

Kinetic Studies of Carbonization of Pure Aromatic Hydrocarbons

D.K. BANERJEE

Institute of Oil and Gas, Ploiesti, Romania
Presently: Department of Chemistry,
University of Ottawa,
Ottawa, Ontario, Canada.

Introduction

Carbonization of petroleum is a highly complex process involving a large number of chemical reaction intermediates. To understand the reaction mechanism of carbonization of aromatic compounds like naphthalene, dimethyl naphthalene¹, anthracene², and phenanthrene³ the studies have already been carried out. Kinetics and mechanism of anthracene carbonization is well known.^{4,5,6}

In the present work, kinetics of carbonization of model compounds like: toluene, ethylbenzene and n-butylbenzene were carried out, to examine the different types of intermediate reactions that taking place towards the formation of coke. These studies illustrate the role of aromatic nucleus and the effect of side chain substituents on the early stages of carbonization.

Experimental

Pyrolyses of pure toluene, ethylbenzene and n-butylbenzene, were carried out in presence of nitrogen, in a quartz tubular reactor. The temperature of the reactor was maintained between 600-750°C. The flow of the aromatics was controlled by a dosing pump and that of nitrogen by a flow-meter. Aromatic vapour was mixed with nitrogen in the molar ratio 1:1, before entering the reaction zone of the reactor.

At the exit of the reactor products were cooled immediately with dry ice. Both the gaseous and liquid products were collected and analysed by gas chromatographic method.

The reactor was taken out of the furnace, cooled and the tar formed on the wall of the reactor was extracted with toluene. The toluene soluble portion of the tar was also analysed by chromatographic method.

Material balance calculation was done to determine the exact amount of tar formed due to the carbonization reaction.

Results

The distribution of the products show that, toluene pyrolysis produces about 5 to 10 wt% gaseous product, consisting mostly of hydrogen and methane. Ethylbenzene and n-butylbenzene produces about 10 to 20 wt% gaseous products, mostly consisting of hydrogen, methane and ethylene. From the toluene pyrolysis the major liquid products obtained were: benzene, bibenzyl, stilbene and small amounts of diphenyl, diphenylmethane, anthracene and phenanthrene. Ethylbenzene and n-butylbenzene pyrolyses produced all the products obtained from toluene and also styrene, tetraline and naphthalene.

Some part of the alkylbenzenes is converted into thermally stable solid products called tar, which remain on the wall of the reactor. Part of the tar is soluble in toluene. The insoluble portion is called coke.

Upto 600°C, tar formation is not of much significance. Toluene pyrolysis produces about 5 wt% of the products as tar at 750°C. From ethylbenzene and n-butylbenzene about 5 to 10 wt% of tar is formed between 650-700°C.

Large spectra of the products show that before the carbonization reaction (tar formation), four major types of intermediate reactions take place. At 600°C, decomposition (formation of free radicals) and dehydrogenation (specially formation of styrene) are favoured. As the temperature increases, condensation and dehydrocyclization reactions are more prominent. The latter is particularly noticable for n-butylbenzene.

It is found that from n-butylbenzene pyrolysis at 700°C, the total amount of tar obtained is almost 10 wt% of the total products. The yield of styrene is the highest for the ethylbenzene and n-butylbenzene pyrolyses.

Table 1 shows that the rate of styrene formation decreases with the increases of time and temperature of the reaction. On the other hand, the rate of formation of polycondensed products increases. The rate of tar formation also increases with the conversion level of the feed.

Thus, polymerisation of styrene is one of the important reactions, under the present reaction conditions, which leads to the formation of large aromatic molecules, which ultimately converts into tar.

n-butylbenzene pyrolysis shows that, the dehydrocyclization reaction is followed by various polycondensation reactions to form polycyclic aromatics. The above series of reactions is responsible for carbonization reaction. This is supported by the fact that, rate of tar formation from n-butylbenzene is 2 to 3 times higher than the ethylbenzene.

The rate of tar formation is almost double for n-butylbenzene than ethylbenzene and about four times than toluene. It shows that, as the length of the side chain increases the rate of tar formation also increases. It can be concluded that i) the chemical condensation of the aromatic nucleus to polyaromatics and ii) cross linking to form insoluble carbon rich residue are mostly responsible for the carbonization reaction.

References

1. R.A.Greinke and I.C.Lewis, 16th Conference on Carbon, pp 7, 1983.
2. A.W.Scaroni, P.L.Walker Jr. and R.G. Jenkins, 15th Conference on Carbon, pp 140, 1981.
3. J.Jastrzebski, K.Kubica, M.Stompel and Z.J.Stompel, 16th Conference on Carbon, pp 9, 1983.
4. I.C.Lewis, Carbon, Vol.16, pp 503, 1978.
5. S.E.Stein and L.L.Griffith, 16th Conference on Carbon, pp 13, 1983.
6. S.E.Stein, Carbon, Vol.19, pp 421, 1981.

Table 1. Kinetic data for the pyrolyses of alkylbenzenes.

	Temp./°C	Conv./wt%	Tar/wt%	k_s	$k_c \cdot 10^3$	$k_t \cdot 10^3$
Toluene	700	8.3	3.54	-	0.02	1.0
	700	10.1	3.70	-	0.05	1.2
	700	16.7	4.54	-	0.06	1.3
	750	12.3	4.66	-	0.04	2.3
	750	20.2	4.99	-	0.06	3.0
	750	32.3	5.09	-	0.08	3.2
	750	32.3	5.09	-	0.08	3.2
Ethylbenzene	650	35.1	5.36	0.23	0.2	2.2
	650	43.3	6.02	0.12	0.5	2.4
	650	50.8	6.28	0.10	0.6	2.8
	700	57.3	6.65	0.21	1.1	3.8
	700	69.7	6.90	0.19	1.5	4.1
	700	85.5	7.35	0.10	1.8	5.2
	700	85.5	7.35	0.10	1.8	5.2
n-Butylbenzene	650	42.0	6.70	0.23	2.2	7.0
	650	66.8	7.68	0.16	2.9	7.1
	650	79.7	7.82	0.14	3.6	7.6
	700	52.2	8.48	0.08	8.4	8.6
	700	63.6	8.83	0.07	9.2	8.9
	700	75.4	9.57	0.06	10.1	9.2
	700	75.4	9.57	0.06	10.1	9.2

k_s - rate constant for styrene formation

k_c - rate constant for total amount of condensed products formation

k_t - rate constant for tar formation

All the rate constants are in min^{-1} .