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

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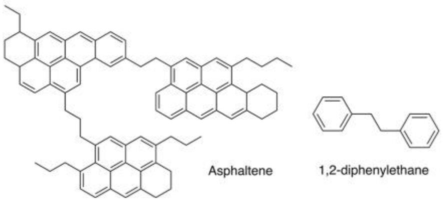
## Progress: Exploring free energy profile of petroleum thermal cracking mechanisms

Understanding the mechanisms of petroleum thermal cracking is critical to develop more efficient and eco-friendly petroleum cracking processes. Asphaltenes are the main component of petroleum subjected to cracking processes. During this period of research, we explored the thermal cracking mechanisms of petroleum by computational methods using 1,2-diphenylethane (DPE) as a model molecule. As the continuous effort to explore the free energy surface of the DPE thermal cracking mechanisms, we carried out extensive quantum chemistry calculations at high levels of theory to accurately explore the minimum energy pathways as the mechanisms of the proposed reactions. The overall mechanisms were divided into four steps including initiation, H-transfer reaction, H-ipso reaction and termination represented by seven reactions (illustrated in our previous annual report). The reaction energy and barriers in terms of enthalpy and free energy and their temperature dependence were calculated in both polar and nonpolar solvents using the polarizable continuum model (PCM) method. The reaction barriers and reaction energies of reactions (1-7) are listed in the Table 1 respectively as $\Delta E^{\ddagger}$ and ΔE.



**Scheme 1.** the chemical formulas of asphaltene and 1,2-diphenylethane (DPE)

**Table 1.** The reactions (1-7) in B3LYP, MP2, CBS-QB3 and CCSD methods with 6-31g+(d,p) basis set: $\Delta E^{\ddagger}$ represents the reaction barrier (kcal/mol), $\Delta E$ represents the reaction energies (kcal/mol).

| Reaction Barriers/Energies (kcal/mol) | B3LYP | | MP2 | | CBS-QB3 | | CCSD | |
|---|---|---|---|---|---|---|---|---|
| | $\Delta E^{\ddagger}$ | $\Delta E$ | $\Delta E^{\ddagger}$ | $\Delta E$ | $\Delta E^{\ddagger}$ | $\Delta E$ | $\Delta E^{\ddagger}$ | $\Delta E$ |
| Reaction (1) | 62.188 | 58.590 | --- | ---- | ---- | ---- | --- | --- |
| Reaction (2) | 19.856 | 16.476 | 20.527 | 2.213 | 20.892 | 13.756 | 34.664 | 20.467 |
| Reaction (3) | 10.674 | 3.520 | 15.161 | -4.093 | 11.696 | 2.617 | 16.375 | 0.650 |
| Reaction (4) | 3.780 | -25.831 | 18.859 | -15.410 | 5.907 | -21.569 | --- | --- |
| Reaction (5) | 18.587 | 6.745 | 28.285 | -7.847 | 22.083 | 12.090 | --- | --- |
| Reaction (6) | 18.894 | -1.690 | --- | --- | --- | --- | --- | --- |
| Reaction (7) | 7.363 | -48.500 | --- | --- | --- | --- | --- | --- |

The reaction barriers and reaction energies of reactions (1-7) are listed in the Table 1 respectively as $\Delta E^{\ddagger}$ and $\Delta E$. The energy profiles are optimized using four levels of theory including B3LYP, MP2, CBS-QB3 and CCSD methods with 6-31G+(d,p) basis set. Reaction (1) of homolytic C-C bond dissociation leading to two radicals is very endothermic with reaction energy around 60 kcal/mol to essentially break C-C single bond. Reaction (2), in which benzyl radical extracts a hydrogen atom from $H_2$ molecule to produce a toluene and regenerate a H• radical, is rather endothermic based on the results from CCSD, B3LYP, and CBS-QB3 methods. However, the MP2 results suggest that this step reaction is only slightly endothermic by more than 2.2 kcal/mol. The reaction (3), in which 2-phenylethyl free radical extracts a hydrogen atom from $H_2$ molecule to produce ethylbenzene and regenerate a H• radical, is chemically similar to the reaction (2), and is endothermic based on CCSD, B3LYP, and CBS-QB3 methods. For MP2 method, the results indicate that reaction (3) is exothermic by less than 5 kcal/mol. The reaction (4), in which H• radical binds with DPE to produce a new radical, is an exothermic reaction with a low reaction barrier. The calculated barriers range from effectively 3.78 kcal/mol using MP2 method to 18.859 kcal/mol using CBS-QB3 method (Table 1). The exothermicity of this step of reaction is also shown by all three levels of theory ranging between -15.410 kcal/mol and -25.831 kcal/mol. The barriers generated by B3LYP and CBS-QB3 methods of reactions (5), in which radical product of reaction (4) breaks into benzene and 2-phenylethyl free radical, are 18.6 kcal/mol and 22.1 kcal/mol, respectively, with difference as 3.5 kcal/mol. As comparison, the MP2 method overestimates the barriers by about 10kcal/mol than B3LYP method. The reaction (5) is endothermic based on the results of both B3LYP and CBS-QB3 methods, but exothermic based on the result of MP2 method. In the reaction (6), benzyl radical extracts a hydrogen atom from DPE to produce toluene and generate another radical. Due to the chemical complexity, only B3LYP calculations were successfully completed for reaction (6). This step of reaction has 18.9 kcal/mol barrier and is slightly exothermic by less than about 1.6 kcal/mol. To obtain higher accuracy of the reaction barrier information for the DPE thermal cracking reactions, the single point energy profiles of reactant, transition state and product at two high levels of theory, uB3LYP/aug-cc-pvtz and CCSD(T)/6-311G+(d,p), are calculated and plotted in the Figure 1. The single point calculations largely confirms the energetic profiles of these reactions using various levels of theory listed in Table 1.

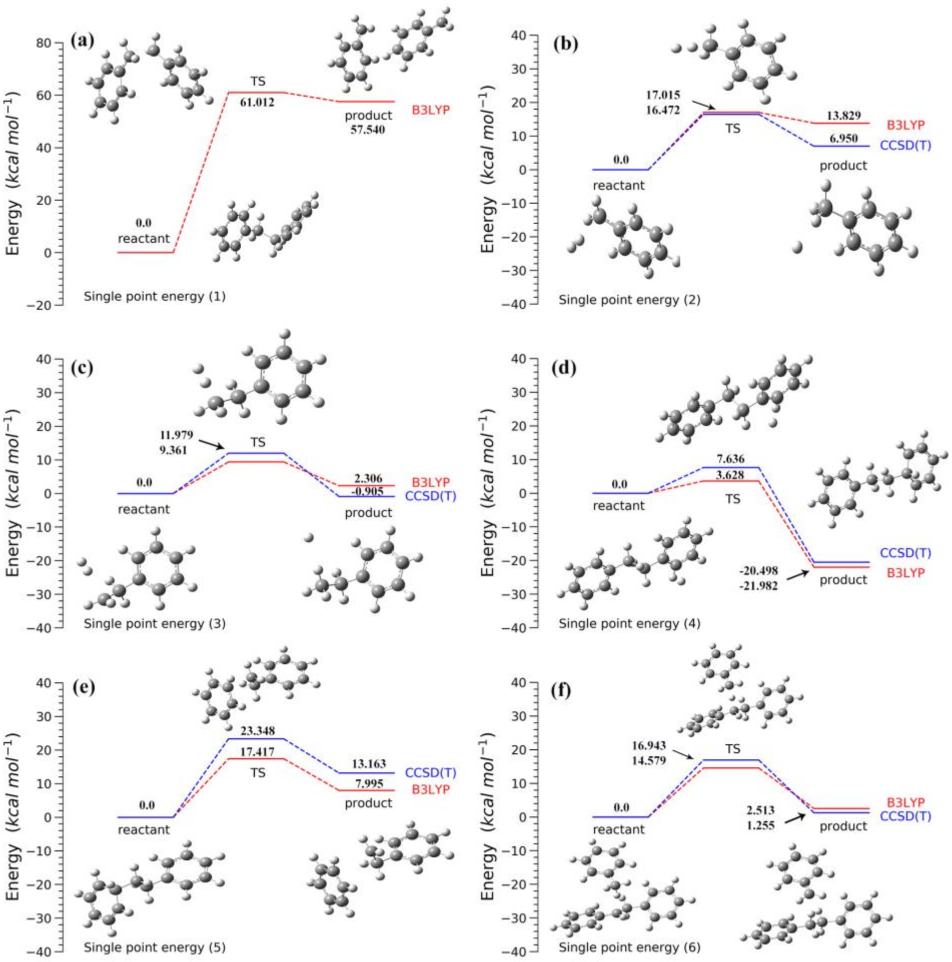


**Fig 1.** The single point energies of reactant, transition state and product geometries along the reaction pathway (1-6) at uB3LYP/aug-cc-pvtz (red line) and CCSD(T)/6-311+g(d,p) (blue line) levels of theory.

As the next step of exploring the potential energy surfaces of the DPE thermal cracking mechanism, the minimum energy pathways of H-transfer, H-ipso and termination including reactions (2-5) are constructed using IRC method and plotted and illustrated in the Figures 2-5. The pathways of reactions (2-4) were generated by both MP2 and DFT methods with 6-31G+(d,p) basis set. The pathway for reaction 5 was obtained at B3LYP/6-31G+(d,p) level of theory only.

As the first systematic investigation of petroleum cracking mechanisms, this study provided a comprehensive theoretical description of petroleum cracking processes, and is currently under peer review process for publication.

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

The reported research progress have put important impacts on PI's career development in computational chemistry related to petroleum study. The student (Ms. Feng Wang) who carried out the systematic computational studies of DPE thermal cracking reactions has developed comprehensive scientific skills for high standard scientific research investigations. Feng also presented her finding at the 257th ACS National Meeting in Fall 2019 in the Energy and Fuels Division of ACS and symposium of "Simulations of Materials & Processes for Energy Applications". This experience has greatly sharpened her interpersonal skills and extended her career development and networking.

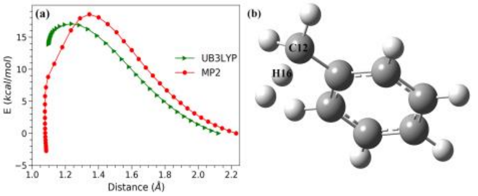


**Fig 2.** Reaction 2 profile.

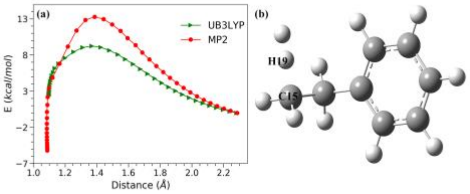


**Fig 3.** Reaction 3 profile.

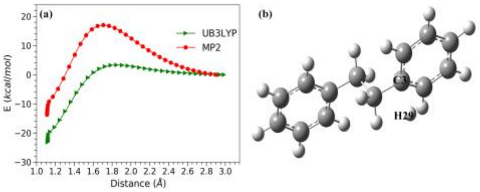


**Fig 4.** Reaction 4 profile.

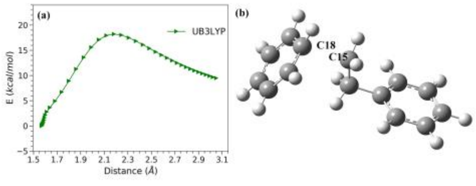


**Fig 5.** Reaction 5 profile.