The Effect of the Reactor Type on the Selectivity of Thermal Reactions of *p*-Xylene in Temperature Gradient Systems

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Thermal reactions of *p*-xylene were investigated in two kinds of reactors, batch type and flow type, with a large temperature gradient. Excellent differences of the resulting products were observed between these two types of reactors. As for a batch type reactor, 4,4′-dimethylbibenzyl was produced in a high yield with [2.2]paracyclophane and toluene as by-products, and as for a flow type reactor, toluene was obtained as a major product with a low selectivity of 4,4′-dimethylbibenzyl, respectively. These results were different from those of the conventional fast flow pyrolysis method in which [2.2]paracyclophane or poly(3,6-dimethylene-1,4-cyclohexadiene) was formed as a major product. These differences can be accounted for by the partial separation of a reaction mixture caused by the thermal diffusion effect, which arises when the mixture is subject to a temperature gradient.

Thermal diffusion arises when a mixture is subjected to a temperature gradient, leading to partial separation of the components. In a reactor, which has a large temperature gradient, partial separation of the components of the reaction mixture due to the thermal diffusion effect prevents such side reactions as reverse reactions and successive reactions. By such a reactor, the reaction products are expected to be different from those in the conventional ones. In 1941 Hirota reported the formation of oily aromatic hydrocarbons and hydrogen from methane using a Clusius–Dickel type thermal diffusion column as a reactor.[1–3] His success in getting the oil in a high yield was attributable to the prevention of the recombination reaction by the instant separation of produced hydrogen from hydrocarbon residues owing to thermal diffusion effect caused by the temperature gradient. His works ought to be regarded as one of the earliest examples of application of a thermal diffusion column as a reactor. However, they had been left unnoticed until very recently. In 1988 Yamaguchi (one of the authors) reexamined Hirota's process, confirming the conversion of methane to C2 compounds.[4] The thermal reactions of simple aromatic hydrocarbons in a temperature gradient system were developed in this laboratory.[5–7] In the preceding paper,[6] we reported the formation of 4,4′-dimethylbibenzyl in a high selectivity by the dehydrogenative coupling of *p*-xylene in a temperature gradient system. The present paper deals with the thermal reactions of *p*-xylene using two kinds of reactors (termed as a batch type reactor and a flow type reactor in this paper), in which the thermal diffusion effect is expected.

Experimental

Batch Type Reactor. The reactions were carried out in a reaction system shown in Fig. 1, where a steep temperature gradient was expected between the surface of the heater and the cold wall of the flask. The spiral heater, made of a nickel chromium steel wire of 0.5 mm in diameter and 25 cm in length was placed horizontally inside of a 1 L three-necked separable flask fitted with a reflux condenser. This reactor is termed as a batch type reactor in this paper, and is characterized by the vertical contact of *p*-xylene vapor with the heater. The flask containing 1 mole of *p*-xylene was heated by a heating mantle under nitrogen. After the boiling of *p*-xylene was started, the power of the heater inside was turned on, and vapored *p*-xylene was contacted with the heater. The surface temperature of the heater was measured

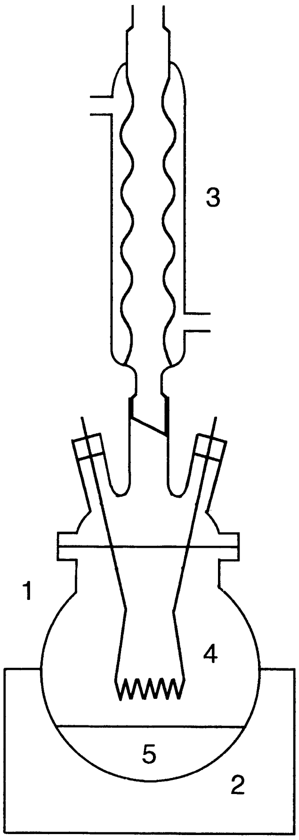

Fig. 1. Batch type reactor. 1: Separable flask, 2: Heating mantle, 3: Reflux condenser, 4: Heater, 5: Reactant.

by a radiation pyrometer (Minolta IR-120) and set at a desired reaction temperature. During the reaction the temperature was monitored by the radiation pyrometer and controlled. The reaction products were identified by GC-MS and GC-IR analysis using authentic samples. After the reaction, the reaction mixture was mixed with chloroform of twice volume of originally employed xylene to dissolve solid products, and analyzed by a gas chromatograph. Gaseous products were also analyzed by a gas chromatograph.

Flow Type Reactor. The flow type reactor used in this experiment is schematically shown in Fig. 2. In brief, the reactor consists of a Pyrex glass-made Liebig condenser (60 cm in length and 5.0 cm in inner diameter) and a heater made of a nickel chromium steel wire (42 cm length and 1.0 mm diameter) mounted at the axis of the condenser. In the flow type reactor, *p*-xylene vapor flowed parallel to the heater. The inlet of *p*-xylene and the outlet of gaseous product were placed at the level 2 cm lower from the top of the heater. The air in the reactor was first replaced by nitrogen and cooling water was supplied. The power of the heater was turned on. The temperature of the heater was measured by a radiation pyrometer and set at a desired temperature. *p*-Xylene was charged downward at a constant rate, and the surface temperature of the heater was further monitored and controlled. The heater was kept at the temperature for two hours by maintaining the voltage and the currency of the electric current. Reaction products were collected every 30 minutes; gaseous products from the upper outlet and liquid products from the lower outlet, and analyzed by gas chromatography.

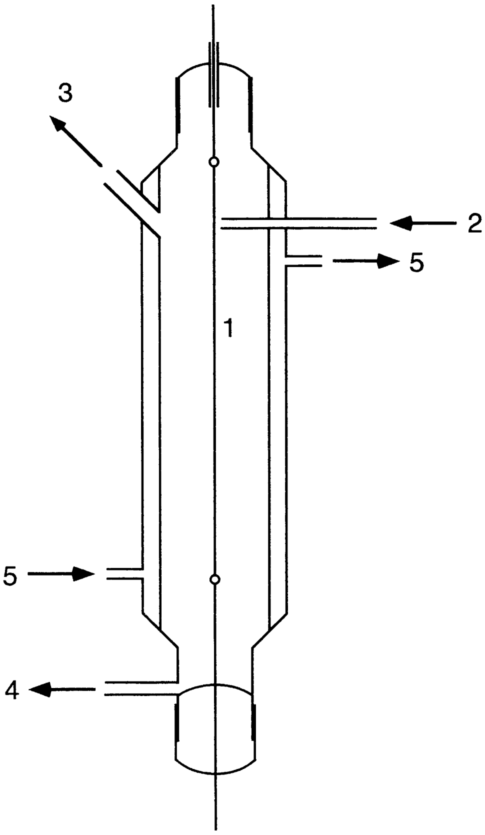

Fig. 2. Flow type reactor (Thermal diffusion column). 1: Heater, 2: *p*-Xylene, 3: Gaseous products, 4: Liquid products, 5: Cooling water.

Results and Discussion

Products of the Batch Type Reactor. The results of the batch type reactor are summarized in Table 1 with experimental details. The reaction started substantially at 1000°C, producing two ring aromatic compounds for the most part. The main product from *p*-xylene was 4,4′-dimethylbibenzyl (**1**). Among other major products were [2.2]paracryclophane (**2**), bis(4-methylphenyl)methane (**3**), *p*-methylstyrene, and toluene. The product, which remained insoluble in the reaction mixture after the addition of chloroform, was identified as poly(3,6-dimethylene-1,4-cyclohexadiene) (**4**) by IR analysis. With the raise of temperature, the selectivity of **1** decreased, while that of **3**, and the sum of **2**+**4** increased. As long as the reaction temperature remained unchanged, the constant selectivity of the products was obtained, even when the conversion of *p*-xylene increased with the prolonged reaction time.

It was shown by GC analysis that the main gaseous products were hydrogen and methane with a small amount of ethane and ethylene. The ratio of hydrogen to methane was approximately 6 to 4, which was consistent with other previous experimental results.[8,9] It should be noted that this ratio slightly decreased with the increase of the conversion of *p*-xylene by the temperature raise.

The formation of hydrogen is best accounted for by the reactions (Eqs. 1 and 2) postulated by Szwarc.[8] Most of the components of the reaction mixture can be traced to a common intermediate, *p*-methylbenzyl radical. This intermediate is formed by thermal scission of the benzylic hydrogen. Most of these radicals recombines to form **1** (Eq. 3), the product of the highest selectivity in the present temperature gradient system. Some of these radicals are converted to 3,6-dimethylene-1,4-cyclohexadiene by dispropor-

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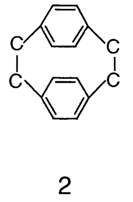

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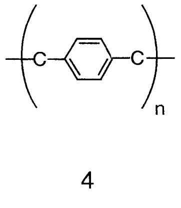

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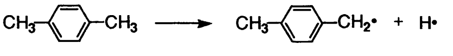
Table 1. The Thermal Reactions of *p*-Xylene in a Batch Type Thermal Diffusion Reactor

Reaction Temp./°C	1050	1050	1100	1150	1150
Reaction time/h	5	10	5	2	5
Conversion/%	5.0	10.2	10.9	12.8	32.7
Selectivity/%[a]					
Benzene	0.2	0.3	0.8	1.0	1.1
Toluene	20.1	20.0	20.3	22.1	22.0
o-Xylene	1.9	2.0	1.7	1.3	1.3
m-Xylene	2.3	2.3	2.2	2.3	2.4
Styrene	1.9	1.8	2.0	2.3	2.2
p-Methylstyrene	3.2	3.3	3.6	5.0	5.1
Naphthalene	ND[b]	ND	TR[c]	0.2	0.3
Methylnaphthalenes	ND	ND	TR	0.1	0.1
Biphenyl	ND	ND	0.1	0.1	0.1
Methylbiphenyls	ND	ND	0.2	0.5	0.6
Diphenylmethane	ND	ND	TR	0.2	0.2
Fluorene	ND	ND	0.2	0.5	0.5
Dimethylbiphenyls	ND	ND	0.2	0.5	0.4
Bibenzyl	ND	ND	0.1	0.1	0.1
Methylbibenzyls	1.1	1.1	1.3	1.7	1.8
Bis(4-methylphenyl)methane	5.9	5.8	6.1	6.6	6.6
4,4′-Dimethylbibenzyl	44.2	44.0	42.7	33.2	33.1
[2.2]Paracyclophane	10.0	9.8	9.3	8.4	8.4
Poly(3,6-dimethylene-1,4-cyclohexadiene)	1.7	1.9	2.0	6.0	6.2
Dimethylanthracenes	0.5	0.6	0.7	1.1	1.2
Others	7.1	7.1	6.5	6.8	6.3
Selectivity of gaseous product/mol%					
H_2	61.6	61.5	60.7	57.0	56.8
CH_4	37.9	37.8	38.6	42.5	42.4
Others	0.5	0.7	0.7	0.5	0.8

a) Values for selectivity were based on the weight of the products. b) Not detected. c) Trace.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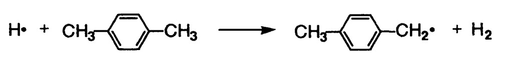
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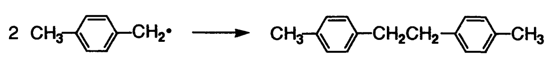
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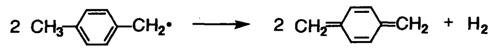
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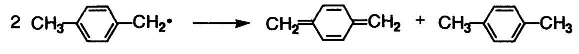
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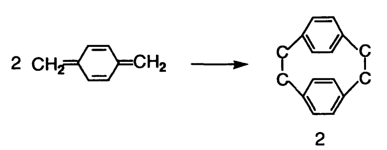
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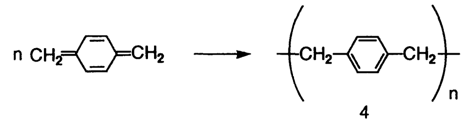
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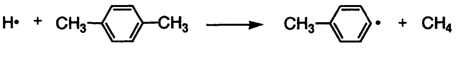
tionation (Eq. 4) or further dehydrogenation of the radicals (Eq. 5).[8,10] 3,6-Dimethylene-1,4-cyclohexadiene is either converted to **2** (Eq. 6) or polymerized to **4** (Eq. 7).

The formation of methane can be accounted for by the reaction (Eq. 8) as suggested by Szwarc[8] or by the reaction (Eq. 9) as suggested by Schaefgen.[9] The *p*-methylphenyl radical thus formed is further converted to toluene (Eq. 10), some of which is further changed to benzene. The radical is also responsible for the formation of **3**.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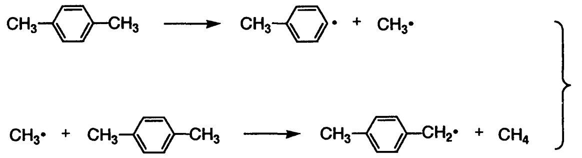
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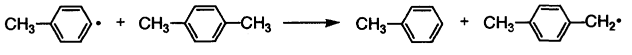
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Comparison with the Results of Fast Flow Pyrolysis. In a conventional reaction method such as fast flow pyrolysis, where *p*-xylene was pyrolyzed in a vapor phase without temperature gradient, the main products were [2.2]paracyclophane (**2**) and poly(3,6-dimethylene-1,4-cyclohexadiene) (**4**), supposed to be derived from 3,6-dimethylene-1,4-cyclohexadiene.[8–13] 4,4′-Dimethylbibenzyl (**1**) was described as only one of the by-products, the selectivity of which was only 2.9%,[12] although some reference was made to the formation of the compound.[9,11–13]

Contrary to these results, **1** was the main product in the present experiment. The high selectivity of **1** should be attributable to the thermal diffusion effect. In the conventional method, where little temperature gradient is present, *p*-methylbenzyl radical can accept enough energy to undergo dehydrogenation (Eq. 4) or disproportionation (Eq. 5) to be converted to 3,6-dimethylene-1,4-cyclohexadiene, the predecessor of **2** and **4**. Moreover, if **1** is produced from *p*-methylbenzyl radical, it is subject to successive reactions,[9] resulting in the low selectivity of **1**.

On the other hand, in the temperature gradient system as shown in Fig. 1, the thermal diffusion effect, caused by the temperature gradient between the surface of the heater and the cold wall of the vessel, brings about the quenching of the components of the reaction mixture immediately after their production. Thanks to the effect, *p*-methylbenzyl radical leaves the heated surface of the heater for the cold wall to be prevented from further conversion to 3,6-dimethylene-1,4-cyclohexadiene. No process other than the coupling to **1**, which requires almost no reaction energy, should be allowed for the quenched *p*-methylbenzyl radical. 4,4′-Dimethylbibenzyl (**1**), thus produced, is prevented from successive reactions due to the thermal diffusion effect, leading to its high selectivity.

Results of the Flow Type Thermal Diffusion Reactor. Table 2 lists the results of the flow type reactor (a thermal diffusion column), which were quite different from those of the batch type reactor. Toluene was the main product of the reaction under the reaction conditions studied. Only a few quantities of 4,4′-dimethylbibenzyl (**1**), which was the main product of the batch type reactor, was produced. As for gaseous products, a sample (corresponding to the experiment of the fifth column from the left in Table 2) comprised 61.6% of methane, 36.0% of hydrogen, 0.3% of ethane, and 2.1% of butanes. These results contrasted sharply with those of the batch type reactor (shown in Table 1), in which hydrogen occupied about 60% of gaseous products. The results of the flow type thermal diffusion reactor were also inconsistent with those of the conventional fast flow pyrolysis where **2** and **4** were major reaction products.

Thermal Diffusion Effect in the Reactors with the Temperature Gradient. The high selectivity of toluene should also be attributable to the thermal diffusion effect. Thermal diffusion arises when a mixture is subjected to a temperature gradient leading to partial separation of the components. In this process, the component of smaller molecular weight concentrates in the hotter region. In the thermal diffusion reactor of our experiment, molecular hydrogen or atomic hydrogen, evolved in the course of reactions, are separated and concentrated on the surface of the heater

Table 2. The Thermal Reactions of *p*-Xylene in a Flow Type Thermal Diffusion Reactor

Reaction temp.	1080	1080	1150	1150	1240	1240
Flow rate/mol h^{-1}	0.054	0.102	0.104	0.181	0.105	0.191
Conversion/%	6.6	4.2	12.7	8.2	24.2	16.4
Selectivity/%[a]						
Benzene	4.1	2.9	9.1	8.9	16.2	16.0
Toluene	60.5	60.7	51.3	53.2	39.8	40.9
o-Xylene	6.2	8.0	4.2	5.0	2.8	3.2
m-Xylene	2.3	3.6	1.9	2.6	1.4	1.5
Styrene	4.8	4.8	7.7	8.4	10.4	12.0
Trimethylbenzenes	10.6	8.7	6.3	5.8	3.9	2.8
p-Methylstyrene	4.5	3.1	4.9	3.1	3.9	2.7
Indene	1.1	0.5	4.6	3.3	7.0	7.4
Naphthalene	0.5	TR[c]	1.6	2.0	4.5	5.5
Methylnaphthalenes	ND[b]	ND	ND	ND	0.5	0.4
Biphenyl	ND	ND	ND	ND	1.2	0.4
Methylbiphenyls	ND	ND	ND	ND	0.7	TR
Diphenylmethane	ND	ND	ND	ND	0.1	ND
Fluorene	ND	ND	ND	0.2	0.7	0.6
Dimethylbiphenyls	ND	ND	ND	ND	0.2	ND
Bibenzyl	ND	ND	ND	ND	ND	ND
Methylbibenzyls	0.3	ND	0.5	0.4	0.2	ND
Bis(4-methylphenyl)methane	ND	ND	ND	ND	ND	ND
4,4′-Dimethylbibenzyl	2.0	3.4	1.9	2.2	0.7	0.6
[2.2]Paracyclophane	2.7	4.1	3.2	2.6	0.7	0.6
Unidentified	0.4	0.2	2.6	2.5	5.1	5.4

a) Values for selectivity were based on the weight of the products. b) Not detected. c) Trace.

due to thermal diffusion effect. They can retard the formation of p-methylbenzyl radicals (Eq. 2) and 3,6-dimethylene-1,4-cyclohexadiene (Eq. 4), and promote the production of p-methylphenyl radicals by hydrogenolysis of p-xylene (Eq. 8), resulting in the high selectivity of toluene. In other words, in the thermal diffusion column, p-xylene appears to have undergone hydrogenative cracking due to the condensation of hydrogen, without supplying hydrogen as a reactant. The analysis of the gaseous products also supports the consumption of hydrogen and the formation of methane. Furthermore, when half amount of hydrogen was added to p-xylene at 1150 °C (corresponding to the third column of Table 2), the selectivity of toluene rose to 83.7%, suggesting that hydrogen was responsible for the demethylation.[14)]

In the batch type reactor, where the heater was placed horizontally as shown in Fig. 1, gaseous products leave the high temperature region around the heater more immediately than in the flow-type reactor, on account of their low weight and the upward flow of p-xylene vapor convection. Hydrogen is less concentrated in the vicinity of the heater and less p-methylphenyl radicals are formed in the former reactor than in the latter reactor. This difference of hydrogen concentration is responsible for the difference of products distribution between the two reactors.

Conclusions

Thermal diffusion effect can account for the following difference of product of thermal reactions of p-xylene. In a temperature gradient system, p-xylene gave as a major product 4,4′-dimethylbibenzyl in the batch type reactor and toluene in the flow type reactor, respectively. However, thermal diffusion effect worked differently, in each reactor in a temperature gradient system. In the former, the effect brought about the quenching of p-methylbenzyl radical which was converted to 4,4′-dimethylbibenzyl. In the latter, the effect resulted in the concentration of hydrogen around the heater, and caused p-xylene to undergo hydrogenative cracking. Anyway, both results contrast sharply to those of the conventional fast flow pyrolysis of p-xylene, where [2.2]paracyclophane and poly(3,6-dimethylene-1,4-cyclohexadiene) were produced mainly, probably because of the little temperature gradient.

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