Methylcyclohexane pyrolysis and oxidation in a jet-stirred reactor

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Abstract: Alkylated cycloalkanes are an important chemical class in conventional fuels. Methylcyclohexane (MCH) is a simple alkylated cycloalkane that is a potential candidate to represent the naphthenic content in transportation fuel surrogates. Detailed experimental speciation data for MCH gas-phase oxidation and pyrolysis is still lacking in the literature. This work investigates the high-temperature pyrolysis and low-temperature oxidation of MCH in a jet-stirred reactor. Under low-temperature conditions, highly oxygenated intermediate species indicative of “alternative isomerization” of hydroperoxyalkylperoxy (OOQOOH) radicals and the subsequent third sequential O₂ addition are presented. Furthermore, a detailed chemical kinetic model capable of predicting MCH combustion was developed using new thermodynamic group values and recently published rate coefficients. Alternative isomerization of OOQOOH radicals and third sequential O₂ addition pathways were incorporated into the reaction mechanism. Additionally, an approach for reducing the complexity of the MCH low-temperature chemical pathways has been investigated to limit the arduousness of developing kinetic models. The experimentally measured species concentration profiles at atmospheric pressure, equivalence ratios of 0.25, 1.0, 2, and ∞ , and temperatures in the range of 500–1100 K were used to validate and improve the chemical kinetic model. The model was further tested against rapid compression machine ignition delay times taken from literature.

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1. Introduction

Emerging combustion modes in internal combustion engines, such as Homogeneous Charge Compression Ignition (HCCI), promise a reduction in the emission of harmful pollutants. Combustion phasing for this combustion mode is dominated by the chemical reaction kinetics of the fuel; its auto ignition plays a particularly significant role in controlling the performance and emissions [1]. Thus, there is a continued interest in developing accurate and detailed kinetic models for fuel oxidation chemistry.

Cycloalkanes (naphthenes) are an important class of compounds in transportation fuels [2, 3]. They make a significant fraction of practical fuels, including jet fuels (~20%), gasoline (~10%), and depending on the crude source and degree of hydro processing, may constitute one-third or more by weight of diesel fuels [4]. Naphthenes play an important role in the formation of aromatic pollutants and polycyclic aromatic soot precursors [5]. Gasoline fuels typically contain significant amounts of C₅-C₇ cycloalkanes, such as cyclopentane [6, 7], methylcyclopentane, cyclohexane [8] and methyl and ethylcyclohexane [9, 10]. Amongst these, MCH is a simple alkylated cycloalkane frequently suggested as a candidate surrogate to represent the naphthenic content in transportation fuels [2, 3].

Various fundamental studies have been conducted for MCH gas-phase reactions, such as experimental measurements of its pyrolysis [9, 11], laminar premixed flame speciation profiles [9, 12], ignition delay times [13, 14], and laminar flame speeds [15]; reduced, skeletal, and detailed kinetic modeling of MCH combustion [9, 13, 16, 17]; and theoretical calculations of important reaction pathways [9, 18-20]. Details of published studies about MCH can be found in the papers of Wang et al. [9] and Narayanaswamy et al. [17].

The motivation of the present work is to (1) measure the detailed speciation products of MCH low- and high-temperature oxidation, and pyrolysis in a jet-stirred reactor (JSR). The literature lacks experimental speciation data for the low-temperature oxidation chemistry of MCH. Gas

Chromatography (GC) was used to measure the stable oxidation intermediates. In addition, synchrotron vacuum ultraviolet photoionization molecular beam mass spectrometry (SVUV-PI-MBMS), which has been widely used in combustion studies [21-25], was used to detect the peroxide species in MCH oxidation. Such data is lacking in literature, and is needed to understand MCH reaction pathways and test kinetic models. The JSR pyrolysis data measured in this work by GC complements previous flow reactor data [9] measured by SVUV-PI-MBMS. Both data are adopted to validate the kinetic model in this work; and (2) develop a preliminary kinetic model of MCH oxidation. The rate constants for some key reactions, e.g., R+O₂ reaction network, were taken from recent quantum chemistry calculations [19, 20, 26]. Additional reaction classes such as the “alternative isomerization” of OOQOOH to P(OOH)₂ radical and subsequent reactions of P(OOH)₂ radical including a third sequential O₂ addition reaction network [27, 28] were also included. In addition, the thermodynamic data was updated by using new group values from Burke et al. [29] in the calculation of Benson’s group additivity. Furthermore, a step-wise method, grounded in “chemical knowledge”, for reducing the number of reactions and species was investigated during the kinetic model development. The kinetic model was tested using the JSR pyrolysis and oxidation data obtained in this work, as well as ignition delay times taken from literature [13, 14]. The discussion focuses on the low-temperature oxidation kinetics of MCH and the methodology behind developing the kinetic model.

2. Experimental methods

Pyrolysis and oxidation of MCH at atmospheric pressure were studied in three fused silica JSRs using different analytical tools. The three experiments are complementary, i.e., KAUST JSR-1 coupled with an Agilent refinery gas analyzer (RGA) can measure pyrolysis products, Nancy JSR-2 coupled with three GCs provides data of stable oxidation products, and Hefei JSR-3 with SVUV-PI-MBMS can measure highly reactive peroxide intermediates. Details of the three JSRs and the experimental procedures can be found in literature [25, 30, 31].

MCH pyrolysis was studied in JSR-1 (volume of 76 cm³) with N₂ as the dilution gas. A

residence time of 1 s was chosen and the initial mole fraction of MCH was kept at 1000 ppm to reduce coking in the JSR at high temperature. After pyrolysis, further gas reactions were frozen by a pressure-drop in the sonic-throat gas sampling, then the sample gas was analyzed online using Agilent RGA and Agilent 7890B GC. The RGA system, following ASTM D1945, D1946, and UOP 539 methods, was used to quantify H₂, methane, acetylene, ethylene, ethane, propene, 1,3-butadiene. The Agilent 7890B system was equipped with a DB-1 column to measure MCH. The uncertainty on reactants is $\pm 5\%$, whilst for the pyrolysis products is estimated to be around $\pm 15\%$.

For the Nancy experiment, MCH oxidation at three equivalences (i.e., 0.25, 1.0, and 2.0) was investigated from 500-1100 K with helium as the dilution gas. The initial MCH mole fraction for the three experiments was kept at ~ 5700 ppm. The oxidation products were analyzed online by three GCs equipped with different columns (i.e., carboxsphere packed column, PlotQ capillary column, HP-5 capillary column) and detectors (thermal conductivity detector, flame ionization detector, and mass spectrometer), to measure C₁–C₄ hydrocarbons, small oxygenated compounds, as well as hydrocarbons and oxygenated species with more than five heavy atoms (i.e., carbon and oxygen atoms), and to identify the structure of unknown intermediates. Calibration was performed by injecting known amounts of pure substances when available; otherwise, the method of the effective carbon number was adopted. The uncertainty of the species mole fractions was about $\pm 5\%$ with online analysis of reactants and C₁–C₂ hydrocarbons, and about $\pm 10\%$ for analysis of other species.

In the Hefei experiment, the JSR was coupled with SVUV-PI-MBMS. During the experiments, the reactor and the cone were insulated using an oven. A nickel skimmer with a 1.25 mm diameter aperture was located about 15 mm downstream from the sampling nozzle (50 μm tip orifice). The formed molecular beam was then measured by the SVUV-PI-MBMS, which enables the measurement of peroxides, especially those with three to five oxygen atoms. The Hefei experiments were performed with an initial MCH mole fraction of 0.01, equivalence ratio of 1.0, and temperature of 500-800 K.

3. Kinetic model and simulation method

137 The MCH mechanism in this study was built on top of a previously developed *n*-heptane
 138 oxidation mechanism [32]. The high-temperature chemistry of MCH incorporates the
 139 high-temperature mechanism developed by Wang et al. [9], with the addition of extra reaction classes
 140 taken from Weber et al. [13]. The low-temperature mechanism was developed referring to Weber et
 141 al.'s mechanism and to the low-temperature reaction classes proposed by Sarathy et al. for *n*- and
 142 iso-alkanes [33]. The low-temperature oxidation scheme was extended to include the "alternative
 143 isomerization", concerted elimination, and third O₂ addition pathways for OOQOOH radicals [28],
 144 as shown in Scheme 1. The "alternative isomerization" pathway involves an alternative
 145 isomerization step in which the OOQOOH internally abstracts an H-atom that is not α to the OOH
 146 group. The reaction class numbers in Scheme 1 are taken from [33]. Additionally, rate constants have
 147 been updated to incorporate recently published information [19, 20, 26], and thermodynamic data
 148 were estimated from the group additivity method implemented in THERM [34] using the updated
 149 group values by Burke et al. [29]. Lastly, a knowledge-based approach to reduce the complexity of
 150 the low-temperature chemistry of MCH was investigated. Details of the reaction mechanism and the
 151 sources of rate parameters for MCH pyrolysis are provided in Table S1 of Supplementary Material-1
 152 (SM-1).

153

154 **Scheme 1.** General reaction mechanism of MCH oxidation. Species with molecular formula detected
 155 in this work are highlighted in blue. The numbers on arrows denote the reaction class discussed in
 156 this text.

158 Previous studies have shown that the sterically hindered cyclic structure of cycloalkanes greatly
 159 affects the low-temperature oxidation [19, 20]. Ring strain energy and frozen rotors imposed by the
 160 cyclic structure lead to remarkable deviations from rate constants estimated by analogy to linear
 161 alkanes. Investigations are needed to explore rate rules for individual cyclic alkane's
 162 low-temperature oxidation. Xing et al. [19, 20] recently studied the low-temperature oxidation
 163 chemistry of three typical MCH radicals (CYCHEXCH₂, MCHR1, MCHR2) using theoretical
 164 calculations. They provided temperature and pressure dependent rate constants involving the radicals,
 165 CYCHEXCH₂ ( )[•], MCHR1 ( )[•] and MCHR2 ( )[•], for the following reaction classes: 11,
 166 15, 16, 23, 24, and 25 (see Scheme 1). Hence, these rates were adopted in the proposed reaction
 167 mechanism. The cyclohexane rate constants computed by Fernandes et al. [26] were used for R + O₂
 168 and subsequent reactions involving the ring in MCH for MCHR3 ( )[•] and MCHR4 ( )[•].
 169 Adjustments were required for class 15 [alkylperoxy (ROO) ↔ hydroperoxyalkyl (QOOH)]
 170 isomerization reactions due the presence of a methyl branch in MCH compared to cyclohexane. The
 171 activation energy was reduced by 2 kcal·mol⁻¹ for reactions involving a tertiary C-H based on
 172 Evans-Polanyi correlation with a secondary C-H, and the degeneracy of hydrogen atoms were
 173 corrected when necessary following symmetry differences.

174 The MCH reaction network for ROO ↔ QOOH isomerization becomes increasingly complex
 175 due to the large number of reaction pathways. Typically, isomerization pathways proceeding via 5, 6,
 176 7, and 8 membered-ring transition states should be included. However, upon comparison of the rate
 177 constants for the isomerization pathways of ROO radicals of MCH, 6 membered-ring transition
 178 states were found to have considerably larger rate constants (see Fig. S1 in Section 1 of SM-2). To
 179 reduce the complexity of the low-temperature chemistry, only 6 membered-ring isomerizations and
 180 isomerizations leading to products detected in the Nancy JSR-2 experiment were included. Tests
 181 were conducted to verify that neglecting the non-six membered isomerization pathways has limited
 182 effect on ignition delay times (IDT) across a wide range of temperatures and pressures (Fig. S2 in

183 Section 1 of SM-2).

184 The second O₂ addition to QOOH intermediates (class 26) leads to low-temperature chain
185 branching. Here, the second O₂ addition rate coefficients are identical to those of the first O₂ addition,
186 however the pre-exponential factors were divided by 2 based on the findings of Goldsmith et al. [35].
187 Following the second O₂ addition, keto-hydroperoxide (KHP) and an OH radical are formed
188 following an OOQOOH isomerization step. In the previously developed low-temperature MCH
189 mechanism [13], rates were obtained using estimations based on acyclic analogues rates. As stated
190 previously, this may be inaccurate. In this mechanism, the rate coefficients for isomerizations of
191 OOQOOH to KHP + OH were assigned using the same rate coefficients as those of the
192 isomerizations of ROO to QOOH. However, due to weakened C-H bond strength (abstracted
193 hydrogen is bound at the α -site to the hydroperoxy group), an additional reduction of 3 kcal·mol⁻¹, as
194 proposed by Sarathy et al. [33], was implemented for isomerization *not* involving the cyclic ring.
195 Isomerizations involving the cyclic ring need to be further scrutinized as the second added O₂ must
196 be in an appropriate position to enable an internal H-abstraction transition state (both groups axially
197 positioned), or else this will lead to significant ring strain. The published literature on this subject is
198 minimal, so an attempt has been made to estimate rates. Again, the same rate coefficients as those of
199 isomerization of ROO to QOOH were used; however, in consideration of the potential ring strain, the
200 activation energy was reduced by 2 kcal·mol⁻¹, instead of 3 kcal·mol⁻¹.

201 In most alkane oxidation mechanisms [33], the hydroperoxyalkylperoxy radical (OOQOOH)
202 only undergoes internal H-atom migration from the weakest hydrogen at the alpha site to the peroxy
203 group, producing a KHP and an OH radical. However, recent studies involving acyclic and cyclic
204 alkanes, have shown that the intramolecular migration of H-atoms from other carbon sites in
205 OOQOOH radicals could be competitive [36]. Yang et al. [37] stated that the formation of a KHP for
206 cyclohexane is “*sterically unlikely as the axial hydroperoxy group stands in the way and prevents the*
207 *equatorial hydrogen from being reached by the peroxy group*”. With this path closed, it is likely that
208 the chain branching will proceed via an “alternative isomerization” pathway to produce

209 dihydroperoxyalkyl radicals ($P(OOH)_2$). Secondly, following the first O_2 addition to a tertiary site
210 (e.g., MCHR1), $ROO \leftrightarrow QOOH$, and subsequent second O_2 addition, there will be no α -hydrogen
211 present for abstraction. To continue with chain branching pathways, the suggested “alternative
212 isomerization” pathway seems probable. Thus, “alternative isomerization” of $OOQOOH$ and
213 subsequent reaction pathways of $P(OOH)_2$ species have been included in this mechanism (see
214 Scheme 1). This is in accord with the experimental measurements of intermediates which are likely
215 to have formed following the reaction network of the “alternative isomerization” of $OOQOOH$ to
216 $P(OOH)_2$, and the third sequential O_2 addition of $P(OOH)_2$ in the literature [28] and also in this work
217 (see Results and Discussion). Analogies and estimations have been used to formulate rate
218 coefficients of all added reactions due to the limited published data, see SM-1.

219 Further reduction to the mechanism was applied by analyzing whether the second O_2 addition
220 to $QOOH$ and third O_2 addition to $P(OOH)_2$ were major pathways. For example, upon the formation
221 of a $QOOH$ species, there are three reaction pathways: $QOOH + O_2 = OOQOOH$ or $QOOH =$ cyclic
222 ether + OH or $QOOH =$ olefin + HO_2 . The sources for the rate constants of these three reactions are
223 from Xing et al. [19, 20] and Fernandes et al. [26]. The analysis shows that the unimolecular
224 reactions of β - $QOOH/\beta$ - $P(OOH)_2$ to cyclic ether and OH was more favorable than the O_2 addition
225 pathways (see Fig. S3 in Section 1 of SM-2). Here, β - $QOOH/\beta$ - $P(OOH)_2$ denotes the
226 $QOOH/P(OOH)_2$ that the radical site is β to the nearest $-OOH$ group. Thus, in this work, the O_2
227 additions to β - $QOOH$ and β - $P(OOH)_2$ were not included. In addition, certain intermediates were
228 lumped to reduce the complexity of the reaction scheme. Details of the lumped species are presented
229 in Table S2 of SM-1. Developing kinetic mechanisms is a time-consuming task and reducing the
230 reaction pathways, wherever appropriate, during the development can reduce the complexity and size
231 of the mechanism. The inclusion of all theoretically possible reaction pathways is cumbersome,
232 especially when the pathways do not play a significant effect. The present knowledge-based
233 approach could prove invaluable when developing kinetic mechanism of fuels that produce many
234 radical isomers.

JSR simulations were performed by CHEMKIN-PRO [38] using the perfectly stirred reactor module (transient solver with an end time of 30 s). In certain simulations above 1000 K, the transient solver was hard to converge, so the steady state solver was adopted. The RCM IDT of MCH were simulated using the closed batch reactor and the supplied volume profiles [13, 14].

4. Results and discussion

The low-temperature oxidation chemistry of MCH is more complex than its pyrolysis and oxidation at high temperature. Elucidating the intermediate species pool at low temperatures is the first step to developing comprehensive reaction mechanisms and to examine kinetic modeling predictions. In the SVUV-PI-MBMS analysis, the mass spectrum of MCH oxidation in JSR-3 at 570 K was measured at 10.5 eV, corresponding to a fuel conversion of ~30%, as shown in Fig. S4 in Section 2 of SM-2. The major intermediates at the early stage of oxidation are oxygenated compounds, which include C₁-C₅ species with one to two oxygen atoms (CH₃OOH, C₂H₄O, C₃H₆O, C₃H₈O, C₄H₆O, C₄H₈O, C₅H₈O, and C₅H₁₀O) and C₇ species with zero to five oxygen atoms (C₇H₁₂, C₇H₁₀O, C₇H₁₂O, C₇H₁₀O₂, C₇H₁₂O₂, C₇H₁₄O₂, C₇H₁₂O₃, C₇H₁₀O₄, and C₇H₁₂O₅). In the Nancy JSR-2 experiment, the oxidation intermediates from C₁-C₇ were also measured. The major component for C₂H₄O is acetaldehyde, while oxirane is a minor component. Acrolein is the only isomer for C₃H₄O while both methacrolein and methyl vinyl ketone were observed for C₄H₆O. For C₃H₆O, C₄H₈O and C₅H₁₀O, both aldehyde and ketone compounds were measured, e.g., propanal and acetone for C₃H₆O, butanal and butanone for C₄H₈O, and pentanal and 2-pentanone for C₅H₁₀O. Furthermore, two kinds of intermediates with the same carbon atoms of MCH were measured, i.e., C₇H₁₂ and C₇H₁₂O. The C₇H₁₂ intermediates were detected as methylcyclohexenes. 1-methyl-cyclohexene was separated from the GC analysis while other isomers were not separated and their mole fractions were summed together. For C₇H₁₂O, eight isomers were observed, including MCH-aldehyde (cyclohexanecarboxaldehyde), MCH-ketone (2-methyl-cyclohexanone and 3-methyl-cyclohexanone), MCH-cyclic ethers with three and five membered rings (1-oxaspiro[2,5]octane, 1-methyl,7-oxabicyclo[2.2.1]heptane, 1-methyl,7-oxabicyclo[4.1.0]heptane).

261 The four membered ring MCH-cyclic ether (e.g., 1-methyl,7-oxabicyclo[3.1.1]heptane) was not
262 detected from the experiment due to its instability. The GC analysis measured its two isomerization
263 products: 6-heptenone and 5-methyl,5-hexenal. The structure of these $C_7H_{12}O$ intermediates are
264 presented in Table S1 in Section 2 of SM-2. The separation and quantification of these $C_7H_{12}O$
265 intermediates are valuable to understand the first O_2 addition process of MCH, especially to elucidate
266 the branching ratios of unimolecular decomposition and O_2 addition to QOOH radical.

267 The mass peaks corresponding to C_7H_{12} and $C_7H_{12}O$ were also observed from the
268 SVUV-PI-MBMS experiment. In addition, several highly oxygenated intermediates were detected
269 during MCH oxidation. In the previous work by Wang et al. [28], the highly oxygenated
270 intermediates were measured by atmospheric pressure chemical ionization orbitrap mass
271 spectrometer. Compared to this previous work, new data of the signal profiles of the C7
272 intermediates are presented in Fig. 1. These data are valuable to validate the model. We note that the
273 mole fraction of MCH was quantified while that of the C7 intermediates was not evaluated due to
274 unknown photoionization cross sections. Similar to a previous comprehensive SVUV-PI-MBMS
275 investigation for hydrocarbons and oxygenated compounds [28], $C_7H_{12}O_3$, $C_7H_{10}O_4$, and $C_7H_{12}O_5$,
276 correspond to intermediates with one $-OOH$ (e.g., KHP/hydroperoxy cyclic ether), one $-OOH$ (e.g.,
277 diketo-hydroperoxide/keto-hydroperoxy cyclic ether), and two $-OOH$ s (e.g.,
278 keto-dihydroperoxide/dihydroperoxy cyclic ether), respectively. The detection of $C_7H_{12}O_5$ is further
279 evidence of second O_2 addition to a QOOH radical, “alternative isomerization” of $OOQOOH$ to
280 $P(OOH)_2$ radical, and a third sequential O_2 addition, as shown in Scheme 1. The SVUV-PI-MBMS
281 experiment detected four other intermediates: $C_7H_{14}O_2$, $C_7H_{12}O_2$, $C_7H_{10}O_2$, and $C_7H_{10}O$. These
282 species can be produced via secondary reactions. The $C_7H_{14}O_2$ intermediates could be
283 methylcyclohexyl peroxides that are produced from the cross combination of RO_2 with HO_2 radicals
284 (e.g., $RO_2 + HO_2 = ROOH + O_2$). The $C_7H_{10}O_2$ species could be produced from the OH radical
285 assisted water elimination of KHP [39]. Based on the recent study of *n*-heptane [40] and theoretical
286 calculation for the H-atom abstraction of KHP from *n*-pentane oxidation [39], the $C_7H_{10}O$

intermediates could be formed from the H-atom abstraction of KHP and the subsequent decomposition of KHP radicals via the loss of HO₂ radical.

289

Figure 1. Symbols are SVUV-PI-MBMS mole fraction of MCH and signal profiles of C7 intermediates, while lines are model prediction by the tuned kinetic model (refer to text). The represented structure of these intermediates are shown.

The simulation for the low-temperature oxidation of MCH in Nancy JSR-2 and the RCM IDT of MCH by Mittal and Sung [14], and Weber et al. [13] is presented in Fig. 2. Although we updated the rate constants using theoretical calculations and estimated the rate constants for some reactions from literature knowledge and experience, the model prediction in dashed lines for MCH profiles in JSR is more reactive than the measurement (Fig. 2a). Additionally, the predicted IDTs are shorter than the measurements, especially in the negative-temperature coefficient zone.

To resolve the aforementioned discrepancies, the model was tuned to improve the fitting to the experimental data. This tentative tuning is based on the sensitivity analysis, and refers to the work of Mohamed et al. [41]. The temperature sensitivity analysis of MCH ignition delay time at 25.5 bar and equivalence ratios of 1.0 and 0.5 was carried out (Fig. S5 in Section 2 of SM-2). The initial temperature is 830 K at the NTC zone, where the largest deviation between simulation and experiment was observed. The sensitivity coefficient at the time just before ignition occurs was adopted for analysis. Apart from the reactions related to MCH (e.g., MCH + OH and MCH + HO₂)

306 and reactions of H_2O_2 in the base chemistry, the reactions related to the formation of HO_2 and OH
307 radicals have large effect on the ignition. For example, concerted elimination of ROO radicals that
308 promoting HO_2 production have a large negative effect on the ignition. In contrast, the reactions
309 promoting the OH radical formation, e.g., the isomerization of ROO to QOOH and the second O_2
310 addition to QOOH, have large positive effect on ignition delay time. The positive sensitivity value
311 increases the fuel reactivity and shortens the ignition delay time, and versus visa. The rate constants
312 selected for tuning are those initially estimated based on analogies, and therefore have larger
313 uncertainties. We did not tune rate constants that were assigned from previous theoretical
314 calculations.

315 Details of the tuning are as follows: (1) The pre-exponential term was increased by a factor of
316 4 for $\text{RO}_2 + \text{HO}_2 = \text{ROOH} + \text{O}_2$; (2) The pre-exponential term of second and third O_2 additions was
317 reduced by a factor of 2 (i.e., the rate is 4x slower than $\text{R} + \text{O}_2 = \text{RO}_2$); (3) an activation energy of
318 $41.6 \text{ kcal}\cdot\text{mol}^{-1}$ was used for KHP decomposition, which is the same value as that used in Weber et
319 al's [13] MCH kinetic model. The solid lines in Fig. 2 represent the tuned model predictions. An
320 improvement is evident for both JSR and RCM IDT simulations. However, there is still a
321 discrepancy for the IDT under some conditions. The initial oxidation products of MCH in Nancy
322 JSR-2 measurements, e.g., alkenes and cyclic ethers, are satisfactorily predicted by the tuned model.
323 We note that the simulated mole fraction for the three-membered ring cyclic ethers (Fig. 2d) and the
324 unsaturated keto/aldehyde compounds (Fig. 2e) are a summation of all isomers. It is interesting to
325 note the high concentration of three-membered ring cyclic ethers, which is comparable to that of the
326 four-membered ring cyclic ethers (i.e., Fig. 2d and 2e). However, the kinetic analysis reveals that
327 pathways to three-membered ring cyclic ethers are unfavorable. The under-prediction of these
328 intermediates is probably due to deficiencies in the kinetic model, and more study for their reaction
329 mechanism is necessary.

330 The purpose of the present model development was not presenting a perfectly tuned model.
331 More experimental data, for MCH and other cycloalkanes, is needed to tune the model and establish

reasonable rate rules for cycloalkane auto-ignition. In addition, the kinetic information on the low-temperature reaction pathways of cycloalkanes and their rate constants are still lacking. In any case, the kinetic model developed in this work could be used as a basis for further model development (SM-3). The glossary and SMILES notation of the species in MCH sub-mechanism are shown in SM-4.

337

Figure 2. (a-f), experimental and predicted mole fractions of MCH and its initial oxidation products in Nancy JSR-2, $\phi = 0.25, 1.0$, and 2.0 . (g-i), experimental and simulated IDT of MCH in RCM [13, 14]. Pressures of $15.1, 25.5$ and 50 bar, MCH/O₂/N₂/Ar mixture, $\phi = 0.5, 1.0$, and 1.5 . Symbols represent experimental measurements. Dashed and solid lines represent the un-tuned and tuned model predictions respectively. The experimental and simulated profiles of C₇H₁₂ in Fig. 2 c are summed mole fraction of the molecule shown in the figure. The experimental profiles of C₇H₁₂O in Fig. 2d and Fig. 2e are summed mole fraction of the molecule shown in the figures, while that for simulation is the summation of all the isomers with similar structures.

The tuned model was also used to predict the MCH oxidation in Hefei JSR-3. As shown in Fig. 1, the model captures the consumption of MCH before the NTC. However, MCH consumption is over-predicted in the NTC regime. The model also captures the signal profiles of the initial C7 intermediates, except that C₇H₁₂ and C₇H₁₂O in the NTC zone.

The reaction pathway for MCH consumption was analyzed at 600 K, $\phi = 1.0$ in Nancy JSR-2. As shown in Fig. S6 in Section 2 of SM-2, MCH is consumed by OH radical via H-atom abstraction and several MCH radicals are formed. At 600 K, these radicals react with O₂ to form ROO radicals.

353 Three reaction class participates in the subsequent reaction of ROO, i.e., concerted elimination to
 354 form C_7H_{12} olefin and HO_2 radical, intramolecular isomerization to form QOOH radicals, and
 355 bimolecular reactions with HO_2 to form $C_7H_{13}OOH$ peroxide. Similar to MCH radicals, the dominant
 356 reaction for the QOOH radicals is O_2 addition to the radical site leading to OOQOOH radicals. The
 357 OOQOOH radicals are consumed by concerted elimination to $C_7H_{12}O_2$ olefinic hydroperoxides,
 358 decomposition to $C_7H_{12}O_3$ keto-hydroperoxides, and further isomerization to $P(OOH)_2$ radicals. A
 359 specific example for the reaction pathways of the ROO radical generated from MCHR3 ($\text{C}_7\text{H}_{13}\text{O}_2^\bullet$) are
 360 presented in Fig. 3. The various isomers of C_7H_{12} , $C_7H_{12}O$, $C_7H_{12}O_2$, and $C_7H_{12}O_3$ are produced. For
 361 the $P(OOH)_2$ radical, its decomposition forms another isomer of $C_7H_{12}O_3$ while its third O_2 addition
 362 leads to $C_7H_{12}O_5$ intermediates. All these intermediates have been detected from the
 363 SVUV-PI-MBMS experiment. The represented structure of these intermediates are also presented in
 364 Fig. 1

366 **Figure 3.** Reaction pathway analysis of the ROO radical produced from MCHR3 ($\text{C}_7\text{H}_{13}\text{O}_2^\bullet$) in MCH JSR
 367 oxidation in Nancy JSR-2. The equivalence ratio is 1.0 and temperature is 600 K.

368 The discussion of the pyrolysis and high-temperature oxidation chemistry is presented in
 369 Section 3 and Fig. S7 of SM-2. In addition, the flow reactor pyrolysis of MCH at various pressures in
 370 the literature [9] were also simulated. The prediction for MCH conversion and the formation of
 371 intermediates and final products is also satisfactory (Fig. S8 and S9 in Section 3 of SM-2). The GC

372 measured mole fractions of MCH pyrolysis and oxidation are presented in SM-5.

373 **5. Conclusions**

374 In this work, we investigated the combustion chemistry of MCH by measuring species distribution
375 from JSR pyrolysis and oxidation. Initial hydrocarbon and oxygenated intermediates, indicative of
376 the first, second, and third O₂ addition reactions in MCH low-temperature oxidation, were measured
377 by GC and SVUV-PI-MBMS analysis. The measurements of dozens of species are valuable to
378 examine kinetic models for MCH gas-phase oxidation and pyrolysis. A preliminary kinetic model for
379 MCH pyrolysis and oxidation has been built based on literature studies. Specifically, rate constants
380 of key reactions of MCH low-temperature oxidation were taken from theoretical calculations,
381 thermodynamic data were estimated from Benson group additivity with implemented new group
382 values, and “alternative isomerization” of OOQOOH and a third sequential O₂ addition reaction
383 network were included on the basis of the experimental observation. However, the model’s
384 prediction for MCH JSR oxidation and RCM IDT was faster compared to the experimental
385 measurements, which indicates unreasonable branching ratios in low-temperature pathways
386 governing OH and HO₂ radical concentrations. A tentative tuning of the rate constants for three
387 reactions, initially estimated based on analogies, resulted in a better prediction of the measurements.
388 Further tuning of the model with systematic rate rules can be developed when additional
389 experimental measurements and theoretical calculations of cycloalkane auto-oxidation are made
390 available. It is recommended that theoretical studies focus on the kinetics of MCH+HO₂, second and
391 third O₂ addition reactions, KHP decomposition, and alternative isomerizations. Additional
392 experimental data in JSR and shock tube ignition delay times at high pressures and low temperatures
393 are necessary to improve the model’s performance.

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453

Figure Captions

(Color figures in electronic version only)

Scheme 1. General reaction mechanism of MCH oxidation. Species with molecular formula detected in this work are highlighted in blue. The numbers on arrows denote the reaction class discussed in this text.

Figure 1. Symbols are SVUV-PI-MBMS mole fraction of MCH and signal profiles of C7 intermediates, while lines are model prediction by the tuned kinetic model (refer to text). The represented structure of these intermediates are shown.

Figure 2. (a-f), experimental and predicted mole fractions of MCH and its initial oxidation products in Nancy JSR-2, $\phi = 0.25, 1.0, \text{ and } 2.0$. (g-i), experimental and simulated IDT of MCH in RCM [13, 14]. Pressures of 15.1, 25.5 and 50 bar, MCH/O₂/N₂/AR mixture, $\phi = 0.5, 1.0, \text{ and } 1.5$. Symbols represent experimental measurements. Dashed and solid lines represent the un-tuned and tuned model predictions respectively. The experimental and simulated profiles of C₇H₁₂ in Fig. 2 c are summed mole fraction of the molecule shown in the figure. The experimental profiles of C₇H₁₂O in Fig. 2 d and Fig. 2e are summed mole fraction of the molecule shown in the figures, while that for simulation is the summation of all the isomers with similar structures.

Figure 3. Reaction pathway analysis of the ROO radical produced from MCHR3 ( ) in MCH JSR oxidation in Nancy JSR-2. The equivalence ratio is 1.0 and temperature is 600 K.

Supplemental Material

SM-1: Rate constant source and lumped species. **SM-2:** Addition information for model development, low-temperature oxidation, and pyrolysis and high-temperature oxidation of MCH.

SM-3: Kinetic model. **SM-4:** Species glossary and SMILES notation. **SM-5:** Experimental data.