Exploring petroleum thermal cracking and coal pyrolysis mechanisms on free energy surfaces

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Progress 1: Methodology Development for Dynamics Sampling in Transition Pathway Space

We first developed a computational method that will be employed in the proposed research to explore the potential energy surface (PES) of the petroleum cracking procedure through dynamics simulations.

The minimum energy pathway contains important information describing the transition between two states on a PES. Chain-of-states methods were developed to efficiently calculate minimum energy pathways connecting two stable states. However, multiple pathways may exist connecting two existing states and should be identified to obtain a full view of the transitions. Therefore, we developed an enhanced sampling method, named as the direct pathway dynamics sampling (DPDS) method, to facilitate exploration of a PES for multiple pathways connecting two stable states as well as addition minima and their associated transition pathways. In the DPDS method, molecular dynamics simulations are carried out on the targeting PES within a chain-of-states framework to directly sample the transition pathway space. The simulations of DPDS could be regulated by two parameters controlling distance among states along the pathway and smoothness of the pathway. One advantage of the chain-of-states framework is that no specific reaction coordinates are necessary to generate the reaction pathway, because such information is implicitly represented by the structures along the pathway. The chain-of-states setup in a DPDS method greatly enhances the sufficient sampling in high-energy space between two end states, such as transition states. By removing the constraint on the end states of the pathway, DPDS will also sample pathways connecting minima on a PES in addition to the end points of the starting pathway. This feature makes DPDS an ideal method to directly explore transition pathway space. Three examples demonstrate the efficiency of DPDS methods in sampling the high-energy area important for reactions on the PES. In summary, the DPDS method provides a simple and effective means to directly sample transition pathways for complex systems and can be easily combined with various levels of theory. The development of DPDS method has been published (*J. Chem. Theory Comput.* **2018**, *14*, 14−29 DOI: 10.1021/acs.jctc.7b00606).
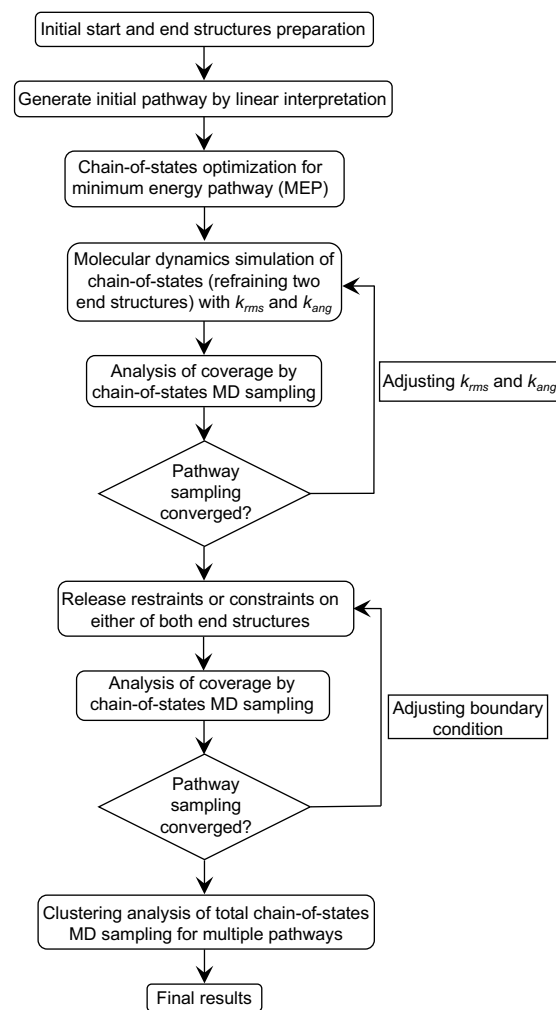

Figure 1. Flow chart for direct pathway dynamics sampling (DPDS) method.

Progress 2: Methodology Development for Dynamics Sampling in Transition Pathway Space

We carried out systematic computational studies to map the PES of thermal cracking reaction mechanisms of model molecule 1, 2-diphenylethane, illustrated in Figure 2a. Intrinsic Reaction Coordinate (IRC) method was employed to obtain the minimum energy pathway (MEP) of each fundamental reaction illustrated in Figure 2a. All the calculations were carried in gas phase using density functional theory (DFT) with UB3LYP and 6-31+g(d,p) basis set. The MEPs of reactions a2, a3, a4 and a5 are plotted in Figure 2b. All reactions have relatively low reaction barriers with a5 having the highest reaction barrier as 18.22 kcal/mol. Reactions a2, a3, a5, and a6 are endothermic, and reaction a4 is exothermic with ΔE as −23.11 kcal/mol. Reaction a1 represents a computational challenge, because it is homolytic breaking of a single carbon-carbon bond producing two radicals as product from a closed shell reactant. Therefore the ground state of the reactant is singlet, and the two radicals as product form a triplet state. Because there is no existing method to construct the MEP for this surfacing crossing reaction, we carried out preliminary calculations to explore the PES of both singlet and triplet states (Figure 2c). Clearly, two surfaces cross at the middle of the reaction process, indicating that the surfacing hoping is likely to occur during the bond breaking. The intersection structure of these two surfaces provides important information about the transition state (TS) of this reaction.

We also investigated the temperature dependence of barriers for reactions a2, a3, a4, a5, and a6 (Figure 3). The reaction barrier enthalpy (H) increases along temperature in all five reactions. From 100K to 800K, the reaction barriers in enthalpy for these reactions increase about 40 kcal/mol for a2 through a5. The increase is significantly larger for reaction a6 with 80 kcal/mol. Interestingly, the reaction barriers in free energy (G) for a2, a3, a4, and a6 show a minimum in high temperature range (400K-500K). This observation supports the hypothesis of this research that there is optimum temperature range for thermal cracking procedure of petroleum.
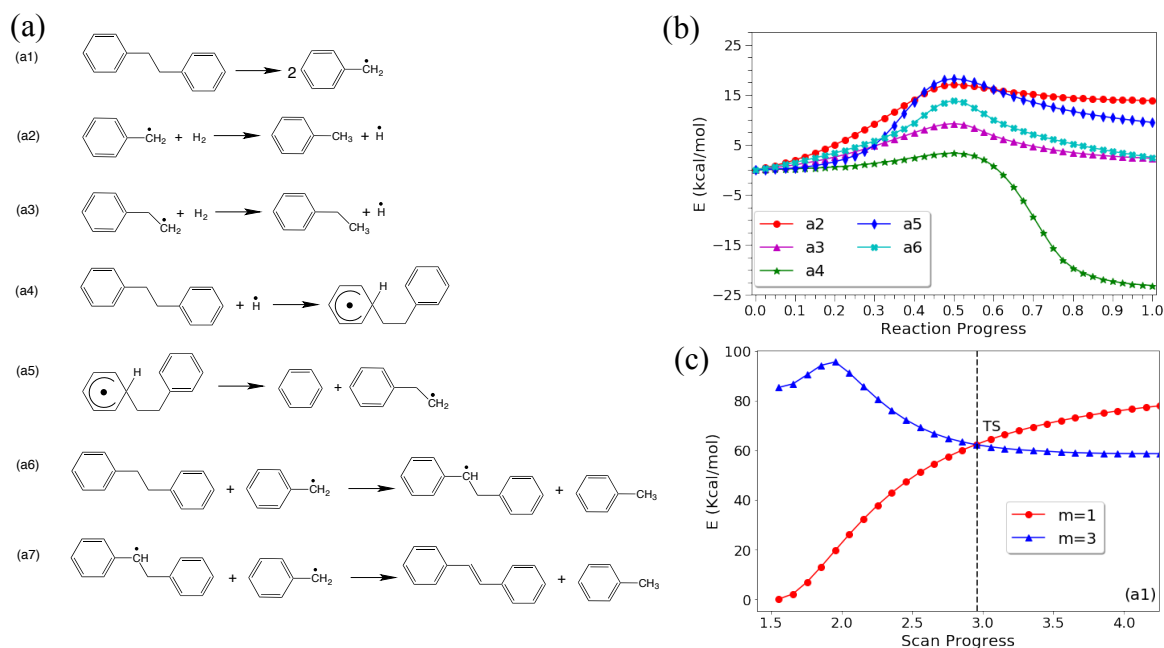

Figure 2. (a) Thermal cracking reaction scheme of 1, 2-diphenylethane; (b)The reaction progress of a2, a3, a4 and a5 reactions; (c) Singlet (m=1) and triplet (m=3) potential energy surfaces of reaction a1.
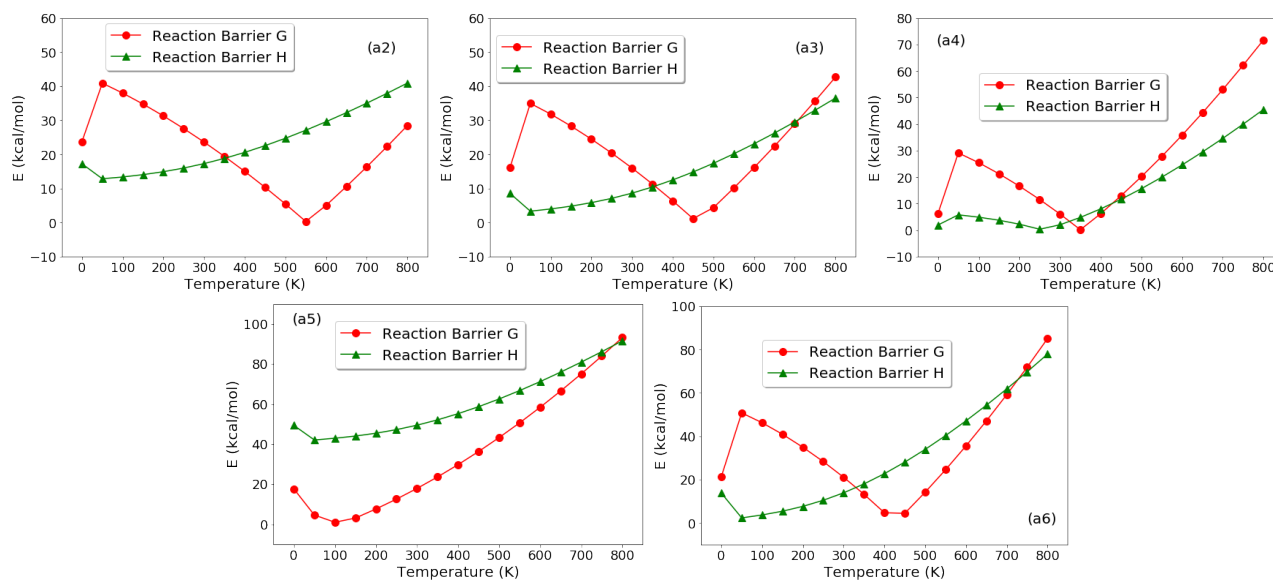

Figure 3. Temperature dependence of reaction barriers for reactions a2, a3, a4, a5 and a6.

Impact research on PI's career and the student who participated in the project

The reported research progress exerted significant impacts on PI's career development in both computational methodology development and applications in computational chemistry related to petroleum study. The developed DPDS method has attracted positive feedback from the community with great interest for its further development. The student who worked on the DPDS method has sharpened his program skills and deepened his understanding of reaction kinetics and statistical mechanics. The student who carried out the calculations to explore the reaction mechanisms has developed strong computational chemistry skills using advanced methods to systematically explore complexed reaction systems.