Structure-dependence in Initial Decomposition of trans-1,2-Dimethylcyclohexyl Isomers: Kinetic Exploration and Conformational Analysis

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Abstract

Cyclohexyl radicals are crucial primary intermediates in combustion of fossil and alternative fuels. They would present the inherent conformation feature, i.e. diverse conformers retained in inversion-topomerization pathways, jointly controlled by the varying radical site and specific spatial positions of alkyl side chains on "easy-distortion" cyclic ring. These conformers for one radical have different energies and thermodynamics, and are highly expected to influence their subsequent decomposition reactions in terms of energetics and kinetics. To reveal such impact, all conformational structures and their interconversion mechanisms for trans-1,2-dimethylcyclohexyl isomers were explored by employing quantum chemical calculations coupled with transition state theory. Originated from distinct conformers, all accessible transition states were explicitly identified in different reaction paths for each type of intramolecular H-transfer or β-scission, and then were carefully used in computing rate coefficients. The kinetic predictions demonstrate that the fairly speedy equilibrium among conformers would be established for one isomer via conformation before they proceed the initial decomposition over 300-2500 K. This allows thoroughly evaluating the contribution of various conformers to the kinetics for multiple paths in one reaction regarding to their thermodynamic properties. Moreover, conformational analysis elucidates that H-transfers exhibit strong structure dependence. Note that the most favorable 1,5 H-transfer is only feasible for one twist-boat with radical site in axial side chain accompanied by one isoclinal methyl group. The results for β-scissions are affected by steric energies and substituent effects remained in conformational structures. These findings facilitate to finally suggest the proper kinetic parameters for each decomposition reaction with the aim of their potential implication in kinetic modelling.

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