THF. After stirring for 3.5 hr, this solution was added slowly to 2.19 ml (0.04 mol) of bromine dissolved in 100 ml of dry THF at −40°. Stirring at this temperature was continued for 4 hr and then the solution was allowed to warm to 25°. The solvent was removed *in vacuo;* the residue was taken up in 200 ml of chloroform and extracted with water. After the extract was dried ($MgSO_4$) and decolorized with charcoal, the solvent was removed. The remaining oil crystallized on standing at 0° and was recrystallized from ethanol to yield 6.01 g (81.3%) of α-bromo-α-nitrobenzyl benzyl sulfone, mp 108–109°.

**B.**—In 500 ml of Spectrograde carbon tetrachloride was suspended 10 g (0.0342 mol) of **3** and 13 g (0.07 mol) of N-bromosuccinimide. The suspension was refluxed under nitrogen and irradiated with a sun lamp for 14 hr. After chilling, the solution was filtered, the solvent was removed *in vacuo,* and the residue was recrystallized from ethanol to give 9.6 g (80%) of α-bromo-α-nitrobenzyl benzyl sulfone.

*Anal.* Calcd for $C_{14}H_{12}BrNO_4S$: C, 45.42; H, 3.27; N, 3.78; Br, 21.58; S, 8.66; mol wt, 370.2. Found: C, 45.52; H, 3.50; N, 3.68; Br, 21.70; S, 8.65; mol wt, 372.

**α-Chloro-α-nitrobenzyl Benzyl Sulfone.**—Compound **3** (5 g, 0.0171 mol) and N-chlorosuccinimide (4.55 g, 0.0342 mol) dissolved in 250 ml of carbon tetrachloride were refluxed and irradiated under nitrogen for 19 hr. Cooling, filtration, and removal of solvent yielded an oil. Eluting through a silica gel column with chloroform and recrystallizing from ethanol gave 4.1 g (73%) of α-chloro-α-nitrobenzyl benzyl sulfone, mp 81–82°.

*Anal.* Calcd for $C_{14}H_{12}ClNO_4S$: C, 51.6; H, 3.72; N, 4.30; Cl, 10.9; S, 9.85. Found: C, 51.8; H, 3.81; N, 4.38; Cl, 10.95; S, 10.09.

**4-Octene-4-sulfonamide.**—Stirring 9.0 g (0.03 mol) of 1-bromo-1-nitrobutyl butyl sulfone with potassium amide (0.09 mol) in 150 ml of liquid ammonia for 1 hr at −33° gave a brown solution. Solid ammonium chloride (0.1 mol) was slowly added at −50°, the ammonia was replaced by ether, and glacial acetic acid was added until the ether solution was neutral. After filtration, the ether layer was concentrated to 40 ml and extracted with two 30-ml portions of 10% aqueous potassium hydroxide. The aqueous layer was acidified with acetic acid and extracted with ether. The extract was concentrated to 30 ml and 30 ml of petroleum ether (bp 60–70°) was added. Further concentration to 40 ml and cooling gave 2.2 g (40%) of colorless crystals, mp 94.5–97°. Recrystallization from a 1:1 benzene–petroleum ether (60–70°) mixture and subsequent sublimation at 80° (0.2 mm) gave pure product: mp 97–98°; ir (KBr) 3330 and 3213 ($NH_2$), 2940 (CH), and 1317 and 1167 $cm^{-1}$ ($SO_2$); nmr ($CDCl_3$) δ 6.64 (t, 1, HC=C), 5.07 (s, 2, $NH_2$), 1.90–2.60 (m, 4, $CH_2C$=C), 1.17–1.90 (m, 4, $CH_2$), and 0.76–1.17 (t, 6, $CH_3$).

*Anal.* Calcd for $C_8H_{17}NO_2S$: C, 50.19; H, 8.96; N, 7.36; S, 16.86. Found: C, 49.98; H, 9.06; N, 7.11; S, 16.91.

**Registry No.**—**1**, 21272-78-6; **2**, 21272-79-7; **3**, 21272-80-0; **4**, 21272-81-1; **6**, 21272-82-2; **7**, 21272-83-3; **8**, 21272-84-4; **9**, 21272-85-5; **10**, 21272-86-6; **11**, 21272-87-7; α-bromo-α-nitrobenzyl phenyl sulfone, 21272-88-8; 1-bromo-1-nitrobutyl butyl sulfone, 21272-89-9; dibromonitromethyl methyl sulfone, 21272-90-2; α-bromo-α-nitrobenzyl benzyl sulfone, 21272-91-3; α-chloro-α-nitrobenzyl benzyl sulfone, 21272-92-4; 4-octene-4-sulfonamide, 21272-93-5.

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# The Isomerization of the Xylenes Using Zeolite Catalysts

M. A. LANEWALA AND A. P. BOLTON

*Union Carbide Corporation, Linde Division, Molecular Sieve Department, Tonawanda, New York 14150*

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The isomerization of the xylenes, catalyzed by partially multivalent metal cation exchanged, partially decationized Type Y zeolites, is invariably accompanied by transalkylation, and the degree of isomerization is proportional to the extent of transalkylation. An equilibrium distribution of the xylenes is obtained when over 50% transalkylation has occurred in agreement with calculated values. Data from the transalkylation of the trimethylbenzenes with benzene indicated that this reaction proceeds *via* a bimolecular mechanism. Such a mechanism, involving a diphenylalkane-type transition state, is proposed for xylene isomerization and satisfactorily accounts for the observed results.

The isomerization of the xylenes has received considerable attention in the literature, and the xylenes are used as model compounds in the elucidation of reaction mechanisms for the positional isomerization of alkylaromatics. The usually accepted mechanism[1] involves the addition of a proton, furnished by an acid catalyst, to the alkylbenzene at the ring carbon holding the alkyl group, followed by a 1,2 shift of the methyl group. However, such a mechanism neglects to account for the presence of transalkylation products which are considered to be derived from side reactions. Unseren and Wolf[2] have shown that 1,2 shifts can only compete with the transalkylation reactions, and Allen, Yats, and coworkers[3,4] have shown that the product isomers derived from the isomerization of alkylaromatics can be due to both intra- and intermolecular reactions, the individual contributions being a function of the structure of the alkylaromatic. Recent work on the isomerization of the diethylbenzenes[5] and *t*-butylphenols[6] has shown that a mechanism for positional isomerization *via* transalkylation satisfactorily accounts for the occurrence of transalkylated products. The objective of this study was to follow closely the composition of the transalkylation products formed during the isomerization of xylenes with a crystalline catalyst derived from a Type Y zeolite and determine the role of transalkylation in this reaction.

## Results

Initial experiments showed that the isomerization of the xylenes over a zeolite catalyst is accompanied by a transalkylation reaction. To determine the extent of

(1) A. P. Lien and D. A. McCauley, *J. Amer. Chem. Soc.*, **74**, 6246 (1952).
(2) E. Unseren and A. P. Wolf, *J. Org. Chem.*, **27**, 1509 (1962).
(3) R. H. Allen, L. D. Yats, and D. S. Erley, *J. Amer. Chem. Soc.*, **82**, 4853 (1960).
(4) R. H. Allen, *ibid.*, **82**, 4856 (1960).
(5) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *J. Org. Chem.*, **33**, 1513 (1968).
(6) A. P. Bolton, M. A. Lanewala, and P. E. Pickert, *ibid.*, **33**, 3415 (1968).

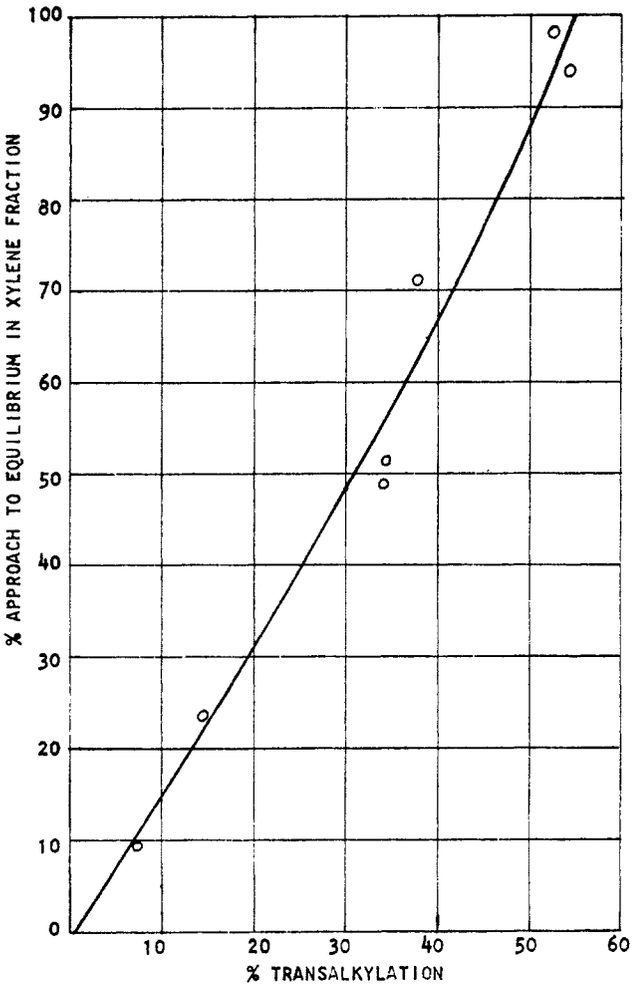



Figure 1.—Dependence of *o*- and m-xylene isomerization on extent of transalkylation (batch reactor).

transalkylation at equilibrium distribution of the xylene isomers, the batchwise isomerization of *o*-xylene was carried out at 250° for varying periods of time. The results, plotted in Figure 1, show that a good correlation is obtained between the per cent approach of *o*-xylene to its equilibrium value and the extent of transalkylation. Figure 1 also shows that over 50% transalkylation is required before *o*-xylene reaches its equilibrium value. Table I shows that the principal transalkylation products obtained from the isomerization of *o*- and *m*-xylenes at 300° are toluene and the trimethylbenzenes.

TABLE I

THE ISOMERIZATION OF *o*- AND *m*-XYLENE

| Feed | Product composition, mol %, after 20 hr at 300° and 190 psig: *o*-Xylene | *m*-Xylene |
|---|---|---|
| Benzene | 1.7 | 2.6 |
| Toluene | 16.3 | 18.9 |
| *o* | 9.6 | 9.8 |
| *m* Xylenes | 27.8 | 25.6 |
| *p* | 9.3 | 9.8 |
| 123 | 2.7 | 2.7 |
| 124 Trimethylbenzenes | 22.6 | 20.4 |
| 135 | 9.9 | 9.8 |
| | —Translkylation, %— | |
| | 53.2 | 54.8 |
| | —Normalized distribution, %— | |
| *o* | 23.5 | 21.6 |
| *m* Xylenes | 53.8 | 56.8 |
| *p* | 22.7 | 21.6 |
| 123 | 7.5 | 8.1 |
| 124 Trimethylbenzenes | 64.3 | 61.3 |
| 135 | 28.2 | 30.6 |

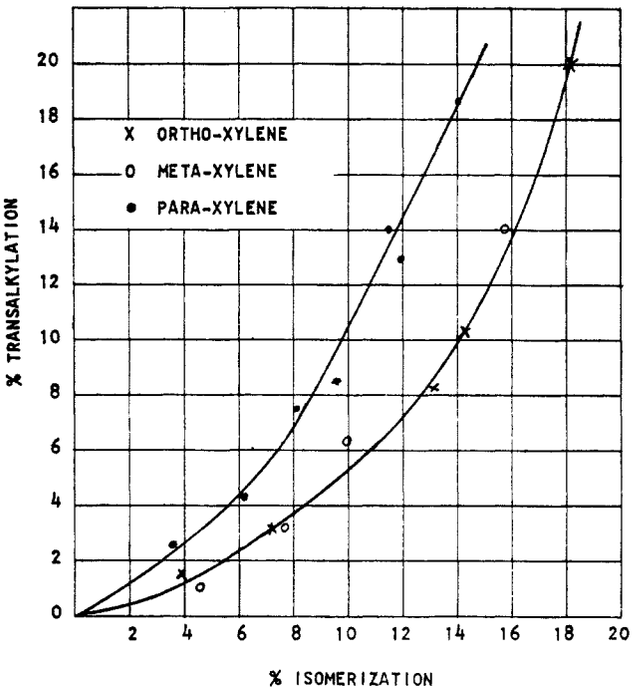



Figure 2.—Dependence of extent of isomerization upon transalkylation for the xylene isomers.

The isomerization of the three xylene isomers was also studied in a continuous flow reactor, principally to follow the composition of the xylene and the trimethylbenzene fractions at low conversions. The space velocity of the feed was varied to obtain different conversion levels. The results obtained using *o*-xylene (Table II) show that both the extent of transalkylation and the per cent approach to equilibrium in the xylene fraction increase with conversion. At low conversion, the concentration of the *p*-xylene in the xylene fraction approaches zero while the concentration of the 1,2,4 isomer in the trimethylbenzene fraction approaches 100%; the 1,3,5 isomer concentration decreases with decreasing conversion while that of the 1,2,3 isomer remains constant. The *meta* isomer (Table III) yields both *o*- and *p*-xylene at low conversions; the trisubstituted fraction is predominantly the 1,2,4 isomer, but contains a significant amount of the 1,3,5 isomer. At low conversions, the *para* isomer (Table IV) yields both the *o*- and the *m*-xylene, unlike the products from $AlCl_3$ and related catalyst systems. Both the 1,3,5 and the 1,2,3 isomers in the trisubstituted fraction approach zero concentration at low conversions, leaving the 1,2,4 isomer as the principal product.

The data from the isomerization of the xylenes under nonequilibrium conditions show a higher amount of transalkylate accompanying *p*-xylene isomerization than is found with the *ortho* and the *meta* isomers. These data are shown in Figure 2, and similar results have previously been observed with different catalyst systems.[7]

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

TABLE II

THE ISOMERIZATION OF *o*-XYLENE AT 300°

| % conversion | Product distribution, mol % | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Xylenes | | | Trimethylbenzenes | | |
| | Benzene | Toluene | Xylenes | Trimethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 20.0 | 0.8 | 8.8 | 80.0 | 11.2 | 81.8 | 15.8 | 2.3 | 16.3 | 79.7 | 4.0 |
| 10.2 | 0.4 | 4.6 | 89.8 | 5.4 | 85.6 | 12.5 | 1.9 | 14.6 | 81.7 | 3.7 |
| 8.2 | 0.3 | 3.7 | 91.8 | 4.3 | 86.8 | 11.9 | 1.3 | 12.0 | 84.0 | 4.0 |
| 3.2 | 0.1 | 1.5 | 96.8 | 1.6 | 92.8 | 6.7 | 0.5 | 8.0 | 87.7 | 4.3 |
| 1.5 | 0.1 | 0.5 | 98.5 | 0.8 | 96.1 | 3.7 | 0.2 | 3.5 | 91.5 | 5.0 |

TABLE III

THE ISOMERIZATION OF *m*-XYLENE AT 300°

| % conversion | Product distribution, mol % | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Xylenes | | | Trimethylbenzenes | | |
| | Benzene | Toluene | Xylenes | Trimethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 14.0 | 0.7 | 7.3 | 86.0 | 6.1 | 8.9 | 84.1 | 7.0 | 31.1 | 63.1 | 5.8 |
| 6.7 | 0.1 | 4.2 | 92.3 | 4.1 | 5.5 | 89.9 | 4.6 | 30.1 | 63.0 | 6.9 |
| 6.3 | 0.1 | 3.4 | 93.7 | 2.9 | 5.3 | 90.3 | 4.4 | 28.2 | 68.6 | 3.2 |
| 3.2 | 0.0 | 1.8 | 96.8 | 1.3 | 4.0 | 92.3 | 3.4 | 15.8 | 81.2 | 3.0 |
| 0.9 | 0.0 | 0.5 | 99.1 | 0.4 | 3.4 | 95.4 | 1.2 | 11.0 | 87.5 | 1.5 |

TABLE IV

THE ISOMERIZATION OF *p*-XYLENE AT 300°

| % conversion | Product distribution, mol % | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Xylenes | | | Trimethylbenzenes | | |
| | Benzene | Toluene | Xylenes | Trimethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 18.8 | 2.7 | 7.8 | 81.2 | 8.3 | 3.1 | 11.0 | 85.9 | 15.7 | 78.2 | 6.1 |
| 14.0 | 2.6 | 5.6 | 86.0 | 5.8 | 2.5 | 9.1 | 88.4 | 14.0 | 80.1 | 5.9 |
| 7.5 | 0.4 | 3.6 | 92.5 | 3.5 | 1.8 | 6.3 | 91.9 | 13.5 | 81.6 | 4.9 |
| 4.3 | 0.5 | 1.9 | 95.7 | 2.0 | 1.5 | 4.7 | 93.8 | 10.5 | 85.5 | 4.5 |
| 2.6 | 0.5 | 0.9 | 97.4 | 1.2 | 0.9 | 2.7 | 96.4 | 5.3 | 91.2 | 3.5 |

TABLE V

THE TRANSALKYLATION OF 1,2,3-TRIMETHYLBENZENE WITH BENZENE AT 300°

| % conversion | Product distribution, mol % | | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Xylenes | | | Trimethylbenzenes | | |
| | Benzene | Toluene | Xylenes | Trimethylbenzenes | Tetramethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 7.6 | 45.7 | 4.5 | 5.7 | 42.4 | 1.8 | 33.5 | 51.0 | 15.5 | 6.8 | 39.0 | 54.2 |
| 5.6 | 46.8 | 3.1 | 4.3 | 44.4 | 1.4 | 42.3 | 45.3 | 12.4 | 4.3 | 30.9 | 64.8 |
| 3.9 | 47.7 | 2.1 | 2.9 | 46.1 | 1.1 | 46.8 | 43.1 | 10.1 | 3.1 | 25.3 | 71.6 |
| 2.9 | 48.1 | 1.5 | 2.3 | 47.1 | 1.0 | 48.7 | 40.7 | 10.6 | 2.8 | 24.3 | 72.9 |
| 2.6 | 48.3 | 1.2 | 2.1 | 47.4 | 1.0 | 49.7 | 40.3 | 10.0 | 2.5 | 22.2 | 75.3 |
| 1.8 | 48.8 | 0.8 | 1.4 | 48.2 | 0.7 | 53.1 | 38.5 | 8.4 | 1.8 | 20.0 | 78.2 |

TABLE VI

THE TRANSALKYLATION OF 1,3,5-TRIMETHYLBENZENE WITH BENZENE AT 300°

| % conversion | Product distribution, mol % | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | Xylenes | | | Trimethylbenzenes | | |
| | Benzene | Toluene | Xylenes | Trimethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 27.1 | 29.7 | 21.6 | 25.7 | 22.9 | 22.7 | 55.5 | 21.8 | 42.3 | 52.0 | 5.7 |
| 15.6 | 39.6 | 12.5 | 13.5 | 34.4 | 22.0 | 56.6 | 21.4 | 63.8 | 33.4 | 2.8 |
| 6.1 | 46.2 | 4.5 | 5.4 | 43.9 | 23.5 | 59.2 | 17.3 | 75.6 | 22.7 | 1.7 |
| 2.1 | 47.4 | 2.1 | 2.6 | 47.9 | 22.9 | 60.4 | 16.7 | 84.7 | 14.0 | 1.3 |
| 1.7 | 48.4 | 1.3 | 2.0 | 48.3 | 25.6 | 61.7 | 12.7 | 87.7 | 11.5 | 0.8 |
| 1.4 | 49.2 | 1.0 | 1.4 | 48.6 | 26.4 | 62.3 | 11.3 | 90.0 | 9.3 | 0.7 |

Since it was the objective of this study to determine the role of transalkylation in the isomerization of the xylenes, the reactions between the three trimethylbenzene isomers and benzene were studied. Benzene was chosen in preference to toluene in order to differentiate between the xylene isomer formed by the removal of a methyl group from the trimethylbenzene and that formed by the transfer of a methyl group to toluene. These experiments were also carried out in a flow reactor using equivalent amounts of benzene and the trimethylbenzene isomer. The 1,2,3-trimethylbenzene–benzene feed yielded a xylene fraction containing a higher than equilibrium amount of the *ortho* isomer, the concentration increasing to over 50% with decreasing conversion (Table V). With the 1,3,5-trimethylbenzene–benzene feed, a xylene fraction consisting of equilibrium distribution was obtained, but the relative concentrations of the *ortho* and the *meta* isomers increased as the conversion approached zero (Table VI). The 1,2,4-trimethylbenzene–benzene feed produced an equilibrium distribution of the xylene isomers, but at low conversion levels a significant increase in the relative concentration of the *o*-xylene occurred (Table VII). This experiment was repeated substituting toluene in

TABLE VII

THE TRANSALKYLATION OF 1,2,4-TRIMETHYLBENZENE WITH BENZENE AT 300°

| | Product distribution, mol % | | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Xylenes | | | Trimethylbenzenes | | |
| % conversion | Benzene | Toluene | Xylenes | Trimethylbenzenes | Tetramethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 15.4 | 35.0 | 14.8 | 14.1 | 34.6 | 1.5 | 22.6 | 56.8 | 20.6 | 30.0 | 65.1 | 1.9 |
| 7.4 | 43.3 | 5.9 | 6.6 | 42.6 | 1.5 | 29.8 | 50.5 | 19.8 | 13.1 | 84.2 | 2.7 |
| 5.9 | 45.0 | 3.8 | 5.5 | 44.1 | 1.5 | 34.0 | 48.1 | 17.9 | 6.4 | 91.1 | 2.5 |
| 5.5 | 45.3 | 3.6 | 5.2 | 44.5 | 1.4 | 32.6 | 48.9 | 18.7 | 7.1 | 87.8 | 3.1 |
| 3.5 | 46.7 | 2.5 | 3.5 | 46.5 | 0.8 | 36.1 | 47.3 | 16.6 | 4.6 | 93.0 | 2.4 |
| 2.1 | 47.5 | 1.8 | 2.2 | 47.9 | 0.6 | 37.7 | 46.4 | 15.9 | 3.4 | 94.2 | 2.4 |

TABLE VIII

THE TRANSALKYLATION OF 1,2,4-TRIMETHYLBENZENE WITH TOLUENE AT 300°

| | Product composition, mol % | | | | | Isomer distribution (normalized) | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Xylenes | | | Trimethylbenzenes | | |
| % conversion | Benzene | Toluene | Xylenes | Trimethylbenzenes | Tetramethylbenzenes | *o* | *m* | *p* | 1,3,5 | 1,2,4 | 1,2,3 |
| 19.6 | 1.39 | 33.1 | 31.6 | 30.4 | 4.4 | 25.4 | 48.4 | 26.2 | 23.2 | 69.8 | 7.0 |
| 16.9 | 1.03 | 35.6 | 27.1 | 33.1 | 3.2 | 26.5 | 46.9 | 26.6 | 20.1 | 71.8 | 8.1 |
| 13.6 | 0.76 | 37.4 | 22.2 | 36.4 | 3.2 | 27.8 | 45.6 | 26.6 | 17.1 | 75.0 | 7.9 |
| 10.9 | 0.55 | 41.5 | 12.7 | 39.1 | 3.2 | 28.0 | 45.0 | 26.5 | 13.0 | 80.0 | 7.0 |
| 8.5 | 0.46 | 43.1 | 12.0 | 41.5 | 2.8 | 31.5 | 42.1 | 26.4 | 8.8 | 84.9 | 6.3 |
| 7.3 | 0.38 | 43.2 | 10.8 | 42.7 | 2.4 | 32.3 | 42.1 | 25.6 | 8.2 | 86.3 | 6.0 |

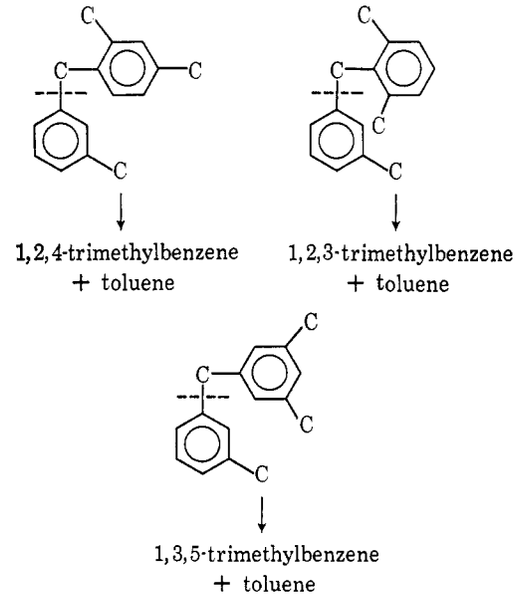
the feed for benzene (Table VIII). The results show that both the *ortho* and the *para* isomers are formed in excess of the equilibrium distribution.

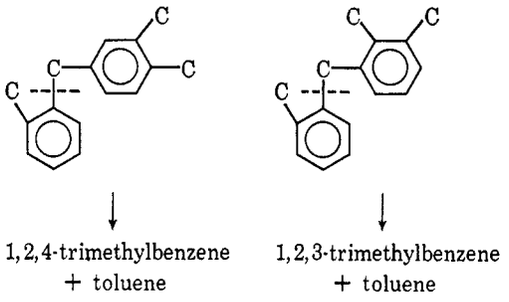
## Discussion

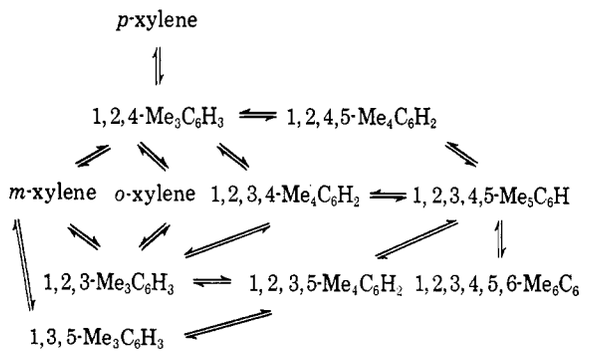
The initial results with zeolite catalysts show that xylene isomerization does not occur in the absence of transalkylation and that the more extensive the transalkylation, the greater the degree of isomerization. Since the trimethylbenzenes are present during xylene isomerization and since it has been demonstrated that under the same reaction conditions they reconvert to the xylene isomers, at least part of the isomerization must be intermolecular over a zeolite catalyst.

The isomerization of the xylenes may be explained by transalkylation mechanisms similar to those previously proposed;[5,8,9] these mechanisms, involving diphenylalkane-type intermediates, impose limitations on the possible isomers that may be derived from the transalkylation reactions and satisfactorily account for the observed results.

Starting with the *meta* isomer, all three trisubstituted isomers may be derived from this intermediate. *o*-Xylene produces an intermediate which can yield only the 1,2,3- and the 1,2,4-trimethylbenzene, while *p*-xylene, having four equivalent unsubstituted ring positions, can yield only the 1,2,4 isomer. Similarly, the possible isomers that may be derived from a bimolecular transalkylation reaction may be tabulated for all the polymethylsubstituted benzenes. Using these limitations imposed on the transalkylated products, the following reaction scheme may be derived.




Such a scheme presents a complex interaction of various species in equilibrium. An equilibrium product distribution could be calculated if the required thermodynamic data were available for all the constituents. However, because of the lack of such data for most of

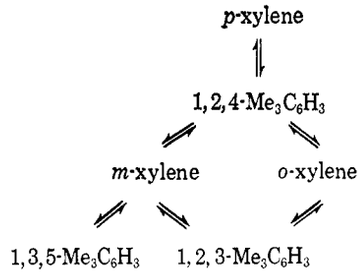
(8) H. Pines and J. T. Arrigo, *J. Amer. Chem. Soc.*, **80**, 4369 (1958).
(9) A. Streitwieser and L. Rief, *ibid.*, **86**, 1988 (1964).

TABLE IX

CALCULATED EQUILIBRIUM PRODUCT DISTRIBUTIONS FOR XYLENE–TRIMETHYLBENZENE SYSTEM

| Temp, °K | % xylene in product | % transalkylate in product | Normalized product distributions: Xylene fraction: o | m | p | Trimethylbenzene fraction: 1,2,3 | 1,2,4 | 1,3,5 |
|---|---|---|---|---|---|---|---|---|
| 300 | 45.5 | 59.4 | 16.4 | 59.8 | 23.8 | 5.4 | 57.6 | 36.9 |
| 350 | 46.1 | 53.8 | 17.6 | 58.3 | 24.1 | 7.1 | 59.4 | 33.5 |
| 400 | 46.5 | 53.4 | 18.9 | 56.8 | 24.2 | 8.8 | 60.8 | 30.5 |
| 450 | 46.5 | 53.6 | 20.1 | 55.7 | 24.2 | 10.0 | 61.6 | 28.3 |
| 500 | 46.4 | 53.6 | 21.2 | 54.8 | 24.0 | 11.2 | 62.4 | 26.4 |
| 550 | 46.5 | 53.6 | 22.0 | 54.0 | 24.0 | 12.6 | 62.1 | 25.4 |
| 600 | 46.6 | 53.4 | 22.9 | 53.2 | 23.8 | 13.9 | 61.7 | 24.4 |

the polysubstituted methylbenzenes, a modified system connecting the xylenes and trimethylbenzenes may be




used to calculate equilibrium product distributions. A computer program using a method of successive elimination was used to calculate the various equilibrium constants from available thermodynamic data[10] using standard procedures.[11] The results of these calculations at various temperatures are shown in Table IX, where the extent of transalkylation and isomerization is given together with the equilibrium product distribution in both the xylene and the trimethylbenzene fractions.

The results in Table I and Figure 1 and the calculated values in Table IX correlate well and show that in order to achieve a 95% approach to equilibrium in the xylene fraction, it is necessary to have over 50% transalkylation.

The experimental results obtained from the transalkylation of the trimethylbenzenes substantiate the proposed reaction scheme. The xylene isomers derived from the 1,2,3 isomer are predominantly *ortho* and *meta*, as required. The xylene isomer distribution from the 1,3,5 isomer is higher in *o*- and *m*-xylenes than the equilibrium values. That the xylene fraction does not tend toward 100% *m*-xylene at low conversions must indicate that the rate of the transalkylation step 1,3,5 → *meta* is significantly slower than the step *meta* → 1,2,4. The data from the 1,2,4 isomer show that the *meta* and the *ortho* isomers are formed preferentially, the concentration of the latter being far above its equilibrium value. Since it is proposed that the *para* isomer is derived from the 1,2,4-trimethylbenzene, an explanation is required of its absence in the initial products from the isomerization of *o*-xylene. The greater extent of transalkylation under nonequilibrium conditions undergone by *p*-xylene compared to the *ortho* and the *meta* isomers, as shown in Figure 2, satisfactorily accounts for this anomaly. The *para* isomer would thus require a relatively higher concentration of transalkylate than the other isomers before its formation. From a system containing 100% transalkylate, 1,2,4-trimethylbenzene, and toluene (Table VIII) the *p*-xylene is formed in high concentration at low conversion. These data also show that the transfer of a methyl group from the trimethylbenzene to the toluene occurs in a kinetic and not an equilibrium distribution. The data in Tables II, III, and IV show that the 1,2,4 isomer is the trimethylbenzene formed initially from the *o*- and *p*-xylenes and that both the 1,2,4 and the 1,3,5 isomers are initially formed from *m*-xylene. Thus, a transalkylation mechanism for the isomerization of the xylenes adequately accounts for the observed data.

It has previously been observed[5] that, unlike the $AlCl_3$ and similar catalysts systems, there are no zeolite–alkylbenzene complexes which may mask reaction mechanisms. The experimental equilibrium distribution of the trimethylbenzene fraction produced from the zeolite-catalyzed isomerization of the xylenes agrees reasonably well with the calculated values. Lien and McCauley[1] have observed that the concentration of the 1,2,4 isomer in the product from the $BF_3$–HF catalyzed isomerization of the trimethylbenzenes is dependent upon the catalyst concentration, and that the experimental value of its equilibrium distribution only matches the calculated value after extrapolating to zero catalyst concentration. It was also demonstrated that xylene isomerization catalyzed by high catalyst concentrations results in *m*-xylene contents greatly in excess of equilibrium distribution. It is possible that the intramolecular mechanism observed for xylene isomerization with acid catalysts is a result of the enhanced stability of the *m*-xylene and 1,3,5-trimethylbenzene $\sigma$ complexes[12] compared with those of the other isomers. The principal evidence for the intramolecular isomerization of the xylenes is the apparent absence of direct conversion of the *para* isomer to the *ortho* isomer or *vice versa*. However, starting with either of these isomers, the products will be the *m*-xylene $\sigma$ complex and the mesitylene $\sigma$ complex until a 1:1 mole ratio of these isomers to the acid catalyst is established.[1] After this step, equilibration between the acid phase and the hydrocarbon phase will take place and the formation of equilibrium distributions of the isomers will begin in the hydrocarbon phase. Further support for a transalkylation mechanism is the measurement of second-order kinetics in the $AlCl_3$-catalyzed isomerization of the xylenes in toluene solution.[13] Thus, the transalkyla-

(10) "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," American Petroleum Institute, Research Project 44, Carnegie Press, Carnegie Institute of Technology, Pittsburgh, Pa., 1953.

(11) O. A. Hougen, K. M. Watson, and R. A. Ragatz, "Chemical Process Principles," Part II, John Wiley & Sons, Inc., New York, N. Y., 1959, pp 1001–1002.

(12) S. V. Choi and H. C. Brown, *J. Amer. Chem. Soc.*, **88**, 903 (1966).

(13) H. C. Brown and H. Jungk, *ibid.*, **77**, 5579 (1955).

tion mechanism proposed for the isomerization of the xylenes using a zeolite catalyst may also be operative in an acid-catalyzed system but obscured by hydrocarbon–catalyst complex formation.

### Experimental Section

The di- and trimethylbenzenes were obtained from Matheson Coleman and Bell, Norwood, Ohio, and were used without further purification. The xylenes were all over 99.8% pure and the trimethylbenzenes were all over 96.7% pure. The crystalline catalyst was synthesized from Type Y zeolite with a $SiO_2/Al_2O_3$ molar ratio of 5.0 by partial rare earth cation exchange (45% rare earth) and partial decationization (50%). The balance of the cations was sodium. The preparation and pertinent properties of this material have been previously reported.[5,6]

The batch experiments were carried out in a 250-ml Hartalloy Magnadash, a magnetically stirred autoclave fitted with a dip-tube for withdrawing samples. Five grams of catalyst powder was used for 0.5 mol of xylene.

The flow experiments were carried out in a high-pressure stainless steel fixed bed reactor of conventional design. For these experiments the catalyst was used in the form of $^1/_8$ in. × $^1/_8$ in. tablets. The reaction temperature and pressure were maintained at 300° and 500 psig respectively in all experiments. The hydrogen to hydrocarbon ratio was held at 5:1 while the space velocities varied between 0.5 and 20 g of feed/g of catalyst/hr.

The analyses were made on a Perkin-Elmer 880 chromatograph equipped with 150-ft [*m*-bis(*m*-phenoxyphenoxy)benzene–Apiezon L] capillary column and a flame ionization detector.

**Registry No.**—*o*-Xylene, 95-47-6; *m*-xylene, 108-38-3; *p*-xylene, 106-42-3; 1,2,3-trimethylbenzene, 526-73-8; 1,3,5-trimethylbenzene, 108-67-8; 1,2,4-trimethylbenzene, 95-63-6.

# The Stereochemistry of Free-Radical Additions of Thiols to Substituted Cyclohexenes[1]

Norman A. LeBel, Robert F. Czaja, and Andrew DeBoer

*Department of Chemistry, Wayne State University, Detroit, Michigan 48202*

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Radical chain addition of hydrogen bromide to 2-chloro-4-*t*-butylcyclohexene (**1**) gave exclusively 2$^c$-chloro-4$^c$-*t*-butylcyclohexyl bromide (**8**), the product of *trans*-diaxial addition. AIBN- and uv-initiated free-radical additions of benzyl mercaptan (A), hydrogen sulfide (B), methanethiol (C), and thiolacetic acid (D) to 1- and 2-chloro- and 1- and 2-methyl-4-*t*-butylcyclohexene (**3**, **1**, **4**, and **5**, respectively) were investigated. The relative proportions of the diastereomeric adducts produced under varying reaction conditions were determined for the following reactions: A and **1**; B and **3** and **1**; C and **3** and **1**; D and **1** and **3**–**5**. In all cases, *trans*-diaxial addition predominated, and the relative proportions of products were shown to be dependent upon the addendum to olefin ratio. Conformational energy factors associated with the transition state appear to be responsible for preferential axial attack by a thiyl radical. The lower stereoselectivity of thiol additions, as contrasted to those of hydrogen bromide, are best explained in terms of a reversal of the thiyl-radical addition step. Differences in the extent of this reversibility appear to be dependent upon the relative stabilities of the thiyl radicals and the 2-thiyl-1-substituted cyclohexyl radicals, as well as on the rate of chain transfer. Bridged thiyl radical intermediates are not considered important in these additions. The concentration and temperature effects observed for free-radical additions of thiols to 1- and 2-chloro-4-*t*-butylcyclohexene compared with those observed for additions to 1- and 2-methyl-4-*t*-butylcyclohexene are of the same order of magnitude, but in opposite directions. The energy difference between the cyclohexyl-radical intermediates arising from "equatorial" thiyl-radical attack is probably responsible for the opposing trends. The extent of reversibility of the initial radical addition step is greatest for hydrogen sulfide and thiolacetic acid, less for methanethiol, and nonexistent for hydrogen bromide.

Free-radical additions of hydrogen bromide to various 1-substituted cyclohexenes have been reported to proceed exclusively in a *trans*, anti-Markovnikov manner.[2,3] On the other hand, the addition of thiol compounds was shown to be nonstereospecific;[4,5] a mixture of isomers was obtained in which the *trans*-addition product predominated. Several explanations have been offered to account for these results.[4-6] One of the factors taken into consideration was a chair–chair interconversion of the intermediate radical formed in the addition step. The importance of such chair–chair interconversions in the nonstereospecific additions of thiols can presumably be ascertained by causing the six-membered ring to prefer a single conformation.[7] To this end, we have chosen to study the stereochemistry of the radical-chain additions of hydrogen bromide to 2-chloro-4-*t*-butylcyclohexene (**1**), and of several thiols to **1**, 1-chloro-4-*t*-butylcyclohexene (**3**), 1-methyl-(**4**), and 2-methyl-4-*t*-butylcyclohexene (**5**). The light-catalyzed addition of hydrogen bromide to **3** has been reported to give predominantly, *but not exclusively*, 2$^c$-chloro-5$^t$-*t*-butylcyclohexyl bromide,[8] and a bromine-bridged, radical intermediate nicely accommodated the data.[9] Sulfur-bridging has been invoked to rationalize the high degree of stereoselectivity observed in the addition of methanethiol to 1-chloro-4-*t*-butylcyclohexene (**3**).[10] Only two adducts were identified as products of the reaction between thiolacetic acid and 1-methyl-4-*t*-butylcyclohexene (**4**); the major isomer was that resulting from diaxial addition, namely 2$^c$-methyl-5$^t$-butylcyclohexanethiol acetate.[11] In methanethiol

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(7) *Cf.* E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 219–227.

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