIN-Pro [20] keyword utilized to perform such simulations. In this VPRO simulation, the compression stroke and post-compression heat transfer are modeled as an isentropic compression and expansion of the reaction chamber, respectively. To effect this process, the volume time history derived from the nonreactive pressure trace is applied to a closed homogeneous batch reactor in CHEMKIN-Pro v 15131 [20] and an IdealGasReactor in Cantera v2.2.0 software [21]. Both software packages provide identical results. This method faithfully reproduces the thermodynamic conditions present in the reaction chamber, provided that the experiments are conducted under conditions for which the adiabatic core hypothesis holds, as demonstrated by Das *et al.* [12].

The second method of simulation is a constant volume, adiabatic reactor initialized to the pressure and temperature conditions at the EOC (i.e., P_C and T_C), referred to as CONV simulations. This type of simulation is conducted using the Cantera v 2.2.0 software [21]. The point of ignition in both VPRO and CONV simulations is defined as the time when the derivative of the simulated pressure reaches a global maximum.

A comparison of these two simulation methods is shown in Fig. 8. For the case shown in Fig. 8a, ignition was not observed in the VPRO simulation during the experimental duration and the ignition delay from the CONV simulation was about a factor of four greater than that from the experiment. For the case shown in Fig. 8b, the ignition delay for the VPRO simulation was about a factor of five higher than the experimental value while the value from the CONV simulation was about a factor of four times greater than the experimental value.

Figure 9 shows the comparison of the ignition delays from experiments and VPRO simulations for the diluted conditions. It is noted that some of the VPRO simulations did not ignite within the computational duration (300 ms); simulated results for these cases are not shown on Figure 9. The simulated ignition delays are seen to be consistently greater than those from experiments showing that this mechanism is significantly less reactive than experiments.

Figure 10 shows a comparison of the ignition delays measured in this study with the ignition delays from the study of Wang *et al.* [3] in a shock tube, as well as a comparison of both experiments with the predictions from the CONV simulations. CONV simulations are used for this comparison to have a consistent simulation method across the entire temperature range. Wang *et al.* [3] conducted their experiments at nominal pressures of 13 bar and near 38 bar. For the experimental data comparison shown in Fig. 10, the ignition delays from Wang *et al.* [3] were scaled to the current compressed pressures using the scaling factors suggested therein. It can be seen that the current RCM measurements at low-to-intermediate temperatures complement well with the literature shock tube data at high temperatures.

By comparing the model with the RCM experiments on the right of Figs. 10a and 10b, it is seen that the model over-predicts the ignition delay uniformly at both the equivalence ratios investigated in the current study, and the pressure dependence of the ignition delays at low temperatures is not well captured by the model. It is also noted that the mechanism performs relatively better at low pressures and low equivalence ratios. The discrepancy between experiments and simulations is likely due to the lack of detailed description of the low-to-intermediate temperature chemistry, which is known to be promoted by increase in equivalence ratio and pressure. Hence, the differences in experimental and simulated ignition delays are

expected to be more severe at higher pressures and higher equivalence ratios, and less severe at lower pressures and lower equivalence ratios.

Figures 10a and 10b also show the performance of the mechanism in estimating the ignition delays at conditions investigated by Wang *et al.* [3]. As noted by Wang *et al.* [3], for the conditions investigated in their study the mechanism of Dagaut *et al.* [4] performed relatively better at high pressures, in opposition to the findings of the present study targeting at low-to-intermediate temperatures. The reason for this characteristic difference in the performance of the mechanism with pressure is currently unclear.

4.2 Reaction path analysis

Integrated reaction pathway analysis was conducted to understand the important oxidation reactions of tetralin predicted by the reaction mechanism of Dagaut *et al.* [4]. This analysis helps in identifying the relative contributions of various reactions in production or consumption of species for the current experimental conditions. Analysis was conducted using the CONV simulation for an initial pressure of 35 bar and an initial temperature of 835 K, at an equivalence of $\phi=0.5$ in air. Moreover, analysis was conducted from the initial condition to the point of 10% fuel conversion. The 10% fuel conversion point was chosen to identify controlling chemistry during the chemical induction time and also because the point of 10% fuel conversion is isolated from thermal runaway.

Figure 11 shows the results of the integrated reaction path analysis. H-abstraction reactions from the alkyl chain of tetralin by O, OH, and HO₂ lead to the formation of tetralyl radical. It should be noted that the mechanism of Dagaut *et al.* [4] lumps the two possible tetralyl radicals into a single molecule called RTETRALIN. Reactions of RTETRALIN with oxygen (O₂) consume nearly all (>99.7%) of the tetralyl radicals. About 8% of tetralyl radical reacts with O₂

leading to the formation of carbon monoxide (CO), phenyl radical (C₆H₅), hydrogen (H₂), and ethylene (C₂H₄) as shown in (R1): $\text{RTETRALIN} + \text{O}_2 \rightarrow 2\text{CO} + \text{C}_6\text{H}_5 + \text{H}_2 + \text{C}_2\text{H}_4$.

The phenyl radical produced from (R1) is consumed entirely by reactions with oxygen (O₂). Reactions of phenyl radical with oxygen result in formation of highly reactive O radical as shown by (R2): $\text{C}_6\text{H}_5 + \text{O}_2 \rightarrow \text{C}_6\text{H}_5\text{O} + \text{O}$. About 87% of tetralyl radical reacts with oxygen to form tetralyl peroxy (denoted as RTETRAOO) as shown in (R3): $\text{RTETRALIN} + \text{O}_2 \rightarrow \text{RTETRAOO}$, which subsequently undergoes several dissociation reactions. The majority of the tetralyl peroxy, about 75%, dissociates to form dialin (C₁₀H₁₀) and hydroperoxyl radical (HO₂) as shown in (R4): $\text{RTETRAOO} \rightarrow \text{C}_{10}\text{H}_{10} + \text{HO}_2$. The next important consumption reaction path way of tetralyl peroxy is the dissociation reaction which leads to formation of formyl radical (HCO), benzaldehyde (C₆H₅CHO), and ethylene (C₂H₄) as shown in (R5): $\text{RTETRAOO} \rightarrow \text{C}_2\text{H}_4 + \text{HCO} + \text{C}_6\text{H}_5\text{CHO}$. A small amount (<1%, not shown in Fig. 11) of tetralyl peroxy dissociates to form benzofuran (denoted as BZFUR), ethylene (C₂H₄), and OH radical by (R6): $\text{RTETRAOO} \rightarrow \text{C}_2\text{H}_4 + \text{OH} + \text{BZFUR}$.

As discussed previously, most of the tetralyl peroxy reacts to form dialin by (R4). Dialin is highly unreactive at the current conditions and only small amounts of it are consumed by the following reactions, (R7): $\text{C}_{10}\text{H}_{10} + \text{OH} \rightarrow \text{H}_2\text{O} + \text{C}_{10}\text{H}_8 + \text{H}$, (R8): $\text{C}_{10}\text{H}_{10} + \text{OH} \rightarrow \text{C}_6\text{H}_4\text{CH}_3 + \text{C}_2\text{H}_3\text{CHO}$, and (R9): $\text{C}_{10}\text{H}_{10} + \text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{C}_6\text{H}_5\text{C}_2\text{H}_2$. Reaction path analysis shows that dialin is predominantly consumed by (R7). Reactions of dialin with hydroxyl (OH) radical, including (R7)–(R9), consume highly reactive OH radicals and produce relatively lesser reactive species. In addition, more than 16% of dialin consumption is via its reaction with HO₂, (R10): $\text{C}_{10}\text{H}_{10} + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{C}_{10}\text{H}_8 + \text{H}$, resulting in the formation of naphthalene (C₁₀H₈), H₂O₂, and H radical. While (R10) leads to the formation of H₂O₂, this reaction is not the most important contributor to H₂O₂ build-up.

For the temperatures currently investigated, the H radical produced from (R7) does not facilitate chain-branching reaction (R11): $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$, but instead undergoes (R12): $\text{H} + \text{O}_2(+\text{M}) \rightarrow \text{HO}_2(+\text{M})$ followed by (R13): $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ and (R14): $\text{H}_2\text{O}_2(+\text{M}) \rightarrow \text{OH} + \text{OH}(+\text{M})$ [22]. Thus, (R7) can be classified as chain propagating for the current conditions. As a consequence, the reactions of dialin tend to reduce the availability of OH for other reactions, such as H-abstraction from the fuel.

4.3 Brute force sensitivity analysis

Brute force sensitivity analyses have been carried out to identify the controlling chemistry at varying pressures, temperatures, and equivalence ratios. The pre-exponential factors of the reactions were separately multiplied by a factor of 5.0 and 0.2 one at a time and ignition delays with the modified reactions were computed from the CONV simulations. The sensitivity index representing the effect of change of the reaction rate coefficient on ignition delay (hence on reactivity) is defined as $\left(\ln \frac{\tau_{5.0}}{\tau_{0.2}}\right) / \left(\ln \frac{5.0}{0.2}\right)$, where $\tau_{0.2}$ and $\tau_{5.0}$ are the simulated ignition delays using the reaction rate multiplied by 0.2 and 5.0, respectively. A negative (positive) sensitivity index implies that increasing the reaction rate accelerates (decelerates) ignition resulting in a shorter (longer) ignition delay. Brute force sensitivity indices were calculated for the 129 core reactions which describe the oxidation of tetralin in the mechanism of Dagaut *et al.* [4]. These reactions represent all of the reactions of tetralin, tetralyl radical, tetralyl peroxy, and dialin, and are outlined as 30 reaction types in Table 1 in the work of Dagaut *et al.* [4]. We consider only these reactions because we are interested in investigating the effect of changes in the fuel chemistry; the chemistry of small radicals (e.g., H, OH, etc.) is known to be important to the low-to-intermediate temperature of hydrocarbons [22], so we do not consider it in this analysis.

The first set of sensitivity analyses was conducted to identify the controlling chemistry at several initial temperatures. Figure 12 shows the sensitivity indices for three initial temperatures (835 K, 1100 K, and 1500 K) at an initial pressure of 35 bar for $\phi=0.5$ mixtures of tetralin in air. The first two temperatures (835 K and 1100 K) are chosen because they are representative of the temperatures investigated in the current study and those from Wang *et al.* [3]; the final temperature of 1500 K is chosen as in the range where high-temperature reaction paths take over from the low-to-intermediate temperature pathways. Similar analysis was conducted at 15 bar and largely similar results were found.

Figure 12 shows the sensitivity indices of the 10 reactions with the highest sensitivity at 835 K. H-abstraction from tetralin by hydroperoxyl radical (HO_2) exhibits the highest sensitivity and has a negative sign, as it leads to build-up of hydrogen peroxide that controls ignition through (R13) and (R14). It is interesting that the competing reactions concerning oxygen reaction with RTETRALIN, (R1) and (R3), exhibit opposite sensitivity indices. Specifically, the breakdown of RTETRALIN, (R1), exhibits high negative sensitivity index (accelerating ignition) while the oxygen addition pathway, (R3), exhibits positive sensitivity index (decelerating ignition).

The integrated reaction path analysis shown in Fig. 11 helps in understanding the chemical kinetic reason for the observed results. The phenyl (C_6H_5) radical formed from (R1) participates in an exothermic reaction with oxygen molecule via (R2), leading to production of highly reactive oxygen atom (O). The O radical formed from (R2) abstracts hydrogen from the tetralin molecule leading to the formation of OH and tetralyl radicals. As such, the phenyl (C_6H_5) radical formed from (R1) initiates a chain-branching cycle and hence exhibits negative sensitivity (enhancing ignition).

On the other hand, the tetralyl peroxy produced from (R3), which competes with the reaction (R1), is predominantly consumed by the elimination reaction (R4) resulting in the formation of less reactive dialin and HO₂ radical. It should be noted that the dissociation reaction of tetralyl peroxy through (R4) exhibits a positive sensitivity index. The differences in reactivities of the products formed from (R1) and (R3) explain their contrasting sensitivity index signs. All the reactions of tetralyl peroxy which compete with the elimination reaction to form dialin, (R4), exhibit negative sensitivity. This can be explained on the basis that dialin, one of the products of (R4), acts as a radical scavenger (as discussed earlier) and products of the other competing dissociation reactions do not exhibit similar radical scavenging effect.

It is also of interest to note that, at 835 K and 1100 K, the reaction leading to formation of the tetralyl peroxy adduct, (R3), exhibits a positive sensitivity index while its reverse reaction (dissociation to tetralyl radical and O₂) exhibits a negative sensitivity index. These results are interesting as the reactions between fuel radicals and oxygen (O₂) leading to formation of the peroxy adduct are thought to accelerate the oxidation of hydrocarbons in the low-to-intermediate temperature range, including normal and branched alkanes [23,24], cycloalkanes [25,26], and unsaturated species [27]. This surprising result may be an artifact of the mechanism employed herein, arising due to the lack of comprehensive treatment of the low temperature reactions of tetralin oxidation. In particular, the mechanism considered here does not include any isomerization reactions of the tetralyl peroxy that are the typical entry point to the low-temperature chain branching processes. In addition, reaction (R3) has a small negative sensitivity at 1500 K and its reverse reaction has a small positive sensitivity. This is most likely because, at the higher temperature, only 5% of the tetralyl radical is directed into the oxygen addition pathway. This reduces the importance of the dialin formation pathways from tetralyl peroxy as

shown by the small value of the sensitivity index for the formation of dialin from tetralyl peroxy, (R4), at 1500 K.

Furthermore, it is interesting to note that the reaction of OH with tetralin to form water and tetralyl radical has a positive sensitivity at 835 K, but a negative sensitivity at the other two higher temperatures. This indicates that consuming OH radicals to form the primary fuel radical causes a decrease in the reactivity of the system at 835 K. This is most likely because the highly reactive OH consumed in this reaction is primarily turned into a dialin molecule through the reaction pathways discussed previously. The sensitivity of this reaction to form tetralyl radical is in contrast to the reaction of HO₂ with the fuel to form H₂O₂ and tetralyl radical. Although this reaction consumes one radical (HO₂) and the reaction pathways of tetralyl radical primarily form dialin, it also forms hydrogen peroxide, which is the primary source of hydroxyl in the system. Therefore, at low temperatures this reaction functions as a chain-branching reaction, whereas the reaction of hydroxyl with the fuel is effectively chain-terminating.

Finally, the sensitivity indices at 835 K shown in Fig. 12 do not change significantly with change in pressure (although not shown here). This weak change in sensitivity indices implies that the controlling chemistry does not change with pressure and indicates that the performance of the mechanism in predicting the ignition delays should not change with pressure. This is consistent with the observations in the current study that the mechanism is consistently less reactive than experiments at all pressures for temperatures investigated in the current work. Comparison of sensitivity indices at 1100 K for the two pressures also shows that the sensitivity indices do not change significantly with change in pressure. From this analysis, it is not clear why this mechanism performs relatively better at high pressures for the high temperature conditions investigated in the shock tube study of Wang *et al.* [3].

As mentioned previously, the simulated ignition delays were about a factor of four longer than the experimental values for the temperatures investigated in the current work. The factor of five change in the reaction rate for the reaction of HO₂ with the fuel to form H₂O₂ and tetralyl radical considered in this analysis causes approximately a 60% decrease in ignition delay at 835 K. Since a 400% improvement is required, changing the reaction rate of H-abstraction by HO₂ from the fuel to improve the result would require a change well outside the uncertainty range of this reaction rate. Furthermore, it is unclear how the uncertainty of the reaction (R1) may be estimated from the work of Dagaut *et al.* [4] because it is not an elementary reaction and thus the uncertainty of this reaction rate is not known explicitly.

A second set of sensitivity analyses was conducted to study the change in controlling chemistry with change in equivalence ratio, as it was found that the mechanism performs better at lower equivalence ratios. To identify the change in controlling chemistry, brute force sensitivity analysis based on the CONV simulations was conducted at initial pressure and temperature of 35 bar and 835 K, respectively, at two equivalence ratios of $\phi=0.5$ and 1.0 for tetralin/air mixtures. Comparison of brute force sensitivity indices with change in equivalence ratio is shown in Fig. 13. Figure 13 demonstrates that the controlling chemistry is similar to the results discussed in Fig. 12 and does not change with change in equivalence ratio.

From the sensitivity analyses it appears that simple modification of reaction rate coefficients is not enough to increase the fidelity of the mechanism and a more comprehensive description of oxidation of tetralin, especially at low temperatures, is needed. The need for more comprehensive description of oxidation at low-to-intermediate temperatures is supported by the evidence of pre-ignition heat release at low temperatures observed in the current study. The mechanism of Dagaut *et al.* [4] was developed on the premise that low temperature oxidation of

tetralin is not effective as reported by Yang and Boehman [2]. This premise has been found to be inappropriate for the conditions in the current study. Furthermore, earlier studies have shown that the inclusion of low temperature reactions may be necessary for developing a high fidelity chemical kinetic model even for fuels that do not exhibit exothermicity in a CFR engine [28].

5. Conclusion

Ignition delays of tetralin/O₂/N₂ mixtures were measured using a heated rapid compression machine at varying pressures from 15 bar to 50 bar, temperatures between 763 K and 950 K, and equivalence ratios of $\phi=0.5$ and 1.0. The effect of dilution was also studied by varying the initial concentrations of tetralin and oxygen independently. Pre-ignition heat release has been observed in the current study at the low end of the temperature range investigated; however, no evidence of NTC behavior of the ignition delays was found. Comparison of ignition delays of tetralin and *n*-butylbenzene was also conducted to understand the effect of molecular structure on ignition propensity. In addition, comparison of experimental and simulated ignition delays showed the available chemical kinetic model to be significantly less reactive than experiments. Reaction path analyses and brute force sensitivity analyses were conducted to understand the controlling chemistry of low-temperature tetralin autoignition. Brute force sensitivity analyses showed that simple modifications of reaction rate coefficients are not sufficient to improve the fidelity of the mechanism and a comprehensive model describing the low temperature reactions is needed to generate a high fidelity chemical kinetic model to predict the ignition delays and pre-ignition heat release observed in the present experiments.

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 583 Figure 1: Definition of ignition delay. Experimental conditions: tetralin/O₂/N₂=0.8/20.84/78.36
 584 by mole, $P_0=2125$ Torr, $T_0=380$ K, $P_C=50$ bar, $T_C=796$ K, and $\tau=43$ ms.

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587 Figure 2: Plot showing the experimental repeatability. Same experimental conditions as Fig. 1.

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Figure 3: Representative pressure traces at three of the experimental conditions from Table 1. It can be seen that no evidence of two-stage ignition is found in the pressure traces.

Figure 4: Pre-ignition heat release identified by comparison of pressure histories obtained from reactive and nonreactive experiments, for $T_C=763$ K and 802 K. The pressure trace for $T_C=802$ K is offset by +5 bar to clarify differences in the pressure traces. Conditions: $\phi=1.0$ in air, $X_{\text{tetralin}}=1.6\%$, and $P_C=35$ bar.

599 Figure 5: Arrhenius plots of ignition delays of tetralin/oxidizer mixtures at varying pressures and
600 equivalence ratios.
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(a) $\phi=1.0$, Fuel/Air Mixtures

(b) $\phi=0.5$, Fuel/Air Mixtures

Figure 6: Comparison of ignition delays of *n*-butylbenzene and tetralin.

Figure 7: Schematic of important reactions in tetralin and *n*-butylbenzene low-temperature ignition. Note that chain branching steps are possible from any carbon in the butyl chain for *n*-butylbenzene; for further discussion of the reaction pathways of *n*-butylbenzene, the interested reader is referred to the work of Husson *et al.* [19].

Figure 8: Comparison of measured pressure traces and computed profiles using CONV and VPRO simulations.

Figure 9: Comparison of experimental and simulated ignition delays for the diluted experiments – tetralin/O₂/N₂ mixtures with X_{O₂}=10.42%.

Figure 10: Arrhenius plots showing the complementary nature of ignition delays measured in this RCM study with the shock tube (ST) data taken from Wang *et al.* [3] at different pressures and equivalence ratios. All mixtures are tetralin/air. Computational results based on the CONV simulations are also plotted for comparison.

Figure 11: Integrated reaction path analysis up to 10% fuel conversion from an initial condition of 35 bar and 835 K for a $\phi=0.5$ tetralin/air mixture in the CONV simulation.

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631 Figure 12: Brute force sensitivity of the ignition delay for $\phi=0.5$ tetralin/air mixtures at an initial

632 pressure of 35 bar for three initial temperatures in the CONV simulations.

Figure 13: Brute force sensitivity of the ignition delay for $\phi=0.5$ and $\phi=1.0$ tetralin/air mixtures at an initial condition of 35 bar and 835 K in the CONV simulations.

637 Table 1: Equivalence ratios, oxidizer types, component mole percentages, and compressed
 638 pressures studied in this work. Note that $X_{\text{component}}$ indicates the mole percentage of that
 639 component.

ϕ	Oxidizer	X_{tetralin} (%)	X_{O_2} (%)	X_{N_2} (%)	P_C (bar)
0.5	Diluted	0.40	10.42	89.18	35, 50
1.0	Diluted	0.80	10.42	88.78	35, 50
0.5	Air	0.80	20.84	78.36	15, 35, 50
1.0	Air	1.60	20.67	77.73	15, 35

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