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Conformational inversion-topomerization mechanism of ethylcyclohexyl isomers and its role in combustion kinetics

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Abstract

With the "strain-free" cyclic structure, cyclohexane and alkyl cyclohexanes (and their radicals) have various conformers (e.g. chair, boat, and twist etc.) by pseudorotation of the alkyl ring. Noting that different conformers will undergo different types of H-migration reactions, the mechanism of conformational change may impact the distribution of cyclohexyl and the branched cyclohexyl radical isomers during cyclohexane and alkyl cyclohexanes combustion. Consequently, it will influence the formation of subsequent decomposition products. In this work, the conformational inversion-topomerization mechanism and H-migration reactions for six ethylcyclohexyl radical isomers were systematically studied by ab initio calculations and the transition state theory. The updated sub-mechanism of these conformational changes is incorporated into an ethylcyclohexane pyrolysis model. By comparing the simulated results of the "complete" model including the sub-mechanism of conformational changes and the simplified model ignoring these processes, the effect of inversion-topomerization mechanism on the relative concentrations of various ethylcyclohexyl radicals and the formation of subsequent decomposition products were revealed.

Keywords: Ethylcyclohexane; Conformation; H-migration; Ab initio calculation; Kinetic modeling

1. Introduction

Cycloalkanes (usually with long side chains) make up 20–30% of jet and diesel fuels and are also commonly found in gasoline [1,2]. Comparing with chain-like alkanes or aromatic compounds with planar rings, cycloalkanes present unique chemical and physical properties during combustion

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[3–6]. For example, previous studies have shown that cycloalkanes combustion tends to produce a large amount of carcinogenic pollutants and precursors of polycyclic aromatic hydrocarbons (PAHs), such as benzene and toluene by stepwise dehydrogenation or dealkylation [6–9]. As suggested recently [3,9–13], the detailed mechanism of cycloalkanes combustion deserves much more effort not only by experimental measures but also by theoretical calculations.

With the "strain-free" cyclic structure, cyclohexane has multiple conformers (e.g. chair, half-chair, boat and twist-boat conformers), and those with alkyl substituents even have more conformers due to the orientation of the side chain. The conformational structures and conformational reactions of cyclohexane and methylcyclohexane (MCH) have been extensively studied, focusing on their thermodynamics and spectroscopy [14–17]. For instance, the chair-equatorial conformer is the most stable structure for MCH, while other conformers with half-chair, boat and twist structures have higher energies (6–14 kcal/mol) [15,17]. Similar levels of conformational energies can be expected for corresponding cycloalkyl radicals. Considering that typical barrier height for 1,5 H-migration of an alkyl radical is 12–18 kcal/mol [18], the inversion-topomerization conformation might be competitive with these H-migration reactions and changes the reaction flux in the combustion process. On the other hand, some H-migration reactions can only occur from specific conformers due to the steric effect, for example, only the methylcyclohexyl radical in twist-axial conformer can undergo 1,5 H-migration [2]. These two facts inspire us to think through the role of the conformational inversion-topomerization mechanism of cyclic alkyl radicals in cycloalkanes combustion. Unfortunately, such conformational reactions have been rarely concerned by the previously used kinetic models [3].

Recently, a few studies provided some evidence for this issue. Sirjean et al. [19] and Kiefer et al. [20] studied the ring opening reaction of cyclohexane by considering both chair and boat conformers, and found that the global rate constant for the reaction of $c\mathrm{C_6H_{12}} \rightarrow 1\text{-}\mathrm{C_6H_{12}}$ is largely influenced by the reactant and intermediate conformers. Davis et al. [2] studied H-migration reactions of methyl and ethyl branched cyclopentyl and cyclohexyl radicals by considering the conformational effect. The computed rate coefficients for the same type of H-migrations from various conformers show notable differences. Yang et al. [5] studied the effect of molecular structure on the low temperature oxidation reactivity of cycloalkanes, in particular 1,5 H-migration of cyclic alkylperoxyl radical. The numbers of H atoms available for H-migration reactions were explored with regard to the ring pseudorotation. Kang et al. [3] conducted conformational analysis to explain the reactivity difference in three ethylcyclohexane (ECH) isomers, which results in different fractions of intermediates.

In this work, we aim to fundamentally understand the conformational inversion-topomerization mechanism of ethylcyclohexyl radicals and reveal its effect on ECH combustion. The conformational processes of six ethylcyclohexyl radicals were systematically studied by theoretical kinetic studies. H-migration reactions corresponding to various conformers were computed for each radical, since these reactions are strongly governed by the conformations of cyclic alkyl radicals. Finally, we compared proportions of the consumption pathways and mole fractions of subsequent products of six ethylcyclohexyl radicals resulted from kinetic modeling simulations with or without considering the sub-mechanism accounting for the different conformations.

2. Theoretical calculations

The equilibrium geometries of all stationary points were first optimized at B3LYP/6-31G(d, p), followed by IRC calculations at the same level to ensure that the computed transition states (TS) connect the desired reactants and products. Analysis of vibrational frequencies confirmed that all transition states have only one imaginary frequency. Based on these initial geometries, two high-level composite methods, i. e. CBS-QB3 [21] and G4 [22] were applied to re-optimize the structures and compute energies. Previous works suggested that the methods of CBS-QB3 and G4 can properly describe the unimolecular reactions of cycloalkyl radicals [2,12]. The CBS-QB3 method involves the geometry optimization and Hessian matrix analysis at B3LYP/6-311G(2d,d,p), a series of high level single point energy corrections (MP2, MP4 and CCSD(T)), and a complete basis set extrapolation to correct energies [21]. The G4 method includes geometry optimization at B3LYP/6-31G(2d,p), an extrapolation procedure to obtain the Hartree–Fock limit, and a series of single point correlation energy calculations based on MP4/6-31G(d), and a high level correction [22]. The Cartesian coordinates and frequencies of optimized structures for all reactants, products and TSs are provided in *the Supplemental material-II.* Quantum chemical computations were carried out with the Gaussian 09 software [23].

Thermal rate coefficients at the high-pressure limit were calculated using the conventional transition state theory (TST) with the 1D asymmetric Eckart tunneling [24,25]. For all reactants, products and transition states, the torsional modes corresponding to the internal rotations involved in the side-chain were assumed as one-dimensional hindered rotors, and their hindrance potentials were obtained by the relaxed potential energy scan at the