Investigation of ignition behavior of dimethyl and ethyl isomers of cycloalkanes and furans

Mazen A. Eldeeb, Ben Akih-Kumgeh
Department of Mechanical and Aerospace University
Syracuse University, Syracuse, NY 13244, USA

Abstract

The high-temperature auto-ignition delay times of dimethyl and ethyl isomers of cyclohexane and furan are carried out behind reflected shock waves at average pressures of 5.0 and 12.0 atm. The study is aimed at establishing reactivity differences between these dimethyl and ethyl isomers which could further be explored in chemical kinetic modeling. The two hydrocarbon classes are designed to test whether the observed trend is indicative of general reactivity differences between dimethyl and ethyl isomers of cyclic hydrocarbons, oxygenated or non-oxygenated. It is observed that 2,5-dimethyl furan ignition delay times are up to 5 times longer than those of the more reactive ethyl furan. The dimethyl cyclohexane investigated is a mixture of 1,3-cis-dimethyl and 1,3-trans-dimethyl cyclohexane. In the case of the cyclohexanes, a similar trend is observed such that 1,3-dimethyl cyclohexane has longer ignition delay times than the ethyl isomer, albeit to a lesser extent than observed with the furans. These observations align with another literature study of alkyl benzene isomers by Shen and Oehlschlaeger [Combust. Flame, 2009], showing that the ignition delay times of 1,3-dimethyl benzene (m-xylene), are up to 3 times longer than those of ethyl benzene. The pronounced differences in the high-temperature ignition delay times of these isomers are clearly established using the shock tube technique and motivate further mechanistic explorations of distinguishing reaction pathways, without necessarily invoking the more complex low-temperature chemistry.

1 Introduction

The shock tube technique plays a crucial role in advancing our understanding and enabling us to develop accurate combustion chemistry models [1]. A typical chemical kinetic model for combustion applications consists of a tentative mechanistic description, a large number of kinetic parameters, and thermo-transport properties of the various species. This poses a challenge to the project of predictive chemical kinetic model development so that a strong synergy between experiments and modeling is indispensable for progress. Chemical kinetic model validation using shock tube ignition measurements is bound by the associated experimental uncertainties, mainly related to the determination of the post-reflected shock temperature. For typical high-temperature ignition, the temperature uncertainty is approximately 20-30 K, which can be translated into 20-30% uncertainty in ignition delay times [2], if a known global activation energy or temperature sensitivity is assumed.

Correspondence to: bakihkum@syr.edu

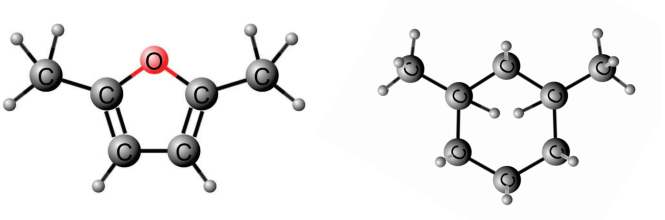
One approach to improving mechanistic schemes and model predictions makes use of relative reactivity indicators, such as trends in ignition behavior for a selected class of fuel components. The results of such comparative studies can also be directly applied to combustion system design, since fuel technology is largely focused on relative combustion properties of various fuels and fuel blends. If the fuels to be compared are not isomeric, observed reactivity trends need to be interpreted in terms of molecular structure and constraints imposed on mixture compositions. In the case of isomers, this task is simplified and one can focus on the effect of pressure, temperature, and equivalence ratio. Most shock tube ignition studies are carried out at high-temperatures because of limited test times. As a result, differences in ignition delay times are easily identified under these conditions if they are significant. It should be noted, however, that reactivity differences can be better resolved through ignition delay measurements compared to laminar burning velocities where differences are often in percentages compared to shock ignition where delay times can differ by integer factors. Thus, an interesting case presents itself for comparative study of fuel components when the delay times differ by a factor of 2 or more over a reasonable experimental temperature range. The observed trends can be more extensively explored in model development and their subsequent analysis, without the initial complication introduced by the rather complicated low-temperature chemistry.

In this work we investigate the ignition delay times of dimethyl and ethyl isomers of furans and cyclohexanes. We initially hypothesize that differences between ignition delay times of dimethyl and ethyl isomers will be factors of 2 or more, based on previous ignition studies of alkyl benzenes by Shen and Oehlschlaeger [3]. They established that ignition delay times of dimethyl benzenes (xylenes) are longer than those of ethyl benzene, with the ignition delay times of m-xylene being up to 5 times longer at some conditions. We discuss some possible reasons for the observed trend.

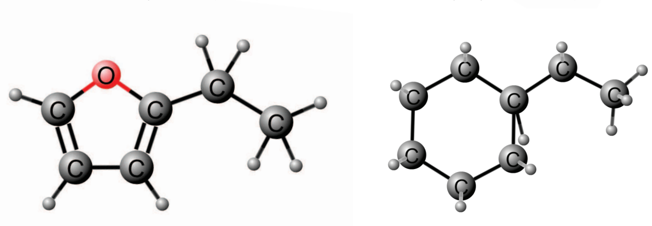
Of the systems investigated here, 2,5 dimethyl furan has been extensively studied using experiments, modeling, and simulations as reviewed by Qian et al. [4]. Furans are considered as promising bioderived fuels for spark-ignition engines and have been a subject of many recent investigations. A previous study of the trend among furan, methyl furan, and 2,5-dimethyl furan has been reported by the current authors [2], establishing that 2,5-dimethyl furan is the least reactive (longest ignition delay times). More recently a study of dimethyl furan, iso-octane, and their blends have been investigated by the authors [5], indicating that 2,5-dimethyl furans have longer ignition delay times than iso-octane. The second group of interest, cyclohexanes, are key components in transportation fuels. Similar to aromatics, their proportion in fuels is often quoted without specification of the make up with respect to their individual molecular structures. It is of interest to identify the isomer effect on the reactivity of cyclohexane. The mono alkylated cyclohexanes have been the subject of many experimental and modeling studies [6–10], resulting in shock tube and rapid compression machine ignition data sets and models with varying degree of prediction abilities. The study by Hong et al. [10] includes species concentration profiles aimed at linking observed ignition delay trends to the role of key radicals such as OH. Ignition delay times of methyl and ethyl cyclohexane and air mixtures have been investigated by Vanderover and Oehlschlaeger [11], showing that ignition delay times of methyl cyclohexane are longer than those of ethyl cyclohexane. However, studies including ethyl furan and dimethyl cyclohexanes have not been reported. This work expands the database of the systems already investigated and establishes the relative ignition behavior of the isomers considered. The structures of the systems investigated in this work are show in Fig. 1.

2 Experimental technique

Experiments are carried out in a shock tube facility with an inner diameter of 10 cm, a test-section length of 4 m and a driver of 2.67 m. Homogeneous gaseous test mixtures are prepared in a 150-liter



2,5-dimethyl furan (DMF) 1,3-dimethyl cyclohexane (DMCHXN)



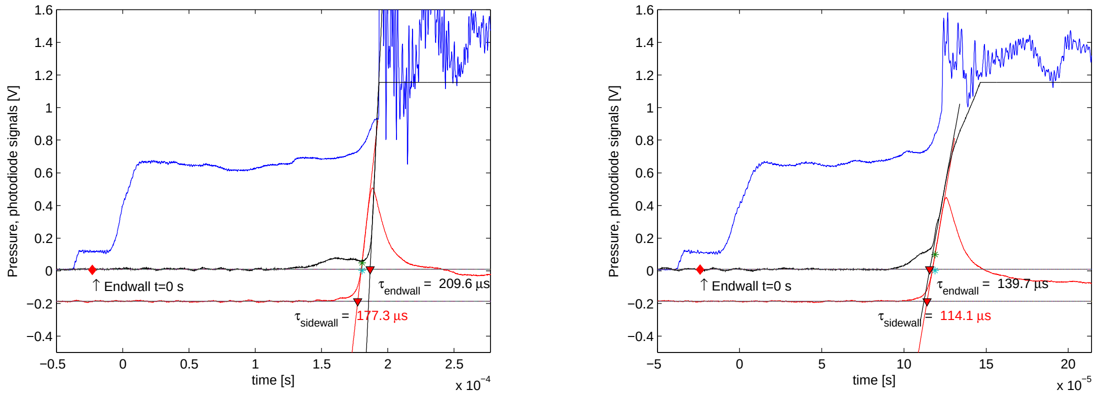
2-ethyl furan (2-EF) ethyl cyclohexane (ECHXN)

Figure 1: Molecular structures of fuel isomers investigated.

mixing tank using the partial pressure technique. Mixing is achieved by the convective current induced during the filling and subsequent molecular diffusion processes over a time period of 18-24 hours. Fuel samples of 99+%-purity were obtained from Sigma Aldrich. Shock arrival times are captured by four fast-response pressure transducers mounted 40 cm apart. Ignition events are monitored using an optical fiber connected to an assembly of a photo diode and a narrow band filter at 431 ± 10 nm, characteristic of CH chemiluminescence which peaks during ignition. Simultaneous sidewall and endwall delay time measurements are carried out but the results shown hereafter employ the sidewall measurements. The discrepancy between endwall and sidewall ignition delay times is generally well known [12, 13]. One of the least discussed features of this problem is illustrated in Figs. 2a and 2b for a stoichiometric mixture of ethyl cyclohexane, oxygen, and argon. Viewed from the sidewall, the photo diode captures the ignition of an approximately cylindrical gas volume, whose diameter is that of the optical fiber and length is that of the tube inner diameter. Ignition is marked by a sharp rise and fall of the chemiluminescence signal as the volume is burned out. Viewed from the endwall, the situation is different; closest to the endwall with the earliest established high temperature is a small volume visible to the optical fiber. This view is extended into the tube to regions with a different temperature history. The earliest ignition signal is thus relatively weak, becomes stronger as the subsequent sequence of ignition processes down the tube is captured. The convolution emerges as a longer ignition delay time compared to the sidewall measurement. As shown in the figures, the observed differences are comparable with shock tube uncertainties, so that this percentage difference is not as big as typical deviations of chemical kinetic model predictions from experiments. In the current shock tube, the sidewall is centered approximately 1 cm away from an endwall insert.

3 Results and discussions

The ignition measurements of the furan isomers are first presented, followed by those of the cyclohexanes. The reported results are for stoichiometric mixtures of fuel and oxidizer in which the molar ratio of argon to oxygen, D, is kept constant. Figures 3a and 3b show the ignition delay times of stoichiometric mixtures of 2,5-dimethyl and ethyl furans at post-reflected pressures of 5 atm and 12 atm, respectively, over a temperature range of 1044–1390 K. It is observed that in both cases, the ignition delay times of the dimethyl isomer are longer than those of ethyl furan. At 5 atm the difference is up to a factor of 5 while at 12 atm, evidence of a difference in temperature sensitivity is observed, with the dimethyl

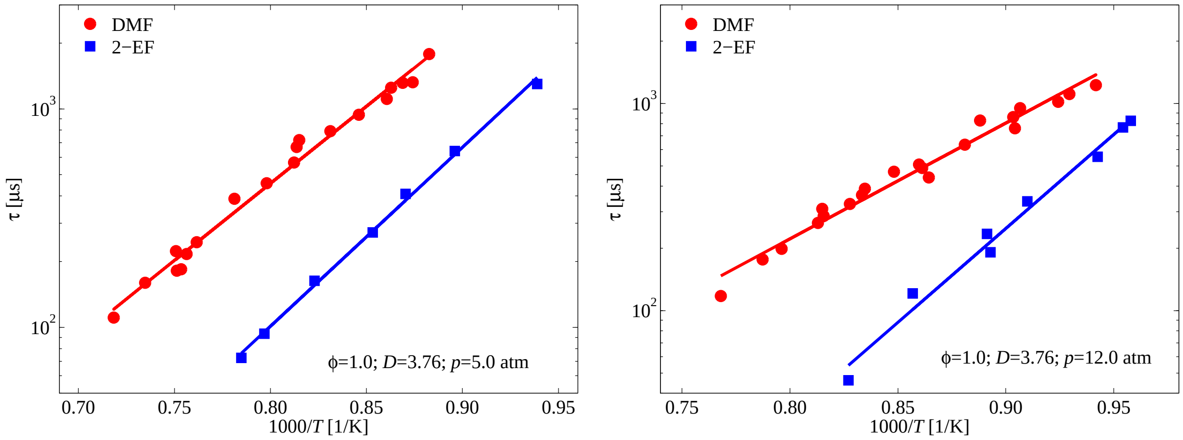


(a) T=1288 K (b) T=1315 K

Figure 2: Simultaneous endwall and sidewall ignition delay time measurement, illustrated for ignition of stoichiometric mixtures of ethyl cyclohexane /O_2/Ar at average pressures of 5 atm. Differences are observed partly due to cumulative ignition of the gas column viewed by the endwall photo diode, whereas the sidewall views a cross section well defined by the optical fiber line of sight.

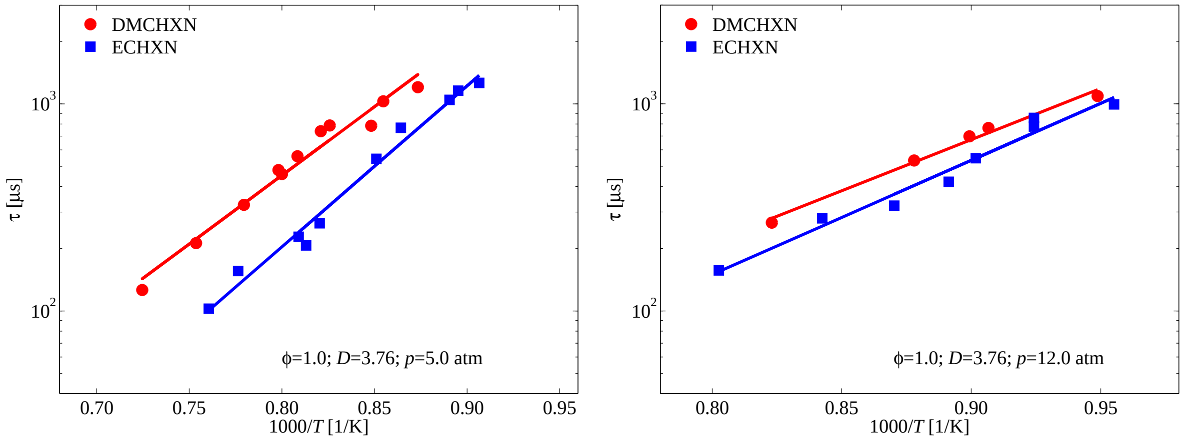
isomer displaying a weaker temperature sensitivity. This marked difference originating from structural differences presents a good opportunity to further explore the oxidation of alkyl furans.

We rationalize the observed differences in a number of ways. Firstly, the alkyl radicals liberated by direct bond cleavage are methyl radicals for the dimethyl and ethyl radicals for the ethyl isomer. Whereas the ethyl radical can undergo beta-scission to yield ethylene and an H atom, methyl radicals can recombine to form stable ethane molecules or undergo a slower beta-scission to yield H atoms and methylene radicals. Secondly, whereas the dimethyl isomer presents terminal C–H bonds for radical attack, weaker C–H bonds in the ethyl radical present a more favorable site for H-abstraction by radicals. Thirdly, it is also feasible that ring-opening of the primary fuel radicals (those obtained after first H-abstraction) is easier for the radicals of ethyl furan compared to those of the 2,5-dimethyl furan.



(a) p=5 atm (b) p=12 atm

Figure 3: Ignition delay times of stoichiometric mixtures of fuel, oxygen, argon with an argon/oxygen ratio of 3.76. Ignition delay times of 2,5-dimethyl furan are significantly longer than those of 2-ethyl furan. Solid lines represent Arrhenius fits.



(a) p=5 atm

(b) p=12 atm

Figure 4: Ignition delay times of stoichiometric mixtures of fuel, oxygen, argon with an argon/oxygen ratio of 3.76. Ignition delay times of dimethyl cyclohexane (DMCHXN) are longer than those of ethyl cyclohexane (ECHXN), especially at 5 atm. Solid lines represent Arrhenius fits.

The results of the stoichiometric cyclohexane studies are shown in Figs. 4a and 4b, where it can be seen that the ethyl isomer ignites more readily than the 1,3-dimethyl isomer over a temperature range of 1057–1395 K. However, in this case it is observed that the differences are not as pronounced as those of the furan isomers, with the delay times of the dimethyl isomer being only approximately 2 times longer than those of the ethyl under similar conditions. Similar to the furans, differences are more pronounced at the lower pressure of 5 atm over the investigated temperature range. From Fig. 1, we see that one of the differences between the furan structures and the cyclohexanes is the C=C bond structure which is present in furans and absent in cyclohexanes. Radical addition reactions to these double bonds can facilitate ring opening or radical propagation. Thus if more radicals are initially produced during the oxidation of the ethyl isomers of furans and benzenes, these would tend to more effectively accelerate oxidation through attack of the C=C double bonds. Further work is ongoing to develop ethyl furan and dimethyl cyclohexane models to couple with existing models of 2,5-dimethyl furan and ethyl cyclohexane for more quantitative analysis of these tentative explanations.

4 Conclusions

The reflected shock tube technique has been employed in the investigation of the effect of molecular structure on ignition propensity for dimethyl and ethyl isomers of the cyclic compounds, furans and cyclohexanes. It observed that the ignition delay times of the dimethyl isomers are generally longer than those of the ethyl isomers under similar experimental conditions. A more pronounced difference is seen between the ignition delay times of 2,5-dimethyl and ethyl furans, where a difference of up to a factor of 5 is observed compared to the difference between dimethyl and ethyl cyclohexane, which is approximately a factor of 2. The observations also align with a previous study on the ignition of alkyl benzene isomers, which established that m-xylene ignition delay times can differ from those of ethyl benzene by up to a factor of 3, or 5 under some conditions. There are, however, other factors in play in these trends, such as bond types, resonance stabilization, and strain. The experimental results present an opportunity to further explore mechanistic pathways and rate processes controlling the oxidation of cyclic hydrocarbons of relevance to combustion systems.

Acknowledgement

Acknowledgment is made to the Donors of the American Chemical Society Petroleum Research Fund for partial support of this research.

References

[1] D. F. Davidson and R. K. Hanson, “Interpreting shock tube ignition data,” *Int. J. Chem. Kinet.*, vol. 39, pp. 510–523, 2004.

[2] M. A. Eldeeb and B. Akih-Kumgeh, “Reactivity trends in furan and alkyl furan combustion,” *Energy & Fuels*, vol. 28, no. 10, pp. 6618–6626, 2014.

[3] H.-P. S. Shen and M. A. Oehlschlaeger, “The autoignition of c_8h_{10} aromatics at moderate temperatures and elevated pressures,” *Combustion and Flame*, vol. 156, no. 5, pp. 1053–1062, 2009.

[4] Y. Qian, L. Zhu, Y. Wang, and X. Lu, “Recent progress in the development of biofuel 2, 5-dimethylfuran,” *Renewable and Sustainable Energy Reviews*, vol. 41, pp. 633–646, 2015.

[5] M. A. Eldeeb and B. Akih-Kumgeh, “Investigation of 2,5-dimethyl furan and iso-octane ignition,” *Combust. Flame*, 2015, http://dx.doi.org/10.1016/j.combustflame.2015.02.013.

[6] M. Colket, T. Edwards, S. Williams, N. P. Cernansky, D. L. Miller, F. Egolfopoulos, P. Lindstedt, K. Seshadri, F. L. Dryer, C. K. Law *et al.*, “Development of an experimental database and kinetic models for surrogate jet fuels,” in *45th AIAA Aerospace Sciences Meeting and Exhibit*, 2007, pp. 8–11.

[7] W. J. Pitz, C. Naik, T. N. Mhaoldúin, C. K. Westbrook, H. J. Curran, J. P. Orme, and J. Simmie, “Modeling and experimental investigation of methylcyclohexane ignition in a rapid compression machine,” *Proceedings of the Combustion Institute*, vol. 31, no. 1, pp. 267–275, 2007.

[8] S. S. Vasu, D. F. Davidson, Z. Hong, and R. K. Hanson, “Shock tube study of methylcyclohexane ignition over a wide range of pressure and temperature,” *Energy & Fuels*, vol. 23, no. 1, pp. 175–185, 2008.

[9] B. Sirjean, E. Dames, D. Sheen, F. Egolfopoulos, H. Wang, D. Davidson, R. Hanson, H. Pitsch, C. Bowman, C. Law *et al.*, “A high-temperature chemical kinetic model of n-alkane, cyclohexane, and methyl-, ethyl-, n-propyl and n-butyl-cyclohexane oxidation at high temperatures, jetsurf version 1.1, september 15, 2009.”

[10] Z. Hong, K.-Y. Lam, D. F. Davidson, and R. K. Hanson, “A comparative study of the oxidation characteristics of cyclohexane, methylcyclohexane, and *n*-butylcyclohexane at high temperatures,” *Combustion and Flame*, vol. 158, no. 8, pp. 1456–1468, 2011.

[11] J. Vanderover and M. A. Oehlschlaeger, “Ignition time measurements for methylcylcohexane-and ethylcyclohexane-air mixtures at elevated pressures,” *International Journal of Chemical Kinetics*, vol. 41, no. 2, pp. 82–91, 2009.

[12] E. L. Petersen, D. F. Davidson, and R. K. Hanson, “Ignition delay times of ram accelerator ch/o/diluent mixtures,” *Journal of Propulsion and Power*, vol. 15, no. 1, pp. 82–91, 1999.

[13] E. Petersen, “Interpreting endwall and sidewall measurements in shock-tube ignition studies,” *Combust. Sci. Technol.*, vol. 181, no. 9, pp. 1123–1144, 2009.