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Uniqueness in the low temperature oxidation of cycloalkanes

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This work examines the inherent features in the low temperature oxidation of cycloalkanes which distinguish cyclic alkanes from open-chain alkanes. The first part of the discussion is based on the recent motored-engine studies of cyclic hydrocarbons, [Yang and Boehman, Proc. Combust. Inst. 32, p. 419; Yang and Boehman, Combust. Flame, 157, p. 495], and focuses on the formation of conjugate olefins in low temperature oxidation. While less reactive than linear alkanes of similar size, cyclic hydrocarbons produced significant amounts of conjugate olefins during low temperature oxidation, which is uncharacteristic of linear alkanes. Conformational analyses in this paper and in a companion paper reveal that the inhibited low temperature chain branching and the promoted olefin formation are due to the steric structures of the cyclic compounds limiting the number of hydrogens available to the (1,5) H-shift but alternatively enhancing the opportunity for the (1,4) H-shift during the isomerization of the fuel peroxy radicals, $ROO^{\cdot} \rightarrow {}^{\cdot}QOOH$.

The second part of this work focuses on the role of methyl substitution in low temperature oxidation of cycloalkanes, which is drastically different from that of linear alkanes. *Ab initio* calculations are conducted on cyclohexane and methylcyclohexane to compute the activation energy of the (1,5) and (1,4) H-shift with full consideration of species conformation. The presence of the methyl group is found to enable low activation-energy channels in the (1,5) H-shift. Next, the impact of methyl substitution on the formation of conjugate olefins is discussed for methylcyclohexane and methylcyclopentane. Based on the experimentally determined yields of conjugate olefin isomers, estimations are made of the fraction of each fuel radical that is converted to conjugate olefins. For both compounds, more tertiary radicals are converted to conjugate olefins than secondary radicals, and primary radicals have the least fraction being converted.

1. Introduction

Oxidation of cyclohexane and related compounds is attracting increasingly attention in recent years. This is largely driven by the interest in kinetic modeling of the combustion of practical liquid fuels [1–3], and the six-membered ring hydrocarbons being selected as the representative compounds for the least investigated cycloalkanes. Meanwhile, with the increasing amount of oil sands derived materials being processed as a refinery feedstock, cycloalkanes will account for a more significant fraction in liquid fuels [4].

Studies of cyclohexane oxidation have revealed two major differences between cyclohexane and n-hexane. First, the reactivity in low temperature oxidation of cyclohexane is significantly lower than that of n-hexane, as indicated by the long ignition delay observed in rapid compression machines (RCM) [5] and the high octane number in combustion engines [6]. Low temperature reactivity is determined by degenerate chain branching, in which a key step is the intramolecular (1,5) H-shift of fuel peroxy radical ($ROO^{\cdot} \overset{(1,5)}{\rightarrow} {}^{\cdot}QOOH$). Second, formation of conjugate olefins, e.g., cyclohexene vs. cyclohexane, 1-hexene vs. n-hexane, is a more important reaction channel for cyclohexane than for n-hexane. Formation of conjugate olefins requires (1,4) H-shift during $ROO^{\cdot} \overset{(1,5)}{\rightarrow} {}^{\cdot}QOOH$ and subsequent elimination of HO_2, or a direct (concerted) elimination of HO_2, $ROO^{\cdot} \rightarrow \text{olefin} + HO_2^{\cdot}$, which also requires a transition state similar to that of (1,4) H-shift. These observations suggest differences between cyclohexane and n-hexane starting in the early steps of low temperature oxidation.

The literature has not provided a clear answer as to why cyclohexane is less reactive and forms more olefins during low temperature oxidation. Table 1 lists the rate constants of intramolecular hydrogen shift for cyclohexane proposed by Handford-Styring and Walker [7] from their closed-vessel experiments, which has been adopted by other groups [8–10] in kinetic modeling of cyclohexane oxidation. Also shown are the rate constants of similar reactions for open-chain alkanes on secondary hydrogens, proposed by Curran et al. [11]. The rate constants of cyclohexane were based on the

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Table 1
Rate constants of internal hydrogen abstraction, ROO· → ·QOOH, in cyclohexane [7] and open-chain alkanes [11].

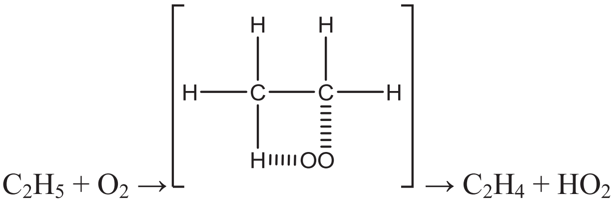
	E_a, kJ/mol	A, per C-H, s^{-1}	k at 800 K, s^{-1}	$k/k_{(1,4)}$
Cyclohexylperoxy				
(1,4)[a]	135.7 ± 5.9	8.71×10^{11}	1.2×10^3	1
(1,5)	123.5 ± 4.1	6.46×10^{11}	5.6×10^3	4.7
(1,6)[b]	112.5 ± 5.7	7.59×10^{10}	3.4×10^3	2.8
Akylperoxy, secondary H				
(1,4)	112.3	1.00×10^{11}	4.7×10^3	1
(1,5)	87.2	1.25×10^{10}	2.5×10^4	5.4
(1,6)	79.7	1.56×10^9	9.8×10^3	2.1

[a] Formation of cyclohexene was not included in this (1.4) H-transfer.
[b] This channel could be overestimated because much lower yields of 1,4-epoxycyclohexane were later reported [19,20].

relative yields of 1,2-epoxycyclohexane, 5-hexenal, and 1,4-epoxycyclohexane, which corresponds to the (1,4), (1,5) and (1,6) channels, respectively. Without accounting for cyclohexene as a (1,4) product, the (1,5) channel was argued as the most favored channel due to the highest yield of 5-hexenal. Recent detailed cyclohexane mechanisms [8,10] put even more weight on the (1,5) channel over the other two. Table 1 shows a smaller rate constant for cyclohexane in the (1,5) isomerization than for chain alkanes, which can explain the less pronounced lower low temperature reactivity of cyclohexane. However, the ratio of the (1,4) and (1,5) rate constants for cyclohexane is no different from that for chain alkanes, which is inconsistent with the dominant formation of cyclohexene and the greater importance of the (1,4) channel in cyclohexane oxidation. Clearly, the discrepancy arises from the exclusion of cyclohexene as a product of the (1,4) H-shift.

Conventionally, three channels are considered responsible for the formation of conjugate olefins. Take ethyl radical as an example,

$$C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2 \quad \text{(R1)}$$
$$C_2H_5 + O_2 \rightarrow C_2H_5OO \rightarrow C_2H_4OOH \rightarrow C_2H_4 + HO_2 \quad \text{(R2)}$$



(R3)

R1 is direct H-abstraction which requires high activation energy and is unimportant at low temperature [12,13]. R2 and R3 both involve peroxy radicals but R2 completes the (1,4) H-shift and eliminates HO_2 in a subsequent reaction, while R3 does not complete the (1,4) H-shift but undergoes a similar transition state and eliminates HO_2 directly from the peroxy radical. Recent studies from ethyl peroxy radical [12–16] to cyclohexyl peroxy radical [17] showed that the R3 route, which is termed *direct* or *concerted* HO_2 elimination, is more important than R2 in low temperature oxidation. Nevertheless, both reactions require a similar transition state in which a bonding is established between the peroxy group and a hydrogen atom on the adjacent carbon.

In closed-vessel experiments, if cyclohexene was taken into account, which accounts for over 50% of products formed [7,18], the (1,4) route would be significantly favored over the (1,5), while the (1,6) is the least favored.[2]

The purpose of this work is to uncover the fundamental reasons behind the difference in low temperature oxidation between cyclic and acyclic hydrocarbons by experiment, conformational analysis, and quantum calculations. Detailed product analyses of low temperature oxidation of five cyclic hydrocarbons, methylcyclopentane (MCP), cyclohexane (CH), methylcyclohexane (MCH), 1,2,3,4-tetrahydronaphthalene (tetralin), and decahydronaphthalene (decalin), are recently reported in a motored engine [20,21]. Based on these results, conformational analysis on the impact of cyclic structures on low temperature reactivity is conducted in a companion paper [22]. Discussion in this work focuses on the unusual formation of conjugate olefins. Results of these two papers illustrate how cyclic structures affect hydrogen accessibility for the (1,5) and (1,4) H-abstraction, which leads to the different low temperature reactivity and olefin formation for cyclic structures than for open chain structures.

Methyl substitution alters low temperature oxidation of cycloalkanes in a drastically different way than does with linear alkanes. For example, methyl substitution increases low temperature reactivity of cycloalkanes but does the opposite to linear alkanes [22]. Two topics related to methyl substitution are discussed in this work. First the role of methyl substitution on the (1,5) and (1,4) H-abstractions is investigated for cyclohexane and methylcyclohexane with *ab initio* calculations and full consideration of species conformation. Second, effect of methyl substitution on conjugate olefin formation is discussed based on the motored engine results of methylcyclohexane and methylcyclopentane.

2. Experimental

2.1. Experimental setup

The experimental setup for the current study has been described in previous publications [20,23]. The prominent features 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 is controlled by varying compression ratio or intake temperature. Reaction heat release and cylinder temperature were calculated from measured cylinder pressure. Complete heat release results can be found in [24].

Reaction products were collected from the engine exhaust in condensed and gaseous phases and analyzed by GC techniques. Two capillary columns, Restek VMS (30 m, 1.4 μm) and Rtx-5 (29 m, 0.25 μm), were used for species separation. Product identification and quantification were made by mass spectrometry (MS) and flame ionization detection (FID). An internal standard method was used for species quantification. A detailed description of exhaust gas sampling and methods for GC analysis can be found in [24].

2.2. Test fuels and test conditions

Table 2 lists the cyclic compounds investigated in this work 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 (as determined by GC-FID in this work). Impurities in tetralin are naphthalene and decalins.

The engine was run at a constant speed of 600 rpm, atmospheric intake pressure, and equivalence ratio of 0.25. Oxidation products were obtained from the engine exhaust as the compression ratio was varied. The intake temperature was set at 200 °C for all compounds except MCH, for which the intake temperature

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[2] Note that if cyclohexene is not counted, the (1,6) channel would be favored over the (1,4) channel because the yield of 1,4-epoxycyclohexane is higher than that of 1,2-epoxycyclohexane. However, opposite results were reported in a RCM [19] and a motored engine [20] where more 1,2-epoxycyclohexane was produced than 1,4-epoxycyclohexane.