Kinetics of Xylene Isomerization over Silica-Alumina Catalyst

K. L. HANSON and A. J. ENGEL

Pennsylvania State University, University Park, Pennsylvania

Eleven mixtures of the three isomers of xylene and ethylbenzene were isomerized over a silica-alumina catalyst in a differential tubular reactor at temperatures from 700° to 900°F. and pressures from 0 to 100 lb./sq. in. gauge. Analysis showed that meta-xylene isomerizes reversibly to ortho- and para-xylene, but the direct interconversion of ortho-xylene to meta-xylene does not occur. Further, it appears that the isomerization reactions are first order and, by the Hougen-Watson technique, follow a single-site reaction model.

Considerable interest has developed in recent years in the isomerization of xylenes, mainly because of a greatly increased demand for para-xylene as an intermediate in the manufacture of polyester fibers and films. The individual xylene isomers are usually obtained by separation from mixtures of xylenes that result from the catalytic reforming of petroleum naphtha. The production of any particular isomer of xylene could be greatly increased by the isomerization of mixtures of xylenes, with subsequent separation of the desired isomer. Because of this, xylene isomerization processes are expected to become more attractive economically as the demand for para-xylene increases.

The isomerization of xylenes is greatly aided by the use of an acid catalyst and can be carried out in either the liquid or vapor phase. The purely thermal isomerization of xylenes does occur (*10, 32*) but is of very little interest because extreme conditions are required and the yields are poor. The liquid phase isomerization of xylenes can be carried out under either homogeneous or heterogeneous phase conditions with a combination of Lewis acids as a catalyst, for example, HF/BF_3. Such reactions have been observed to be first order with respect to xylene concentration (*2, 8, 21, 30*) and first order with respect to catalyst concentration for homogeneous phase conditions (*8*). The disproportionation of xylenes to toluene and trimethylbenzenes, a side reaction, can be effectively suppressed by the use of a toluene diluent (*2, 8, 21*). When the xylene isomerization reactions are allowed to proceed to completion in the liquid phase under heterogeneous conditions, a product results which corresponds closely to thermodynamic equilibrium (*2, 21, 30*) as calculated by Taylor (*31*). If sufficient catalyst is used to produce homogeneous phase conditions and the temperature level is moderate, the product will be essentially 100% meta-xylene (*8, 29, 30*). This upsetting of the normal equilibrium is attributed to complexing of the meta-xylene, the most basic isomer, with the acid catalyst.

Isomerization of xylenes in the liquid phase suffers from the disadvantages of slow reaction rates and poor yields. In recent years interest has turned from liquid phase to vapor phase isomerization. A suitable catalyst is a typical oxide cracking catalyst, such as silica-alumina, silica-magnesia, or silica-alumina-zirconia (*6*). The activity of silica-alumina for xylene isomerization has been improved by steam treating the catalyst prior to its use (*4, 15, 25*). Addition of hydrogen to the xylene feed (*7, 9, 16, 18, 22, 26*) suppresses side reactions, reduces coke formation, and increases the rate of xylene isomerization. Steam dilution (*7, 9*), or small amounts of water in the feed (*3*), also improve the reaction, whereas nitrogen dilution does not (*16, 18*).

The isomerization of ethylbenzene to xylenes is much more difficult to achieve than the interisomerization of xylenes (*5, 7, 9*). Pitts (*27*) concluded that ethylbenzene and xylenes interconvert only when hydrogenation of aromatics also occurs. Otherwise, ethylbenzene tends to crack to ethylene and benzene rather than isomerize to xylenes (*5, 13*). Cracking of xylenes will also occur over silica-alumina, but the main side reaction is disproportionation (*5, 11, 12, 20*).

Nearly all of the work on the vapor phase isomerization of xylenes has been limited to catalyst and process modifications to improve yield and to increase the isomerization

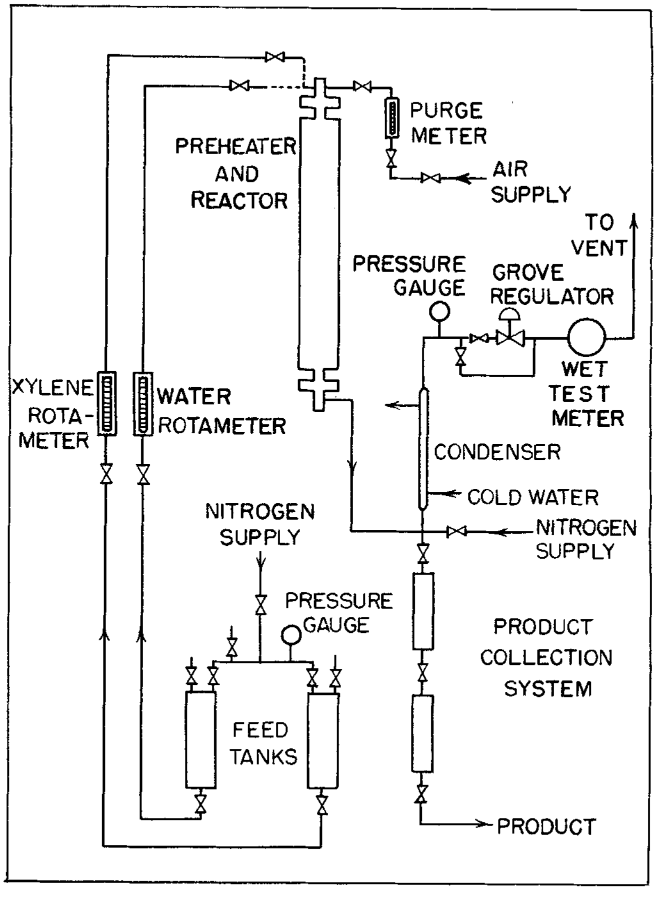

Fig. 1. Schematic diagram of apparatus.

K. L. Hanson is with Swift and Company Research Laboratories, Chicago, Illinois.

Table 1. Composition of Feed Mixtures

Feed No.	Mole fraction Ortho-xylene	Meta-xylene	Para-xylene	Ethyl-benzene
1	0.436	0.467	—	0.097
2	—	0.623	0.280	0.097
3	—	1.000	—	—
4	0.060	0.880	0.060	—
5	0.120	0.760	0.120	—
6	0.180	0.640	0.180	—
7	0.300	0.400	0.300	—
8	0.400	0.200	0.400	—
9	0.500	—	0.500	—
10	1.000	—	—	—
11	—	—	1.000	—

rate. Some relatively limited kinetic studies have shown that the isomerization reactions are pseudo first order (*5*), including the conversion of ortho-xylene to para-xylene (*23*). Hence this study (*14*) was undertaken to investigate the kinetics of the vapor phase isomerization of xylenes over a silica-alumina catalyst. The kinetic model for heterogeneous catalysis as developed by Watson (*17*) was selected for data correlation to provide a more rational rather than a strictly empirical basis for the study.

EXPERIMENTAL PROCEDURE

The equipment for carrying out continuous vapor phase xylene isomerization consisted of a catalytic differential reactor and auxiliary equipment including rotameters for measuring the flows of feed and water to the reactor, feed tanks, product collection tanks, a product condenser, a Grove pressure regulator and cylinder nitrogen system to maintain constant pressure, and a wet-test meter to measure the volume of by-product gases (see Figure 1). All equipment in contact with the process fluid was made of 300 series stainless steel.

The reactor was fabricated from a 43-in. piece of ½-in. Schedule 160 304 stainless steel pipe, flanged at either end. The top of the reactor consisted of a block of stainless steel welded to a flange and machined to provide for three process stream entrances to the reactor and one inlet for a 3/16-in. thermowell tube. The feed flowed downward and was preheated in an annular preheat section. On either side of catalyst bed, which, depending on catalyst volume, occupied the middle 1 to 10 in. of the reactor, was a 1 to 2-in. bed of crushed unglazed earthenware to provide for uniform flow distribution. Three 60-mesh stainless steel screens kept the earthenware and the catalyst in fixed positions during a run. Below the reaction zone another annular heating section helped to maintain a uniform temperature in the reaction zone. Reactor temperatures were measured with five 24-gauge iron-constantan thermocouples inserted into thermowells. The reactor was closely wound with nichrome resistance wire in three separate sections to provide feed preheat and maintain isothermal conditions in the catalyst bed. The entire length of the reactor was covered with 2 in. of an asbestos-calcium silicate type of insulation. The catalyst was Houdry S-90 silica-alumina pellets crushed to — 20 + 40 mesh size (0.83 to 0.42-mm. in diameter).

In preparation for a series of runs, a weighed amount of catalyst was charged to the reactor, which was then heated and held overnight at 900°F. to stabilize partially the activity of the catalyst. Prior to starting a run, steam was fed to the reactor for at least 15 min. to purge the reactor of air and develop a temperature profile that corresponded to flow conditions. To make a run, feed was passed through the reactor at a rate of 1 to 5 ml./min. for 30 min., and a sample was collected during the last 15 min.

The catalyst bed temperature was controlled to within 3°F. of the desired temperature and the isomerizations were carried out at 700°, 800°, or 900°F. After each run the catalyst was regenerated for 1 hr. with a mixture of steam and air. In taking the kinetic data a maximum of five runs was made with any one charge of catalyst, and no charge of catalyst was used for more than one day. Isomerization under pressure was carried out by pressuring the reactor with nitrogen to either 50 or 100 lb./sq.in.gauge prior to starting the water flow.

The feeds were prepared by mixing pure xylenes and ethylbenzene in the desired proportions. Table 1 gives the feed compositions used. Component purity was rated by the supplier as 99% or better and was checked by infrared analysis.

The product was analyzed by infrared absorption spectroscopy (*28*) on a P.E. model 21 spectrophotometer. The average precision and accuracy of the analytical technique were found to be within 0.3% of the total sample for the three xylenes and ethylbenzene. The product was also analyzed for small amounts of benzene and toluene. The values of the optical densities used in calculating the concentrations were averages of four scans for each sample. It was assumed that the optical densities of the individual components were additive, but it was not necessary to assume that Beer's law was valid for a component at its analytical wavelength. Solution of the set of six simultaneous equations was performed with the aid of an IBM 7074 computer.

The maximum conversion of any of the xylenes that was observed was 16% but nearly all of the values were 4% or less, so that the rate data could be analyzed on the basis of a differential reactor system, and the composition of the reactant stream was assumed to be the arithmetic average of the feed and product compositions.

RESULTS AND DISCUSSION

Catalyst Activity

The activity of Houdry S-90 silica-alumina catalyst for xylene isomerization was defined by isomerizing a mixture of xylenes and ethylbenzene, feed 1, at fixed operating conditions. Selection of the feed composition and operating conditions was based on data reported by Luzar (*23*) on the isomerization of ortho-xylene to para-xylene over Houdry S-90 catalyst. The mole fractions of ethylbenzene and meta-xylene in feed 1 are the concentrations calculated to exist in a mixture of the three xylenes and ethylbenzene in thermodynamic equilibrium at 900°F. (*31*). It was observed by Luzar and by us at the beginning of this study that isomerization of this feed produced an overall conversion of ortho-xylene to para-xylene with little net change in the concentrations of meta-xylene and

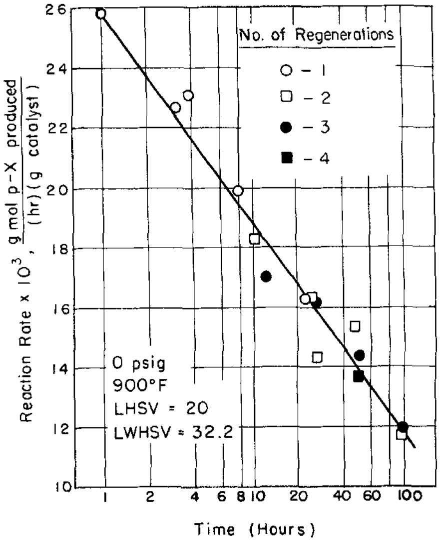

Fig. 2. Decrease of catalyst activity with time at 900°F.

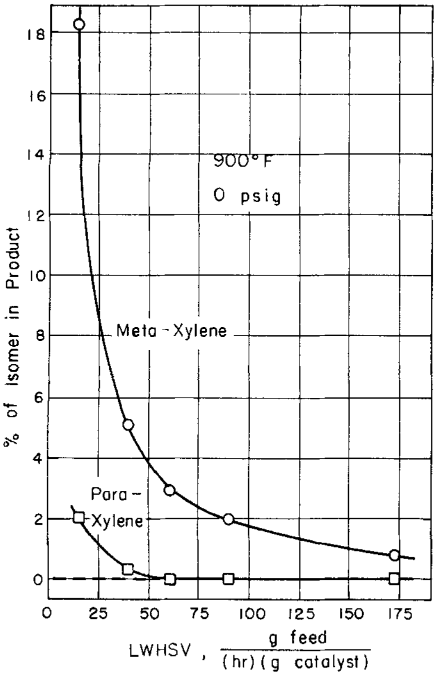

Fig. 3. Conversion of ortho-xylene to meta-xylene.

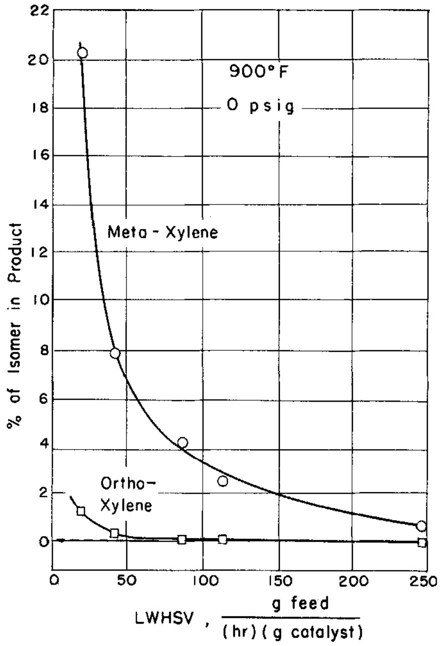

Fig. 4. Conversion of para-xylene to meta-xylene.

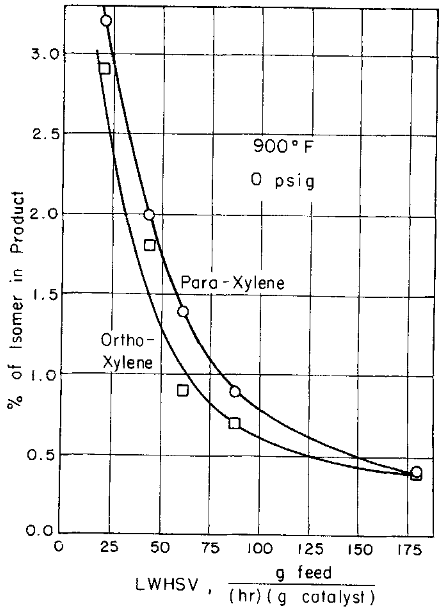

Fig. 5. Conversion of meta-xylene to para-xylene and ortho-xylene.

ethylbenzene. The conversion to para-xylene was selected as an indication of catalyst activity.

The data used to define catalyst activity are shown in Figure 2. The least-squares line defines activity by

$$a = 1.00 - 0.270 \log_{10} t \qquad (1)$$

It should be observed that the catalyst was contacted with feed for brief periods of time but was maintained at 900°F. for long periods. Shown as a parameter in Figure 2 is the number of times a catalyst charge was contacted with feed and regenerated. If there had been a step decline in catalyst activity due solely to contact with feed and subsequent regeneration, the data would be expected to correlate as a family of curves. Since the data correlate along a single line, it appeared that merely holding the catalyst in the reactor at 900°F. caused the observed decline in catalyst activity. In view of this activity decline, attempts were made to stabilize large batches of catalyst by calcining them in an oven at 900°F. for approximately 100 hr. The anticipated activity decline did not occur; in fact, the calcining improved the initial catalyst activity by approximately 30%. The improvement in activity of silica-alumina for the isomerization of xylenes by calcining has also been observed by Iwasaki (*19*). Thus, it seems unlikely that the decline in activity of the catalyst in the reactor was due solely to a time-temperature aging phenomenon. Rather, the activity decline is attributed to steam sintering of the catalyst, as it is very probable that residual amounts of steam were entrapped in the reactor between runs.

Equation (1) was used to correct all the kinetic data to the common value of unity for the catalyst activity. In applying the activity correction, it was assumed that the catalyst activity was constant during a run, and was independent of reaction rate, temperature, and pressure. These assumptions are not entirely valid, but they were quite necessary in the absence of additional catalyst activity data. The actual level of catalyst activity was maintained generally in the range of 0.6 to 0.7. This made all the activity adjustments of the same order of magnitude and minimized errors arising from the activity correction.

Isomerization Reactions

The isomerization of each of the three pure xylenes was studied to determine the overall nature of the isomerization reactions. Two alternate reaction schemes have been proposed in the literature. In one (5) the xylenes isomerize mutually, as shown:

$$\begin{tikzcd} & \text{meta} \arrow[dl, shift left] \arrow[dr, shift left] & \\ \text{ortho} \arrow[ur, shift left] \arrow[rr, shift left] & & \text{para} \arrow[ul, shift left] \arrow[ll, shift left] \end{tikzcd}$$

The second isomerization scheme proposes that ortho-xylene and para-xylene do not directly interconvert, that is, the migrating methyl group moves around the benzene ring in steps of one ring position at a time. This is represented schematically as

$$\text{ortho} \rightleftharpoons \text{meta} \rightleftharpoons \text{para}$$

This study supports the second reaction scheme. Several investigators (*1*, *2*, *8*, *21*, *24*, *30*) have proposed the second model for liquid phase isomerization, but none have reported it for the vapor phase.

Data demonstrating the accepted scheme are shown in Figures 3, 4, and 5. For the ortho-xylene and para-xylene feeds the product was entirely meta-xylene over the range of higher space velocities. Production of ortho-xylene from a para-xylene feed and vice versa did not become noticeable until there were substantial amounts of meta-xylene in the products. In contrast, isomerization of meta-xylene resulted in approximately equal conversions to ortho-xylene and para-xylene over the entire range of space velocities used. The obvious interpretation of this is that ortho-xylene and para-xylene do not directly interconvert.

The extent of the isomerization of xylenes to ethylbenzene was also investigated. None of the three xylenes was observed to isomerize to ethylbenzene, even for conversion levels of 6, 18, and 20% for the meta, ortho, and para isomers, respectively. This agrees with the findings of other workers (5, 27).

As has been discussed, there are only two xylene isomerization reactions that occur. Each of these reactions can be represented by the following monomolecular reaction model:

$$A \rightleftharpoons B \quad \text{(in the presence of } C\text{)}$$

A was chosen to represent meta-xylene and B is either ortho-xylene or para-xylene, depending upon the reaction being considered. C represents the third xylene isomer, since in general all three isomers of xylene were present in a feed mixture. The two reactions occur simultaneously and independently, which made it possible to observe the kinetics of both reactions at the same time. Selection of the feed compositions was influenced by this factor. Approximately equal conversions were obtained for both reactions if the ortho-xylene and para-xylene mole fractions in the feed were the same.

Analysis of the Kinetic Data

A heterogeneous catalytic reaction is considered to occur in a series of mass transfer and kinetic steps. If one step has a resistance that is dominant, it is a rate controlling step.

The diffusion of the xylenes from the bulk of the vapor stream to the catalyst surface and the diffusion into the pores of the catalyst were investigated in order to separate the mass transfer effects from the kinetic effects. The minimum necessary partial pressure of a xylene reactant to eliminate bulk diffusion resistance under typical reaction conditions was estimated to be 0.01 atm. from the generalized calculation technique described by Satterfield and Sherwood (33). Since the reactant partial pressure was always much higher than this value, bulk diffusion was not considered to be a controlling factor. Experimental data on the effect of a fourfold vapor velocity increase on reaction rate at a fixed space velocity also eliminated bulk diffusion as a significant rate factor. These data showed a 16% decrease in rate with the increased vapor velocity, whereas an increase in rate would be anticipated. This decrease in rate was judged to be not significant and was not pursued any further. The importance of pore diffusion was tested by observing the effect on reaction rate of decreasing the average catalyst particle size from 0.63 to 0.32 mm. A 7% increase in rate was observed for the smaller particle size for the isomerization of pure para-xylene, the most reactive xylene, at 900°F. and 0 lb./sq. in. gauge. Application of a modified Thiele method (33) for the prediction of catalyst effectiveness factors was also used to indicate the relative unimportance of pore diffusion. The effectiveness factors for the two catalyst sizes were estimated to be 0.85 and 0.98 for the isomerization of para-xylene at 900°F. Therefore, pore diffusion effects were considered small and were neglected in the analysis of the kinetic data.

In mathematically describing the kinetic steps of a reaction it is customary to assume that one step is slow and that the other steps are essentially at equilibrium conditions. Although this is a rather tenuous assumption, the analysis becomes unwieldy and impractical if it is not made. The equations describing the kinetic steps of a monomolecular reversible reaction are shown below, and are a straightforward application of the theory of heterogeneous catalysis as developed by Watson (17).

Adsorption of A controlling:

$$r = \frac{k_A L}{1 + P_B\,(K_A/K + K_B) + P_C K_C}\left(P_A - \frac{P_B}{K}\right) \quad (2)$$

Adsorption of B controlling:

$$r = \frac{k_B L K}{1 + P_A\,(K_A + K_B K) + P_C K_C}\left(P_A - \frac{P_B}{K}\right) \quad (3)$$

Single-site reaction controlling:

$$r = \frac{k L K_A}{1 + P_A K_A + P_B K_B + P_C K_C}\left(P_A - \frac{P_B}{K}\right) \quad (4)$$

Two-site reaction controlling:

$$r = \frac{k s L K_A}{(1 + P_A K_A + P_B K_B + P_C K_C)^2}\left(P_A - \frac{P_B}{K}\right) \quad (5)$$

The values used for the overall reaction equilibrium constant K were calculated by Taylor (30) and are shown in Table 2. The presence of the adsorption equilibrium constant K_C in the rate expressions is due to the xylene isomer which does not participate in the reaction.

All the rate expressions were inverted and reduced to forms that were suitable for multiple regression analyses. These were carried out for both isomerization reactions under each of the postulated rate controlling assumptions. In performing the regressions, data were used from twenty-five runs at 900°F., nine runs at 800°F., and nine runs at 700°F. The data at 900°F. included four runs at 50 lb./sq. in. gauge and four runs at 100 lb./sq. in. gauge. No data were excluded in order to obtain an improved correlation, and considerable effort was spent in developing a suitable method for obtaining the data. The original data and a more detailed description of the regression analyses are available elsewhere (14).

The least suitable model was the adsorption and desorption of meta-xylene (adsorption of A) as a rate controlling step. The multiple correlation coefficient for this model was very low for both reactions. In addition, the regression coefficients for this model were nearly all negative. All of the physical constants in the accepted rate expression should be either zero or positive, as negative constants are inconsistent with the theoretical development. Hence, this model clearly did not fit the data.

The single-site and two-site rate models are identical except for the squared denominator in the two-site model. As a result the correlations would be expected to be quite similar, but discrimination between the two models is greatly aided by a determination of the effect of pressure on reaction rate. The data at 900°F. and at pressures of 0, 50, and 100 lb./sq. in. gauge showed that the single-site mechanism gave a somewhat better fit than the two-site mechanism, since the multiple correlation coefficients for the former mechanism were 0.943 and 0.967 for the isomerization of meta-xylene to para-xylene and ortho-xylene, respectively, while the corresponding values for the latter mechanism were 0.923 and 0.937.

The regression coefficient associated with meta-xylene was always positive, always much larger than the values for ortho-xylene and para-xylene, and always statistically significant at the 95% confidence level, as judged by the

TABLE 2. EQUILIBRIUM DATA FOR THE XYLENES

Temp., °F.	Equilibrium mole fraction of xylene isomer			Equilibrium constant K	
	Meta	Para	Ortho	Meta ⇌ Para	Meta ⇌ Ortho
700	0.527	0.237	0.236	0.450	0.448
800	0.521	0.235	0.244	0.451	0.469
900	0.517	0.233	0.250	0.451	0.484

Table 3. Rate and Adsorption Equilibrium Constants

	$k' \times 10^3$, g.-moles/ (hr.)(g. catalyst) (lb./sq. in.)		K_A, (lb./sq. in.)$^{-1}$	
	Observed	Smoothed	Observed	Smoothed
Isomerization of: Meta-xylene to para-xylene				
700°F.	0.352	0.386	0.140	0.210
800°F.	2.33	1.93	0.182	0.089
900°F.	6.50	7.31	0.0336	0.044
Isomerization of: Meta-xylene to ortho-xylene				
700°F.	0.266	0.265	0.195	0.210
800°F.	1.29	1.31	0.112	0.089
900°F.	4.87	4.91	0.0367	0.044

value of the partial correlation coefficient. The regression coefficients for ortho-xylene and para-xylene were sometimes negative and in general were not statistically significant. This indicates that meta-xylene is much more extensively adsorbed on the catalyst surface than either ortho-xylene or para-xylene. This is consistent with the relative basicity of the three xylenes. Meta-xylene is definitely the most basic isomer and might be expected to have the greatest affinity of any of the xylenes for an acid catalyst.

In view of the dominance of meta-xylene adsorption, the kinetic data were analyzed by linear regression with the meta-xylene partial pressure as the independent variable. This is equivalent to assuming a value of zero for the equilibrium adsorption coefficients for para-xylene and ortho-xylene. Very little in the way of data fitting accuracy was lost in simplifying the correlation model from a multiple regression to a linear regression. The multiple correlation coefficients for the single-site reaction mechanism, reported as 0.943 and 0.967, were only reduced to 0.938 and 0.960 for the linear regression. The final correlation of the kinetic data was by linear regression and the corresponding single site reaction model is

$$r = \frac{k'}{1 + P_A K_A} \left(P_A - \frac{P_B}{K} \right) \tag{6}$$

The single-site model and the adsorption-of-B model are mathematically indistinguishable when the data are correlated by linear regression, since the resulting equation can be applied to either rate model. However, the single-site mechanism was preferable, because it is easier to visualize and is intuitively more acceptable than the adsorption mechanism.

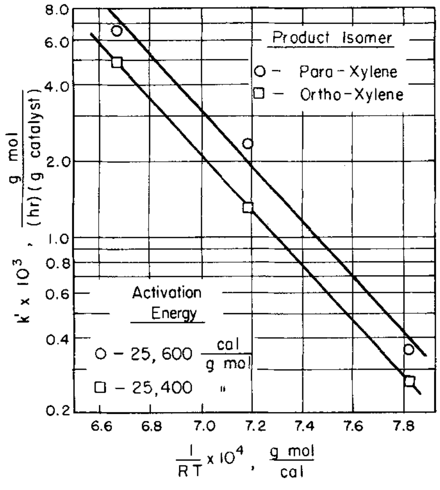

Fig. 6. Activation energy diagram for the izomerization of meta-xylene.

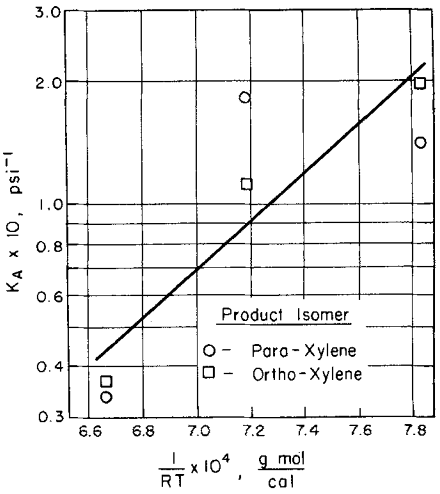

Fig. 7. Meta-xylene adsorption enthalpy diagram.

The average deviation between reaction rates as calculated from the simplified rate model and the observed kinetic data averaged 15% for the isomerization of meta-xylene to ortho-xylene and 16% for the isomerization to para-xylene. The values used for k' and K_A in these calculations are shown in Table 3 and were calculated from the values for the linear regression coefficients.

The effect of temperature on the rate constants for the two isomerization reactions is shown in Figure 6. The activation energies for the isomerization of meta-xylene to para-xylene and to ortho-xylene are virtually identical at 25,600 and 25,400 cal./mole, respectively. This is to be expected, since the two reactions are so similar, and it is taken as an indication of the general validity of the data interpretation and the suitability of the simplified single-site mechanism as a reaction rate model.

The effect of temperature on the meta-xylene adsorption equilibrium constant is shown in Figure 7. The data exhibit considerable scatter about the least-squares line, as is typical of these kinds of data. Ideally, the values for K_A should be the same for both reactions and should plot in a straight line. However, the general agreement in the values of K_A for the two reactions is considered good, relative to what can be realistically expected from kinetic data. The slope of the line in Figure 6 yielded a value of −13,600 cal./mole for the enthalpy of activated adsorption of meta-xylene on the catalyst surface.

A listing of smoothed values for k' and K_A as taken from Figures 6 and 7 is shown in Table 3. These values were used to calculate the overall activation energy of the isomerization reaction on the catalyst surface, k'/K_A, as 39,000 cal./mole.

Since the thermal isomerization rate was observed to be less than 2% of the corresponding catalytic rate at a catalyst activity of unity, it was not necessary to correct the kinetic data for any thermal isomerization that occurred independently of the catalytic isomerization.

Disproportionation of Xylenes

The main side reaction of xylene isomerization is the disproportionation of xylenes to toluene and trimethylbenzene, although some xylene cracking does occur (*13, 20*). The amounts of toluene observed in the product samples were small, usually less than 1% of the sample. With such small conversions any kinetic interpretation of the data is bound to be inexact. However, a large amount of data were available (eighty-nine runs at 900°F.), since all the data taken during the study could be used to calculate toluene production rates, not just the data used to define the kinetics of xylene isomerization. A regression analysis was made to determine if the data would fit the following model:

$$r_D = (k_p X_p + k_m X_m + k_o X_o) P \qquad (7)$$

The linear effect of pressure was based on a superficial examination of the data and the fact that Johanson (*20*) reported an essentially linear effect of pressure, up to 300 lb./sq. in. gauge, on the rate of disproportionation of xylenes over silica-alumina. Although there are six disproportionation reactions (six permutations of two molecules among three isomers), and the rate model neglects that disproportionation is reversible, we believed that this simple model was sufficiently suitable to correlate the data empirically. No attempts were made to adjust the data for catalyst activity differences, as this refinement did not seem justified.

The following values for rate constants for xylene disproportionation were obtained by multiple regression analysis of the kinetic data on toluene production at a temperature of 900°F. and pressures of 0, 50, and 100 lb./sq. in. gauge:

$$k_p = 4.2 \times 10^{-4} \text{ (lb./sq.in.)}^{-1}$$
$$k_m = 0.90 \times 10^{-4} \text{ (lb./sq.in.)}^{-1}$$
$$k_o = 1.4 \times 10^{-4} \text{ (lb./sq.in.)}^{-1}$$

The multiple correlation coefficient and all three partial correlation coefficients associated with the three xylenes were statistically significant at the 95% confidence level. Qualitatively, the rate constants agree with the work of Amemiya (*5*), who found para-xylene to be the easiest isomer to disproportionate and meta-xylene the most difficult. From the rates of toluene production at 700°, 800°, and 900°F. the average activation energy for xylene disproportionation was estimated to be 17,700 cal./mole.

CONCLUSIONS

1. Meta-xylene isomerizes reversibly to ortho-xylene and para-xylene over silica-alumina, but direct interconversion between ortho-xylene and para-xylene does not occur.

2. The isomerization of xylenes to ethylbenzene over silica-alumina at 900°F. either does not occur or the rate is so slow as to be negligible.

3. The kinetic behavior of the two xylene isomerization reactions is first order and is suitably described by the rate model for a single-site reaction mechanism.

4. The overall activation energy for the isomerization of meta-xylene is essentially the same for both isomerization reactions and averages 25,500 cal./g.-mole.

5. Meta-xylene adsorbs on the surface of silica-alumina to a much greater extent than para-xylene or ortho-xylene and has an enthalpy of activated adsorption of −13,600 cal./g.-mole. The values of the adsorption equilibrium constants for para-xylene and ortho-xylene are negligibly small between 700° and 900°F.

6. The disproportionation of xylenes to produce toluene (and trimethylbenzenes) over silica-alumina has an average activation energy of 17,700 cal./g.-mole and occurs at a rate that is approximately proportional to absolute pressure for pressures ranging from 0 to 100 lb./sq. in. gauge.

7. The activity of the silica-alumina catalyst for the isomerization of xylenes is strongly dependent on the combined effects of time, temperature, and gaseous environment.

ACKNOWLEDGMENT

We thank the National Science Foundation for the financial support given during the major portion of this investigation. The support provided by The Pennsylvania State University and E. I. du Pont de Nemours and Company, Inc., is also gratefully acknowledged.

NOTATION

a = catalyst activity
A = meta-xylene
B = reaction product of meta-xylene isomerization
C = xylene isomer not participating in the isomerization reaction
k = rate constant for reaction on the catalyst surface
k' = overall rate constant for the isomerization of meta-xylene, g.-mole/(hr.) (g. catalyst) (lb./sq. in.)
k_A, k_B = rate constant for the adsorption of A or B on the catalyst surface
K = homogeneous reaction equilibrium constant
K_A, K_B, K_C = adsorption equilibrium constant for component A, B, or C, (lb./sq.in.)^{-1}
L = molal concentration of active sites on the catalyst surface, g.-mole/g. catalyst
$LHSV$ = liquid hourly space velocity, ml. fluid/(hr.) (ml. catalyst)
$LWHSV$ = liquid weight hourly space velocity, g. fluid/(hr.) (g. catalyst)
P = absolute pressure, lb./sq.in.
P_A, P_B, P_C = partial pressure of component A, B, or C in bulk fluid, lb./sq.in.
r = average rate of isomerization of meta-xylene, g.-mole/(hr.) (g. catalyst)
r_D = average rate of disproportionation of xylenes to toluene, g.-moles/(hr.) (g. catalyst)
s = geometric factor related to orientation of active sites
t = catalyst age at 900°F., hr.
X_o, X_m, X_p = mole fraction of ortho-xylene, meta-xylene, or para-xylene

LITERATURE CITED

1. Akiyoshi, Saburo, Akito Kobayashi, and Mikio Matsukane, *J. Chem. Soc. Japan Ind. Chem. Sec.*, **59**, 28-30 (1956).
2. Allen, Robert, and Larry Yats, *J. Am. Chem. Soc.*, **81**, 5289-5292 (1959).
3. Amemiya, Tozo, et al., *Japan. Pat. 3771* (1959).
4. ———, *Japan. Pat. 13,914* (1960).
5. ———, *Bull. Japan Petrol. Inst.*, **3**, 14-26 (1961).
6. Anglo-Iranian Oil Co., Ltd., *Brit. Pat. 653,499* (1951).
7. Bennett, Clarence, and William Bailey, Jr., *U. S. Pat. 2,564,388* (1951).
8. Brown, Herbert, and Hans Jungk, *J. Am. Chem. Soc.*, **77**, 5579-5584 (1955).
9. N. V. De Bataafsche Petroleum Maatschappij, *Dutch Pat. 76,170* (1954).
10. Dobryanski, A. F., and F. Y. Saprykin, *Oil Gas J.*, **39**, No. 13, 48 (1940).
11. Given, P. H., and D. L. Hammick, *J. Chem. Soc. (London)*, **1949**, 1779-1783.
12. Greensfelder, B. S., G. M. Good, and H. H. Voge, *Ind. Eng. Chem.*, **37**, 1168 (1945).
13. Hansford, R. C., C. G. Myers, and A. N. Sachanen, *ibid.*, 671.
14. Hanson, K. L., Ph.D. thesis, Pennsylvania State Univ. (1965).
15. Hill, R. W., and A. J. Engel, *U. S. Pat. 2,837,582* (1958).
16. Holzman, George, and George Good, *U. S. Pat. 2,656,397* (1953).

17. Hougen, O. A., and K. M. Watson, *Ind. Eng. Chem.*, **35**, 529 (1943).
18. Iwasaki, Takahisa, and Rikijiro Hatta, *Kogyo Kagaku Zasshi*, **63**, 1975-1979 (1960).
19. *Ibid.*, 1980-1985.
20. Johanson, L. N., and K. M. Watson, *Natl. Petrol. News, Tech. Sec.*, **38**, No. 32, 629 (1946).
21. Kemp, J. D., *U. S. Pat. 2,527,824* (1950).
22. Langlois, G. E., *U. S. Pat. 2,585,899* (1952).
23. Luzar, R. V., M.S. thesis, Pennsylvania State Univ. (1961).
24. McCaulay, D. A., and A. P. Lien, *J. Am. Chem. Soc.*, **74**, 6246-6250 (1952).
25. Octafining (Anon.), *Hydrocarbon Processing Petrol. Refiner*, **42**, 206 (Nov., 1963).
26. Pfennig, Reuben, *U. S. Pat. 2,632,779* (1953).
27. Pitts, P. M., Jr., J. E. Conner, Jr., and L. N. Leum, *Ind. Eng. Chem.*, **47**, 770-773 (1955).
28. Schnurmann, Robert, and Edward Kendrick, *Anal. Chem.*, **26**, 1263 (1954).
29. Schrieshiem, Alan, *J. Org. Chem.*, **26**, 3530-3533 (1961).
30. Takita, Kinichi, *Japan. Pat. 17,227.*
31. Taylor, W. J., et al., *J. Res. Natl. Bur. Standards*, **37**, 95-118 (1946).
32. Tsutsumi, Shigeru, and Masanobu Nakamura, *Technol. Rept. Osaka Univ.*, **10**, 509-513 (1960).
33. Satterfield, C. N., and T. K. Sherwood, "The Role of Diffusion in Catalysis," Addison-Wesley, Reading, Mass. (1963).

Manuscript received October 25, 1965; revision received July 25, 1965; paper accepted July 25, 1965. Paper presented at A.I.Ch.E. Minneapolis meeting.

Electrokinetic-Potential Fluctuations Produced by Pipe Flow Turbulence

HSING CHUANG and J. E. CERMAK

Colorado State University, Fort Collins, Colorado

The distribution across a pipe of turbulent intensities, shearing stress, and energy spectra are inferred from measured electrokinetic-potential fluctuations in a fully developed flow of distilled water in a 2.54-cm. diameter glass pipe. These quantities are shown to be in good agreement with those obtained by Laufer and Sandborn with hot-wire anemometers for air flows at the same mean Reynolds number. A tentative analytical model of the phenomenon is constructed and analyzed by Maxwell's electrodynamic field equations for a nonmagnetized medium moving with a velocity which is much smaller than the velocity of light. A set of equations governing the interrelation between the electrokinetic-potential fluctuations and the turbulent velocity-fluctuation components of the flow field in fully developed pipe flow is deduced. Fourier transforms are then introduced and simple relations between the electrokinetic-potential fluctuations and velocity fluctuations are obtained.

The electrokinetic phenomenon was first observed early in the 19th century. The basic idea of an electrical double layer or diffused double layer arising from adsorption of fluids in contact with solid walls was formed and developed during the last hundred years. The fundamental formulation of the electrokinetic phenomenon is attributed to Helmholtz. However, all early experiments and theories of the electrical double layer were concerned with either a laminar flow through a small tube or a flow through a porous diaphragm connecting two liquid containers. Only recently has the study of electrokinetics been extended to turbulent shear flow.

The instantaneous fluctuations of the streaming potential which occur in a turbulent flow were first observed and recorded by Bocquet (*1*). Binder (*2*) was the first researcher to use electrokinetic measurements to infer velocity fluctuations near the wall in a turbulent fluid. Chuang used it to infer velocity fluctuations in a fully developed pipe flow (*3*) and an open channel flow (*4*).

Because of the many experimental difficulties which arise, it is impossible to explore the characteristics of turbulent motion very close to a wall with existing techniques. Our present knowledge of turbulent shear flow in close proximity to a wall is still insufficient to be the basis for a sound and complete theory. It was this particular problem which motivated this study of electrokinetics in a turbulent flow of distilled water.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental equipment consists of the flow system, the electrodes, and the electrical measurement equipment. The flow system is a self-circulating facility as shown in Figure 2. It has a constant-head tank, 15 cm. in diameter, which provides a constant head of 360 cm., upstream and down-

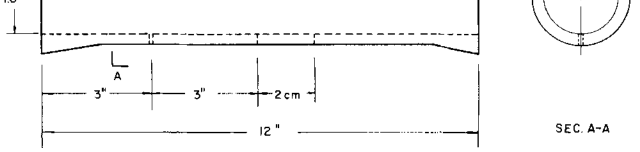

Fig. 1. Test section.

Hsing Chuang is at the University of Louisville, Louisville, Kentucky.