



Oxidation chemistry of cyclic hydrocarbons in a motored engine: Methylcyclopentane, tetralin, and decalin

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ABSTRACT

This work, which parallels a recent study of cyclohexane and methylcyclohexane by the authors, concerns the oxidation chemistry of methylcyclopentane (MCP), 1,2,3,4-tetrahydronaphthalene (tetralin), and decahydronaphthalene (decalin) in a motored engine at low to intermediate temperatures. The experiment is conducted with variable compression ratio from 4 to 15 at equivalence ratio of 0.25 and fixed intake temperature. Results show dramatically different reactivity in low temperature oxidation for the three compounds. MCP and tetralin show little low temperature reaction prior to autoignition, while decalin shows significant low temperature reactivity. Detailed product analysis showed that conjugate olefins, the olefin having the identical structure with the reactant except the only C=C bond, account for over 70% of the products from MCP and an even higher percentage of the products from tetralin. Tetralin oxidation under the present conditions is essentially oxidative dehydrogenation with little oxygenated cyclic compound being formed. Hydronaphthalenes with various degrees of unsaturation are detected in the products from decalin, but are not as prevalent as in the case of MCP and tetralin, because of the high selectivity toward low temperature chain branching. The ring-opening paths in decalin oxidation are discussed, suggesting that breaking the common C–C bond of the two rings is more likely than opening the two rings one after the other. Methyl substitution on the ring was found to significantly promote the formation of propene relative to ethene. Reaction mechanisms are proposed to explain the major products formed from each compound.

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1. Introduction

Oxidation of cycloalkanes has attracted increasing interest in recent years as kinetic modeling of hydrocarbon combustion has extended from linear alkanes, whose oxidation chemistry is best known, to cyclic hydrocarbons, whose oxidation has been the least investigated. The increasing production of Canadian oil sands also forecasts the presence of enhanced amounts of cyclic hydrocarbons in liquid fuels in portions of the United States and elsewhere. Understanding the combustion chemistry of these compounds is therefore of considerable scientific and practical importance.

Most studies on cycloalkane oxidation so far were focused on a single compound, cyclohexane. Cyclopentane and substituted cyclohexanes were also studied but to a much lesser extent. Few results have been reported for gas-phase oxidation of bicyclic compounds, e.g., decalin, although performance in internal combustion engines with some of these compounds has been reported. Bicyclic hydrocarbons, in particular, decalin and tetralin, are important

constituents in the present diesel fuel and are expected to play a more significant role in the future. Decalin and tetralin, which are considered as candidate endothermic fuels with superior thermal stability, are of high interest for advanced jet fuels [1].

Among the few experiments on cycloalkane oxidation, most concerned the global oxidation reactivity, e.g., ignition delays, and very few dealt with the oxidation chemistry, e.g., product speciation. Detailed mechanisms covering both low temperature and high temperature oxidation were not developed until recently for cyclohexane, and essentially no such comprehensive mechanisms have been developed for five-membered ring or bicyclic hydrocarbons. These observations, together with the recent reviews from the combustion chemistry community [2], indicate the imperative need to study cyclic hydrocarbons.

This work focuses on the low temperature reactivity and product speciation of cyclic hydrocarbons oxidized in a motored engine. The pre-ignition processes cover both the *low temperature* and *intermediate temperature* regimes, which is collectively called *low temperature oxidation* in this work. Results have been reported earlier for cyclohexane and methylcyclohexane [3]. Presented here are the results for methylcyclopentane (MCP), 1,2,3,4-tetrahydronaphthalene (tetralin), and decahydro-naphthalene (decalin).

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Early studies on cyclopentane [4] and methylcyclopentane [5] in closed vessel reactors reported carbon oxides, aldehydes, and olefins including cyclopentene as oxidation intermediates. With their classic slow oxidation method, Handford-Styring and Walker [6] studied cyclopentane oxidation by adding 0.5 vol.% cyclopentane to a slowly reacting H_2/O_2 mixture in a closed vessel reactor at 500 torr and 673–783 K. The major reaction intermediates were cyclopentene, 1,2-epoxycyclopentane, cyclopentadiene, smaller olefins and aldehydes, and CO. At 5% fuel conversion, the conjugate olefin, cyclopentene, accounts for 79% of the products while 1,2-epoxycyclopentane and cyclopentadiene account for 5% and 8%, respectively, indicating that the ring structure remains intact during the early stage of oxidation, and dehydrogenation of the ring is the dominant reaction path. Rate constants for reactions between cyclopentane and OH, H [6] and HO_2 [7] radicals were obtained by comparative methods. DeSain and Taatjes [8] studied the reaction of $c-C_5H_9 + O_2 \rightarrow c-C_5H_8 + HO_2$, $c-C_5H_9 + O_2 \rightarrow c-C_5H_8 + HO_2$, under <60 torr and at 296–723 K with *in situ* product analysis. The rate constant was derived based on the yield of HO_2 measured by infrared frequency modulation spectroscopy as a function of temperature. Burcat et al. [9] used a shock tube to study ignition delay of cyclopentane and other cyclic hydrocarbons for diluted stoichiometric mixtures at >1200 K and 4 atm. The results showed that cyclopentane is more resistant to autoignition than iso-octane and cyclohexane, and its ignition delay is about the same as benzene. Recently two shock tube studies of cyclopentane and cyclohexane were reported. Sirjean et al. [10] measured the ignition delays at 1230–1840 K, 7.3–9.5 atm, and equivalence ratios of 0.5, 1 and 2. They found that the ignition delay of cyclopentane is 2–10 times longer than that of cyclohexane under the same conditions of shock pressure, oxygen concentration and fuel loading. A high temperature oxidation mechanism for cyclopentane was proposed based on the automatic mechanism generation program EXGAS [10]. Daley et al. [11] reported the ignition delay at lower temperature (847–1379 K) but higher pressure (11–61 atm) and equivalence ratios of 0.25, 0.5 and 1.0. Longer ignition delay was also observed with cyclopentane, about 2–3 times of that of cyclohexane, in stoichiometric mixtures with constant oxygen concentration. Apart from these shock tube studies, low temperature oxidation of cyclopentane or methylcyclopentane has not yet been reported at atmospheric or higher pressures, nor has a low temperature mechanism been proposed.

Decalin was recently studied in a shock tube by Oehlschlaeger et al. [12]. The ignition delays were reported at 990–1300 K, 9–48 atm, and equivalence ratio of 0.5 and 1.0. A semi-detailed high temperature mechanism was generated by an automatic program, the MAMA code, for decalin oxidation. Gas-phase oxidation of decalin was conducted by Agosta [13] and Natelson et al. [14] in a pressurized flow reactor at 0.8 Mbar, residence time of 0.12 s, and equivalence ratio of 0.3. CO formation was reported as a function of temperature over 600–800 K [13]. Product speciation was qualitatively analyzed at 648–773 K. Besides small olefins and aldehydes, a number of single ring compounds, including substituted cyclohexanes, cycloalkenes, cyclic ketones, and aromatics, were reported as oxidation intermediates [14]. Decalin and tetralin were also studied together with other hydrocarbons in this flow reactor to simulate oxidation of jet fuels [15]. Gas-phase oxidation of neat tetralin has not been reported in the literature. But experimental and mechanistic studies on the pyrolysis of tetralin [16–22], as well as decalin [16,19,21,23,24], have been reported in gas phase and supercritical conditions.

2. Experiment

The experimental setup for the current study has been described in previous publications [3,25]. The prominent features

are repeated here. A CFR octane rating engine is used with modified air intake and fueling systems. With no spark firing, oxidation of the premixed fuel/air charge is controlled by varying compression ratio or intake temperature. The intake manifold has sufficient length for fuel droplets to vaporize and mix with air at selected intake temperatures [26]. Reaction heat release and cylinder temperature are calculated from measured cylinder pressure with standard methods [27].

Reaction products are collected from the engine exhaust in gaseous and condensed phases and analyzed by a combination of GC techniques. Two capillary columns, Restek VMS (30 m, 1.4 μ m) and Rtx-5 (29 m, 0.25 μ m), are used for separating single-ring and double-ring reactants and their products, respectively. Species identification and quantification are via a mass spectrometer (MS) and a flame ionization detector (FID). Permanent gases (CO, CO_2 , O_2 etc.) are analyzed by a thermal conductivity detector (TCD). An internal standard method is used for species quantification. A detailed description of exhaust gas sampling and methods for GC analysis can be found in [26].

Table 1 lists the cyclic hydrocarbons tested in this work and their relevant properties. Methylcyclopentane (95%) is obtained from Acros Organics with the major impurity being cyclohexane. Decahydronaphthalene (98%) and 1,2,3,4-tetrahydronaphthalene (97%) are obtained from Sigma-Aldrich. Decalin is a mixture of 62% of *trans*- and 38% *cis*- isomers (determined by GC-FID in this work). Impurities in tetralin are naphthalene and decalins. The engine runs with a constant speed of 600 rpm, atmospheric intake pressure, and equivalence ratio of 0.25. This equivalence ratio was chosen because it enables the oxidation of the selected compounds be studied over a wide range of compression ratios. Higher equivalence ratios, approaching stoichiometric, showed a reduced operation range of compression ratio and could cause condensation of the high boiling decalin and tetralin during mixture preparation and reaction. Oxidation products are collected from the engine exhaust as compression ratio is varied. The intake temperature is set at 200 °C. In each case, the compression ratio is adjusted from a point of no reaction to a point of autoignition.




The present exhaust sampling and analysis method recovers $\geq 95\%$ of the fuel carbon in methylcyclopentane. A carbon balance of decalin and tetralin is not obtained because of their high boiling points which cause considerable losses of species in the exhaust sample line. Yields of their products are expressed in terms relative to the unreacted fuel coexistent in the exhaust gases.

3. Results and discussion

3.1. Low temperature heat release

Dramatically different low temperature oxidation reactivity is observed for MCP, tetralin and decalin. As shown in Fig. 1, under similar compression ratios, MCP and tetralin show negligible low temperature reaction, while decalin shows a strong low temperature heat release (LTHR) peak. The maximum cylinder pressure

Table 1
Cyclic hydrocarbons tested in this work.

Compound	Formula	Ring	BP, °C	RON ^a	MON ^a
Methylcyclopentane	C ₆ H ₁₂		72	91.3	80.0
1,2,3,4-tetrahydronaphthalene	C ₁₀ H ₁₂		207	96.4	81.9
Decahydronaphthalene (<i>trans/cis</i>)	C ₁₀ H ₁₈		190	42/ 34 ^b	36/ 34 ^b

^a Research octane number (RON) and motor octane number (MON) are from [30].

^b Blending octane number, definition in [30].

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