UCRL-CONF-216161

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October 13, 2005

2005 Fall Meeting of the Western States Section of the Combustion Institute
Stanford, CA, United States
October 17, 2005 through October 18, 2005

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2005 Fall Meeting of the Western States Section of the Combustion Institute
Stanford University, 17-18 October 2005
Paper # 05F-67

Modeling and Experimental Investigation of Methylcyclohexane Ignition in a Rapid Compression Machine

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Abstract

A new mechanism for the oxidation of methylcyclohexane has been developed. The mechanism combined a newly-developed low temperature mechanism with a previously-developed high temperature mechanism. Predictions from the chemical kinetic model have been compared to experimentally measured ignition delay times from a rapid compression machine. Predicted ignition delay times using the initial estimates of the methylcyclohexyl peroxy radical isomerization rate constants were much longer than those measured at low temperatures. The initial estimates of isomerization rate constants were modified based on the experimental findings of Gulati and Walker that indicate a much slower rate of isomerization. Predictions using the modified rate constants for isomerizations yielded faster ignition at lower temperatures that greatly improved the agreement between model predictions and the experimental data. These findings point to much slower isomerization rates for methylcyclohexyl peroxy radicals than previously expected.

Introduction

Chemical kinetic models are needed to represent the chemistry of practical fuels such as gasoline, diesel, and jet fuel. Since these fuels can contain hundreds, or even thousands of hydrocarbon components, it is not currently possible to represent each of these components using a detailed chemical kinetic mechanism. Instead a small number of fuel components, often called a surrogate fuel, can be chosen to simulate a practical fuel. One method for choosing these components is to select one or more constituents to represent each chemical class in the practical fuel. These chemical classes typically include n-alkanes, iso-alkanes, cyclo-alkanes, alkenes, aromatics, polycyclic aromatics, and oxygenates. Cyclo-alkanes are an important chemical class because they comprise a significant fraction of the hydrocarbons present in diesel fuel and jet fuel [1]. With the emergence of oil-sand derived fuels that have a larger fraction of cyclo-alkanes than conventional fuels [2], they are expected to play a larger role in practical fuel chemistry. Yet to date, only limited experimental investigations and chemical kinetic mechanism development has been made on cycloalkanes [3-9].

We have selected methylcyclohexane (MCH) to represent the cycloalkane class in a surrogate fuel. Methylcyclohexane is one of the simplest cyclo-alkanes and is a starting point for the development of chemical kinetic mechanisms for cycloalkanes. Of the cycloalkanes present in gasoline, the methylcycloalkane component is present in highest concentration [10]. In order to develop a chemical kinetic mechanism for wide temperature ranges required for modeling combustion in homogeneous charge compression ignition (HCCI) engines and diesel engines, we have developed a low temperature oxidation mechanism for MCH and merged it with an recently published high temperature mechanism [3]. The complete mechanism is used to model experiments on the ignition of MCH in a rapid compression machine.

Experiments

The NUIG rapid compression machine (RCM) has a twin-opposed piston configuration described previously [11, 12], resulting in a fast compression time of a little more than 16 ms. In addition, creviced piston heads are used which results in a near-homogeneous post-compression temperature distribution in the combustion chamber [13]. Gases used were supplied by BOC Ireland: nitrogen (CP Grade) 99.95%, argon (Research Grade) 99.9995%, oxygen (Medical Grade) 99.5% and were used without further purification. Methylcyclohexane was obtained from Aldrich Chemical Co. Ltd. and was determined to be 99.6% pure using gas chromatographic analysis. To minimize the presence of atmospheric air in the sample, liquid MCH was subjected to several freeze–pump–thaw degassing cycles before being used. Stoichiometric fuel/'air' mixtures were prepared manometrically in a stainless steel container and allowed to homogenize over a 12 hour period. Experiments were carried out at a compression ratio of 10.5:1 with a compression time of approximately 16.6 ms. In order to investigate compressed gas temperatures in the range 680—980 K, two different parameters were adjusted: (i) the diluent gases were varied in order to alter the overall heat capacity of the fuel and 'air' mixture resulting in a range of compressed gas temperatures; (ii) a thermostat fitted to the combustion chamber allowed the initial temperature to be varied independently. The compressed gas temperature, Tc, was calculated based on the initial temperature and pressure of the chamber. The volume ratio was varied such that the calculated compressed-gas pressure matched that measured at the end of compression using the isentropic compression formula. The variation of specific heat with temperature for MCH, O_2 and diluent was included in the calculation. This temperature, Tc, was then plotted against the measured ignition delay time, to obtain overall reactivity profiles. Pressure–time data were measured using a pressure transducer (Kistler 603B) and recorded digitally using a personal computer. The ignition delay time was defined as the time from the end of compression to the maximum rate of pressure rise at ignition. In general, we found that the ignition delay times were reproducible to within 5% of one another at each Tc.

Chemical kinetic mechanism

The chemical kinetic mechanism used in the present study was developed in a modular fashion where species and reactions needed for the low and high temperature chemistry of MCH were added to previously developed mechanisms at LLNL for C1-C6 [14]. Submechanisms for toluene, benzene and cyclopentadiene were included [15]. The high temperatures reactions for MCH were added from the work of Orme et al. [3]. The main mechanism development in the present work is concerned with the low temperature chemistry of methylcyclohexane and is described below.

Thermodynamic properties, reactions paths and reaction rate constants for the low temperature oxidation of MCH were estimated. The thermodynamic properties of MCH and the species associated with its low temperature oxidation were estimated using THERM [16-18]. Reaction paths and their associated reaction rate constants were added to treat the low temperature oxidation of MCH. These reactions follow the addition of MCH radicals to molecular oxygen and subsequent reactions. The subsequent reactions include isomerization reactions to form hydroperoxy-cyclohexyl radicals (QOOH), decomposition of QOOH to cyclic ethers and other products, addition of hydroperoxy-cyclohexyl radicals to molecular oxygen, isomerization to form carbonyl-cyclohexyl-hydroperoxides (HO2Q'=O + OH) and subsequent decomposition of the carbonyl-cyclohexyl-hydroperoxide to produce a carbonyl-cyclohexoxy radical and an OH radical. (Q and Q' are methylcyclohexyl structures with one and two H-atoms removed, respectively).

Selection of reaction rate constants for key reactions

The rate constants for the isomerization of methyl-cyclohexylperoxy ($MCHRO_2$) radicals were estimated based on the reaction rate rules for alkylperoxy isomerizations [14]. The A-factors were adjusted for the entropy differences between the cycloalkane case and the reference n-/iso-alkane. The A-factors were calculated using the expression

$$A=(kT/h)\exp(\Delta S/R) \qquad (1)$$

where k is Boltsmann's constant, h is Planck's constant, T is temperature, ΔS is the change in entropy from a reactant to the transition state and R is the gas constant [19]. The change in entropy for an RO_2 isomerization rate constant is mainly affected by the number of rotors "tied up" in going from the reactant to the transition state. Typically for hydrocarbons, the ΔS per rotor tied up is approximately 3 to 5 cal-mole^{-1}-K^{-1}. Because the $MCHRO_2$ isomerization only involves one rotor, namely the MCHR-O_2 rotor, the A-factors rules from [14] for 5, 6, and 7-membered ring transition states were corrected according to Eqn. 1 to account for the adjusted number of rotors. This leads to an increased A-factor for MCHR-O_2 isomerizations compared to n-/iso-alkyl isomerizations. A typical A-factor for MCHR-O_2 isomerization was 5×10^{12} per secondary C-H site, compared to 1×10^{11}, 1.2×10^{10}, 1.6×10^{9} for a 5-, 6-, and 7- membered ring in the n-/iso-alkylperoxy isomerization respectively (Table I). Thus, large increases in A-factors are seen for MCHR-O_2 isomerizations compared to n-/iso-alkylperoxy isomerizations. Calculations with these estimated A-factors for MCHR-O_2 isomerizations were found to predict much too slow ignition delay times for MCH under RCM conditions compared to the experiments (results will be shown later).

A second set of MCHR-O_2 isomerization rate constants were tried to solve the problem of too slow ignition times for MCH under RCM conditions. These isomerization rate constants were estimated based on the experimental results of Gulati and Walker [4]. In a subsequent literature search, the later work of Hanford-Styring and Walker was found [5], but the experimental isomerization rates constants are not substantially different that the earlier work. Gulati and Walker determined that the corresponding cyclohexylperoxy isomerization rate constants for 5-, 6-, and 7-membered ring transitions states were 5, 5, and 20 times *slower* at 753 K than their corresponding n-/iso-alkylperoxy isomerizations. This difference was attributed to increased strain in the transition state in the 5-, and 6-membered ring compared to the analogous ring in n-/iso-alkylperoxy transition state. For the six-membered ring, the decrease in isomerization rate for cyclohexylperoxy isomerization was attributed to its occurrence only in the "energenetically unfavorable twisted boat form" of the cyclohexylperoxy radical. Since these differences are enthalpy related rather than entropy related, the activation energies of MCHR-O_2 were all increased by 2.5, 2.5, and 5.0 kcal/mole for the 5, 6, and 7 membered transition state to account for the reduction of 5, 5, and 20 times observed at 753 K (Table 1). The A-factors for the 5, 6, and 7 membered rings MCHR-O_2 isomerizations were kept the same as their n-/iso-alkylperoxy counterparts [14]. Thus the A-factors in the second set of MCHR-O_2 isomerization rate constants were much lower than the first set because the Gulati and Walker experiments gave no indication that they should be increased relative to their n-/iso-alkylperoxy counterparts. This second set of isomerization rate constants lead to a dramatic improvement in agreement with the experimentally measured ignition delay times under RCM conditions.

Results

The predicted and measured ignition delay times are shown in Fig. 1. The predicted ignition delay times for the baseline mechanism were much too slow at low temperatures, but were in good agreement with the experimental data at high temperatures (875-1050 K). When the rate constant rules for methylcyclohexylperoxy radical isomerization were changed from the baseline estimates to those based on the experimental results of Gulati and Walker (Table1) [4], the computed ignition delay times were in much better agreement with the experimental times (Fig. 1). Predictions using the modified (second set) isomerization rate constants show negative temperature coefficient (NTC) behavior similar to that observed in the experiments. In Fig. 2, the results for 10, 15, and 20 atm pressure at the end of compression are shown with the Gulati-Walker-based rate constants. The trend of ignition delay times with increasing pressure agrees well between the experiments and the model for the whole temperature range. The ignition delay times predicted by the model are still overall longer than those measured by the experiments by about a factor of two at 750 K.

Discussion

It is interesting to examine why the model predicts the ignition delay times that are in much better agreement with the experiments using methylcyclohexylperoxy isomerization rate constants based on Gulati and Walker [4]. This result was initially baffling because the revised isomerization rate constants are 10^2 to 10^5 times lower than the original estimates at 750 K (Table 1). Usually, decreasing the rate of alkylperoxy isomerization rate constants increases ignition delay times in the NTC region. To understand this phenomenon, we examined the relative rates of methylcyclohexylperoxy isomerization. Each methylcyclohexylperoxy radical can undergo a 5-, 6-, or 7-membered ring isomerization. The fraction of cyclohexylperoxy radicals that undergoes a specific isomerization depends on the rate constant for the specific ring size. This branching fraction is given in Table 1 at 750 K, the temperature at the beginning of the NTC region in the RCM. The results show that for the original isomerization rate estimates, the cyclohexylperoxy radicals mainly isomerize through 7-membered rings while with the Gulati-Walker-based rates, the radicals isomerize through 6-membered rings. This result is important because only the 6-membered ring leads to significant chain branching through the sequence,

$RO_2 \leftrightarrow QOOH$
$QOOH + O_2 \leftrightarrow O_2QOOH \rightarrow HO_2Q'{=}O + OH$
$HO_2Q'{=}O \rightarrow OQ'{=}O + OH$

where two reactive OH radicals are generated that accelerate the autoignition process. The 7-membered ring route also has this sequence, but the sequence is “short-circuited” by the reaction

$QOOH \Rightarrow QO + OH$,

a step that is very fast because it goes through a six-membered transition state (with negligible ring strain) to form the cyclic ether, QO, in this case. Thus, the QOOH goes to QO + OH and does not add significantly to O_2, the path that leads to chain-branching.

Conclusions

The oxidation of methylcyclohexane has been examined experimentally and computationally in a rapid compression machine. To model the oxidation of MCH, a new, low-temperature, oxidation mechanism for methylcyclohexane has been developed. The computational study found that the origin estimates of methylcyclohexylperoxy radical isomerization rate constants gave too long ignition delay times compared to those measured in the rapid compression machine. Rate constants based on the experimental results of Gulati and Walker gave much better predictions compared to the experiments. This difference in predictions was attributed to the relative importance of 7-membered ring isomerizations in the original estimates, compared to 6-membered rings in the Gulati-Walker-based estimates. The 6-membered ring isomerizations lead primarily to chain branching and production of OH radicals which accelerate autoignition process. Our study indicates that the relative rates of 5-, 6-, 7-membered ring methylcyclohexylperoxy isomerizations are critical to prediction of ignition delay times in the NTC region.

Acknowledgements

This work was supported by the U.S. Department of Energy, Office of Freedom CAR and Vehicle Technologies and under the auspices of the U.S. Department of Energy by University of California Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. The authors thank program managers Stephen Goguen and Gurpreet Singh for their support of this work. Ms. T. Ni Mhaoldúin and Prof. John Simmie acknowledge support from the European Union contract NNE5-2001-00869.

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Table 1: Methylcyclohexylperoxy radical isomerization rate constants used in present study (cm-mole-sec units; rate constant is per secondary C-H site)

Ring size in transition state	A	n	Ea	Rate at 750K	Branching fraction
Original estimate:					
5	5.0e12	0	26850	8.0e4	0.4%
6	5.0e12	0	20850	4.5e6	23%
7	5.0e12	0	19050	1.5e7	77%
Gulati and Walker based estimate:					
5	1.00e11	0	29350	3.0e2	12%
6	1.25e10	0	23350	2.1e3	82%
7	1.50e9	0	24050	1.6e2	6%

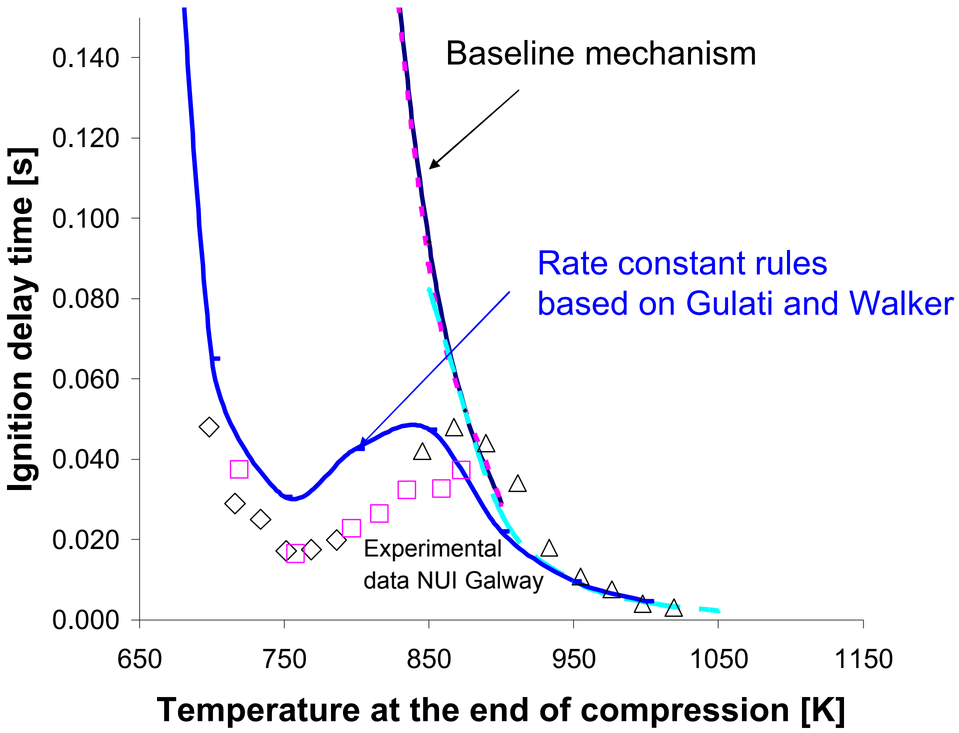

Fig 1: Measured ignition delay times (symbols) for MCH/O_2/diluent stoichiometric mixtures for 10 atm pressure at the end of compression. The predicted ignition delays (curves) are for the baseline mechanism and for isomerization rate constants based on Gulati and Walker.

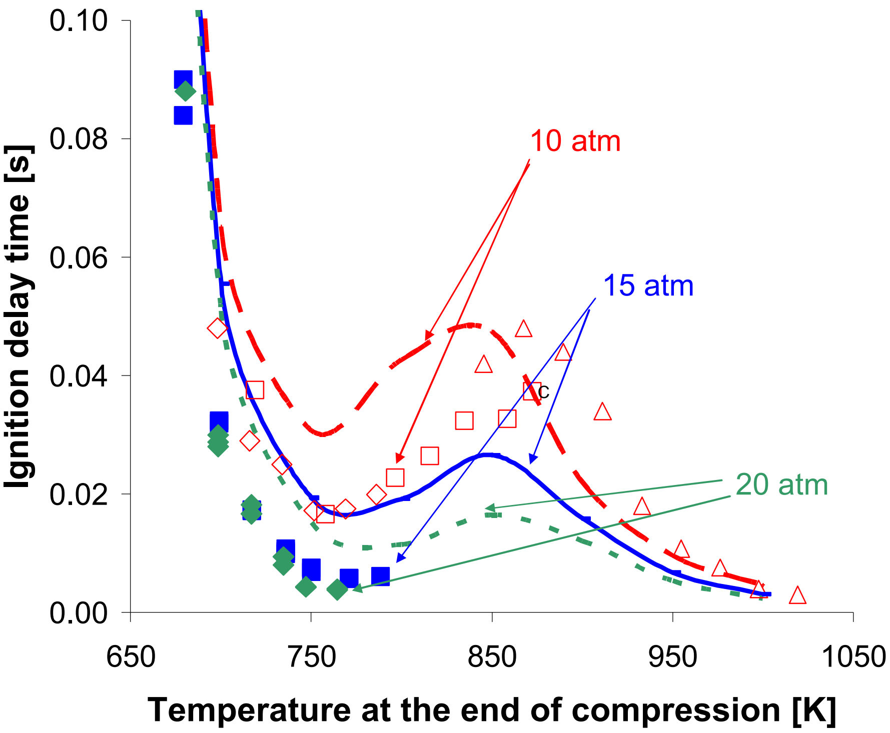

Fig. 2: Comparison of model predictions (curves) and experimental measurements (symbols) for stoichiometric mixtures of MCH/O_2/diluent at 10, 15 and 20 atm pressure at the end of compression.