

Effects of the Structure of the Side Chain on the Pyrolysis of Alkylbenzenes

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INTRODUCTION

The formation of solids from jet fuels under pyrolytic conditions is a subject of intensive research in the years. The deposit formation is attributed to the thermal breakdown of hydrocarbons at temperatures higher than 350°C (1). Petroleum-derived jet fuels generally consist of about 85% paraffins and less than 10% alkylaromatics (2). When paraffins are subjected to pyrolysis, the formation of unsaturated rings is related to the Diels-Alder type reactions of conjugated alkenes and olefins (3). Upon further heat treatment, these unsaturated rings may undergo dehydrogenation reactions to form alkylbenzenes and solid products. Large amounts of alkylbenzenes are detected in the pyrolysis of long chain paraffins such as decane, dodecane and tetradecane (4). These results suggest that alkylbenzenes are the "precursors" of carbonaceous solid products during the pyrolysis of jet fuels.

The thermal chemistry of alkylbenzenes has been extensively studied, but most of the efforts are directed towards primary products obtained on pyrolysis. The length and types of the alkyl side chains can significantly affect the thermal reactions of alkylbenzenes. As the length of the side chain increases, the reactivity also increases. For instance, the activation energy for the pyrolysis reaction of toluene is higher than that of n-butylbenzene (5). Also t-butylbenzene is found to have a much lower thermal reactivity than its isomer n-butylbenzene (6). Another notable feature is that long-chain alkylbenzenes on pyrolysis exhibit pronounced characteristics of paraffins, i.e., cracking reactions (β -bond scission) become more important (7).

Understanding the secondary reactions that lead to the formation of solid deposit is equally crucial in studying the high-temperature thermal degradation process of jet fuels in an aircraft. This objective is achieved in the following study by using high pressure microautoclave reactors to simulate the situation of the fuel line and fuel nozzles in an aircraft. Preliminary pyrolysis reactions have been performed on four isomeric alkylbenzenes (n-, iso-, sec- and t-butylbenzenes) at 450°C and 0.7 MPa nitrogen over pressure. Solid formation tendencies of these compounds have been compared. Fundamental behavior of these alkylbenzenes that lead to their degradation and the formation of solid deposit have been studied.

EXPERIMENTAL

The experimental apparatus, procedures and product work-up were described in the previous paper (6). All chemicals were obtained commercially and used as received. n-, iso- and sec-butylbenzenes (>99% purity) were purchased from Aldrich Chemical Company. t-Butylbenzene (98% purity) was purchased from TCI America.

RESULTS AND DISCUSSION

1. General Scheme in the High Pressure Microautoclave Reactor

Experiments were carried out in the microautoclave reactors (tubing bombs) at 450°C under 100 psi using ultra-high purity (UHP) N₂. Under this condition, the pyrolysis reactions are extremely complex. In a conventional flow reactor, the dominant reactions are scission of β-bonds, while in microautoclave reactors, this reaction is suppressed and secondary reactions are favored. For jet fuels and related model compounds, generally, three groups of compounds are formed in the quenched tubing bomb reactors. They are: (i) low molecular weight gaseous hydrocarbons with the carbon chain length varying from C₁ to C₄, (ii) liquid products of a wide range of molecular weight, and (iii) carbonaceous solid products. As a result of thermal treatment, the reactions proceed to a thermodynamically stable state. If the treatment is severe, a three-phase thermodynamic equilibrium among gaseous, liquid and solid products can be reached. This appears to be the reason for the changes of the color of the liquid products from white to light yellow to brown to dark brown to light brown. The change of color from dark brown to light brown after long reaction times seems to be an indication of the achievement of equilibrium state.

2. Substrate Disappearance and Solid Product Formation

Figures 1 and 2 show the rate of disappearance of model compounds and the yield of solid products formed, respectively. Over a time period from 15 min. to 8 h, n-butylbenzene is quickly converted and t-butylbenzene is the most stable isomer, as shown in Figure 1. As the substrate compounds disappear, carbonaceous solids have been observed to form in the reactors. It can be seen from Figure 2 that each compound has a different induction period for the formation of solid products. The induction period reflects the ability of the compound to resist the formation of carbonaceous solid products. The order for the induction time of the four compounds is: n-<sec-<iso-<tert-butylbenzene. The order is the same as that of the rate of their disappearance. The amount of the solids formed increases with the reaction time for sec-, iso- and t-butylbenzene. This behavior is similar to that of jet fuels, which also exhibit a monotonic increase in the amount of solid products (8). Surprisingly, although solid products are quickly formed in the pyrolysis of n-butylbenzene after a short induction period, the amounts leveled off to an asymptotic value at around 5 h. As a result, the least amounts of solids is formed from the reaction of n-butylbenzene after 8 h at 450°C. The unique behavior of n-butylbenzene will be discussed in the following sections.

3. Major Substrate Consumption Pathways

Major substrate consumption pathways are studied in this paper by pyrolyzing the model compounds at very short residence times where little or no solid products are formed, and examining the compositions of the initial gaseous and liquid products.

(1) n-Butylbenzene (n-BB)

The pyrolysis of n-BB for 15 min. at 450°C indicates that ethane is present in the gas phase as a major product and toluene and styrene are major species present in liquid products. These results suggest that the major pathway of consumption n-BB is by breaking C_α-C_β bonds in the side chain (6).

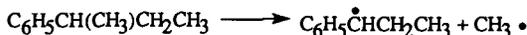
(2) t-Butylbenzene (t-BB)

Although the initiation of t-BB is similar to that of n-BB (C_α-C_β bond cleavage), its initiation process is significantly retarded as shown in Figure 1. This can be explained by the following two reasons. Firstly, the C_α-C_β dissociation energy for t-BB is 73.7±1.5 kcal/mol, which is higher than that for n-BB, 70.0±1 kcal/mol (9). Secondly, the H-abstraction reaction by C₆H₅C(CH₃)₂ radicals formed by the homolysis of t-BB is expected to be much slower simply because of the relatively high stability of C₆H₅C(CH₃)₂ radicals and the poor stability of C₆H₅C(CH₃)₂CH₂ radicals produced. As a result, the

pyrolysis of *t*-BB is mainly carried out by isomerization reaction to form *i*-BB and *s*-BB (6).

(3) *s*-Butylbenzene (*s*-BB)

The composition of gaseous products for the reaction of *s*-BB are shown in Table 1. The major gaseous products after the initial period are methane, ethane and ethylene. As the reaction time increases, the concentration of ethylene decreases. Major liquid products identified include ethylbenzene (0.72 wt%), styrene (0.11 wt%), α -methylstyrene (0.10 wt%), *trans*- β -methylstyrene (0.70 wt%) and α -ethylstyrene (0.16 wt%). According to these results, removing a CH_3 radical from *s*-BB appears to be a dominant initiation process:

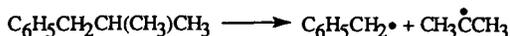


The presence of C_2 species in relatively high concentration in the gas phase indicates that removing a CH_3CH_2 radical also exists as another initiation process:



(4) *i*-Butylbenzene (*i*-BB)

The composition of gaseous products for *i*-BB is also shown in Table 1. Methane and propylene are two major gaseous products. Toluene (1.47 wt%) and *trans*- β -methylstyrene (2.80 wt%) are the major liquid products in the initial period. These data suggest that the following initiation reaction exists in the pyrolysis of *i*-BB.



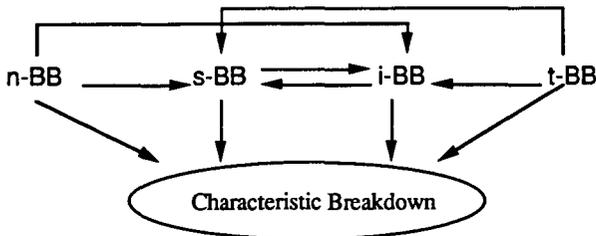
4. Major Liquid Product Selectivities

Liquid products consist mostly of cracking products (4), the molecular weights of which are less than the substrate compounds. Cracking products include mainly benzene, toluene, ethylbenzene, *i*-propylbenzene and *n*-propylbenzene. Figures 3, 4 and 5 show the plot of selectivities of benzene, toluene and ethylbenzene from the pyrolysis of butylbenzenes. *t*-BB has the highest selectivity for benzene as shown in Figure 3. This appears to suggest that the aryl-alkyl bonds in *t*-BB are weakened by the presence of bulky *t*-butyl groups. The formation of benzene may also be due to the attack of H to the ipso position of *t*-BB. In Figure 4, the concentration of toluene increases almost linearly with the increase of conversion except that the slope is lower for *s*-BB. Since β -bond scission to form benzyl radicals is the only initiation process in *n*-BB and it is easy for the benzyl radicals to abstract H from other species in the reaction system, *n*-BB has the highest selectivity to form toluene. In contrast, *i*-BB has two initiation pathways, only one of which forms benzyl radicals that lead to the formation of toluene. This lowers its toluene production. *t*-BB has been known to pyrolyze mainly by isomerization reactions to form *i*-BB (and *s*-BB to a lesser extent). The formation of toluene from *t*-BB might be attributed to the further dissociation of *i*-BB. It is obvious that direct decomposition of *s*-BB does not form toluene. Figure 5 shows the ethylbenzene selectivities. Similar behavior is observed in *n*-BB, *s*-BB and *i*-BB, *t*-BB. This could be understood from the discussion in the last section. It is possible that ethylbenzene can be formed as an initial reaction product for *n*-BB and *s*-BB, while *i*-BB and *t*-BB can only be formed between secondary reaction products.

5. Comparison of Solid Formation Tendencies

Compositions of liquid products seem to demonstrate that the reactivity of a model compound is governed by the initial reaction products. Generally there are two competing sets of reactions in the pyrolysis of all four model compounds at the initial stage, i.e.,

isomerizations and the characteristic breakdown for each specific compounds as shown below.



It is obvious from the previous discussion that for the pyrolysis of t-BB, the isomerization reaction to i-BB is more important than its characteristic breakdown. Therefore, the induction time for the solid formation from t-BB mainly depends on the isomerization reaction and the induction period of i-BB. This might account for its low reactivity and long induction period for solid formation (Figures 1 and 2). n-BB is the one that is most easily converted, but not the one that forms the highest amounts of solids. One reason for this is that it appears to be easy for n-BB to form cracking products such as toluene and ethylbenzene as shown in Figures 4 and 5, and stable high molecular weight compounds such as naphthalene as shown in Figure 6. The other reason is that fewer compounds of styrene-series were found in the liquid products of n-BB. In fact, only styrene is identified, and its concentration decreases rapidly as the reactions proceed. In the case of s-BB and i-BB, large amounts of compounds such as styrene, allylbenzene, α -methylstyrene, β -methylstyrene, and ethylstyrenes were present after the initial reaction period. This may constitute the reason for the formation of large amounts of solid products from the pyrolysis of s-BB and i-BB.

CONCLUSIONS

There is a significant effect of the structure of the side chains on the pyrolysis of alkylbenzenes. The rate of the disappearance or reactivity of an alkylbenzene depends on the ease of the dissociation energy of its initiation reactions. The order of reactivity or conversion of substrate was found to be n->sec->iso->tert-butylbenzenes. This indicates that, in general, branching seems to decrease the thermal reactivity of the alkylbenzenes. The amount of solids produced is related to the stability of the intermediate products especially at the initial stage. It seems that styrene-series compounds formed at the early stage are responsible for the formation of large amounts of solid products during the pyrolysis of sec- and iso-butylbenzenes.

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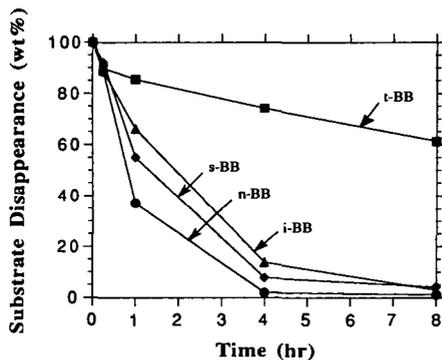


Figure 1. The disappearance of the substrate compounds at 450°C

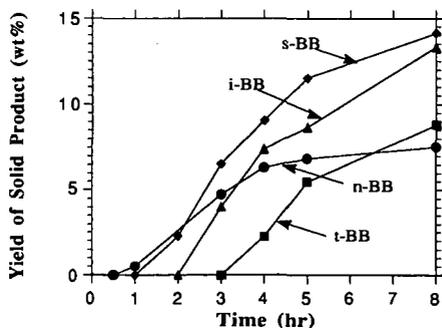


Figure 2. The formation of solid products at 450°C from the pyrolysis of butylbenzenes

Table 1. Composition of Gaseous Products from the Pyrolysis of sec- and iso-Butylbenzenes at 450°C

Time (hr)	CH ₄ (mol%)		C ₂ H ₄ (mol%)		C ₂ H ₆ (mol%)		C ₃ H ₈ (mol%)		C ₃ H ₆ (mol%)		Volume (ml)	
	s-BB	i-BB	s-BB	i-BB	s-BB	i-BB	s-BB	i-BB	s-BB	i-BB	s-BB	i-BB
0.25	83.49	71.84	9.52	0.34	6.04	0.87	0.75	3.02	0.08	21.17	44	42
1.00	86.59	62.85	3.13	0.54	8.07	4.11	1.29	7.18	0.80	19.28	293	203
2.00	84.25	68.25	1.50	0.57	10.79	6.35	1.91	9.61	0.59	10.43	497	355
4.00	83.99	63.39	1.08	0.89	12.16	9.58	2.26	14.60	0.32	4.08	687	601
8.00	82.15	62.67	0.54	0.26	13.36	12.16	3.11	15.32	0.23	4.55	727	733

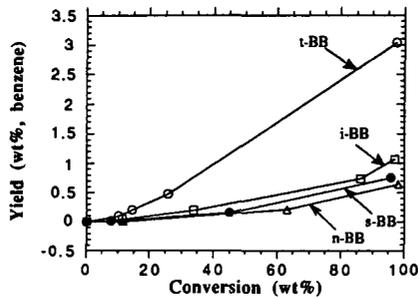


Figure 3. Selectivities of benzene in the pyrolysis of butylbenzenes

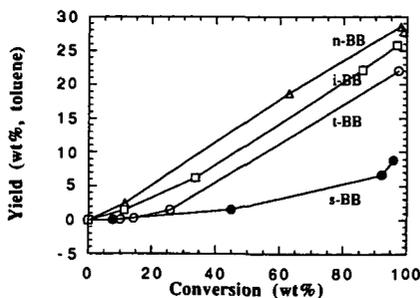


Figure 4. Selectivities of toluene in the pyrolysis of butylbenzenes

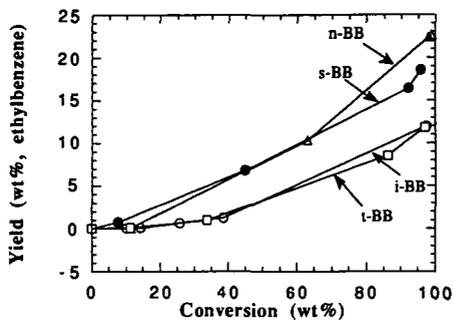


Figure 5. Selectivities of ethylbenzene in the pyrolysis of butylbenzenes

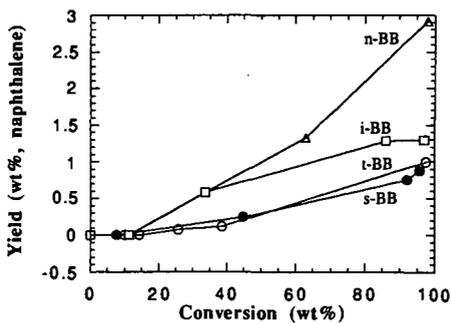


Figure 6. Selectivities of naphthalene in the pyrolysis of butylbenzenes