



Effects of molecular structure on oxidation reactivity of cyclic hydrocarbons: Experimental observations and conformational analysis

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ABSTRACT

This work concerns the pre-ignition reactivity of cyclic hydrocarbons and its dependence on cyclic structures. In the first part, global reactivity of five cyclic hydrocarbons, methylcyclopentane (MCP), cyclohexane (CH), methylcyclohexane (MCH), decahydronaphthalene (decalin), and 1,2,3,4-tetrahydronaphthalene (tetralin), whose detailed product analyses were recently reported [Y. Yang, A.L. Boehman, Proc. Combust. Inst. 32(1) (2009) 419–426; Y. Yang, A.L. Boehman, Combust. Flame 157(3) (2010) 495–505], were compared over a range of compression ratio and intake temperature in a motored engine. Molecular structure exerts a profound effect on low temperature oxidation reactivity. Decalin is the most reactive compound whose extent of oxidation increases monotonically with increasing temperature and pressure. MCH shows higher low temperature reactivity than CH, and both show distinct negative temperature coefficient behavior. MCP and tetralin exhibit little low temperature reaction before critical conditions are reached for autoignition. In the second part, conformational analysis is conducted to understand how molecular structures affect the low temperature oxidative reactivity, in particular the (1,5) H-shift of fuel peroxy radicals ($ROO^{(1,5)}QOOH$), the key step in low temperature chain branching. In comparison with open-chain structures, cyclic structures significantly reduce the total number of hydrogens that can be abstracted in the (1,5) H-shift. This is because the (1,5) H-shift of a cyclohexylperoxy radical requires both the peroxy group and the to-be-abstracted hydrogen locate at an axial position on the cyclohexane ring. The total number of available hydrogens in decalin, MCH, CH, and tetralin is 14, 11, 6, and 4, respectively. Also important is the number of hydrogens available for the (1,5) isomerization of a given peroxy group, i.e., the degeneracy of the (1,5) H-shift. Degeneracy in (1,5) H-shift for decalin, MCH, CH, and tetralin is ~3, 2–3, 2, and 1, respectively. These numbers are in accord with the relative reactivity observed for these compounds. The higher reactivity of MCH relative to CH also results from the equatorial preference of the methyl group which forces the peroxy group to stay at an axial position and facilitates (1,5) H-shift. The last argument is confirmed by quantum mechanical calculations.

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1. Introduction

With the depletion of conventional oil looming ever closer, future transportation fuels (gasoline, diesel and jet) are expected to contain an increasing portion of cycloalkanes from unconventional oil sources such as oil sands, oil shale, and coal liquefaction oils. Oxidation of cycloalkanes, however, has been much less studied in comparison with their aliphatic and aromatic counterparts [1–3].

Oxidation of cycloalkanes follows similar reaction schemes to those of open-chain alkanes. The former, however, possess their own unique kinetic features, in particular during low temperature oxidation (LTO), and it has been reported unreliable to extrapolate

the rate constants of cycloalkanes from those of analogous aliphatic alkanes [4]. For example, formation of conjugate olefins, that is to say olefins with the same molecular structure as the original fuel compound except for the presence of a double carbon bond, is a much more important pathway in oxidation of cycloalkanes, which in practice results in slower autoignition (high octane number, low cetane number) and higher benzene emissions in IC engine combustion with naphthenic fuels [5,6].

A rarely noticed difference between aliphatic and cyclic alkanes is the effect of methyl substitution on oxidation reactivity. Fig. 1 shows the variation of research octane number (RON, from [7]) of *n*-hexane, cyclopentane, and cyclohexane with zero, one and two methyl substitutions. Without substitution, *n*-hexane shows much lower octane number than cyclohexane and cyclopentane. Methyl substitution on normal alkanes reduces oxidation reactivity and enhances RON, as seen from *n*-hexane to methylhexanes

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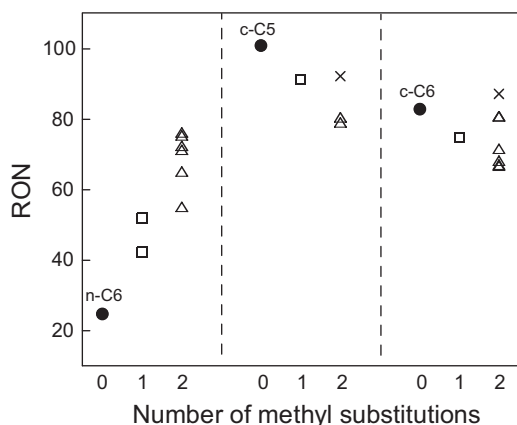


Fig. 1. Impact of methyl substitutions on research octane number (RON). “●” for alkanes with no side chains: *n*-hexane (*n*-C6), cyclopentane (*c*-C5), and cyclohexane (*c*-C6). “□” for alkanes with one methyl side chain: methylhexane isomers, methylcyclopentane, and methylcyclohexane. “△” for alkanes with two methyl side chains: dimethylhexanes, dimethylcyclopentanes, and dimethylcyclohexanes. “×” is co-substituted cycloalkanes: 1,1-dimethyl-cyclopentane and 1,1-dimethyl-cyclohexane. RON values are from Ref [7].

to dimethylhexanes. The opposite is observed in cyclopentane and cyclohexane where RON generally decreases with the number of methyl substitutions. To date the literature has not provided an explanation for such discrepancy.

This work, together with a companion work [8], attempts to understand the fundamental differences during low temperature oxidation between cyclic hydrocarbons and their open-chain analogues, and among cyclic hydrocarbons with different ring structures. The focus is on how cyclic structures affect the key steps in LTO, i.e., (1,5) and (1,4) H-shift reactions of alkylperoxy radicals (ROO●). This work studies the (1,5) step which is closely related to degenerate chain branching and low temperature reactivity, while the companion work deals with the (1,4) step which is responsible for the formation of conjugate olefins. The discussions are based on conformational analysis and motored engine results of five cyclic hydrocarbons, including methylcyclopentane (MCP), cyclohexane (CH), methylcyclohexane (MCH), decahydronaphthalene (decalin), and 1,2,3,4-tetrahydronaphthalene (tetralin). Part of the experimental results has been reported in [9,10] along with detailed product analysis for these compounds.

Oxidation of cyclopentane [11] and cyclohexane [12] were studied in closed vessel reactors by the group at Hull University with their classic slow oxidation method. The major findings were that the cyclic structure is mostly retained during the initial steps of LTO and conjugate olefins make up most of the primary products. Ignition delays in shock tube experiments of cyclopentane and cyclohexane were reported by Burcat et al. [13] and more recently by Sirjean et al. [14] and Daley et al. [15]. These authors reported a longer ignition delay for cyclopentane than for cyclohexane in near stoichiometric mixtures with constant oxygen concentrations. Oxidation of cyclohexane and methylcyclohexane, has been studied in a jet-stirred flow reactor (for CH [16,17]), plug flow reactors (for MCH [18,19]), rapid compression machines (for CH [20], for MCH [4]), a shock tube (for MCH [21–23]), and a motored engine (for both [9]). Ignition delay and species profiles (most for CH) were reported over a wide range of temperature, pressure, and residence time. Detailed oxidation mechanisms have been proposed for CH [24–26] and MCH [4] but remain to be further examined with new experiments [2,3]. Virtually no detailed product results have been reported on the gas-phase oxidation of decalin and tetralin, except some brief results on decalin from the Drexel University flow reactor [27].

The three-dimensional steric structure of hydrocarbon molecules has not often been taken into account when detailed oxidation mechanisms are formulated or individual rate constants are determined. Only in a few limited cases, such as in *ab initio* calculations, have conformational analyses been conducted to help understand the oxidation of small hydrocarbons, for example, in $C_2H_5\bullet + O_2 \rightarrow C_2H_4 + HO_2\bullet$ [28,29]. Knepp et al. recently performed *ab initio* calculations with comprehensive conformational analysis on CH and reported potential energy surface of the species involved in the formation and isomerization of cyclohexylperoxy radicals [30], which is an unusual but valuable practice in studying hydrocarbon oxidation. Such an approach is adopted in the present and a companion paper [8] to understand how the steric structures of cyclic hydrocarbons affect their low temperature oxidation.

2. Experiment

2.1. Experimental setup

The experimental setup for the current study has been described previously [9,31]. The essential features of the approach are repeated here. A CFR octane rating engine with modified air intake and fueling system was used. Without firing of the spark, oxidation of the premixed fuel/air charge was controlled by varying the compression ratio and the intake temperature. Net heat release (or apparent heat release), the difference of heat release from chemical reaction and heat loss to the cylinder walls, was calculated from pressure traces of 40 consecutive cycles using the standard method [32]. Cylinder temperature was estimated based on the in-cylinder charge mass and the ratio of specific heat ($\gamma = c_p/c_v$). Due to the significance at low compression ratio, the residual gas fraction is estimated using the method of Fox et al. [33].

Engine exhaust was collected in the gaseous phase in this study and analyzed by gas chromatography (Shimadzu GC-17A). Hydrocarbon species were analyzed with a flame ionization detector (FID); permanent gases, CO, CO₂, and O₂, were analyzed with a thermal conductivity detector (TCD).

2.2. Test fuels and test conditions

Table 1 lists the cyclic compounds tested in this study and their relevant properties. Methylcyclopentane (95%) was obtained from Acros Organics with the major impurity being cyclohexane. The rest, cyclohexane (99%), methylcyclohexane (99%), decahydronaphthalene (98%), 1,2,3,4-tetrahydronaphthalene (97%), were obtained from Sigma-Aldrich. Decalin is a mixture of 62% of *trans*- and 38% *cis*-isomers (determined in this work). Impurities in tetralin are naphthalene and decalin.

The engine was run at a constant speed of 600 rpm, atmospheric intake pressure, and equivalence ratio of 0.25. For each compound, three sets of tests were conducted:

- (1) Compression ratio (CR) sweep with constant intake temperature (T_{in}) of 120 °C.
- (2) CR sweep with constant $T_{in} = 200$ °C.
- (3) T_{in} sweep with constant CR = 11.85.

In each case, compression ratio or intake temperature was adjusted from a point of no reaction to a point of autoignition. Autoignition, however, was not achieved at $T_{in} = 120$ °C for MCP and tetralin at the highest compression ratio. Also, due to its high reactivity, the intake temperature sweep of decalin was conducted at constant CR of 7.69, instead of 11.85. In T_{in} sweep tests, the fueling rate was reduced to accommodate the decreases in air flow rate

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