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Chemical kinetic modeling of low pressure methylcyclohexane flames

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Abstract

Alkyl cyclohexanes are important components in gasoline, diesel, and jet fuels. With the recent introduction of oil-sand derived petroleum feedstocks, the levels of alkyl cyclohexanes in fuels are likely to increase. Elevated levels of alkyl cyclohexanes in fuels are expected to increase soot emissions when utilized in combustion devices. With expected increases in alkyl cyclohexanes in fuels, more accurate chemical kinetic pathways and rate constants are needed to understand the chemical pathways responsible for increased soot production. To improve the accuracy of chemical kinetic models, low pressure premixed flames with tunable UV molecular beam sampling provides a wealth of speciation data for model validation. This data will help to understand the flame chemistry of alkyl cyclohexanes and their production of soot precursors like benzene, acetylene, fulvene and others. In this study, we have focused on methyl cyclohexane (MCH) which is the simplest alkyl cyclohexane.

In a recently published study of methyl cyclohexane flames by the present authors, the LLNL MCH model and other available literature models were found to be inaccurate in predicting many intermediate species in low pressure MCH flames. This finding has led to improvements of the MCH chemical kinetic model. The following submodels have been replaced in the previous 2007 LLNL model: The C1-C4 base chemistry using the Saudi Aramco version 1, the aromatics base chemistry using the latest LLNL-NUIG base model, and the cyclohexane submodel with the more recent LLNL 2007 version. Also, there are additional updates of the MCH mechanism. The abstraction reactions from MCH were replaced using recent experimentally measured values and standardized using the latest LLNL reaction rate rules. The previous 2007 MCH model lumped many of unsaturated ring products of MCH that lead to soot precursors. These species have now been expanded to include all the relevant isomers with their associated chemical kinetic reaction paths and rate constants. The model now tracks the intermediate unsaturated methylcyclohexane species with much more fidelity and predicts their experimentally measured concentrations with much more accuracy.

The improved MCH chemical kinetic model was employed using Chemkin Pro® and the experimentally measured temperature profile to model the low pressure flames of equivalence ratios of 1 and 1.9. A more accurate experimental temperature profile than previously available was obtained using the FKT transfer function. In the paper, the experimentally measured and predicted cyclic species, aromatics, and soot precursors are compared and discussed. Additionally, the production and consumption of key aromatic species is tracked to identify the important chemical pathways leading to aromatics, and soot precursors in these MCH flames.

1. Introduction

Petroleum-derived fuels like gasoline, jet, and diesel fuels contain significant amounts of cycloalkanes. These are usually in the form of six-membered ring compounds (cyclohexanes); however, gasoline can contain some 5-membered ring compounds (cyclopentanes). In petroleum-based fuels, cycloalkanes are usually substituted with one or more alkyl group (Farrell et al. 2007; Pitz et al. 2007; Pitz et al. 2011). In gasoline fuels, the cycloalkanes are single ring compounds; however, in diesel fuels, some of the cyclohexanes are multi-ring and have two or three fused cyclohexane rings. In addition, transportation fuels derived from oil sands can have larger amounts of cycloalkanes than those derived from conventional petroleum sources (Neill et al. 2003).

To accurately simulate fuel effects in practical combustion devices, chemical kinetic models are needed to represent each chemical class in the practical fuel, including cycloalkanes. Towards fulfilling this goal, chemical kinetic models have been developed for cycloalkanes including methyl cyclohexane (Granata et al. 2003; Neill, Chippior et al. 2003; Pitz et al. 2007; Ji et al. 2011), ethylcyclohexane (Wang et al. 2010), n-propylcyclohexane (Ristori et al. 2001) and n-butylcyclohexane (Wang, Dames et al. 2010) and decalin (Oehlschlaeger et al. 2009). In this work, we focus on the simplest cyclohexane with an alkyl substitution: methyl cyclohexane (MCH). Although it has the simplest molecular structure, there have been issues with the performance of MCH models in the literature, particularly at high pressures where accurate models are needed to simulate combustion in internal combustion engines (Vanderover et al. 2009). Specifically, the ignition delay times of the chemical kinetic model have been too long at high pressure compared to experiments. Also, there have been problems in simulating the flame structure of low-pressure MCH flames (Skeen et al. 2011). Skeen et al. found that Pitz et al. model was unable to reproduce many of the intermediate species measured in the flame. Although it is important to proceed to higher molecular weight alkyl cyclohexane's relevant to diesel fuel, we want to resolve issues with the simplest of the alkyl cyclohexanes so that knowledge acquired can be systematically used for higher molecular weight alkyl cyclohexanes. The current study focuses on resolving the issues regarding the agreement of the model with low pressure flame measurements.

2. Chemical kinetic model development

Model development

The following improvements to the MCH chemical kinetic model have been made: First, the C1-C4 base chemistry was replaced with Saudi Aramco version 1.3 (Metcalfe et al. 2013; Metcalfe et al. 2013). This base model well simulates premixed laminar flame speeds (Metcalfe, Burke et al. 2013). Second, the aromatics base chemistry was replaced using a newly developed and validated version (Metcalfe et al. 2013). This aromatics chemistry well simulates the oxidation of toluene, benzene, cyclopentadiene, and phenol. Third, the submodel for cyclohexane was replaced with the Silke et. al version (Silke et al. 2007). This mechanism describes well the ignition of cyclohexane and its oxidation under conditions in a jet stirred reactor. Fourth, many MCH portions of the mechanism have been updated as follows. The abstraction reactions from MCH were replaced using recent experimentally measured values (Sivaramakrishnan et al. 2009) and standardized using the latest LLNL reaction rate rules (Sarathy et al. 2011). The previous 2007 MCH model lumped many of unsaturated ring products of MCH that lead to soot precursors. This led to an inadequate description of many of the unsaturated cyclic products in low pressure MCH flames (Skeen, Yang et al. 2011). These lumped species have now been removed and replaced with the inclusion of all the relevant isomers with their associated reaction paths and rate parameters. As will be seen, this more detailed description of the chemistry of the unsaturated cyclic species gives much better agreement with the measured intermediates in the low-pressure MCH flames.

Transport

The effect of transport on the computed results depends on the transport properties used and the type of transport model used. Transport parameters were estimated for new species now included in the mechanism. To estimate transport properties there are two main correlations available: one for aromatics and one for linear alkanes. Because cyclic species are similar in shape to aromatics, transport parameters of new cyclic species were computed using Wang and Frenklach's recommended correlation for aromatics (Wang et al. 1994). For aliphatic species in the mechanism, the n-alkane correlation recommended by Holley et al. (Holley et al. 2009) was used. Regarding the transport model, the multicomponent model in Chemkin is considered to be more accurate than the mixture averaged model. We tried the multi-component transport model with thermal diffusion included in ChemkinPro® (2010), but the flame calculations did not converge to a solution. Therefore, the mixture-averaged transport model in was used.

Numerical model

The burner stabilized flame model in ChemkinPro® (2010) was used for the flame simulations. The temperature profile in the flame was specified using measured temperature profiles discussed below. The number of grid points on the computational grid was increased to ensure that the calculations were converged. The number of grid points on the stoichiometric flame discussed below was increased from 90 to 229 and the rich flame from 217 to 307. No discernible change was seen on a plot of the methyl radical profile (not shown). The reaction pathway and sensitivity analysis tools in ChemkPro® were used to obtain further information about the flame chemistry.

3. Experimental

We investigated low-pressure premixed MCH/oxygen/argon flames at equivalence ratios of φ = 1.0 and 1.9 and pressures of 15 and 30 Torr, respectively, stabilized on a flat-flame McKenna burner. A summary of the flame conditions is provided in Table 1. Flame A, the stoichiometric flame, provides a more direct investigation of the fuel-consumption/oxidation processes, while the fuel-rich condition is chosen to produce larger amounts of aromatic species. Our previous work (Skeen et al., 2011) focused mainly on the first few steps of MCH composition leading to the aromatic species toluene and benzene. In this work, we present additional experimental results previously unpublished.

Table 1. Flame Parameters

Flame	X_{MCH}	X_{O2}	X_{Ar}	φ	p / Torr	Mass flow rate / g cm^{-2} s^{-1}
A	0.035	0.365	0.60	1.0	15	$4.1\text{x}10^{-3}$
B	0.060	0.340	0.60	1.9	30	$4.3\text{x}10^{-3}$

The experimental set-up and procedures used to study the chemical composition of such flames have been described in several previous papers (Cool et al. 2005; Cool et al. 2005; Osswald et al. 2007; Hansen et al. 2009). The gas flow rates are controlled using calibrated mass flow controllers, and the liquid MCH is metered using a syringe pump, vaporized, and quantitatively added into the oxidizer/Ar stream. Gases from within these flames are extracted using a quartz probe with an orifice diameter of approx. 0.8 mm. The gas-phase species are ionized by single photons with energies between 8-17 eV using tunable synchrotron radiation at the Chemical Dynamics Beamline of the Advanced Light Source located at Lawrence Berkeley National Laboratory. The resulting ions are subsequently separated and detected using a time-of-flight mass spectrometer with a detection limit of ~1ppm (Cool, McIlroy et al. 2005).

As in previous work, we measured the integrated and photon-current normalized ion signals as a function of the photon energy, and used the resulting photoionization efficiency (PIE) curves to identify the isomeric composition of the combustion intermediates. We measured the gas composition at different positions within the flame by moving the burner relative to the sampling cone, and the ion signal was then converted into chemical species spatial mole fraction profiles. The photoionization cross sections, including fragmentation patterns, needed for a quantitative analysis were taken from Refs.(Cool, McIlroy et al. 2005; Wang et al. 2008; Zhou et al. 2010; Yang 2011). For some intermediates, the cross sections were estimated by the empirical method of Koizumi or from those of similar molecules (Cool, McIlroy et al. 2005; Wang, Yang et al. 2008; Zhou, Zhang et al. 2010; Yang 2011). These estimates are summarized in Table 2.

Table 2: Estimated Photoionization Cross-Sections for MCH Combustion Intermediates

Mass	Species	Energy / eV	σ / Mb
98	2-Methyl-1-Hexene	9.5	9.1
98	1-Heptene	9.5	2.5
96	C_7H_{12} (1,3-dienes)	8.8, 9.5, 9.8	8.8, 19.0, 21.0
96	Methyl-Cyclohexenes	9.5, 9.8	9.3, 11.3
94	Lumped C_7H_{10} isomers	8.8	20.0

Mole fraction profiles as a function of distance from the burner were obtained for these two flames for more than 40 species (including radicals) with ion masses ranging from 1 (H) to 98 (C_7H_{14}). Whenever feasible the isomeric contributions at a given ion mass were resolved. For example, contributions from allene, vinyl alcohol, and fulvene are separated from propyne, acetaldehyde, and benzene, respectively; however, for some of the heavier ion masses the mole fraction profiles can only be considered partially resolved because of ambiguities in isomeric identification as discussed previously (Skeen, Yang et al. 2011). Nevertheless, based on previous experience attempting to model the detailed chemistry of low-pressure flames (see Ref. (Hansen, Cool et al. 2009) and examples therein), the accuracies of the experimentally determined mole fraction profiles (within 20% for the major species, but as large as a factor of two for intermediates with unknown photoionization cross sections) should be sufficient for assessing the predictive capabilities of MCH combustion chemistry models.

Flame temperatures, which are important input parameters in modeling calculations, are measured using OH laser-induced fluorescence. A detailed description of the setup is available in the literature (Hansen et al. 2009). Briefly, light near 306 nm is generated at 10 Hz by an optical parametric oscillator (Continuum, Sunlite EX, FX-1) to excite the OH *A-X* (0,0) transition. Measurements are taken approx. 3 cm upstream from the sampling cone tip, thus the temperatures should represent unperturbed conditions. Uncertainties in temperature are estimated to be ± 150 K in the reaction region and post-flame and larger in the preheat zone where the OH concentration diminishes and gradients steepen. At times, a more accurate temperature profile near the burner can be obtained by normalizing a transfer function, used in the analysis of species mole fraction data, to the post flame OH LIF temperature measurements. The transfer function can be related to the temperature by applying the relationship for an isentropic adiabatic expansion through a nozzle (Struckmeier et al. 2009). In this work, the transfer function was used to obtain an improved temperature profile for the $\varphi = 1.0$ flame relative to that used in Skeen et al. (2011).

4. Results and Discussion

In this section, we compare species profiles across the two flames that are computed using the updated mechanism and measured experimentally. The results are presented by the different classes of species.

Unsaturated cyclic species

Unsaturated cyclic species are important in MCH oxidation because they lead to precursors to the formation of soot. McEnally and Pfefferle (McEnally et al. 2003) reported that soot correlates well with benzene formation in doped methane flames for aliphatic dopants. They found that cycloalkanes (e.g. methylcyclohexane) formed much more benzene than their acyclic counterparts in doped methane flames (McEnally et al. 2006). In the flame, MCH dehydrogenates through unsaturated cyclic species forming the aromatics benzene and toluene. Therefore, it is important to validate the MCH mechanism for the formation of unsaturated cyclic species that lead to benzene and toluene in the flame.

Figure 1 compares the predicted and measured species profiles for cyclohexene. The computed results for the stoichiometric flame compare well with the measurements, but the rich flame concentrations are overpredicted. In the rich flame, cyclohexene is mainly formed by hydrogen abstraction from the MCH ring, followed by ejection of a methyl group to form cyclohexene. It is consumed by hydrogen abstraction by H and OH radicals and by ring opening. The results for 1,3-cyclohexadiene are shown in Fig. 2. The agreement between the simulations and the experiments are reasonable with the model showing the correct trend in peak concentration from the stoichiometric to rich flame. The model and experimental comparison for benzene are given in Fig. 3. The behavior seen in the experiment is well reproduced by the model. The present modeling results are much improved compared to the previous version of the model that underpredicted the peak concentrations of cyclohexene, 1,3-cyclohexadiene and benzene by a factor of 8, 4-20 and 2, respectively (Skeen, Yang et al. 2011). We attribute the better accuracy of model to its higher fidelity description of unsaturated ring intermediates. The improved predictability of the model gives increased confidence in the model simulations of important soot precursors like benzene.

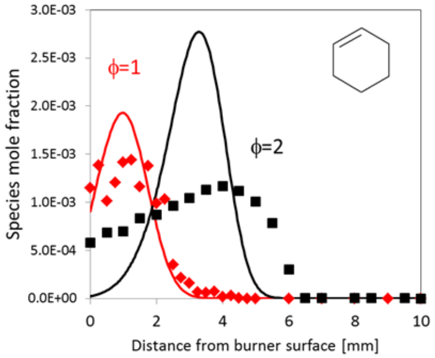

Figure 1. Computed (curves) and measured (symbols) species concentration profiles of cyclohexene.

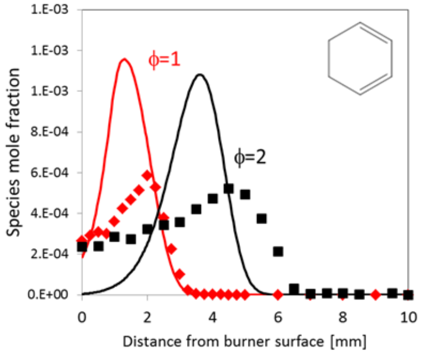

Figure 2. Computed (curves) and measured (symbols) species concentration profiles of 1,3-cyclohexadiene.

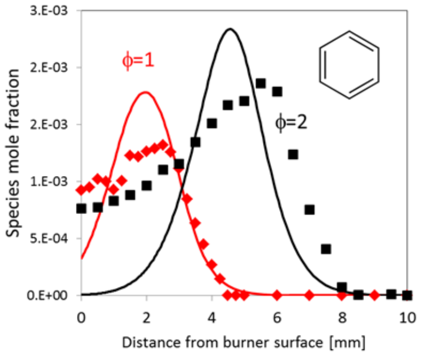

Figure 3. Computed (curves) and measured (symbols) species concentration profiles of benzene.

Small intermediates (C_2H_4 and C_2H_2)

Next, the behavior of small intermediate species in the flames is examined. Ethene is one of the important intermediate species with concentrations of 1 percent in the stoichiometric flame and increasing to 3 percent in the rich flame (Fig. 4). With ethene being a major intermediate with a well-known cross-section, its uncertainty is expected to be +/- 20%. The modeling results are generally within the experimental uncertainty, except near the burner for the rich flame. Acetylene is often reported in the literature as an important precursor for the formation of soot (Wang et al. 1997). The flame profiles for acetylene are given in Fig. 5 with agreement between the model and experiments generally within the experimental uncertainty of 20%, similar to ethene. These results provide confidence in the model for the prediction of soot precursors.

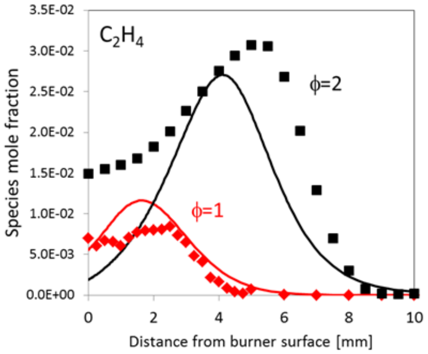

Figure 4. Computed (curves) and measured (symbols) species concentration profiles of ethene.

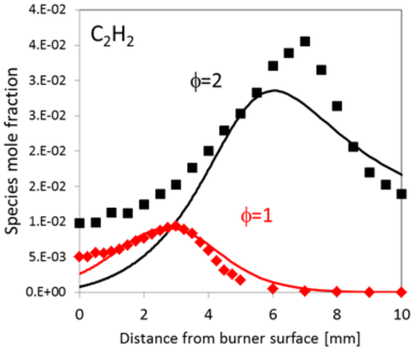

Figure 5. Computed (curves) and measured (symbols) species concentration profiles of acetylene.

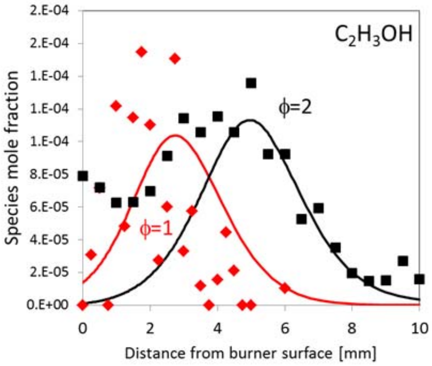

Figure 6. Computed (curves) and measured (symbols) species concentration profiles of ethenol.

The final small species shown is ethenol, which has received much attention in the literature and was first discovered in this experimental facility (Taatjes et al. 2006). Given the low concentration and large scatter for the ethenol experimental data for the stoichiometric flame, the agreement is good. Ethenol was mainly formed in the computed flame by c2h4+oh↔c2h3oh+h. This is the same pathway previously found in an ethene flame (Taatjes, Hansen et al. 2006).The pressure-dependent rate constant is taken from (Senosiain et al. 2006).

Radicals

One of the significant advantages of molecular beam sampling over conventional microprobe sampling is the ability to measure the concentration of radical species. This provides more stringent validation targets for chemical kinetic mechanisms than are usually available. The radical that was measured with the largest concentration in the flames was methyl radical. The experimental data show that its concentration increases from the stoichiometric to rich flame (Fig. 7). The model reproduces this trend and shows good agreement with the experimental data (The peak value is within 30% of the data).

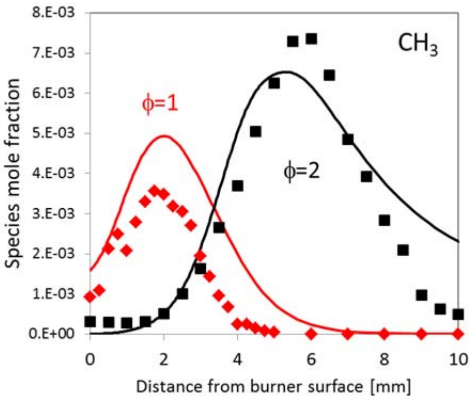

Figure 7. Computed (curves) and measured (symbols) species concentration profiles of methyl radical.

One of the most important radicals in the flame is the propargyl radical because of its role in the formation benzene in flames (Stein et al. 1991; Miller et al. 2003) and the associated need to describe its chemistry accurately in chemical kinetic models. In Fig. 8, the amount of propargyl radical increases significantly from the stoichiometric to rich flames. The model follows this trend, but the predicted peak concentration of the stoichiometric flame is about a factor of 3 too high. The propargyl is mainly formed by $C_6H_5+H \leftrightarrow C_3H_3+C_3H_3$ in the stoichiometric flame. Sensitivity analysis shows that this reaction exhibits the highest sensitivity for propargyl formation in this flame (at 2.5 mm). The pressure-dependent rate constant is specified in the reverse direction from (Miller and Klippenstein 2003). For the rich flame, propargyl is mainly formed by $C_2H_3+C_2H_3 \Leftrightarrow C_3H_3+CH_3$. The rate constant is from Pope et al. (Pope et al. 2000). The agreement between the predicted and experimental propargyl concentrations in the rich flame is relatively good.

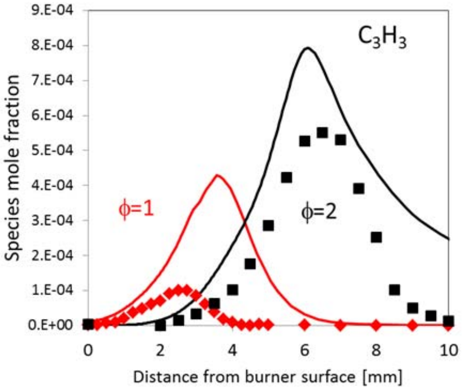

Figure 8. Computed (curves) and measured (symbols) species concentration profiles of propargyl radical.

The allyl radical is also thought to have a significant role in the formation of aromatic rings. The reaction of allyl and propargyl radicals can lead to fulvene and benzene (Georgievskii et al. 2007; Miller et al. 2010; Matsugi et al. 2011). The concentration profiles of the allyl radical are shown in Fig. 9. Again, the peak concentration of allyl increases from the stoichiometric to rich flame. The model reproduces this trend and quantitatively reproduces very well the experimentally measured profiles.

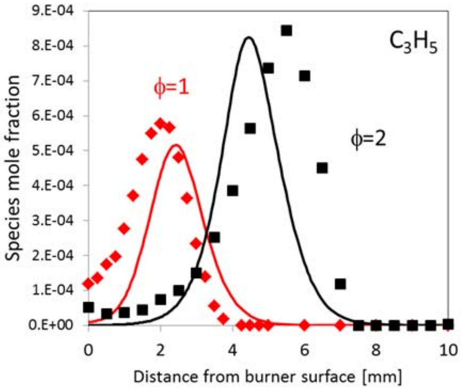

Figure 9. Computed (curves) and measured (symbols) species concentration profiles of allyl radical.

5. Conclusions

Species concentration profiles measured in low pressure flames have been simulated using an updated MCH chemical kinetic model. Improvements to the chemistry submechanism of C_1-C_4 species, cyclohexane, benzene, cyclopentadiene and MCH are responsible for dramatic improvement in the predictions of the model compared to the experimental measurements.

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Disclaimer

This is a work-in-progress paper and is not intended to be an archival publication.

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