

## Modelling the Formation of Two Ring Aromatics in Alkylaromatic Pyrolysis: Importance of Thermochemistry

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### Highlights

- Thermochemistry of fused two ring aromatics are calculated using CBS-QB3 level of theory.
- Thermochemistry of near aromatic radicals calculated using CBS-QB3 level of theory.
- Model generated to observe formation of two ring aromatics in alkylaromatic pyrolysis.
- Model yield of two ring aromatics matches experiments within order of magnitude.

### 1. Introduction

The pyrolysis of oils is highly relevant in the field of crude oil upgrading [1]. In this work, the formation of two ring aromatics is studied during the pyrolysis of hexylbenzene to help understand the formation of coke in crude oil upgrading processes, as two ring aromatics are likely the precursors to coke [2].

### 2. Methods

This work uses Gaussian 03 [3] for the calculation of the thermochemistry and rate constants for species and reactions using the CBS-QB3 level of theory. All hindered rotors are calculated using the B3LYP/CBSB7 level of theory wherever applicable.

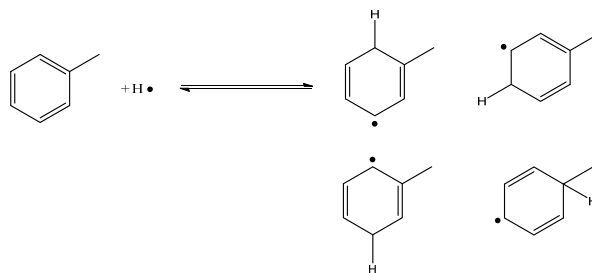
The Cantherm thermochemistry calculation package [4] from the Green Group Reaction Mechanism Generator (RMG) was used to convert Gaussian outputs to heat capacity, enthalpy, and entropy of formation.

Experimental setup was identical to work of Carr et al [1]. In short summary, reaction was carried out in batch reactor provided by SITEC; reactor was heated in sand bath to 450°C, 300bar, and quenched by water at the end of the reaction time. Liquid products were analyzed by GC-MS, whereas gas products were analyzed by GC-FID.

### 3. Results and discussion

This work calculates the thermochemistry of various compounds related to the formation of two ring aromatic species, and uses the updated information in conjunction with RMG to generate reaction mechanisms that can be used to estimate the formation of two ring species.

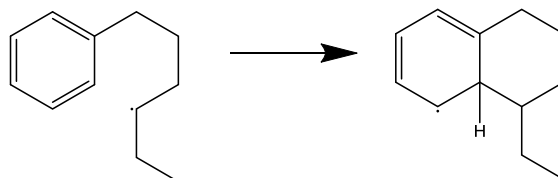
One area of focus are the formation of near aromatic radicals. Near aromatic radicals can form in the pyrolysis of alkylaromatics at 450°C through the addition of hydrogen radicals to aromatic rings, as shown in Figure 1.



**Figure 1.** Method of formation of near aromatic radicals in pyrolysis of alkylaromatics in 450°C; figure shows the addition of a hydrogen radical to the aromatic ring of toluene. One of four products may form based on the location of the hydrogen's addition.

The thermochemistry of eight model compounds were calculated; the eight model compounds are the four H radical addition products to toluene, and four H radical addition products to hexylbenzene. The resulting thermochemistry was used to derive a hydrogen bond increment value for near aromatics, which can be used to correct the thermochemistry for all other near aromatic radicals, yielding better predictions when near aromatics further react to form bridged two ring alkylaromatics.

Another area of focus is the formation of two ring aromatic compounds. It was found that the most relevant route of formation for fused two ring compounds is through intramolecular exocyclic addition, an example is shown in Figure 2.



**Figure 2.** Intramolecular exocyclic addition of a hexylbenzene radical to form a radical precursor of ethyltetralin. This reaction class is the most common method of formation for fused two ring aromatics in pyrolysis of alkylaromatics in 450°C.

Again, the thermochemistry of model compounds were calculated to ensure accurate modeling of the formation of this class of compounds. In this case, the thermochemistry of ethyltetralin, an ethyltetralin radical precursor (shown on Figure 2), indane, and the analogous indane precursor to Figure 2 was calculated. Similarly, the thermochemistry characteristics of these two compounds are captured by a fused ring near aromatic hydrogen bond increment and polycyclic group additivity correction to improve the thermochemistry estimations of future compounds of similar type.

Experiments were performed on hexylbenzene at 450°C, at 15, 20, 30, and 45 minutes to observe the yield of ethyltetralin and indane over time; yields were compared to the estimates of the model generated by this work. Model predictions of both ethyltetralin and indane match experiments within one order of magnitude. However, it appears that the model lacks pathways to consume indane, leading indane yield to monotonically increase and become overpredicted, whereas the rate of formation of ethyltetralin may be too slow to account for ethyltetralin production.

#### 4. Conclusions

The thermochemistry of near aromatics and fused two ring aromatics were calculated using the CBS-QB3 level of theory. These values are used to derive group additivity values and hydrogen bond increments to improve the predictions of analogous compounds. With improved thermochemistry, the prediction of indane and ethyltetralin were shown match experiments within an order of magnitude, and improvements can be made by investigating the kinetics of the formation and consumption of these molecules.

#### References

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#### Keywords

Pyrolysis, Ab initio calculations, Aromatics, Reaction Mechanisms