BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 2635—2637 (1970)

Equilibria of the Isomerization of Xylene at 290°C under a Pressure of 300—6000 kg/cm^2

Haruo TAKAYA,* Naoyuki TODO,* Tadasuke HOSOYA,* Toshio MINEGISHI* and Mikio YONEOKA**

* *The Government Chemical Industrial Research Institute, Tokyo, Mita, Meguro-ku, Tokyo*
** *Japan Gas-Chemical Company Inc., Niigata Laboratory, Enoki-cho, Niigata*

(Received February 23, 1970)

It is known that the isomeric forms of xylene, *i.e.*, *ortho*-xylene, *meta*-xylene and *para*-xylene, can be converted into one other by isomerization over acid catalysts under heterogeneous conditions. However, as has been reported by Taylor,[1] the *para*-xylene content in the mixture of xylene at equilibrium is 23—24% in the temperature range from 100°C to 600°C.

Recently a patent presented by Hepp[2] has reported an improved process for isomerizing xylenes; in this process the yield of the *para* isomer is about 58%, and that of the *ortho* isomer is almost twice that which can be obtained by a conventional operating process, when the reaction is conducted at 327°C and at a pressure of 5400 kg/cm^2. If such a process can be possible, both the economical and thermodynamical interests of the isomerization would be enhanced. However, it has been realized that the influence of the pressure on an equilibrium of a reaction is determined by the difference between the molar volumes of the product and the reactant.[3] The molar volumes of *ortho*-, *meta*- and *para*-xylene at 25°C are 121.2 m*l*/mol, 123.5 m*l*/mol, and 123.9 m*l*/mol respectively.[4] Hence, under a high pressure, the differences between the molar volumes of these isomers seem to be small even at a high temperature of 327°C, where the molar volumes of the xylenes are nearly equal to those at 25°C.

The present authors have previously developed high-pressure equipment for both the batch and the flow reactions and have investigated the rate of the isomerization of xylenes over acid catalysts under heterogeneous conditions.[5,6] This study was undertaken in order to examine the pressure dependency of the compositions of the mixtures of xylenes at equilibrium at 290°C and to confirm the improved process described above.

Experimental

The xylene isomerization was carried out by the contineous-flow method using the high-pressure equipment reported in the previous paper.[5] The catalyst used was powdered Nikki X633L silica-alumina. The feeds were prepared by mixing pure xylenes in the desired proportions; the compositions used are given in the column 2 of Table 1. The products were analyzed by gas chromatography in the same manner as has been described in a previous paper.[6]

Results and Discussion

The compositions of the xylene fraction in the reaction product at 290°C at pressures between 300 and 6000 kg/cm^2 are shown in column 3 of Table 1.

It has been proposed by Hanson that *para*-xylene and *ortho*-xylene do not directly interconvert,[7] that is, that the migrating methyl group moves around the benzene ring in steps of one ring position at a time. This can be represented schematically as;

$$\textit{ortho} \rightleftarrows \textit{meta} \rightleftarrows \textit{para}$$

Hence, the results on the equilibrium composition of xylenes were treated with the following two reactions: *para*$\rightleftarrows$*meta* and *meta*$\rightleftarrows$*ortho*. The ratios of *para*-xylene and *ortho*-xylene to *meta*-xylene are also tabulated in column 2 (Reactant) and 3 (Product) of Table 1 and are shown in Fig. 1. The ratios of the products should approach closer to those at equilibrium than the ratios of the reactants. For example, the ratio of p/m at equilibrium under the pressure of 2000 kg/cm^2 can be obtained by the following procedure. The ratio of p/m

---

[1] W. J. Taylor, D. D. Wagman, M. G. Williams, K. S. Pitzer and F. D. Rossini, *J. Res. Nat. Bur. Stand.*, **37**, 95 (1946).

[2] H. J. Hepp and M. M. Johnson, U. S. 3363017.

[3] S. D. Hamann, "High Pressure Physics and Chemistry," ed. by R. S. Bradley, Academic Press, London and New York (1963), p. 134.

[4] J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 72nd ed., Interscience Publisher, New York (1955), pp. 74—76.

[5] T. Hosoya, T. Minegishi, H. Takaya, M. Yoneoka and N. Todo, *Tokyo Kogyo Shikenjo Hokoku*, **64**, 499 (1969).

[6] H. Takaya, N. Todo, T. Hosoya, T. Minegishi and M. Yoneoka, *Kogyo Kagaku Zasshi*, **73**, 1831 (1970).

[7] K. L. Hanson and A. J. Engel, *A.I.C.E.J.*, **13**, 260 (1967).

Table 1. Compositions and ratios* at 290°C under various pressures

Pressure I kg/cm²	Reactant II						Product** III						W/F IV h.g-cat./g
	%			Ratio*			%			Ratio*			
	p	*m*	*o*	*p*/*m*	*m*/*m*	*o*/*m*	*p*	*m*	*o*	*p*/*m*	*m*/*m*	*o*/*m*	
300	33.3	33.3	33.3	1.00	1.00	1.00	26.8	45.5	27.7	0.59	1.00	0.61	0.45
300	0.2	99.6	0.2	0.00	1.00	0.00	22.0	59.0	18.8	0.38	1.00	0.32	1.24
2000	18.8	55.9	25.3	0.34	1.00	0.45	19.9	54.4	25.7	0.37	1.00	0.47	0.78
2000	33.3	33.3	33.3	1.00	1.00	1.00	23.1	51.1	25.8	0.45	1.00	0.51	0.43
2000	0.3	99.4	0.3	0.00	1.00	0.00	21.8	59.0	19.2	0.37	1.00	0.33	1.13
5000	17.5	58.4	24.1	0.30	1.00	0.41	20.9	53.2	25.9	0.39	1.00	0.49	0.85
5000	52.5	14.9	32.6	3.52	1.00	2.19	29.2	47.1	23.9	0.62	1.00	0.51	0.80
5000	27.7	54.1	18.1	0.51	1.00	0.34	23.9	53.3	22.8	0.45	1.00	0.43	0.80
5000	24.1	53.6	22.3	0.45	1.00	0.42	22.0	52.2	25.7	0.42	1.00	0.49	0.80
5000	20.0	56.0	24.0	0.36	1.00	0.43	20.4	54.6	25.0	0.37	1.00	0.46	0.08
6000	18.2	56.7	25.1	0.32	1.00	0.44	20.8	52.7	26.5	0.40	1.00	0.50	0.81
6000	33.3	33.3	33.3	1.00	1.00	1.00	20.1	54.7	25.2	0.37	1.00	0.46	0.45

* Ratio of *para*-xylene or *ortho*-xylene to *meta*-xylene.

** Xylene fraction of the product.

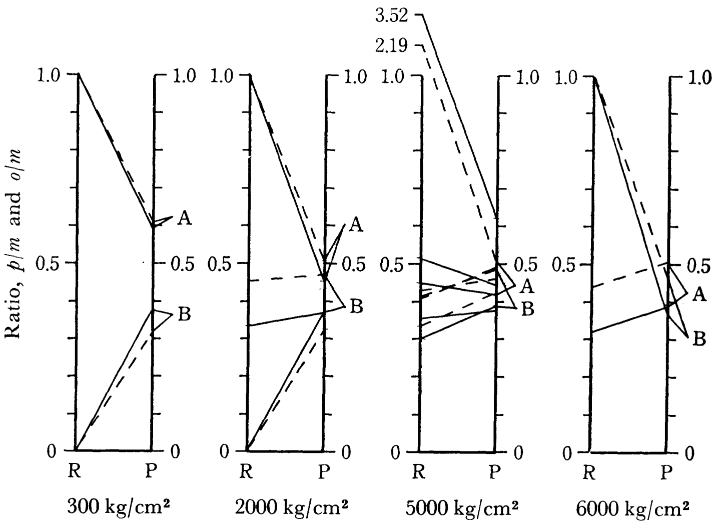

Fig. 1. Ratios, *p*/*m* and *o*/*m*, of reactants and products.
——: *p*/*m*, ----: *o*/*m*
R: Reactant P: Product
A and B are the maximum and the minimum value of the probable ratio at equilibrium respectively.

Table 2. Compositions at equilibrium

Pressure kg/cm²	Composition at B** in Fig. 1						Composition at A* in Fig. 1					
	Ratio			%			Ratio			%		
	p/*m*	*m*/*m*	*o*/*m*	*p*	*m*	*o*	*p*/*m*	*m*/*m*	*o*/*m*	*p*	*m*	*o*
300	0.38	1.00	0.32	22	59	19	0.59	1.00	0.61	27	46	28
2000	0.37	1.00	0.47	20	54	26	0.45	1.00	0.51	23	51	26
5000	0.39	1.00	0.49	21	53	26	0.42	1.00	0.51	22	52	26
6000	0.37	1.00	0.46	20	55	25	0.40	1.00	0.50	21	53	27

* A is the maximum value of the probable ratio at equilibrium.

** B is the minimum value of the probable ratio at equilibrium.

decreases from 1 to 0.45 upon the isomerization; thus, the ratio at equilibrium should be smaller than 0.45 (A in Fig. 1). The ratios of p/m increase from 0 to 0.37 and from 0.34 to 0.37; thus, the ratio at equilibrium should be larger than 0.37 (B in Fig. 1). Consequently, the ratio at equilibrium under 2000 kg/cm^2 should be 0.37(B)—0.45(A). The A and B values obtained from such a procedure, and also the corresponding compositions, are shown in Table 2 and in Fig. 2. Figure 2 clearly indicates that a mixture of xylenes at equilibrium, even under a pressure of 6000 kg/cm^2, consists of 20—21% *para*-xylene, 53—55% *meta*-xylene, and 25—27% *ortho*-xylene; these findings practically agree with those obtained under ordinary conditions, although the experiment in this study was carried out at 290°C, a temperature lower by 37°C than that in Hepp's work. However, it seems unlikely that the difference in the reaction temperature between the both cases greatly influences the equilibrium composition, for it is very difficult to suppose that by such a temperature difference discrete phenomena can occur.

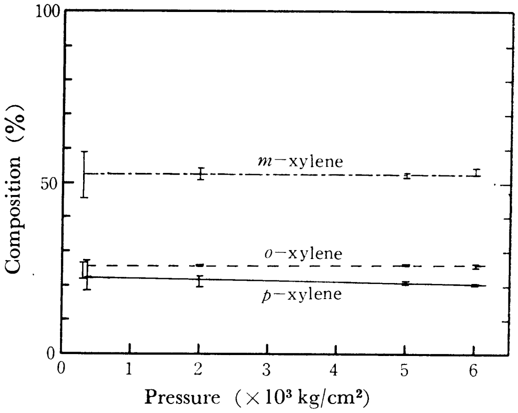

Fig. 2. Pressure dependency of the composition at equilibrium.

This conclusion is consistent with the thermodynamical consideration presented in the first paragraph.