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Xylene Isomerization and Disproportionation over Lanthanum Y Catalyst

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Xylenes have been converted using a LaY zeolite catalyst at a temperature, 350°C, where transalkylation, as well as isomerization, occurs. The relative rates of the isomerization reactions were calculated using the Wei–Prater method. Relative selectivities calculated from the relative rates (Wei–Prater) agree very well with those calculated from rates obtained by extrapolation to low conversions. The trimethylbenzenes obtained at low conversions are those expected from methyl-group-directing influence for the *ortho*-xylene and *para*-xylene reactants; however, with *meta*-xylene an equilibrium trimethylbenzene composition was obtained even at very low conversions. The results are consistent with a series reaction path for the isomerization reaction.

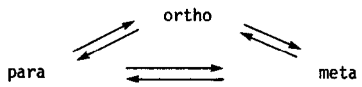
INTRODUCTION

Xylene isomerization has been widely studied because of the importance of this process in aromatics production as well as the academic interest in the kinetics of the interconversions within a three-component system. The catalyst system has ranged from low-temperature liquid-phase homogeneous acid catalysts, e.g., aluminum chloride, to high-temperature liquid- or gas-phase heterogeneous catalysts, e.g., silica–alumina or zeolites.

A number of investigators, for example, Chutoransky and Dwyer (*1*), found their isomerization data were consistent with a simple consecutive, reversible 1,2-methyl shift mechanism:

$$\text{ortho} \rightleftarrows \text{meta} \rightleftarrows \text{para.}$$

Others used a triangular reaction scheme to calculate their rate constants (e.g., Ref. (*2*)):



The Wei–Prater (*3*) technique is extremely useful for calculating relative rate constants for a triangular reaction network.

In addition to isomerization, xylenes undergo disproportionation to toluene and trimethylbenzenes as well as lesser amounts of more extensive disproportionation. Disproportionation, relative to isomerization, usually increases with increasing temperature.

Lanewala and Bolton (*4*) proposed that xylene isomerization occurred by a transalkylation mechanism. Their disproportionation results, at low conversion, show that: *ortho*-xylene yielded only 1,2,4-trimethylbenzene; *meta*-xylene yielded mostly 1,2,4-trimethylbenzene but also significant 1,3,5-trimethylbenzene; and *para*-xylene yielded only 1,2,4-trimethylbenzene.

The purpose of the present study was to obtain xylene isomerization rate data with an acidic zeolite catalyst and to compare these data with those reported for an amorphous silica–alumina catalyst. The reaction

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temperature used in the present study was sufficiently high for disproportionation to be a significant reaction, allowing us to pay particular attention to the trimethylbenzene disproportionation products obtained at low conversions. The Wei–Prater (*3*) technique was used to obtain kinetic rate constants.

EXPERIMENTAL

A commercial NaY zeolite was multiply exchanged with a lanthanum nitrate solution. The exchanged zeolite was stored as a wet cake. It was activated *in situ* by heating the wet cake in the reactor for 6 h at 500°C in an air flow.

The catalyst (1 g wet cake) was held in a plug flow reactor by glass wool plugs. Glass beads were placed on top of the catalyst bed to act as a preheater section. A syringe pump was used to pass the reactant over the catalyst at atmospheric pressure. Liquid products were collected at intervals. Analysis of the aromatics was by gas chromatography using a diisononylphthalate-Bentone-34 column with temperature programming. Initially the temperature was held at 80°C for 7 min, then raised to 120°C at 10°C/min, and held at 120°C until all of the compounds had eluted.

After a run was completed, the catalyst was regenerated. First, the catalyst was flushed with nitrogen at the reaction temperature. After 1 h, the nitrogen flow was replaced by an air flow. The air flow was maintained at reaction temperature for 1 h; the temperature was then increased to 500°C and held at 500°C with air flow for at least 4 h. The catalyst was then cooled to reaction temperature in an air flow. A more detailed description of the procedure is given in Ref. (*5*).

RESULTS

The isomerization of xylene with the LaY catalyst is complicated by secondary reaction(s), for the most part disproportionation. In addition to the xylene isomers, trimethylbenzenes and toluene are major products. Smaller quantities of benzene and tetramethylbenzenes are also formed. The data in Fig. 1 clearly show that, with all three xylene reactants, toluene and trimethylbenzenes are formed in equal molar quantities for all conversions leading up to the xylene equilibrium point (for clarity, only a few of the experimental points are plotted in the figure).

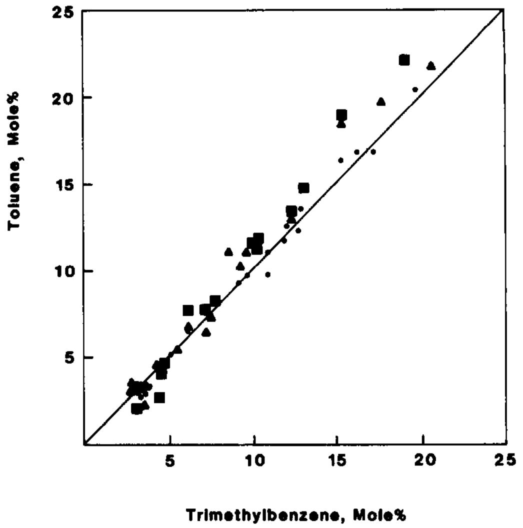


FIG. 1. Formation of disproportionation products, toluene and trimethylbenzene, at increasing conversion of each xylene isomer (straight line is theoretical one for disproportionation; reactant is: ■, *ortho;* ●, *meta;* ▲, *para*).

Plots of the conversion of one xylene isomer to the other two isomers (Fig. 2) show that *ortho*-xylene isomerizes most rapidly while *meta*- and *para*-xylene isomerize at about the same rate. Xylene also disproportionates to trimethylbenzenes (and toluene) more rapidly than do the *meta*- and *para*-xylene isomers; the latter two isomers disproportionate at about the same rate.

A plot of the conversion of each of the three xylenes to the other two xylene isomers *versus* the amount of trimethylbenzene (Fig. 3) also emphasizes the greater reactivity of *ortho*-xylene. Isomerization is about 2.9 times faster than disproportionation for *ortho*-xylene. For *meta*- and *para*-xylene, isomerization is only 1.6–1.7 times greater than disproportionation.

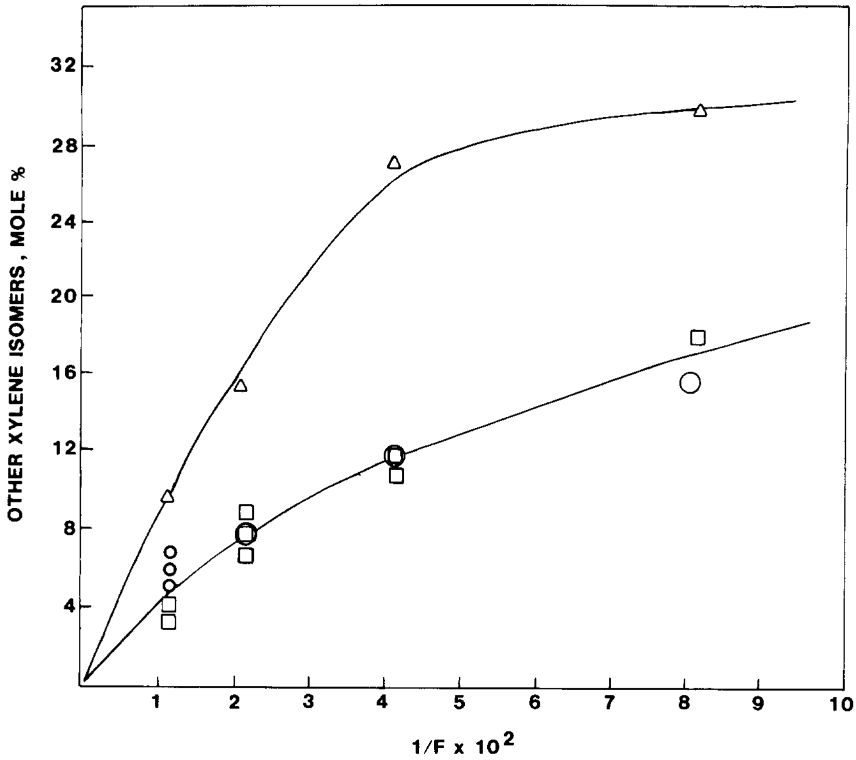


FIG. 2. Influence of space velocity (1/F sec^{-1}) on the isomerization of each of the three xylene isomers to the other two xylenes at 350°C; reactant is: △, *ortho;* ○, *meta;* □, *para.*

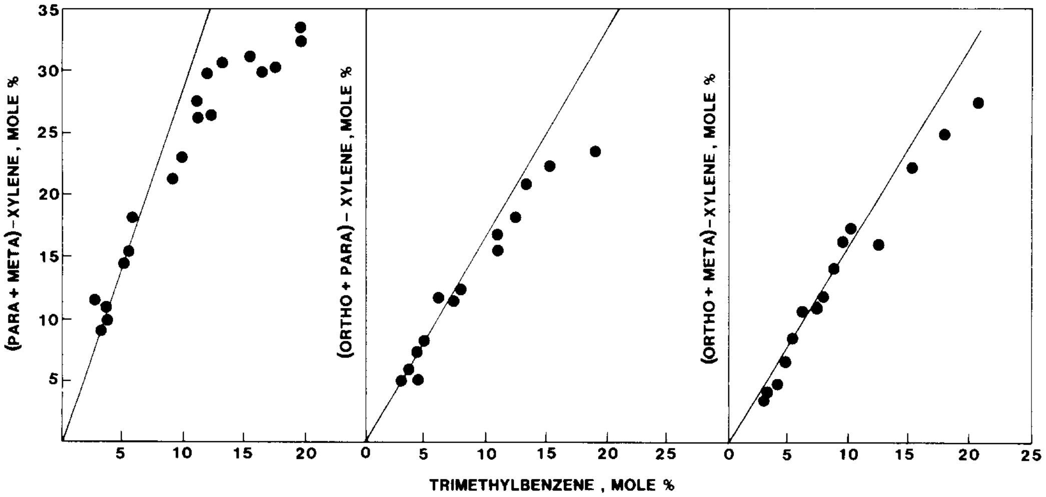


FIG. 3. Isomerization of each xylene isomer to the other two xylene isomers *versus* disproportionation to trimethylbenzenes (left, *ortho*-xylene with slope 2.9; middle, *meta*-xylene with slope 1.7; right, *para*-xylene with slope 1.6).

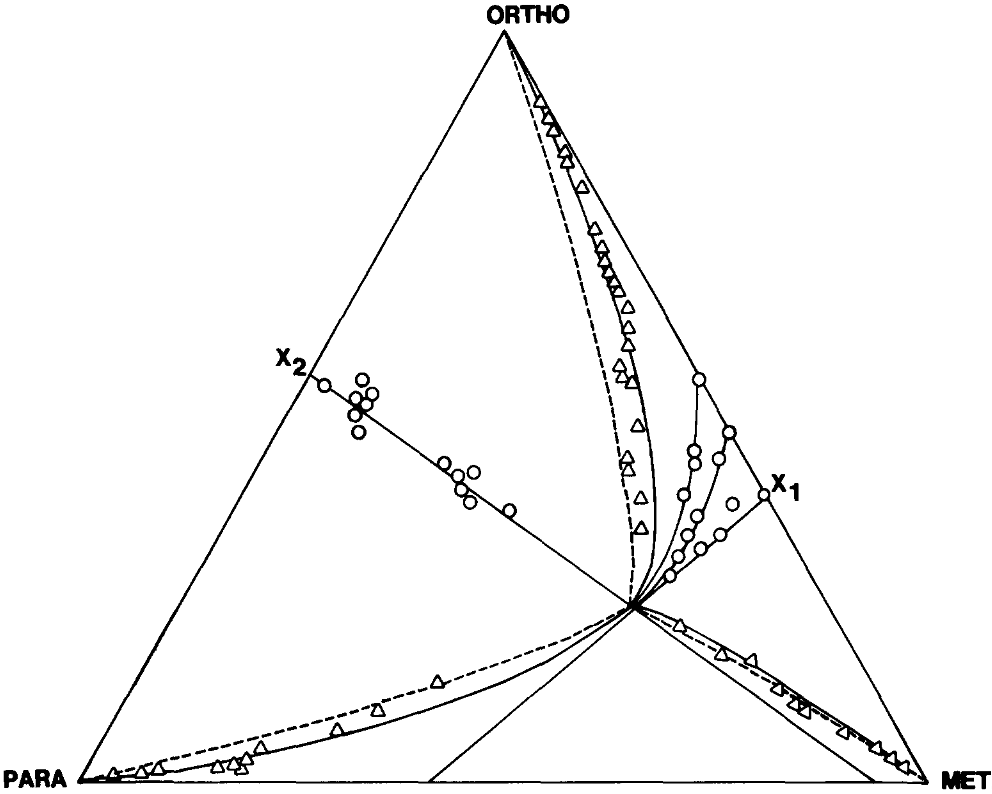


FIG. 4. Wei–Prater plot of the approach to the equilibrium composition for the isomerization of each xylene isomer and xylene isomer mixtures.

A triangular plot for xylene isomerization shows the curved reaction line for the conversion of each isomer at 350°C and atmospheric pressure (Fig. 4). In this plot all nonxylene products are disregarded in calculating the percentage composition; Silvestri and Prater (*2*) showed that this is justified. The *ortho–meta* axis straight-line reaction path was obtained experimentally by estimating the straight-line *ortho–meta*-xylene mixture from the tangent of each improved trial straight-line reaction path mixture. The fourth attempt gave the first straight-line vector:

$$X_1 = (0.39,\ 0.61,\ 0.0)\begin{pmatrix} \textit{ortho} \\ \textit{meta} \\ \textit{para} \end{pmatrix}.$$

The equilibrium vector, calculated from Ref. (*6*) was

$$X_0 = (0.233,\ 0.530,\ 0.237)\begin{pmatrix} \textit{ortho} \\ \textit{meta} \\ \textit{para} \end{pmatrix}.$$

The X_2 vector was calculated; the appropriate *ortho–para*-xylene mixture was prepared and converted to give the experimental points plotted along the previously calculated line X_2E. The experimental points fit this calculated line very well. Following the technique of Wei and Prater (*3*), these reaction vectors were used to calculate the relative rate constants defined in the scheme:

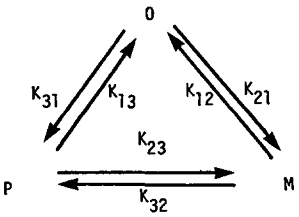


TABLE 1

Relative Rate Constants

Rate constant	Silica–alumina[a]	AP catalyst[b]	LaY[c]	
			<35%	>35%
k_{21}	27.2	19.3	10.9	3.88
k_{12}	13.0	7.27	4.79	1.70
k_{23}	37.1	16.3	8.08	3.36
k_{32}	17.3	7.11	3.61	1.50
k_{13}	1.0	1.0	1.00	1.00
k_{31}	1.03	1.16	1.02	1.02

[a] Data from Ref. (*2*).
[b] Data from Ref. (*1*).
[c] This work: <35% data calculated from data with less than 35% *meta*-xylene in products; >35% was from those data with more than 35% *meta*-xylene.

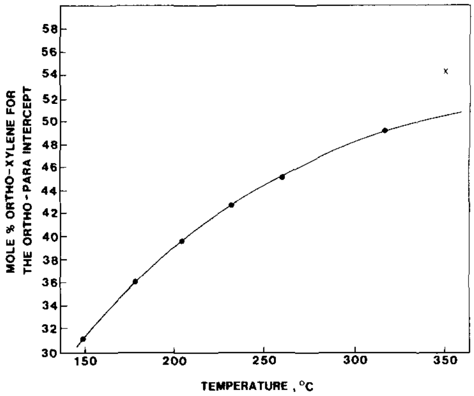


FIG. 5. Influence of temperature on the intercept of the straight-line reaction path on the *ortho–para*-xylene axis (●, data from Ref. (*1*); ×, present study).

Table 1 contains these constants as well as those reported by other authors with other catalysts (*1, 2*).

Data obtained for the isomerization products from each of the pure xylene isomers are presented in Tables 2, 3, and 4. Representative data from these tables are plotted in Fig. 4. Two sets of calculated reaction lines are also presented in this figure. These two lines were calculated using the isomerization data obtained starting with the pure *ortho*-xylene reactant and the value for *X*, and *E* given above. For the broken lines, the xylene isomer compositions containing 35% or more of the *meta* isomer, starting with the *ortho* reactant, were used in the Wei–Prater calculation. The solid lines were calculated using only those compositions containing less than 35% of the *meta*-xylene product. It is clear that neither set of curves will fit the full range of data; however, the calculated solid curves do fit the data for all three starting isomers at the lower conversions. Furthermore, the higher conversion data from the conversion of both the *ortho* and *para* isomers change to fit the broken curve.

Chutoransky and Dwyer (*1*) calculated the *ortho*-xylene: *para*-xylene intercept for a number of temperatures for an AP catalyst (a zeolite in an alumina matrix); the calculated intercepts were in excellent agreement with their experimentally measured intercepts. The *ortho* fraction for the *ortho–para* axis intercept from Ref. (*1*) is plotted *versus* temperature in Fig. 5. It is noted that the value we obtained experimentally at 350°C is only slightly higher than the value obtained by extrapolation of the data from Chutoransky and Dwyer.

The approach of the xylene isomerization to equilibrium is presented as a function of total conversion of the pure xylene reactant in Fig. 6. From this plot, it is clear that the *meta* isomer is converted to the *ortho* and *para* isomers at nearly equal rates; furthermore, the *ortho–para* selectivity does not change up to 40% conversion. The conversions of *para*-xylene and *ortho*-xylene are similar since both form *meta*-xylene faster than the other xylene isomer. The rate of approach to equilibrium of the *ortho*-xylene (from *para*-xylene) and *para*-xylene (from *ortho*-xylene) is initially low. Each of these rates increase with increasing total conversion to approach the rate obtained for the formation of the respective isomer from the *meta*-xylene reactant. The rate of the *meta* isomer approach to equilibrium with total conversion is the same for the *ortho*-xylene and the *para*-xylene reactants.

Disproportionation is a major reaction

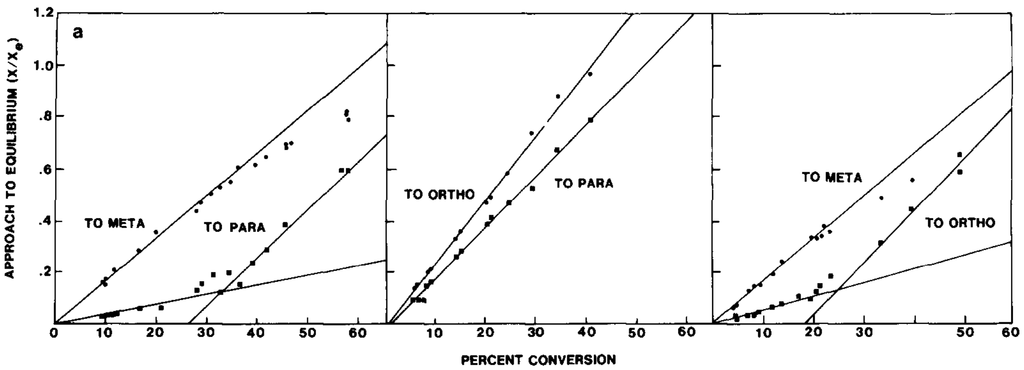


FIG. 6. Approach to equilibrium composition for the two xylene products for increasing total conversion of each xylene reactant for (a) this study (left, *ortho* reactant; middle, *meta* reactant; right, *para* reactant; X_0 is equilibrium percentage of xylene isomers; X is percentage of xylene at each conversion) and (b) data from Ref. (*4*) (figure notation is the same as that for (a)).

TABLE 2

Conversion Products for the Conversion of *ortho*-Xylene over LaY at 350°C[a]

Benzene	Toluene	Xylene			Trimethylbenzene		
		para-	*meta*-	*ortho*-	1,3,5-	1,2,4-	1,2,3-
1.82	22.3	7.96	24.6	23.6	4.65	13.1	2.00
1.01	16.3	6.04	25.2	36.2	3.28	10.1	1.88
0.81	13.7	5.03	25.4	42.2	2.62	8.83	1.40
0.8	11.6	4.45	25.3	45.8	2.35	8.18	1.44
0.61	9.55	3.57	21.3	54.0	2.04	6.86	2.03
1.65	20.5	8.36	24.8	25.3	4.77	12.3	2.67
1.04	16.7	6.01	24.3	34.7	3.84	11.0	2.51
0.40	2.98	0.89	10.0	82.4	0.11	2.62	0.58
0.37	2.73	0.82	8.83	83.9	0.11	2.46	0.76
0.34	2.69	0.81	8.51	89.9	0.09	2.36	0.76
1.52	16.8	6.03	24.0	35.6	3.51	10.8	1.77
0.69	10.9	3.61	22.4	49.0	2.50	7.99	1.47
0.82	12.2	2.81	24.4	47.6	2.19	8.61	1.33
0.49	5.09	1.34	13.8	74.1	0.37	4.01	0.77
0.64	6.40	1.34	16.8	68.8	0.51	4.77	0.73
0.52	5.06	1.29	13.4	74.7	0.33	3.95	0.73
0.41	3.28	0.95	9.84	78.1	0.15	2.83	0.73
0.38	3.22	0.95	9.46	77.9	0.13	2.72	0.69
0.36	2.93	0.97	8.77	83.5	0.13	2.61	0.75
0.30	2.82	0.95	8.31	83.9	0.09	2.71	0.96
0.50	12.3	3.18	21.2	50.2	2.39	8.45	1.51
0.71	10.8	2.98	19.8	55.5	1.72	7.37	1.22
0.63	9.20	2.55	18.6	60.0	1.36	6.58	1.08
3.36	25.7	9.66	25.3	13.9	6.51	13.6	1.98
1.57	20.1	7.41	26.4	21.7	7.49	13.4	2.00
1.30	18.8	6.63	27.2	27.6	4.43	12.3	1.77
0.99	16.3	5.64	27.2	31.8	4.95	11.3	1.82
1.36	18.1	6.65	27.2	30.2	3.96	11.0	1.59
0.84	12.1	4.24	25.7	43.6	4.18	7.92	1.38
0.66	10.7	3.94	26.6	47.6	1.58	6.53	1.02

[a] Mole%.

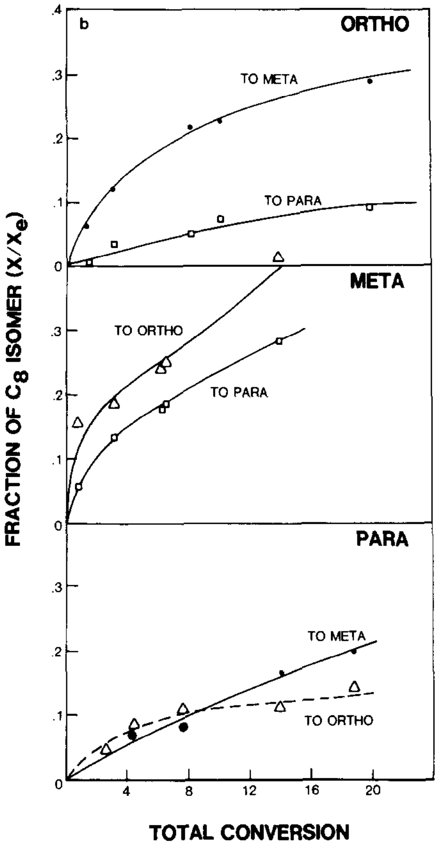


FIG. 6—*Continued.*

pathway for xylene conversion with LaY at 350°C. With the *para* isomer (Fig. 7) both 1,3,5- and 1,2,3-trimethylbenzene concentrations extrapolate to zero at low conversions; thus, the only initial product is the 1,2,4-isomer. However, when 15–20 mole% trimethylbenzenes have been formed, an equilibrium trimethylbenzene mixture is obtained. Thus, the trimethylbenzenes formed from *para*-xylene reach equilibrium at a lower total conversion than that required for the xylene to reach equilibrium; *ortho*-xylene produces a different initial trimethylbenzene composition at low conversion than *para*-xylene. With the *ortho*-xylene reactant, the 1,3,5-trimethylbenzene concentration approaches zero at low conversion while both 1,2,3- and 1,2,4-trimethylbenzenes are initial products. Again, the trimethylbenzene equilibrium composition is attained after about 15% disproportionation has occurred. The trimethylbenzenes obtained from *meta*-xylene at low conversion differ from that obtained with either of the other xylene isomers. With the *meta*-xylene reactant, it appears that an equilibrium trimethylben-

TABLE 3

Products from the Conversion of *meta*-Xylene over LaY at 350°C[a]

Benzene	Toluene	Xylene			Trimethylbenzene		
		para-	*meta*-	*ortho*-	1,3,5-	1,2,4-	1,2,3-
1.35	22.0	11.0	34.4	12.4	4.29	12.3	2.11
0.61	17.7	10.8	44.2	11.5	3.83	9.79	1.60
0.42	14.7	9.10	51.0	11.7	3.30	8.37	1.35
0.36	13.6	8.48	55.7	9.51	3.11	8.06	1.20
0.03	2.96	2.08	88.9	2.99	0.77	2.00	0.27
0.03	3.34	2.12	88.3	3.30	0.85	2.05	0.22
0.03	2.80	2.07	88.0	3.02	1.07	2.27	0.81
0.03	3.53	2.09	87.5	3.57	0.94	2.16	0.23
0.05	4.80	3.41	83.5	4.05	1.23	2.83	0.37
0.05	4.89	3.60	82.5	4.31	1.25	3.03	0.38
0.14	8.24	5.68	71.7	6.67	1.91	4.99	0.66
0.12	7.75	5.47	73.2	6.26	1.89	4.69	0.61
0.11	7.72	5.37	74.4	6.27	0.89	4.71	0.58
0.27	11.6	7.86	62.1	8.52	2.43	6.73	0.92
0.27	11.5	7.36	62.3	8.21	2.22	6.83	0.95

[a] Mole%.

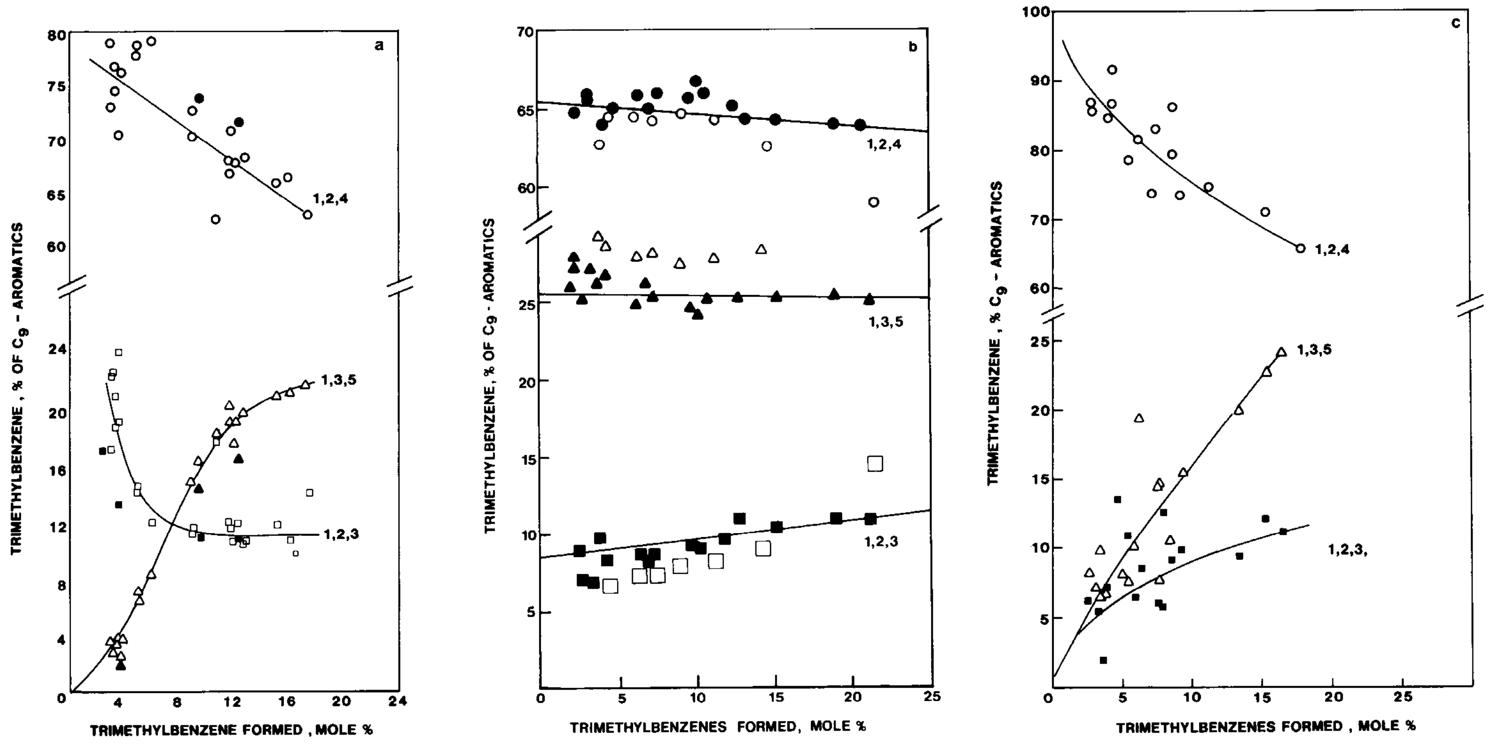


FIG. 7. Trimethylbenzene formed for increasing extent of disproportionation at 350°C from the conversion of each xylene isomer ((a) *ortho*-xylene reactant; (b) *meta*-xylene reactant; (c) *para*-xylene reactant; □■, 1,2,3-; ○●, 1,2,4-; △▲, 1,3,5-; open and solid symbols are for data from runs with different catalyst batch).

TABLE 4

Products from the Conversion of *para*-Xylene with LaY at 350°C[a]

Benzene	Toluene	Xylene			Trimethylbenzene		
		para-	*meta*-	*ortho*-	1,3,5-	1,2,4-	1,2,3-
1.08	21.6	29.1	20.0	7.47	4.51	13.8	2.37
0.64	19.6	37.2	18.7	6.19	4.01	11.6	2.13
0.42	18.5	43.6	17.5	4.61	3.07	10.9	1.42
0.03	3.29	89.5	3.83	0.47	0.23	2.48	0.15
0.03	3.58	88.6	3.99	0.55	0.33	3.32	0.21
0.03	3.32	89.5	3.77	0.50	0.24	2.52	0.18
0.15	12.8	60.5	13.9	2.17	1.72	9.47	1.25
0.12	11.0	66.4	12.2	1.69	1.28	6.91	0.53
0.10	10.0	64.6	14.2	1.75	1.32	6.77	1.18
0.04	5.53	80.6	7.31	1.03	0.44	4.34	0.75
0.03	4.41	85.1	6.05	0.72	0.24	3.45	0.62
0.04	4.31	83.8	6.89	0.77	0.29	3.80	0.29
0.01	2.23	90.2	3.47	0.78	0.23	2.17	0.93
0.07	6.73	76.4	9.30	1.21	0.47	5.11	0.67
0.08	7.45	73.9	10.3	1.43	0.69	5.72	0.45
0.07	6.55	75.0	9.89	1.28	1.32	5.32	0.60
0.20	10.9	61.3	15.6	3.26	0.64	7.60	0.52

[a] Mole%.

zene mixture is obtained even at very low (1–3%) conversions.

DISCUSSION

The set of relative rate constants for the interconversion of the xylene isomers with the LaY zeolite catalyst is different from that calculated by Silvestri and Prater (*2*) for an amorphous silica–alumina catalyst. Chutoransky and Dwyer (*1*) calculated a set of relative rate constants for their zeolite catalyst that was in reasonably good agreement with that obtained by Silvestri and Prater (*2*) for an amorphous silica–alu-

TABLE 5

Xylene Isomerization Products for the LaY Catalyst Used in This Study and Previously Reported Results

Reactant	Selectivity	LaY				AP catalyst[d]	Silica–alumina[e]
		High[a]	Low[a]	Wei–Prater			
				<35%[b]	>35%[c]		
para-Xylene	*meta/ortho*	7.0	2.0	8.1	3.4	16.3	37.1
meta-Xylene	*ortho/para*	1.3	1.3	1.3	1.1	1.02	0.75
ortho-Xylene	*meta/para*	9.7	2.0	11	3.8	16.6	26.2

[a] See text for definition of high and low.

[b] Calculated from data starting with *ortho*-xylene reactant and only those data sets with less than 35 mole% *meta*-xylene.

[c] Same as footnote *b* except only use those data sets with more than 35 mole% *meta*-xylene.

[d] Calculated from data in Ref. (*1*).

[e] Calculated from data in Ref. (*2*).

mina catalyst even though the ratios in Table 5 are lower for the Ref. (*1*) data. However, different temperatures were used for the three studies described above: the results of the present study were obtained at 350°C, those of Chutoransky and Dwyer were at 205°C, and those of Silvestri and Prater were at 510°C. The amorphous silica–alumina has a lower activity than the zeolite catalysts; hence, the higher reaction temperature is required to obtain a reasonable conversion. Because of the limitation of attainable space velocity and the xylene analysis, temperature is a process variable readily changed to study catalysts with widely varying activity. It appears that a similar set of relative rates is obtained for xylene isomerization using amorphous and zeolite silica–alumina if one operates in the lower temperature region where a similar space velocity gives a measurable conversion.

Since the straight-line reaction path intercept we obtained is in excellent agreement with the ones predicted by extrapolating the data of Chutoransky and Dwyer, it seems likely that our kinetic data for xylene isomerization are in good agreement with those of Chutoranksy and Dwyer. However, our data in Table 5 show a lower selectivity than do the data of Chutoransky and Dwyer. This indicates that as temperature is increased within the temperature window that space velocity and analyses permit one to operate in, the rates of the slower reactions approach those of the faster reactions. This could arise because of diffusional limitations or because adsorption-disguised kinetics are altering the true rate constants (*7*). To distinguish the importance of each of these effects is a complex problem that has not been resolved.

The selectivity (ratio of the relative rates of formation of the two xylene isomeric products from the reactant xylene isomer) can be calculated from the slopes in Fig. 6 and from the relative rate constants obtained by the Wei–Prater method. The data in Table 5 show that for *meta*-xylene conversion the two calculation methods give the same selectivity. Two selectivities, one for low and one for high conversion, are obtained with the data in Fig. 6 for the conversion of the *ortho*- and *para*-xylenes.

The lower conversion data provide selectivity ratios that show a higher rate of formation of the *meta*-xylene isomer starting with either *ortho*-xylene (*meta*/*para* ratio) or *para*-xylene (*meta*/*ortho* ratio) reactant. The ratio of slopes for the >35% conversions is lower than that for the <35% conversions and both ratios for the >35% conversions approach one. A selective disproportionation of one (or two) of the xylene isomers does not appear to be responsible for the change of the (*meta*/*para*) and (*meta*/*ortho*) ratios to approach one since (a) trimethylbenzene equilibrium is attained at a lower total conversion than is the xylene equilibrium and (b) the experimental equilibrium point is in excellent agreement with the one calculated from Ref. (*6*) data.

The experimental data used for Wei–Prater calculations were divided into two sets since we did not obtain a good fit of the data to curves calculated with one set of rate constants. The rate constants calculated using the Wei–Prater method with the >35% conversion data show higher *meta*/*ortho* and *meta*/*para* ratios than those calculated from the ratio obtained from the lower conversion slopes in Fig. 6. The selectivities calculated from the Wei–Prater rate constants obtained using the higher conversion data are in good agreement with the values calculated from the ratio of slopes of Fig. 6 (low LaY values of Table 5). Thus, the low and high selectivities obtained from plots of the approach to equilibrium are in good agreement with the corresponding selectivity calculated from Wei–Prater rate constants obtained using the low and high conversion data. However, additional data are not needed to calculate the six relative rate constants using the Wei–Prater method but would be required in order to use the approach to equilibrium plots for this purpose. Thus, the

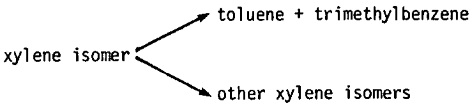
Wei–Prater technique is the preferred method.

For electrophilic substitution, the ring positions *ortho* and *para* to a methyl group are activated. The initial products from *ortho*-xylene (1,2,3- and 1,2,4-trimethylbenzene) and *para*-xylene (1,2,4,-trimethylbenzene) are the ones predicted from the directing effect of methyl groups. In contrast, an equilibrium trimethylbenzene composition is obtained even at very low conversions when *meta*-xylene is the reactant even though 1,2,3- and 1,2,4-trimethylbenzene are the only products predicted by directing effects. Secondary isomerization of the initial products from *meta*-xylene cannot account for the equilibrium distribution since the trimethylbenzene products, once formed, should isomerize at a similar rate whichever of the three xylenes are used as reactant. Since *ortho*-xylene and *para*-xylene products do not extrapolate to an equilibrium trimethylbenzene composition, we eliminate secondary reactions as being responsible for the initial equilibrium distribution obtained from *meta*-xylene. It does not seem likely that shape selectivity should determine the transalklyation product distribution for *meta*-xylene but not for either *ortho*- or *para*-xylene. Thus, it appears that some special effect(s), in addition to directing effects, is also present for the *meta*-xylene transalkylation.

The different trimethylbenzene compositions formed from each of the xylene isomers clearly eliminates a common transition state or a rapid surface equilibrium of the trimethylbenzenes: it also requires that xylene isomerization not occur prior to the transalkylation. Thus, the present results are consistent with, but do not require, the isomerization reaction being a series reaction

$$\underline{\text{ortho}}\text{-xylene} \rightleftarrows \underline{\text{meta}}\text{-xylene} \rightleftarrows \underline{\text{para}}\text{-xylene}$$

and the transalkylation and xylene isomerization being parallel reactions



REFERENCES

1. Chutoransky, P., and Dwyer, F. G., *Advan. Chem. Ser.* **121,** 540 (1973).

2. Silvestri, A. J., and Prater, C. D., *J. Phys. Chem.* **68,** 3268 (1964).

3. Wei, J., and Prater, C. D., *in* "Advances in Catalysis and Related Subjects," Vol. 13, p. 203. Academic Press, New York/London, 1962.

4. Lanewala, M. A., and Bolton, A. P., *J. Org. Chem.* **34,** 3107 (1969).

5. Mulrooney K. J., M. Eng. thesis, University of Louisville, 1980.

6. Taylor, W. J., Wagman, D. D., Williams, M. G., Pitzer, K. S., and Rossini, F. D., *J. Res. Natl. Bur. Stand.* **37,** 115 (1946).

7. Wei, J., *Ind. Eng. Chem.* **58,** 38 (1966).

8. Allen, R. H., and Yats, L. D., *J. Amer. Chem. Soc.* **81,** 5289 (1959).

9. Lien, A. P., and McCaulay, D. A., *J. Amer. Chem. Soc.* **75,** 2407 (1953).

10. McCaulay, D. A., and Lien, A. P., *J. Amer. Chem. Soc.* **74,** 6246 (1952).

11. Watanabe, Y., and Habgood, H. W., *J. Phys. Chem.* **72,** 3066 (1968).