

AROMATIC SELECTIVITIES FOR LaY ZEOLITE CATALYZED DISPROPORTIONATION REACTIONS

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ABSTRACT

Similar LaY zeolite catalyzed xylene isomerization rates are obtained whether a pure xylene reactant or a mixture of a xylene isomer with either ethylbenzene or toluene is used. Trimethylbenzenes formed from xylene disproportionation are kinetically controlled products that conform to a selectivity determined by the ortho-para directing influence of alkyl substituents. Ethyl containing aromatic disproportionation products, formed in nearly equal concentrations and in parallel with trimethylbenzenes, are present in a nearly equilibrium distribution even at low conversions. In these studies, it appears that shape selectivity and diffusion play a dominant role in determining the product distribution for ethyl containing alkyl aromatics.

INTRODUCTION

Kinetics for the isomerization, and in some cases disproportionation, of xylenes have been obtained for a variety of catalysts [1-6]. In most of the studies, it was concluded that isomerization followed a series of 1,2 methyl shifts. However, other isomerization mechanisms have been reported [7]. In general, the relative rate constants departed from those expected for a series reaction and approached those expected for a coupled reaction system (in effect, both 1,2- and 1,3- methyl shifts are allowed) as catalyst pore size decreased until, with the intermediate pore size zeolite HZSM-5, pore diffusion caused all relative rate constants to approach one [5].

Methyl groups direct ortho-para for electrophilic substitution. Hence, this rule permits a prediction of the initial aromatic products that result from disproportionation. For ortho-xylene the allowed substitution products are 1,2,3-trimethylbenzene and 1,2,4-trimethylbenzene but the 1,3,5-trimethylbenzene isomer is not allowed. With aluminum chloride [1] and LaY [4] catalysts it appears that this rule is obeyed. It also appears to apply for trimethylbenzene disproportionation with a LaY catalyst [4]. Little

attention has been paid to the mechanism for disproportionation of aromatics with alkyl groups larger than methyl. This study examines disproportionations where the larger side, present in chain ethylbenzene, may undergo transalkylation reactions.

EXPERIMENTAL

Catalyst Used. A sodium Y zeolite was multiply exchanged with lanthanum nitrate solutions [4]. The exchanged material was calcined in air at 873^oK prior to use. The catalyst particles were very uniform in size and were approximately 80-120 microns in diameter.

Conversion and Analytical Procedures. Conversions were effected in a plug flow reactor containing one gram of catalyst. The catalyst was activated at 775^oK prior to use. Reactant, without diluent, was passed over the catalyst at 623^oK and 101kPa. The reaction mixture, unless otherwise noted, contained equal molar quantities of each reactant. Samples were collected at intervals and these were analyzed by g.c. using either a DB-5 or Bentone/dissodecylphthalate column to obtain conversion and product compositions [4].

RESULTS

Normalized xylene product data are plotted in figure 1 for the three xylene plus ethylbenzene reaction mixtures. Also included in figure 1 are lines representing earlier data [4] for the isomerization of the pure xylenes. Isomerization data obtained for three xylene plus toluene mixtures are similar to that shown in figure 1 except that the agreement between reference 4 data and the data from the present study is not as good. The experimentally determined straight line intercept in figure 1 corresponds to

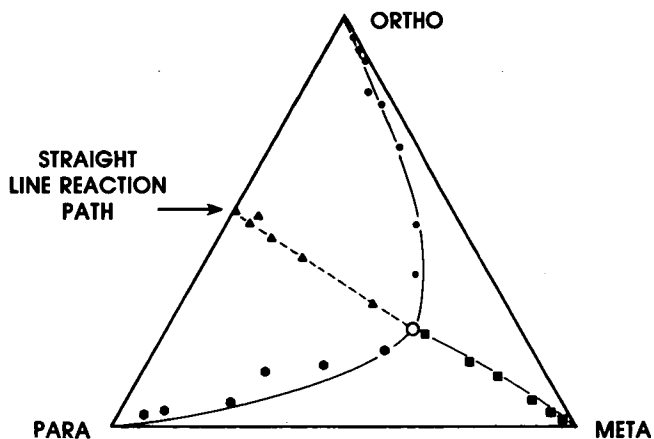


Fig. 1. Wei-Prater plot for xylene products from the conversion of ethylbenzene and xylene mixtures (solid lines from ref. 4).

0.53 fraction of ortho-xylene; this compares to 0.54 (reference 4) and 0.50 (reference 8) for isomerization of pure xylenes. The intercept was the same whether toluene or ethylbenzene was mixed with xylene. The relative rate constants calculated for the pure reactants with $AlCl_3$, LaY and HZSM-5 are presented in Table 1 along with those obtained with the mixed reactants used in the present study. The relative rate constants obtained for the ethylbenzene/xylene reaction mixture using a LaY catalyst are similar to those obtained earlier with the pure xylene reactants using another portion of the same LaY catalyst batch. The constants calculated for xylene plus toluene mixtures are somewhat less indicative of a series isomerization mechanism than when ethylbenzene was used as the diluent.

Table 1
WEI-PRATER RELATIVE RATE CONSTANTS
LaY

Rate Constants	This Study			HSZM-5	$AlCl_3$
	Xylene + Ethylbenzene	Xylene + Toluene	Pure Xylene [4]	Pure Xylene [5]	Pure Xylene [1] 60°C
Ortho → Meta, k_{21}	9.50	5.39	10.9	2.13	2.1(10 ⁵)
Meta → Ortho, k_{12}	4.18	2.35	4.79	1.12	5.8(10 ⁴)
Para → Meta, k_{23}	8.80	4.95	8.08	2.58	2.8(10 ⁵)
Meta → Para, k_{32}	3.93	2.21	3.61	0.84	9.4(10 ⁴)
Para → Ortho, k_{13}	1.0	1.0	1.0	1.0	1.0
Ortho → Para, k_{31}	1.02	1.02	1.02	1.14	1.2

Ethylbenzene disproportionates to form equal molar amounts of diethylbenzene and benzene. A plot of benzene versus diethylbenzene show that the experimental data fit rather well the straight expected for disproportionation. The normalized diethylbenzene product composition (figure 2) is constant for a wide range of ethylbenzene conversions. Toluene can disproportionate to form xylene and benzene. At low conversions, xylene formation appears to be controlled by ortho-para directing effects. With increasing toluene conversion the xylenes approach an equilibrium mixture and attain this equilibrium value when about 30% toluene has been converted.

Normalized diethylbenzene distributions for the conversion of an ethylbenzene ortho-xylene mixture are shown in figure 3. The products resemble those obtained for the conversion of ethylbenzene alone except that slightly less of the meta and para isomers, and more of the ortho isomer, are formed. With ortho-xylene present, the equilibrium composition [9] is obtained whereas the one obtained with ethylbenzene alone has more of the meta isomer and less of the ortho isomer than an equilibrium mixture. Similar diethylbenzene distributions were obtained if either meta-xylene or para-xylene was substituted for ortho-xylene in the reaction mixture.

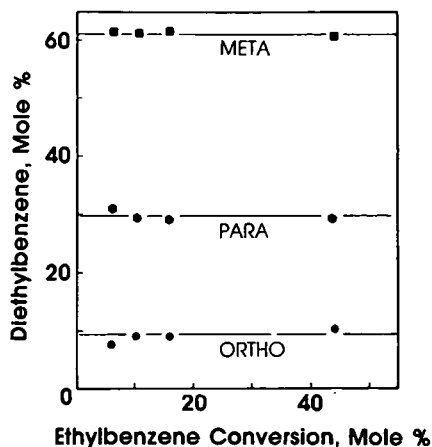


Fig. 2 (left). Disproportionation products from ethylbenzene conversion.

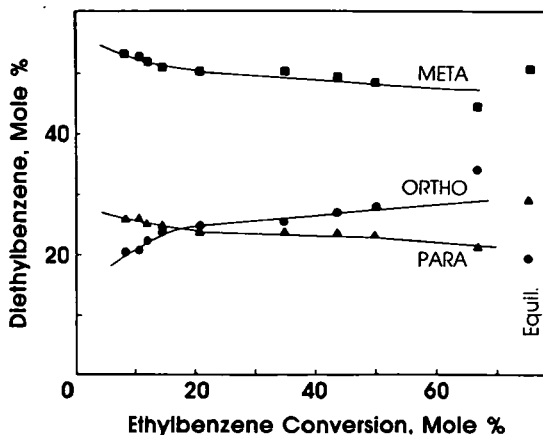


Fig. 3 (right). Diethylbenzenes formed from ortho-xylene/ethylbenzene conversion.

Xylene plus ethylbenzene can disproportionate by two reaction pathways:

- (1) xylene + ethylbenzene = toluene + ethyltoluenes, and
- (2) xylene + ethylbenzene = benzene + ethyldimethylbenzenes.

Three isomers of ethyltoluene and six isomers of ethyldimethylbenzene may be formed by reactions (1) and (2). Each ethyldimethylbenzene isomer was not related to a g.c. peak due to the small amount of these components and to the lack of suitable standards. Thus, the relative importance of the above two reactions was estimated from the benzene/(benzene plus toluene) fraction; this ratio increases with decreasing conversion and it appears that the transfer of the ethyl group is favored over that of the methyl group by a factor of 3 to 4. Both benzene and toluene can be formed by the disproportionation of ethylbenzene and xylene, respectively; however, correcting for the disproportionation (\blacktriangle in figure 4) leads to a similar conclusion. Comparing

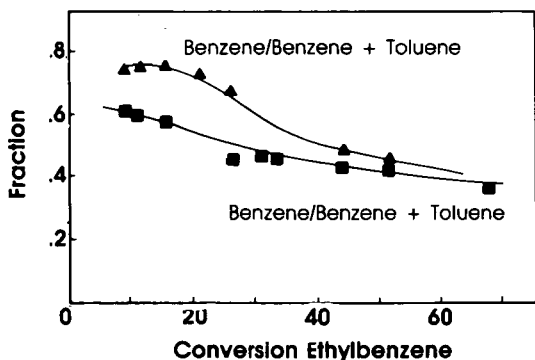


Fig. 4a (left). Fraction of benzene (\blacksquare) and corrected (see text) fraction of benzene (\blacktriangle) for ortho-xylene/ethylbenzene conversion.

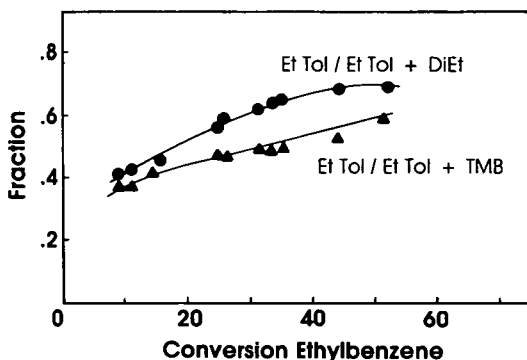
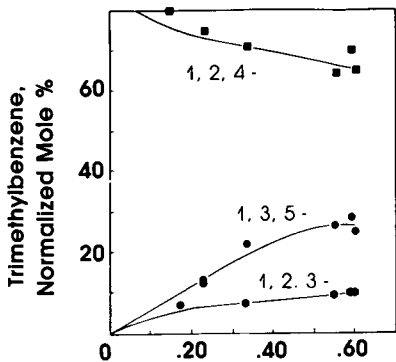
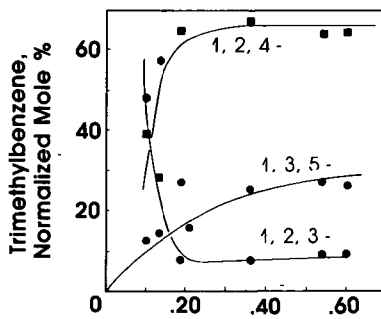


Fig. 4b (right). Ethyltoluene fraction of C_9 aromatics (\blacktriangle), and ethyltoluene plus diethylbenzene (\bullet).



Para-Xylene Conversion, Mole %



Meta-Xylene Conversion, Mole %

Fig. 5 Trimethylbenzene fraction from para-xylene/ethylbenzene conversion. (left)

Fig. 6. Trimethylbenzene distribution from meta-xylene/ethylbenzene conversion. (right)

the self-disproportionation (i.e. trimethylbenzene from xylene or diethylbenzene from ethylbenzene) to the crossed disproportionation (i.e. ethyltoluene) formation shows: (a) that ethylbenzene and xylene undergo disproportionation at about the same rate and (b) that crossed disproportionation is favored by a factor of 2 over self-disproportionation as expected on a statistical basis for the equal-molar mixture used in this study.

Disproportionation of xylene to trimethylbenzenes and toluene has been shown to proceed in a one-to-one molar ratio to produce a trimethylbenzene isomer distribution dictated by the ortho/para directing nature of methyl substituents [4]. From methyl group directing effects, it is expected that only 1,2,4-trimethylbenzene should result from para-xylene disproportionation. The trimethylbenzene distribution data obtained with a para-xylene plus ethylbenzene mixture (figure 5) show that 1,2,4-trimethylbenzene is indeed the predominant product and that its fraction increases with decreasing conversion. Both 1,3,5- and 1,2,3-trimethylbenzene decrease with decreasing conversion and appear to approach zero at zero conversions. The data in figure 6 for meta-xylene plus ethylbenzene conversion also agree with the pattern expected for directing effects since the 1,3,5-trimethylbenzene fraction decreases with decreasing conversion so that the lower conversion products are only the two expected isomers; 1,2,4- and 1,2,3-trimethylbenzene. The ortho-xylene plus ethylbenzene reaction mixture also follows the trend expected for ortho-para directing effects. Thus, the selectivity patterns for disproportionation of xylene to trimethylbenzenes in the xylene/ethylbenzene mixtures are very similar to the ones obtained for pure xylene reactants.

Two reactions must be considered for disproportionation of a xylene plus toluene mixture:

(3) xylene + xylene = TMB + toluene, and

and

(4) xylene + toluene = TMB + benzene.

If pathway (4) applies, disproportionation products, trimethylbenzene and benzene, will form in equal molar amounts. However, the amount of TMB produced is much greater than the amount of benzene (figure 7). Consequently, the predominate pathway for trimethylbenzene formation is via xylene-xylene disproportionation.

Figure 8 illustrates the normalized trimethylbenzene isomer distributions versus total trimethylbenzenes formed for para-xylene disproportionation in the presence of toluene. The data indicate that an equilibrium trimethylbenzene mixtures are formed over the entire conversion range. Similar results were obtained when ortho-xylene or meta-xylene was substituted for the ortho-xylene reactant.

Disproportionation of ethylbenzene and ortho-xylene produces ethyltoluene. From 20% to 70% conversion of ethylbenzene the ethyltoluene distribution is essentially constant and contains more than the equilibrium concentration of meta-ethyltoluene and less than the equilibrium concentration of para-ethyltoluene. It appears that the para isomer concentration increases rapidly as the conversion decreases; parallel to this, the concentration of both the ortho- and para- isomers decreases with decreasing conversion (figure 9). The diethylbenzene products, formed along with the ethyltoluenes shown in figure 9, are at a nearly equilibrium composition; however, at low ethylbenzene conversion the ortho-diethylbenzene fraction is greater, and the

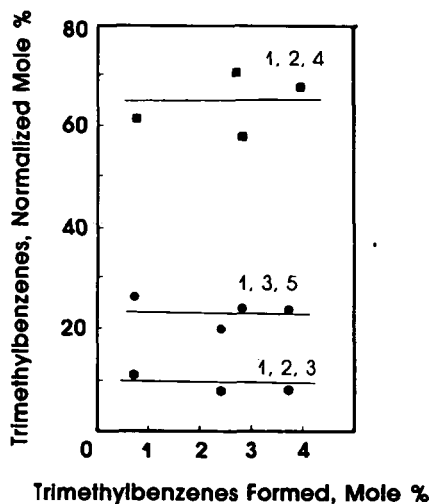
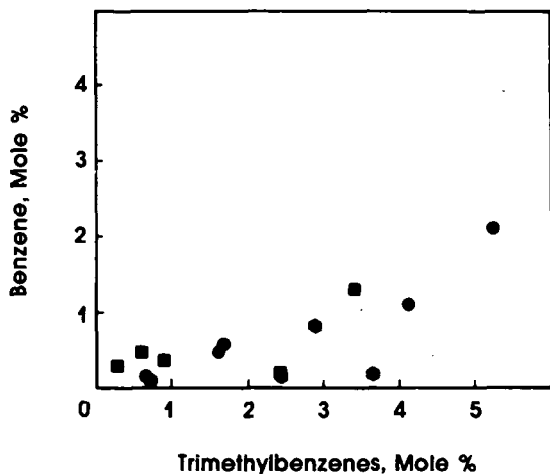


Fig. 7. Disproportionation products from toluene and xylene (ortho, ●; meta, ■; para, ●) conversion. (left)

Fig. 8. Trimethylbenzene distribution from toluene and para-xylene conversion. (right)

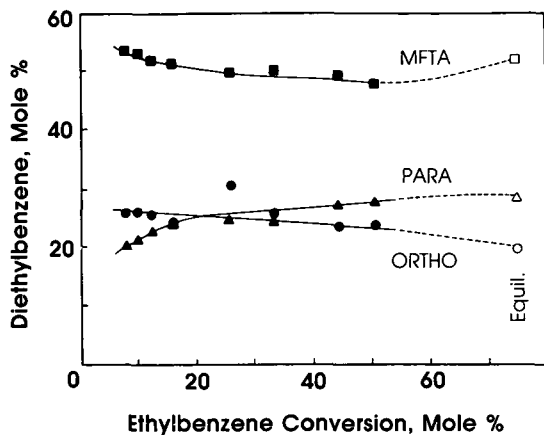
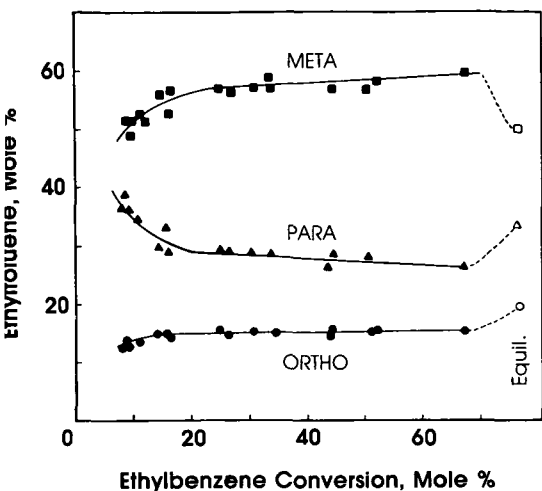


Fig. 9. Ethyltoluene products from the conversion of an ortho-xylene/ethylbenzene mixture. (left)

Fig. 10. Diethylbenzene from the conversion of ortho-xylene/ethylbenzene mixtures. (right)

para-diethylbenzene fraction is less, than the equilibrium amount. Similar results were obtained if either meta- or para-xylene was substituted for ortho-xylene.

The trimethylbenzenes formed in the samples represented in figure 9 and 10 resemble those found earlier [4] with the 1,2,3- and 1,2,4 isomers, both allowed by methyl directing effects, being the dominant, low conversion product (figure 11). 1,3,5-Trimethylbenzene, not allowed by alkyl directing effects, approaches a low, or zero, concentration at low conversions.

An equimolar mixture of toluene and ethylbenzene was also converted over the catalyst at 623^oK. With these reactants the meta isomer, both diethylbenzene and ethylbenzene, was in excess of the equilibrium amount while the ortho isomer was lower than the equilibrium amount (figure 12).

DISCUSSION

The relative isomerization rates of xylene are essentially the same whether the reactant is a pure xylene or a xylene isomer in a mixture with ethylbenzene or toluene. This result suggests that the predominant xylene isomerization pathway with LaY is not by a disproportionation mechanism as has been proposed by some [7]. Rather, the isomerization occurs by a series of 1,2 methyl shifts.

Disproportionation is complex. With xylene reactants initial, primary disproportionation products include only those trimethylbenzene isomers that are allowed by alkyl ortho-para directing influences. Also, rate constants for trimethylbenzene isomerization with LaY are very similar to those for

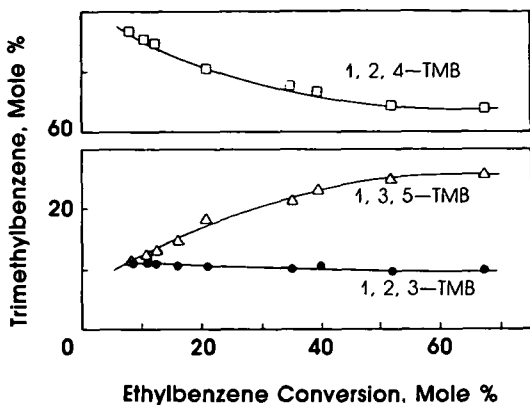


Fig. 11. Trimethylbenzenes formed during the conversion of an ortho-xylene/ethylbenzene mixture. (left)

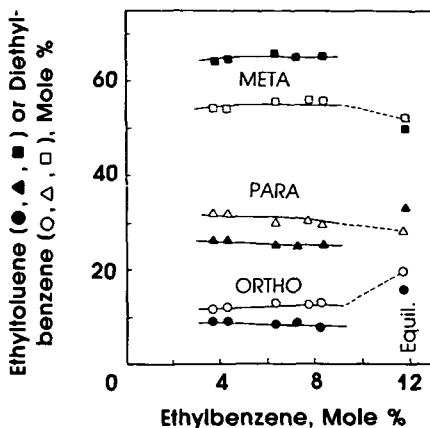


Fig. 12. Ethyltoluene and diethylbenzene product distribution from the conversion of a toluene/ethylbenzene mixture. (right)

xylene [10]. This is the case whether ethylbenzene is present or not. However, for ethyl containing disproportionation products, diffusion as well as chemical selectivity both appear to play a role in determining reaction products.

Kaeding and co-workers [11] show that shape selectivity will favor the isomer with the minimum dimension with intermediate pore size zeolites such as HZSM-5. With ethyltoluene and diethylbenzene, the para isomer has the smallest minimum dimension, followed by the meta and then the ortho isomer. In our study, the products show evidence for a small degree of shape selectivity. In addition, diffusion of ethyl containing products appears to be considerably slower than for trimethylbenzene products. Thus, initial trimethylbenzene distributions are clearly controlled by chemical selectivity and are far removed from the equilibrium values whereas ethyltoluenes or diethylbenzene isomers are produced, in the bulk liquid, in nearly equilibrium concentrations even at low conversions. This is true even though trimethylbenzene and ethyl containing disproportionation products are formed in nearly equal amounts in the catalyst pores. To learn the extent that ortho-para directing effects influence the disproportionation products for the transfer of ethyl or longer carbon-chain substituents will require the use of much smaller size zeolite catalyst particles than employed in the present study on the use a catalyst with pores much larger than those present in this LaY catalyst.

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