

Simultaneous CO and H₂O Laser Absorption Measurements of Pentene Isomers in a Shock Tube

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1 Introduction

The 'straight line' reaction pathways seen for alkane fuels in detailed kinetics mechanisms, where the fuel is successively decomposed and oxidized into smaller fragments until the final combustion products are formed, is a strategy adapted to the structural simplicity of these molecules. However, recent work showed that the combustion of olefins presents markedly different reaction pathways, where isomers can intermix at all levels during the oxidation process [1,2]. Therefore, the kinetics reaction mechanism for any pentene requires the details for the full group of C₅ olefin isomers as possible reaction intermediates. Moreover, a considerable amount of olefin-specific reaction classes are present, and the unusual stability of the allylic species combined with low C-H bond energy at allylic locations (85.5 ± 2 kcal/mol) [3] significantly increases the complexity of the chemical kinetics scheme for olefin fuels. Figure 1 illustrates the molecules 3-Methyl-1-Butene (3M1B), 1-pentene (1-C₅H₁₀), and 2-Methyl-1-Butene (2M1B), cis-2-pentene (cis-2-C₅H₁₀), trans-2-pentene (trans-2-C₅H₁₀), and 2-Methyl-2-Butene (2M2B). In these structures, the H atoms that are not part of a C-H allylic bond have been suppressed, as the chemistry of C₅ olefins is highly connected through allylic radicals.

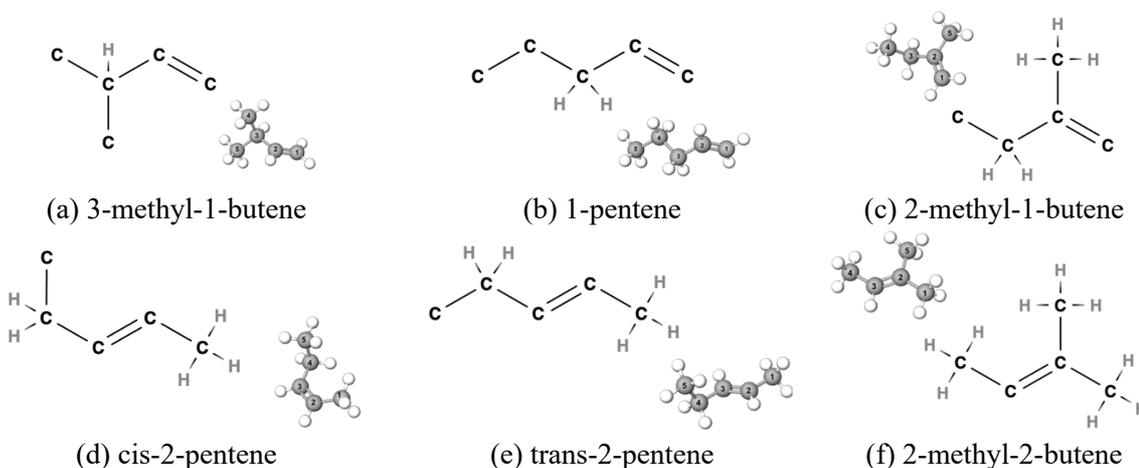


Figure 1: Chemical structures for the pentenes.

Shock tubes are an excellent experimental method to investigate the chemical kinetics of combustion processes. Power *et al.* [4] obtained eight \dot{H} -atom profiles for 1-C₅H₁₀ and 2-C₅H₁₀ pyrolysis (C₂H₅I-pentene-Ar mixtures) via atomic resonance absorption spectroscopy at temperatures ranging from 980 to 1055 K and pressures around 1.5 atm. Later, Arafin *et al.* [5] produced two CO time histories for each branched pentene at 1400 K, 10 atm, $\phi = 1.0$ in 99.3625% Ar. Similarly, a total of seven CO time-history profiles can be found in Dong *et al.* [6] for the oxidation of 1-C₅H₁₀ and 2-C₅H₁₀ at stoichiometric conditions and diluted in 97.88% Ar for temperatures from 1228 to 1372 K and pressures from 8.17 to 10.03 atm. Due to the lack of experiments at similar conditions, the above-mentioned database stringently limits the comparison between all C5 olefin isomers. The work presented herein (new measurements on 1-C₅H₁₀, 2-C₅H₁₀, and 3M1B) will allow for comparing all isomers directly, as similar experimental conditions were studied in the same shock tube for 2M2B [7], 2M1B [2], and both 1-C₅H₁₀ and 3M1B [1]. Data for three different equivalence ratios: 0.5, 1.0, and 2.0, near-atmospheric pressure, temperatures ranging typically between 1300 and 1800 K, and highly diluted mixtures in 99.5% Ar or 20% He and 79.5% Ar were systematically presented in these studies, and the whole set of data gives a unique opportunity to develop a unified model for pentene isomers. This study is organized as follows: the experimental method section introduces the shock-tube facility, the CO and H₂O laser diagnostics, and summarizes the experimental conditions. As the reactivity of the molecules can be determined by measuring the induction delay time from these time-history profiles, models found in the literature can be evaluated. Using the experimental results as a base, error scores are determined for each chemical kinetics mechanism. Finally, the last section shows a discussion on the pentene isomers combustion.

2 Experimental Method

a Shock-Tube Facility

The shock-tube driver section has a 7.62-cm inner diameter and 3.25-m long length, and the driven section has dimensions of 16.2-cm inner diameter and is 7.88-m long. High-temperature oxidation experiments for pentene isomer mixtures were carried near atmospheric pressure using a single diaphragm of 0.25-mm thick-film polycarbonate separating the two sections. The incident shock-wave velocity is determined using five PCB P113A piezoelectric pressure transducers placed along the driven section, and the geometry of the shock tube allows for a 3-ms test time before the reflected expansion wave interacts with the reflected shock. The temperature T₅ and pressure P₅ behind the reflected shock wave were calculated using the normal shock equations. More details can be found in Mathieu *et al.* [8].

b CO and H₂O absorption diagnostics

Quantitative CO and H₂O time histories behind reflected shock waves were recorded using laser absorption diagnostics. A quantum cascade laser producing light at 4566.17 nm to monitor the R(12) line of the CO 1 ← 0 transition band was used to measure CO time histories. Moreover, a tunable diode laser was used to measure H₂O time histories to monitor the 5_{5,1} ← 5_{5,0} transition in the $\nu_1 + \nu_3$ fundamental band of H₂O. The measurements of both CO and H₂O species were done simultaneously thanks to multiple sapphire window ports mounted in the same plane at the end of the shock tube using the direct-absorption optical setup arrangement. The species' quantification is possible using the Beer-Lambert law to process the laser beam intensities and find the species' concentrations, and is defined as

$$\frac{I_t}{I_0} = \exp(-k_\nu PL)$$

Where I₀ represents the time-resolved incident intensity and I_t the time-resolved transmitted intensity. P is the partial pressure, L is the path length, and k_ν is the absorption coefficient. Further details on the computational technique of the absorption coefficient are described in Mulvihill [9]. The wavelengths

of each laser are controlled by two methods: the CO wavelength is centered with a removable cell containing a low-pressure mixture of $\sim 10\%$ CO/90% Ar, and the H₂O wavelength is verified using a Burleigh WA-1000 wavemeter. The beam of the H₂O laser is enclosed in an inert environment to reduce the attenuation of the signal by ambient water and any residual or high-frequency noise is blocked by a 150-kHz bandwidth with all the detectors. More details on both laser diagnostics can be found in Mathieu *et al.* [8,10]. The CO and H₂O induction delay times τ_{CO} and $\tau_{\text{H}_2\text{O}}$ are defined as the time between the rise in pressure from the reflected shock wave at the sidewall location and the intersection obtained from the maximum increasing slope of the CO and H₂O production and the baseline, respectively. An illustration of this definition can be found in Grégoire *et al.* (2021) [1].

c Experimental Conditions

Three compounds, 1-C₅H₁₀, 2-C₅H₁₀, and 3M1B, were chosen to carry out experiments at three different equivalence ratios: 0.5, 1.0, and 2.0, with pressures ranging from 1.11 to 1.41 atm and temperatures ranging from 1311 to 1990 K. New CO measurements on 1-C₅H₁₀ and 3M1B, and both CO and H₂O measurements on 2-C₅H₁₀ were performed, and the details on the experimental conditions covered in this study are reported in Table 1. The liquids 1-C₅H₁₀ and 2-C₅H₁₀ (cis/trans proportion is 30/70) came from Sigma Aldrich with purities of 98.5% and 99%, respectively. The gas 3M1B was also supplied by Sigma Aldrich with a purity of 95%. Finally, the gases O₂, He, and Ar were provided by Praxair, all with 99.999% purity. To maintain high purity for chemical kinetics experiments, the shock tube has a vacuum system utilizing a turbomolecular pump to achieve pressures of 10^{-5} torr prior to each test.

Table 1: Experimental conditions covered in this study for 1-C₅H₁₀, 2-C₅H₁₀, and 3M1B.

Pentene	Diagnostics	ϕ	Temperatures (K)	Pressures (atm)
1-C ₅ H ₁₀	CO	0.5 - 2.0	1321 - 1990	1.12 - 1.38
2-C ₅ H ₁₀	CO, H ₂ O	0.5 - 2.0	1276 - 1984	1.11 - 1.41
3M1B	CO	0.5 - 2.0	1477 - 1761	1.22 - 1.33

d Detailed Kinetics Reaction Mechanisms

These new CO and H₂O profiles are compared with existing chemical kinetics models from the literature that contain all of the pentene isomers. Numerical predictions using up to 6 models are performed. The six detailed kinetics reaction mechanisms are based on AramcoMech 3.0 and are: Cheng *et al.* [11], Dong *et al.* [6], Grégoire *et al.* [2], Power *et al.* [4], and Ruwe *et al.* [12]. It is important to remember that the mechanisms covering the full C5 alkene group are not necessarily designed for each isomer, and discrepancies could come from their different interests. For example, Cheng *et al.* [11] worked on 1-C₅H₁₀ and 2M2B laminar flame experiments, but it will be shown later that their model experiences difficulties in predicting 3M1B. Power *et al.* [4] investigated the hydrogen-atom reactions involved in the 1-C₅H₁₀ and 2-C₅H₁₀ pyrolysis and will also show weaknesses in the branched pentenes' simulations. A more detailed description will continue in the results section.

3 Results and Discussion

New experimental CO measurements for 1-C₅H₁₀, 2-C₅H₁₀, and 3M1B highly diluted in 99.5% He/Ar combined with three literature studies performed in identical conditions with the same apparatus for 2M2B [7] and 2M1B [2], permit the direct comparison of all of the C5 pentene isomers. Figure 2 presents an overview of the CO time-history profiles where low, intermediate, and high temperatures of the temperature span investigated for each equivalence ratio are summarized, along with predictions from six models. The CO profiles at $\phi = 0.5$ and 1.0 follow the same trend where the CO mole fraction is experiencing an increase until reaching a peak and then decreases smoothly. On the other hand, the CO

profiles at $\phi = 2.0$ do not decline after the peak due to the excess in fuel, as opposed to the lean mixtures where the dominant presence of O_2 influences the CO to CO_2 conversion. Figure 2 also shows that the CO mole fraction production increases with equivalence ratio. In parallel, it can be noticed that the increase in the temperature shortens the CO induction time. The authors assessed all the models' performance on predicting the experimental time histories using an error function from Jach *et al.* [13]

$$\bar{E} = \sum_{i=1}^{N_{exp}} \frac{\left| \log_{10} \frac{\tau_{sim}}{\tau_{exp}} \right|}{N_{exp}}$$

Where \bar{E} is the average error that takes into account the numerical predictions τ_{sim} and the experimental induction delay times represented by τ_{exp} . The N_{exp} represents the total number of experiments that are included in the calculations. The evaluation of the six detailed chemical kinetics mechanisms based on all the CO induction times from the experiments is summarized in Table 2.

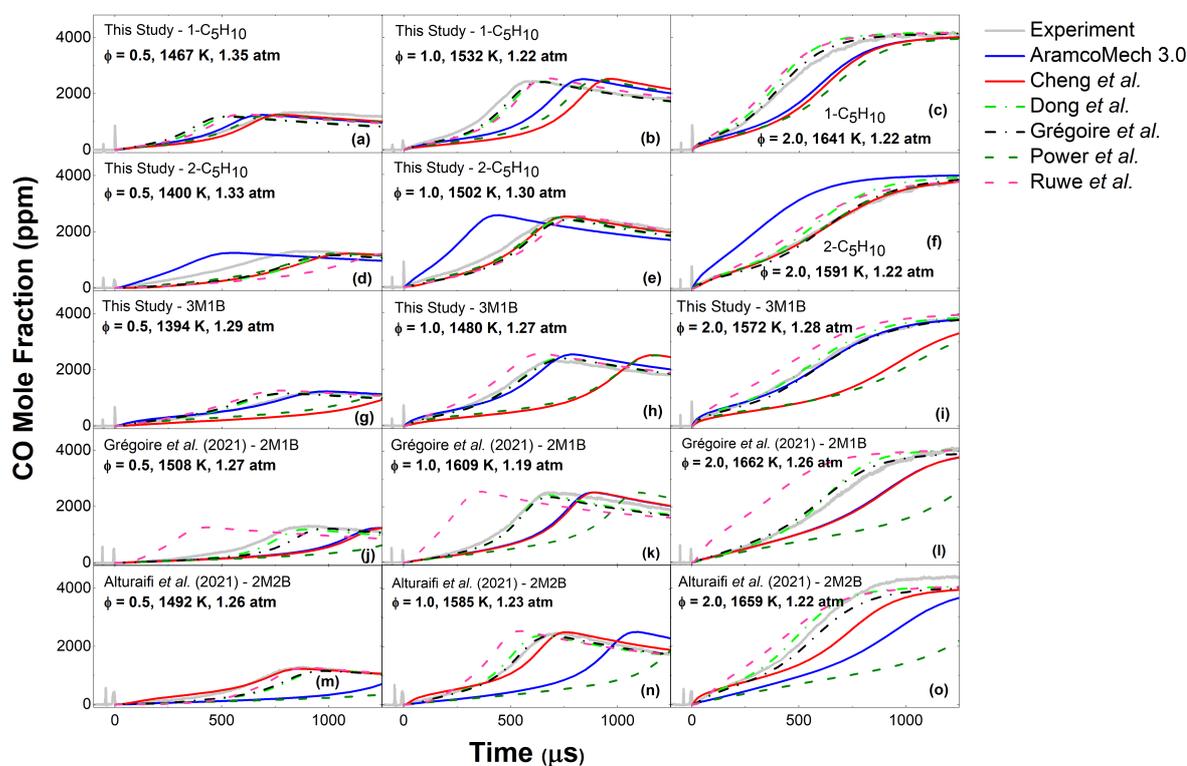


Figure 2: Experimental CO time-history profiles for the oxidation of pentenes in 0.995 He/Ar.

Likewise, a comparison of all the pentene isomers with H_2O experimental time-history profiles is shown in Fig. 3 along with prediction from six models. The shape of the H_2O profiles consists of a linear curve that reaches a constant plateau. This linear growth starts earlier when the temperature increases, decreasing the H_2O induction delays. The final water production mole fractions increase with equivalence ratio. A final evaluation of the six detailed kinetics mechanisms was performed to decide which models are good candidates to predict the entire C5 olefin group. The error scores for the H_2O time-history profiles computed by the authors are reported in Table 2. AramcoMech 3.0 cannot be considered as a good candidate to model the entire C5 olefin group due to its lack of performance on both CO and H_2O measurements for the 2-3 C=C double bond site molecules 2-C₅H₁₀ and 2M2B. The error scores reach 51% and 44% for 2-C₅H₁₀ and 2M2B, respectively. Similarly, the Cheng *et al.* [11] model shows discrepancies for the molecule 3M1B with 40% and 31% of error scores for CO and H_2O , respectively. The Cheng *et al.* work was based on AramcoMech 3.0 and focused on 1-C₅H₁₀ and 2M2B, however the updated model compromised the performance for 3M1B, which ultimately excludes it from

being elected as an adequate model understanding the complete C5 olefin group. In parallel, the Power *et al.* model [4] exhibits difficulties when predicting the production of CO and H₂O for the branched pentene isomers. Finally, the Ruwe *et al.* [12] model experiences high error scores (on average 28% and 41% for CO and H₂O, respectively), and more specifically, the iso-pentene 2M1B is the least accurate with a 53% error score for CO measurements, and 93% for the water measurements. In conclusion, Dong *et al.* [6] and Grégoire *et al.* [2] performed the best, with sufficient accuracy, obtaining $\bar{E}_{CO} = 15$ and 14%, respectively, and $\bar{E}_{H_2O} = 12\%$ for both models. Therefore, both mechanisms can be considered as good candidates for modeling all the pentene isomers, at least for the conditions presented herein.

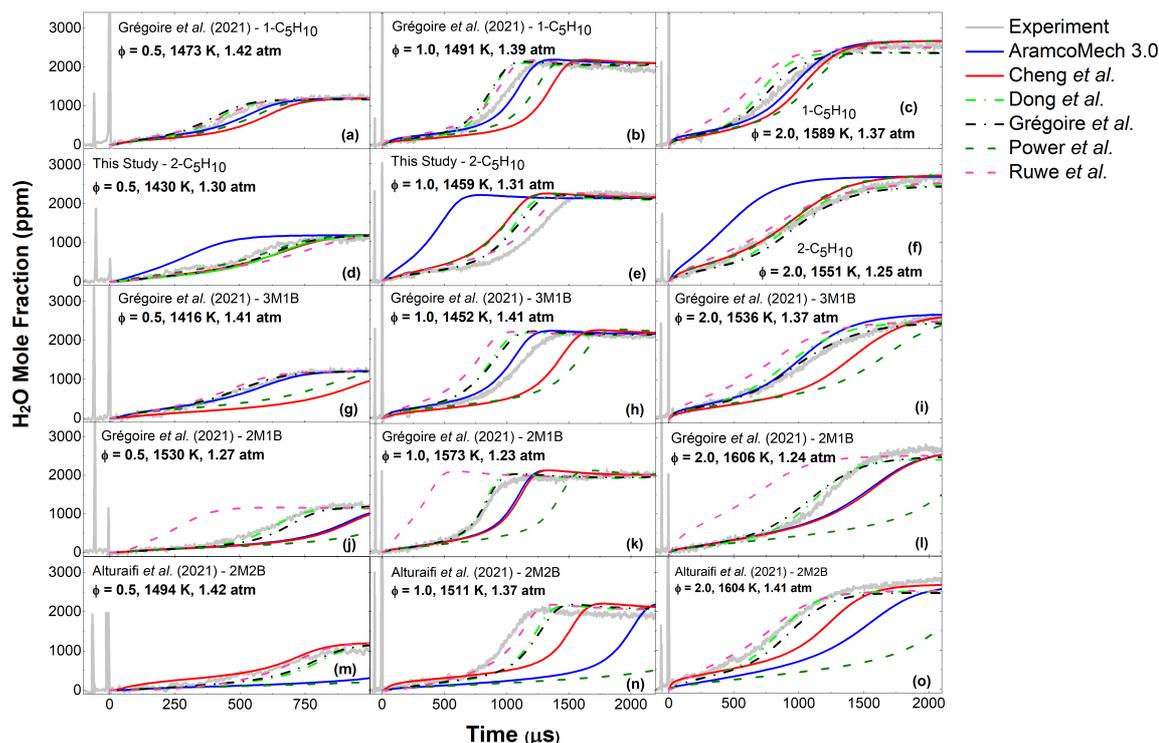


Figure 3: Experimental H₂O time-history profiles for the oxidation of pentenes in 0.995 He/Ar.

Table 2: Error scores computed for CO and H₂O induction delay times for all the pentene isomers, and standard deviations (Std Dev).

Model	1-C ₅ H ₁₀	2-C ₅ H ₁₀	3M1B	2M1B [2]	2M2B [7]	Average	Std Dev
AramcoMech 3.0	13 - 15	51 - 51	21 - 18	20 - 19	44 - 44	30 - 29	18 - 17
Cheng <i>et al.</i> [11]	21 - 20	29 - 11	40 - 31	19 - 22	22 - 17	26 - 20	20 - 11
Dong <i>et al.</i> [6]	17 - 10	24 - 14	15 - 11	10 - 10	7 - 16	15 - 12	13 - 12
Grégoire <i>et al.</i> [2]	22 - 7	22 - 16	11 - 14	9 - 8	8 - 17	14 - 12	13 - 13
Power <i>et al.</i> [4]	19 - 18	21 - 11	43 - 25	33 - 34	58 - 59	35 - 29	19 - 13
Ruwe <i>et al.</i> [12]	17 - 30	34 - 20	13 - 37	53 - 93	21 - 27	28 - 41	17 - 31

4 Conclusion

New CO measurements for 1-C₅H₁₀ and 3M1B oxidation, and both CO and H₂O measurements for 2-C₅H₁₀, combined with published H₂O data obtained in similar conditions for 1-C₅H₁₀ and 3M1B, and both CO and H₂O measurements on 2M1B and 2M2B, permit the unique comparison of the full group of C5 olefins under the same conditions. All experiments were performed in a shock tube, and the oxidation of all the pentenes was carried out in 99.5% He/Ar at three different equivalence ratios and

temperatures ranging from 1311 to 1990 K near atmospheric pressure. Numerical predictions using up to 6 models available in the literature were performed. The use of an error score function from Jach *et al.* [13] shows that the AramcoMech 3.0 model does not have good agreement for 2-3 C=C double bond site molecules. Surprisingly, the performance from updated versions of AramcoMech 3.0 are compromised on different pentene isomers. The Cheng *et al.* [11] model shows discrepancies for the molecule 3M1B, the Power *et al.* (2019) model is not accurate for the branched isomers, and the Ruwe *et al.* (2019) model does not reproduce the H₂O profiles correctly for all pentenes and exhibits weaknesses on CO profiles for 2-C₅H₁₀ and 2M1B. Only two detailed kinetics mechanisms, from Dong *et al.* [6] and from Grégoire *et al.* [2], have consistently good results when compared to all the pentenes, reaching an average error score of 13% for both species presented: CO and H₂O.

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