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Shock tube and laser absorption study of CO time-histories during combustion of branched alkenes

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Combustion experiments of the three isomers of methyl butene compound - 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B), and 3-methyl-1-butene (3M1B), have been carried out in a shock tube using laser absorption technique. Carbon monoxide (CO) time-histories are obtained behind reflected shockwaves over the temperature range of 1350–1630 K near 9.3 atm with stoichiometric mixtures of 0.075% fuel in O_2/Ar. Comparative study of CO time-histories reveals different rates of CO formation indicating different ignition delay time of the methyl butene isomers.

I. Nomenclature

T	=	Temperature (K)
P	=	Pressure (Pa)
ϕ	=	Equivalence Ratio
α_v	=	Absorbance
I_{ref}	=	Intensity of the reference laser beam
I_{tr}	=	Intensity of the transmitted laser beam
v	=	Frequency (Hz)
σ	=	Absorption cross-section of the absorbing species (m^2/mol)
L	=	Path length (m)
R	=	Universal gas constant (J/mol K)
X_{CO}	=	Carbon Monoxide mole-fraction

II. Introduction

Alkenes are important intermediates formed by the combustion of larger hydrocarbons such as alkanes and alcohols [1]. Transportation fuels, such as gasoline, diesel fuel, and aviation fuels contain alkenes, which contribute to determining the ignition properties of these fuels. Smaller, branched alkenes such as methyl butene, exhibit strong octane sensitivity, which is indicative of resistance to knocking behavior in spark-ignition engines. Although they are produced in combustion of many larger hydrocarbon fuels, methyl butenes have not been studied well. There are three isomers of methyl butene as shown in Fig.1, 2-methyl-1-butene (2M1B), 2-methyl-2-butene (2M2B) and 3-methyl-1-butene (3M1B), which are different by the position of C=C double bond in their molecules. Westbrook et al. [2] carried out the ignition delay time measurement for 2M2B oxidation in a shock tube and measured the intermediate product species in a jet-stirred reactor, which were used to develop a detailed chemical kinetic mechanism. Later, Ruwe et al.

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[3] provided detailed chemical insights into fuel consumption and hydrocarbon growth pathways at high temperatures in premixed flames of 2M2B to complement the earlier work [2]. However, oxidation experiments of the other two isomers (2M1B and 3M1B) as well as time resolved measurement of intermediate products in methyl butene oxidation have not yet been performed.

In the present study, we conducted oxidation experiments of three isomers of methyl butene behind the reflected shock waves at high temperature and pressure, and measured the carbon monoxide (CO) concentration-time histories using the laser absorption technique. To our knowledge, this work represents the first set of laser-based species time-history measurements at high temperature during oxidation of methyl butene isomers.

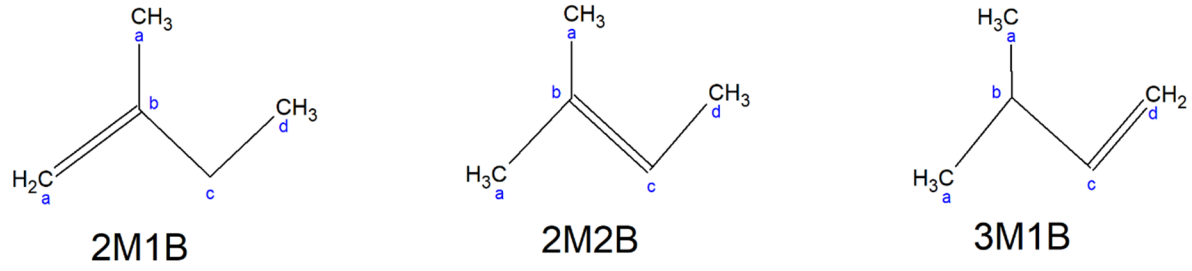

Fig.1. Molecular structures of methyl butene isomers.

III. Experimental setup and procedure

Oxidation experiments of methyl butene isomers were conducted in a double-diaphragm, stainless-steel shock tube of 0.1417 m inner diameter located at the University of Central Florida (UCF), specific details of which can be found in [4, 5]. The last 1.4 m of the shock tube have five equally spaced, piezoelectric, pressure transducers that are connected to four time-interval counters to measure the incident shock velocity. The measured incident shock velocities were linearly extrapolated to obtain the reflected shock velocity at the end wall. Pressure and temperature behind the reflected shock wave (P5 and T5) were calculated using the extrapolated shock velocity and initial temperature and pressure (T1, P1) in 1-D normal shock relations. P5 was also monitored using a Kistler type 603B1 sensor. Eight equally spaced optical ports around the circumference of the tube, 2 cm away from the end-wall, were used for pressure and spectroscopic measurements. Research-grade fuels, O_2 and Ar were used to prepare the test gas mixture manometrically in a 33 L, stainless steel mixing tank for stoichiometric oxidation (0.075% fuel, 0.5625% O_2, 99.3625% Ar) experiments.

A continuous wave, distributed feedback quantum cascade laser from Alpes Lasers (TO3-L-50) operating at 2046.30 cm^{-1} was used to measure CO concentration time-histories. A Bristol 771 Spectrum Analyzer monitored the laser throughout each test to ensure the spectral output from the laser remained stable. CO mole fraction was obtained from the Beer-Lambert law, given in Eq. (1),

$$\alpha_v = -\ln\left(\frac{I_{tr}}{I_{ref}}\right)_v = \sigma(v,T,P)\frac{XPL}{RT} \quad (1)$$

$$\sigma = AP^B T^C \quad (2)$$

The absorption cross-section of CO was measured behind reflected shock waves in the UCF shock tube to characterize its dependence on thermodynamic parameters at temperatures of 1085-1456 K and pressures of 8.6-10.3 atm. A mixture composition of 1% CO/12% He/86% Ar was used for cross-section measurements. A power fit, Eq. (2), in both temperature (K) and pressure (Pa) yields good agreement with experimentally obtained cross-sections (m^2/mol) when $A = 9.112 \times 10^6$, $B = -1.132$, and $C = 0.316$. The uncertainty in measured CO mole fraction was estimated to be < ±10% which results primarily from uncertainty in absorbance, pressure, temperature, and absorption cross-section.

IV. Results and Discussion

CO time-histories are obtained behind reflected shockwaves during oxidation of methyl butene isomers over the temperature range of 1350–1630 K and pressures of 8.9-10.1 atm with stoichiometric mixtures of 0.075% fuel in O_2/Ar. A typical representation of these experiments is shown in Fig. 2, which shows the CO formation and depletion during methyl butene oxidation at similar reflected shock conditions. For all three isomers, CO starts to form gradually,

the rate of which accelerates when combustion begins and reaches its peak level near the ignition point. Higher temperature and pressure due to combustion results in further oxidation of CO to form CO_2, which is seen by the depletion of CO profiles.

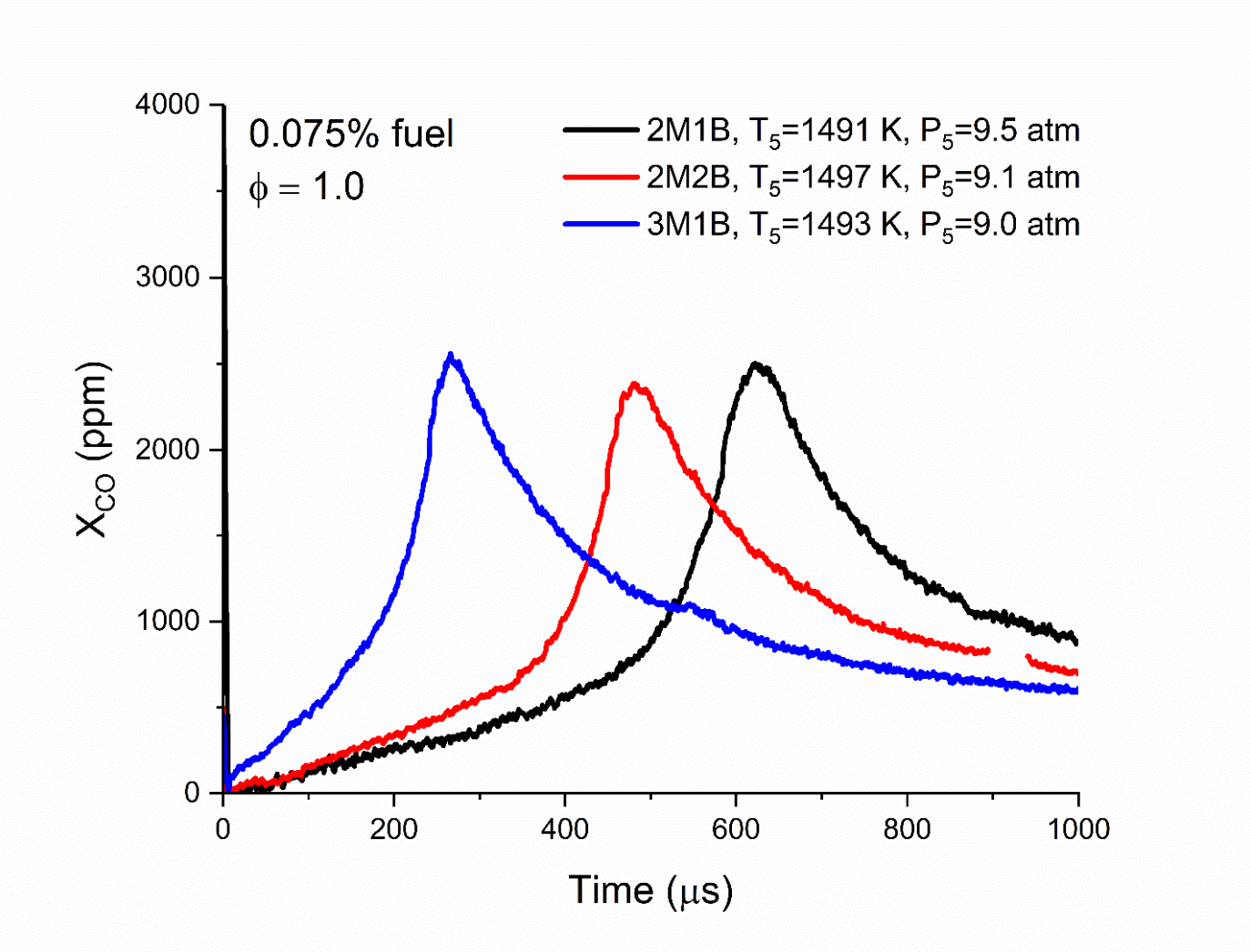

Fig. 2. CO time-histories during oxidation of methyl butene isomers at near 1495K and 9.3 atm.

Since the time at which CO reaches its peak level is indicative of ignition delay time, it is evident from Fig.2. that 3M1B ignites fastest, followed by 2M2B, and 2M1B is the slowest to ignite among the isomers. These isomers have their C=C bond in different positions, which possibly directs different decomposition pathways and ignition time.

V. Summary

Oxidation experiments of methyl butene isomers were performed behind reflected shockwaves at temperatures of 1350-1630 K and pressure of 8.9-10.1 atm to measure the CO time histories. 3M1B has the fastest CO formation rate, followed by 2M2B and 2M1B, respectively. The comparative study of CO time-histories of these isomers highlights the importance of future study on ignition delay time measurement and reaction path analysis of methyl butene

isomers. Experimental data from this study can be used to compare the existing models and as validation benchmark in refining the reaction mechanisms.

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VII. References

1. Li, Y., Zhou, C.-W., Somers, K. P., Zhang, K., and Curran, H. J. "The oxidation of 2-butene: A high pressure ignition delay, kinetic modeling study and reactivity comparison with isobutene and 1-butene," *Proceedings of the Combustion Institute* Vol. 36, No. 1, 2017, pp. 403-411.
doi: https://doi.org/10.1016/j.proci.2016.05.052
2. Westbrook, C. K., Pitz, W. J., Mehl, M., Glaude, P. A., Herbinet, O., Bax, S., Battin-Leclerc, F., Mathieu, O., Petersen, E. L., Bugler, J., and Curran, H. J. "Experimental and Kinetic Modeling Study of 2-Methyl-2-Butene: Allylic Hydrocarbon Kinetics," *J Phys Chem A* Vol. 119, No. 28, 2015, pp. 7462-80.
doi: 10.1021/acs.jpca.5b00687
3. Ruwe, L., Moshammer, K., Hansen, N., and Kohse-Höinghaus, K. "Consumption and hydrocarbon growth processes in a 2-methyl-2-butene flame," *Combustion and Flame* Vol. 175, 2017, pp. 34-46.
doi: https://doi.org/10.1016/j.combustflame.2016.06.032
4. Koroglu, B., Pryor, O. M., Lopez, J., Nash, L., and Vasu, S. S. "Shock tube ignition delay times and methane time-histories measurements during excess CO_2 diluted oxy-methane combustion," *Combustion and Flame* Vol. 164, 2016, pp. 152-163.
doi: https://doi.org/10.1016/j.combustflame.2015.11.011
5. Ninnemann, E., Kim, G., Laich, A., Almansour, B., Terracciano, A. C., Park, S., Thurmond, K., Neupane, S., Wagnon, S., Pitz, W. J., and Vasu, S. S. "Co-optima fuels combustion: A comprehensive experimental investigation of prenol isomers," *Fuel* Vol. 254, 2019, p. 115630.
doi: https://doi.org/10.1016/j.fuel.2019.115630