An *ab initio* Investigation of Hydrocarbon Radical β-scission Reaction Kinetics

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Introduction

Hydrocarbon thermal cracking reactions are the key steps in petroleum refinery processes, and the mechanism is generally accepted to involve free-radical reactions. In general, hydrocarbon radical reactions are very difficult to study experimentally because of the various simultaneous reaction paths and the very short lifetimes of radicals, which makes the quantum chemical approach a good alternative. In this work, the MP2 ab initio method was applied to investigate β-scission reactions of propyl, butyl, and neopentyl radicals.

Results and Discussions

Reaction energetics were obtained using CBS-RAD(MP2), a complete basis set composite energy method. The CBS-RAD(MP2) method was created as a modification of the CBS-RAD method which has proven to give accurate energetics for free radical reactions. It replaces the time-consuming QCISD(fc)/6-31g* method in the geometry optimization and frequency calculation steps with MP2(full)/6-31g* level calculations. The method has the least root mean square error for heats of reaction and activation energy calculations for 15 hydrocarbon cracking reactions with less computational cost compared with the G2 and G3 methods.

Further work applying Transition State Theory and RRKM theory was done to estimate the reaction rate constants for hydrocarbon cracking reactions. The CBS-RAD(MP2) method proved to have excellent agreement with the experimental data, indicating it is a reliable method for studying other large hydrocarbon cracking reactions. Also a reaction kinetic model with pressure and temperature effects was proposed. This model can be easily applied to different reaction conditions without performing additional expensive and complicated calculations.

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