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Thermal Reactions of Xylenes in a Temperature Gradient System

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4,4'-Dimethylbibenzyl was produced in high yield with [2.2]paracyclophane and toluene as by-products by the dehydrogenative coupling of p-xylene under a temperature gradient system, i.e., the thermal diffusion reactor. The results were different from those by the conventional tube reactors where far less selectivity for 4,4'-dimethylbibenzyl was obtained.

In a reactor, which has a large temperature gradient, the 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. Recently we reported the effect of a thermal diffusion reactor on the dehydrogenative coupling of benzene, in which biphenyl was obtained at a high selectivity of more than 94% over the wide range of benzene conversion (3-77%).1) The present paper deals with the preliminary results concerning the thermal reaction of xylenes using a similar reactor.

The reactions were carried out using a thermal diffusion reactor 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 inside of a 1 L three-necked separable flask fitted with a reflux condenser. The flask containing 1 mole of xylene was heated by a heating mantle under nitrogen. After the boiling of xylene was started, the power of the heater inside was turned on, and vapored xylene was contacted with the heater. The surface temperature of the heater was monitored by a radiation pyrometer (Minolta IR-120) and controlled. The reaction products were identified by GC-MS analysis using authentic samples. After the reaction,

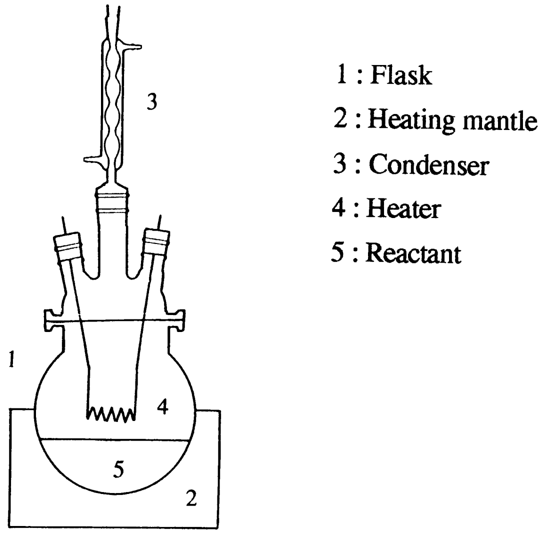
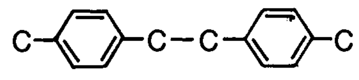


Fig. 1. The reactor.

the reaction mixture was mixed with chloroform of twice volume of originally employed xylene to dissolve solid products, and analyzed by a gas chromatograph (Shimadzu GC-9A).

The results 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]paracyclophane (**2**), 4,4'-dimethyldiphenylmethane (**3**), p-methylstyrene, and toluene. The product, which remained insoluble in the reaction mixture after the addition of chloroform, was identified as poly(p-xylylene) (**4**) by IR analysis.



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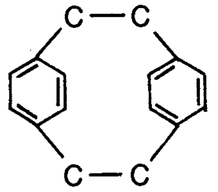

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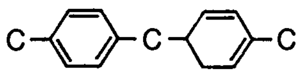

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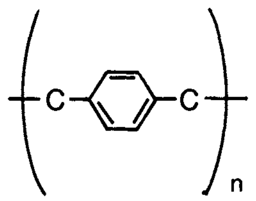

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It was shown by GC analysis that the main gaseous products were hydrogen and methane with a small amount of ethane and ethylene. The ratio of hydrogen to methane was approximately 6 to 4, which is consistent with other experimental results.[2,3] It should be noted that this ratio slightly decreased with the increase of the conversion of p-xylene by the temperature raise.

The conversion of p-xylene and the selectivity of **1** at each reaction temperature is shown in Fig. 2. With the raise of temperature, the selectivity of **1** decreased, while that of **3** and **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.

The formation of **1** is attributable to p-methylbenzyl radical, while that of **3** and toluene to p-methlyphenyl radical. The bond dissociation energy of the C-H in the methyl group of p-xylene is smaller than that of C-C bond. Therefore the dissociation of C-H bond was favored more than that of C-C bond, resulting in the high selectivity of **1**. The experimental result that the ratio of hydrogen to methane decreased with the temperature rise (Table 1) can also be explained by this difference of bond dissociation energy.

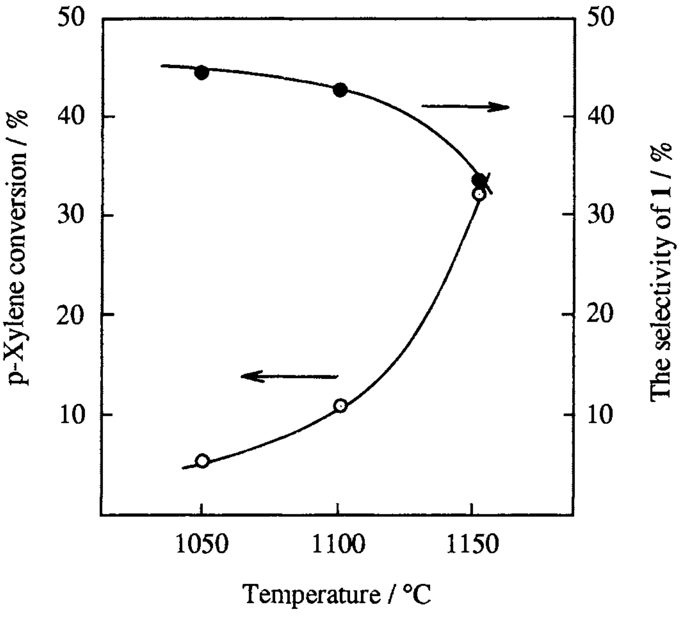


Fig. 2. The conversion of p-xylene and the selectivity of 1 (reaction time 5 h).

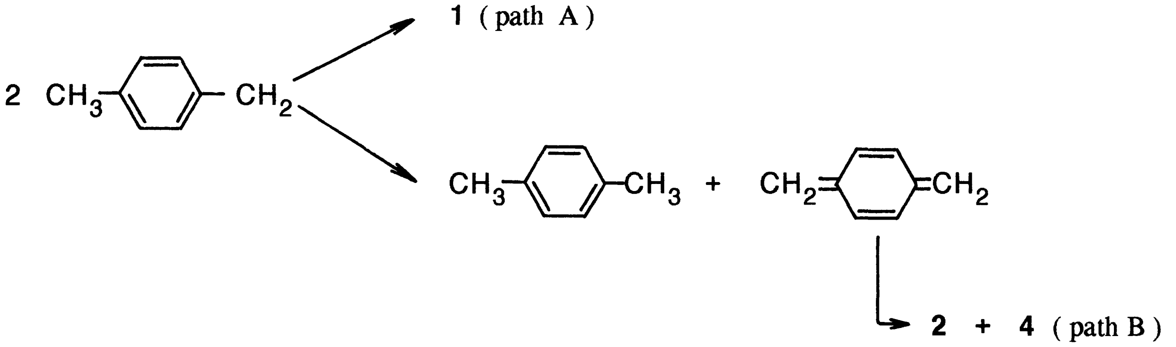
Table 1. Thermal Reactions of Xylenes in a Thermal Diffusion Reactor

Reactant	p-Xylene	p-Xylene	p-Xylene	p-Xylene	m-Xylene	o-Xylene
Reaction temp / °C	1050	1050	1150	1150	1050	1050
Reaction time / h	5	10	2	5	10	10
Conversion / %	5.0	10.2	12.8	32.7	8.6	7.0
Selectivity / % [a]						
Benzene	0.2	0.3	1.0	1.1	0.7	0.6
Toluene	20.1	20.0	22.2	22.1	27.7	24.4
o-Xylene	1.9	2.0	1.3	1.3	3.1	Re[b]
m-Xylene	2.3	2.3	2.3	2.4	Re	2.9
p-Xylene	Re	Re	Re	Re	tr	5.9
Styrene	1.9	1.8	2.3	2.2	1.2	1.7
Methylstyrenes	3.2[c]	3.3[c]	5.1[c]	5.2[c]	7.7[d]	7.8[e]
Naphthalene	ND[f]	ND	0.2	0.3	ND	0.3
Methylnaphthalenes	ND	ND	0.1	0.1	ND	ND
Biphenyl	ND	ND	0.1	0.1	ND	ND
Methylbiphenyls	ND	ND	0.5	0.6	ND	ND
Diphenylmethanes	ND	ND	0.2	0.2	ND	ND
Fluorene	ND	ND	0.5	0.5	ND	ND
Dimethylbiphenyls	ND	ND	0.5	0.4	1.1	ND
Bibenzyl	ND	ND	0.1	0.1	ND	1.5
Methylbibenzyls	1.1	1.1	1.7	1.8	2.9	0.3
Dimethyldiphenylmethanes (**3**)	5.9	5.8	6.7	6.7	2.9	2.7
Dimethylbibenzyls (**1**)	44.2[g]	44.0[g]	33.3[g]	33.2[g]	41.0[h]	37.6[i]
[2.2]Paracyclophane (**2**)	10.0	9.8	8.5	8.5	ND	ND
Poly(p-xylylene) (**4**)	1.7	1.9	6.1	6.3	ND	ND
Anthracene	ND	ND	ND	ND	ND	2.7
Dimethylanthracenes	0.5	0.6	1.1	1.2	ND	ND
Unidentified	7.1	7.1	6.8	6.3	11.7	9.9
Selectivity of gaseous products / mol%						
H_2	61.6	61.5	57.0	56.8	61.0	57.1
CH_4	37.9	37.8	42.5	56.8	61.0	57.1
Others	0.5	0.7	0.5	0.8	0.5	0.7

a) Values for selectivity were based on the weight of the products. b) Reactant. c) 4-Methyl. d) 3-Methyl. e) 2-Methyl. f) Not detected. g) 4,4'-Dimethyl. h) 3,3'-Dimethyl. i) 2,2'-Dimethyl.

In the conventional reaction method such as fast-flow-pyrolysis, the main products were [2.2]paracyclophane (**2**) and poly(p-xylylene) (**4**), supposed to be derived from p-xylylene.[2-7] 4,4'-Dimethylbibenzyl (**1**) was described as only one of the by-products, the selectivity of which was only 2.9%,[6] although some reference was made to the formation of the compound.[3,5-7] In the reaction of toluene using a conventional pyrolysis tube as a reactor, the selectivity of bibenzyl was also low.[8)] 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. p-Xylylene, which is responsible for the production of [2.2]paracyclophane (**2**) and poly(p-xylylene) (**4**) is produced by the disproportionation of p-methylbenzyl radical formed by C-H bond dissociation of p-xylene.[2,4)] The thermal diffusion effect caused by the temperature gradient between the surface of the heater and the cold wall of the reactor 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 p-xylylene by path B. No process other than the coupling (path A) should be allowed for the quenched p-methylbenzyl radical.



o-Xylene and m-xylene also afforded 2,2'-dimethylbibenzyl and 3.3'-dimethylbibenzyl in high selectivity, respectively. Only few reports have been made on the direct formation of these compounds from xylenes, especially in high yield. The thermal diffusion effect can also be responsible for the formation of dimethylbibenzyls in high selectivity from m-xylene and o-xylene.

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