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Kinetics of Mesitylene Isomerization and Disproportionation Over Silica–Alumina Catalyst

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The isomerization and disproportionation of 1,3,5-trimethylbenzene (mesitylene) over silica alumina was carried out at high pressure in the presence of hydrogen. Appreciable catalyst aging was experienced in the first 20–40 hr of operation, after which activity decay was much lower. A bracketing run sequence was adopted to correct data in the latter time period to a common basis. Conversion of mesitylene was dependent upon space velocity, mesitylene partial pressure and temperature, and independent of hydrogen partial pressure or total pressure. Diffusional effects were shown to be negligible.

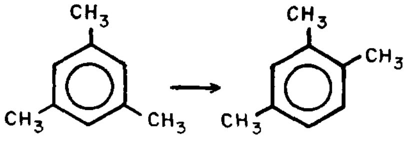
Both isomerization and disproportionation products were obtained with the former predominating. The primary reaction products were 1,2,4-trimethylbenzene (isomerization) and 1,3-di- and 1,2,3,5-tetramethylbenzene (disproportionation). Small secondary isomerization of the primary products was observed. These results are in accord with a single-step, methyl-transfer reaction path.

The isomerization and disproportionation reactions followed a Langmuir-Hinshelwood model with inhibition by reactant. The isomerization reaction showed first-order dependency in reactant while the disproportionation reaction showed second-order dependency in the same. These results are interpreted in terms of an intramolecular surface reaction for isomerization and a bimolecular surface reaction for disproportionation.

INTRODUCTION

The isomerization and disproportionation of trimethylbenzenes over silica–alumina catalysts have been the subject of several papers (*1–4*). At 896°F and atmospheric pressure (*1*), it was found that the main reaction was an isomerization reaction leading to the formation of the two other isomeric trimethylbenzenes. Disproportionation also occurred, though to a lesser extent, and this resulted in the formation of xylenes and tetramethylbenzenes. A decrease in pressure to ~0.1 atm (*1*) suppressed the disproportionation reaction while an increase in pressure to 3 atm (*2*) increased the fraction of disproportionation products, although the isomerization reaction still predominated. From the kinetic study at low pressure and for the temperature range 662–1094°F (*3*), the isomerization reaction was proposed to be first order and the disproportionation reaction second order. Delone, Osityanska, and Petrov (*4*) suggested a free radical mechanism for the disproportionation reaction.

Two primary reactions may be postulated in the isomerization of mesitylene (1,3,5-trimethylbenzene), assuming a single-step methyl transfer in each reaction. The first is an intramolecular reaction (isomerization), which yields 1,2,4-trimethylbenzene as the product.



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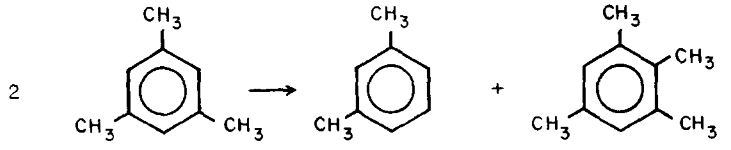
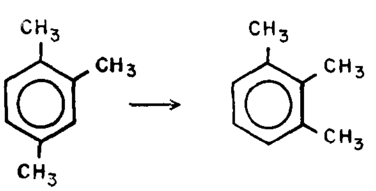
The second is an intermolecular reaction (disproportionation), which predicts the formation of *m*-xylene and 1,2,3,5-tetramethylbenzene.


(2)

Secondary isomerization reactions can also occur. For example, the product formed in reaction (1) may undergo another methyl shift to form 1,2,3-trimethylbenzene.


(3)

Similarly, the products of reaction (2) can undergo methyl shifts: *m*-xylene can isomerize to form the other two xylene isomers, and 1,2,3,5-tetramethylbenzene can isomerize to form 1,2,3,4- and 1,2,4,5-tetramethylbenzene.

In addition to secondary isomerization reactions, secondary disproportionation reactions can also occur. Such reactions could involve methyl transfer between two aromatics of the same or different carbon number. In the present work, contact times were sufficiently low so that these reactions were not significant.

EXPERIMENTAL METHODS

Materials

An American Cyanamid silica–alumina Triple A catalyst (75 wt % SiO_2, 25 wt % Al_2O_3) was used. It was pelleted, crushed to 20–40 mesh sieve size, and calcined at 1000°F for 16 hr. After calcination it had the following physical properties: surface area, 469 m^2/g; pore vol, 0.73 cm^3/g; av pore radius, 36.1 Å; bulk density, 0.54 g/cm^3; and void fraction, 0.57.

Hydrogen was used as a diluent gas. It was purified by passing over a Deoxo catalyst, followed by 5A molecular sieves. Nitrogen, used for pretreatment, was supplied from a large liquid nitrogen source and was passed over 5A molecular sieves. Reagent grade mesitylene (Eastman Organic chemical) was used without further purification. Chromatographic analysis indicated the presence of only 0.05% 1,2,4-trimethylbenzene, about 0.6% of light hydrocarbons with retention times less than that of *m*-xylene, and two unidentified hydrocarbons with retention times between those of 1,2,4- and 1,2,3-trimethylbenzenes and in amounts of less than 0.1%. These impurities did not affect the analyses of products from the mesitylene reaction.

Apparatus and Procedure

A conventional single-pass, fixed-bed catalytic microreactor was used. Details of the reactor, auxiliary equipment and separation system are given by Ackerman, Hartman, and Wright (*5*). Catalyst charges of 5 cm^3 were used for all runs except Run G, which employed 10 cm^3. The catalyst was heated in nitrogen for 2 hr at 950°F. Then the temperature was lowered to the reaction temperature and hydrogen was admitted. After the reaction pressure was attained, the mesitylene was introduced.

A total of seven runs was made. Run conditions are given in Table 1. In each run, conditions were varied, each change constituting a period. In the first three runs, total pressure was varied, as well as space velocity. The next three were carried out at different temperatures but constant space velocity. In the final run, pressure, temperature and space velocity were all varied, and the kinetics were studied over a greater partial pressure range of reactant than in any of the above runs.

Initially, the catalyst aged very rapidly. The duration of the first period was long

TABLE 1
RUN CONDITIONS

Run no.	Total time (hr)	Temp (°F)	Pressure (atm)	Carbon[a] (wt %)
A	55	600	81.8	3.2
B	45	600	61.2	—
C	45	600	40.7	9.8
D	14	500	61.2	12.3
E	18	550	61.2	1.1
F	5	650	61.2	1.6
G	350	600[b]	61.2[c]	8.5

[a] Coke level on catalyst analyzed after run.

[b] Varied from 520 to 625°F later in the run.

[c] Varied from 30.6 to 122 atm later in the run.

for Runs A, B, C and G: 20 hr for the first three and 44 hr for the last. Runs D, E and F consisted of only one period lasting less than 20 hr. For Runs A, B and C, each subsequent period lasted for 5 hr, including a 2-hr off-period for attainment of steady-state conditions (no samples taken), followed by a 3-hr on-period with samples of liquid product taken every hour. For Run G each subsequent period lasted 10 hr, including a 4-hr off-period followed by a 6-hr on-period. Analyses from the last 2 hr of the on-period were used for the kinetic studies. Spot checks on the other samples from the same on-period usually showed good agreement with the last hour sample analysis.

Liquid products were analyzed on an 810 F&M gas liquid chromatograph using a 22-ft FFAP column. Column temperature was maintained at 333°F. Good separation of all liquid products was achieved, except for *m*- and *p*-xylenes, which had identical retention times.

The partial pressure of 1,3,5-trimethylbenzene varied for each run, but was never greater than one twentieth of the total pressure. Since the largest total pressure was 122 atm, the largest value for the partial pressure of the reactant was never greater than 6.12 atm. The vapor pressure at reaction temperature was estimated to be 15.4 and 19.2 atm by extrapolation of vapor pressure data given in Refs. (6) and (7), respectively. Therefore, mesitylene was in the vapor phase at all reaction conditions.

Intraparticle diffusion was estimated by known methods (*8*). Assuming a tortuosity factor of 2, the effective diffusivity was calculated to be 9.6×10^{-4} cm^2/sec for the silica–alumina particles used. From Run B, period 3, the mesitylene conversion rate was 5.8×10^{-7} mole/ml sec and the average mesitylene concentration was 4.2×10^{-5} mole/ml. These values give a Thiele modulus of 0.056 and an effectiveness factor of 1, signifying that diffusional effects on the kinetics of the reaction should be negligible.

Treatment of Data

Because of the low conversions obtained, differential reactor conditions were assumed. The rate of reaction r_x was calculated by,

$$r_x = \left(\frac{F}{V}\right) x, \qquad (4)$$

where F is the liquid feed rate of mesitylene (ml/hr), V is the catalyst volume (ml), and x is the mole fraction conversion to hydrocarbon product. The partial pressure of reactant, $\bar{p}_T$, for a given run was taken as the average of the inlet and outlet conditions. Thus,

$$\bar{p}_T = \left(\frac{1+T}{2}\right)\left(\frac{P}{1+R}\right), \qquad (5)$$

where T is the mole fraction of 1,3,5-trimethylbenzene in the liquid product, P is the total pressure (atm), and R is the feed molar ratio of hydrogen to mesitylene.

As mentioned earlier, catalyst aging occurred during the run, necessitating corrections to the data. The bracketing sequence of Sinfelt (*9*) was adopted for this purpose—periods at a chosen standard condition were repeated between periods at other conditions. Total isomerization and disproportionation products were plotted separately as a function of run time. Smooth curves were drawn through the data of the standard periods to obtain the aging curves. Intermediate run periods were then corrected to a common reference time using the following relationships:

$$\Delta C = C_R^S - C_t^S,$$

$$C_R = C_t + \Delta C,$$

where: ΔC is the correction term; C_R^S and C_t^S are the mole fractions for the standard conditions at the reference time R and another time t, respectively; and C_R and C_t are the mole fractions for any other condition at time R and t, respectively.

Results

Initial Runs

A typical plot of total conversion of mesitylene as a function of run time is presented in Fig. 1 for Run B. An appreciable loss in catalyst activity was experienced in the first 20 hr of reaction, followed by a slower activity decline at later times. Other pressure and temperature conditions gave similar patterns of catalyst aging with the exception of the lowest pressure run which failed to reach the slow activity decline stage even after 45 hr. In general, increasing total pressure and temperature at otherwise identical run conditions resulted in higher conversions. It will be shown later that the total pressure effect can be attributed solely to the increase in partial pressure of mesitylene.

Mass transfer effects were assessed in Run A by running at constant feed partial pressure and varying total space velocity. Calculated rates of isomerization and disproportionation did not vary over a fourfold variation in space velocity, signifying that gas phase diffusional effects were unimportant.

Table 2 presents detailed liquid product analyses for Run B. All nine isomers from di- to tetra-substituted benzenes were found. Inspection of these data reveals the following salient points: (a) the ratio of total isomerization to disproportionation products was about 10/1, indicating isomerization was much faster than disproportionation; (b) the primary isomerization and disproportionation products predicted by Eqs. (1) and (2) predominated; (c) secondary reactions of tetramethylbenzenes were greater that those of tri- or dimethylbenzenes; and (d) the total tetramethylbenzenes recovered were consistently lower than the dimethylbenzenes by a small amount. The last point was noted in all runs and an average value was used in kinetic analyses.

Table 3 includes a comparison of equilibrium and experimental values for product isomer ratios. Typical experimental values are taken from Run B, period 6, and Run G, period 7. It is apparent from the comparison that the two trimethylbenzene isomer products are not in equilibrium with each other, nor is there any equilibrium among the xylenes or tetramethylbenzenes.

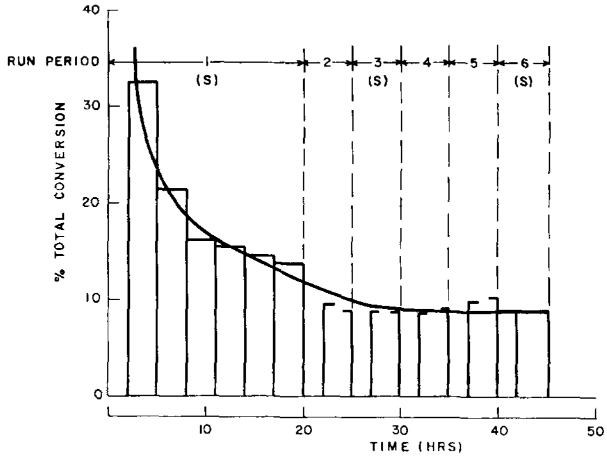


FIG. 1. Total conversion of mesitylene for Run B. Conditions given in Table 2.

TABLE 2

Product Composition Data from Run B[a]

Period:	1(S)	2	3(S)	4	5	6(S)
LHSV:	1.5	2.0	1.5	0.5	1.0	1.5
Methylbenzenes (mole %)						
1,3- + 1,4-	0.998	0.616	0.634	0.599	0.621	0.633
1,2-	0.052	0.031	0.037	0.026	0.038	0.025
1,3,5-	87.6	91.4	91.8	91.2	90.3	91.7
1,2,4-	10.2	7.09	6.77	7.45	8.33	6.92
1,2,3-	0.256	0.143	0.140	0.133	0.165	0.145
1,2,4,5-	0.213	0.134	0.118	0.102	0.118	0.093
1,2,3,5-	0.665	0.573	0.447	0.445	0.421	0.426
1,2,3,4-	0.069	0.049	0.041	0.034	0.033	0.031
Conversion	12.4	8.64	8.19	8.79	9.73	8.27
D	1.05	0.647	0.671	0.625	0.659	0.658
A	0.947	0.756	0.606	0.581	0.572	0.549
$\bar{D}$	0.999	0.701	0.639	0.603	0.616	0.604
I	10.5	7.23	6.91	7.58	8.50	7.07
$I/\bar{D}$	10.5	10.3	10.8	12.6	13.8	11.7
$\bar{p}_T$	—	2.67	2.02	0.693	1.32	2.02
r_I	—	0.129	0.103	0.0373	0.0828	0.103
r_D	—	0.0115	0.0092	0.0030	0.0063	0.0092

[a] Run B, conditions: Temp, 600°F; Pressure, 61.2 atm; H_2 flow rate, 3.40×10^4 ml/hr; charge, 5 cm^3 catalyst. The symbols have the following meanings: D refers to total xylene concentration. A refers to total tetramethylbenzene concentration. I refers to the sum of 1,2,4- and 1,2,3-trimethylbenzene concentration. $D = (D + A)/2$. (S) refers to those run periods which are standard conditions. p_T is the average partial pressure of reactant (atm). r_I and r_D are rates of formation of isomerization and disproportionation products (min^{-1}).

TABLE 3

Comparison of Experimental and Equilibrium Values of Isomer Distributions[a]

Methylbenzene ratios	Isomer ratio		
		Experimental	
	Equilibrium[a]	Run B, period no. 6	Run G, period no. 7
1,2,4-/1,2,3-	8.78	46	54
1,2,3,5-/1,2,3,4-	3.33	13.8	10.0
1,2,3,5-/1,2,4,5-	1.48	4.6	4.0
(1,3- + 1,4)/1,2-	3.56	25	—

[a] Hastings, S. H., and Nicholson, D. E., *J. Chem. Eng. Data 6,* 1 (1961).

Kinetic Run

Since preliminary runs showed appreciable catalyst aging, direct comparison between runs to obtain kinetic information on pressure and temperature effects was rendered impractical owing to differences in catalyst activity in each run. Therefore, a single, extended run was made (Run G) to investigate these effects. A larger catalyst charge (10 cm^3) was employed in order to maintain reasonable conversions for the extensive time required to obtain meaningful kinetic data. Run conditions and results are summarized in Table 4.

In general, individual product distributions were similar to those of Run B discussed previously. However, as a result of the larger partial pressure range covered, a definite variation in the isomerization to disproportionation product ratio ($I/\bar{D}$) was observed in this run, as shown in Fig. 2. A large change in $I/\bar{D}$ ratio occurred when $\bar{p}_T$ was less than 3 atm, while little change occurred above this partial pressure. Values for Run B over a smaller partial pressure range agreed well with Run G as shown in Fig. 2.

The rate data were first subjected to a

TABLE 4
KINETIC DATA FOR RUN G[a]

Period	Temp (°F)	P (atm)	$H_2 \times 10^{-4}$ (cc/hr)	F (ml liq/hr)	$\bar{p}_T$	r_I	r_D
2	600	61.2	1.41	9.0	5.42	0.0223	0.0045
3_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
4_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
5	600	61.2	1.13	5.0	3.84	0.0381	0.00532
6	600	61.2	3.40	6.5	1.79	0.0245	0.00156
7_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
8	600	61.2	0.85	10.0	8.99	0.0470	0.00695
9	600	61.2	4.53	2.5	0.530	0.0107	0.00427
10_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
11	600	61.2	2.83	9.0	2.92	0.0329	0.00349
12	600	61.2	0.85	10.0	9.01	0.0481	0.00596
13	600	61.2	3.40	4.0	1.12	0.0189	0.00099
14_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
15	600	122	1.70	7.5	7.88	0.0462	0.00575
16_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
17	600	30.6	1.70	7.5	1.99	0.0266	0.00188
18_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
19	550	61.2	1.70	7.5	4.02	0.0189	0.0027
20	520	61.2	1.70	7.5	4.04	0.0136	0.0019
21_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
22	575	61.2	1.70	7.5	3.99	0.0280	0.0034
23_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
24_S	600	61.2	1.70	7.5	3.94	0.0375	0.0045
25	625	61.2	1.70	7.5	3.89	0.0646	0.0068
26_S	600	61.2	1.70	7.5	3.94	0.0375	na[b]
27[c]	600	61.2	1.70	7.5	3.74	0.0379	na
28_S	600	61.2	1.70	7.5	3.94	0.0375	na
29[d]	600	61.2	1.70	7.5	3.55	0.0374	na
30_S	600	61.2	1.70	7.5	3.94	0.0375	na

[a] See Table 2 for definition of symbols.
[b] na = not analyzed.
[c] Feed contains a blend of 95% mesitylene and 5% 1,2,3,5-tetramethylbenzene.
[d] Feed contains a blend of 90% mesitylene and 10% 1,2,3,5-tetramethylbenzene.

simple power law rate equation. Plots of log r versus log $\bar{p}_T$ showed noticeable curvature indicating that the kinetic expressions were more complex than simple first- or second-order reactions.

Next, the data were plotted using the Langmuir-Hinshelwood theory of adsorption with reactant inhibition. Best fits were found when isomerization was assumed to occur by a single-site surface reaction mechanism, viz,

$$r_I = \frac{k_I K_1 \bar{p}_T}{1 + K_1 \bar{p}_T}, \tag{6}$$

and disproportionation via a dual-site surface reaction,

$$r_D = k_D \left(\frac{K_1 \bar{p}_T}{1 + K_1 \bar{p}_T} \right)^2 \tag{7}$$

where k_I and k_D are rate constants for isomerization and disproportionation, respectively, and K_1 is the adsorption equilibrium constant for mesitylene. Figures 3 and 4 contain plots of these equations in linearized form. The data fit the proposed equations well. Values for the equilibrium constant K_1 obtained from each plot are in good agreement with each other, and are included in Table 5.

As an independent check of both the correctness of the rate models adopted and the catalyst aging corrections, ratios of the

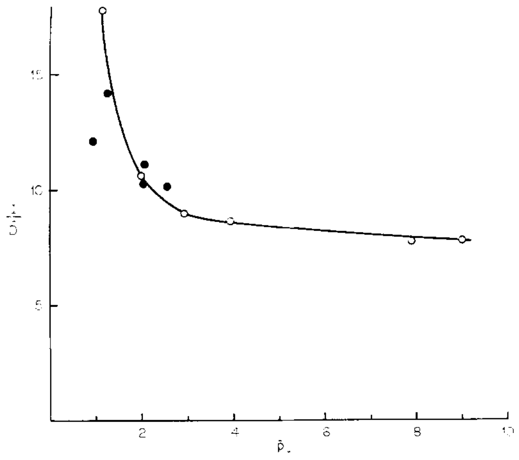


FIG. 2. Variation of the isomerization–disproportionation ratio, $I/\bar{D}$, with partial pressure of mesitylene, $\bar{p}_T$: (●) Run B; (○) Run G.

uncorrected isomerization (I) to disproportionation (D) product concentrations at various periods in a run were calculated and plotted according to Eq. (8),

$$\frac{I}{D} = \frac{k_I}{k_D K_1}\left(\frac{1}{\bar{p}_T}\right) + \frac{k_I}{k_D}. \tag{8}$$

This equation was derived from combination of Eqs. (4), (6) and (7), where $x = I$ for isomerization and $x = D$ for disproportionation. This relationship should hold at all times provided the aging function with time is similar for isomerization and disproportionation, i.e., k_I/k_D = constant. The results are given in Fig. 5. Uncorrected data were used and only values after the ninth reaction period were included as the $I/\bar{D}$ ratio for the standards did not approach a constant value until after this period. The value for K_1 from this plot was in good agreement with those derived from Figs. 3 and 4 as shown in Table 5.

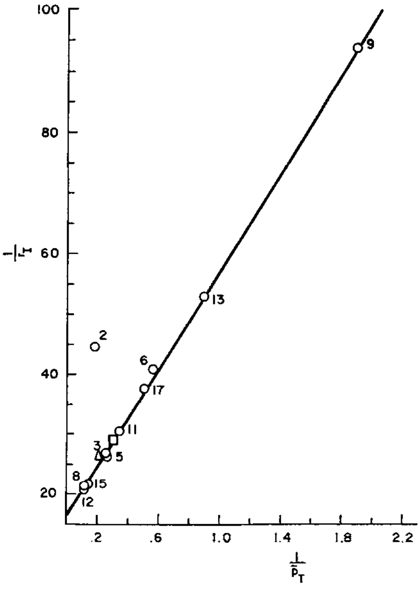


FIG. 3. Correlation of isomerization data with Eq. (6) for Run G: (△) 5% blend; (□) 10% blend.

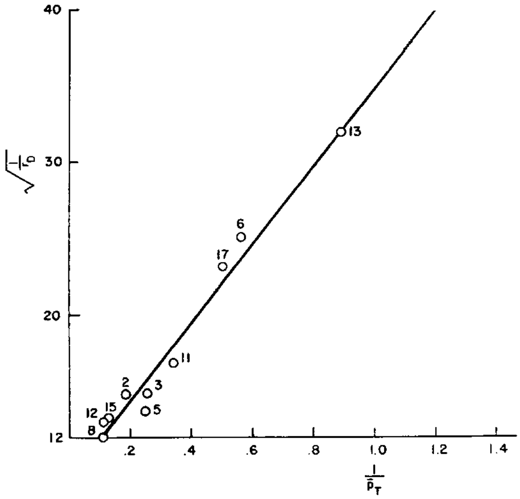


FIG. 4. Correlation of disproportionation data with Eq. (7) for Run G.

In order to check for product inhibition, two blends were prepared consisting of 1,2,3,5-tetramethylbenzene in 1,3,5-trimeth-

TABLE 5
KINETIC RESULTS FOR ISOMERIZATION AND DISPROPORTIONATION OF 1,3,5-TRIMETHYLBENZENE

	600°F		
Reaction	k (min^{-1})	K_1 (atm^{-1})	E_a (kcal/mole)
Isomerization (Eq. 6)	0.0617	0.40	16.9
Disproportionation (Eq. 7)	0.0123	0.35	13.6
Isomerization and Disproportionation (Eq. 8)	—	0.43	—

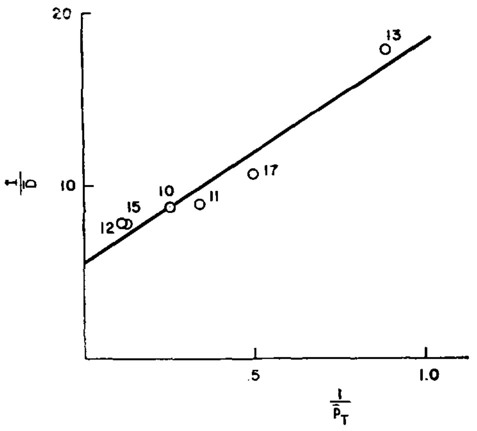


FIG. 5. Correlation of isomerization and disproportionation data with Eq. (8) for Run G.

ylbenzene. One contained 5% of 1,2,3,5-tetramethylbenzene by weight and the other 10%. The reaction was carried out in Run G, periods 27 and 29; standard runs with pure mesitylene were made before, between and after these runs to assure that no unusual catalyst activity changes had resulted. The data are given in Table 4 and shown in Fig. 3. From the plot in Fig. 3, it can be seen that the blends fall on the smooth curve indicating that the tetramethylbenzene does not measurably inhibit the isomerization reaction.

The temperature dependence of the overall isomerization and disproportionation reactions was determined at a single set of run conditions. Plots of log r_I and log r_D versus $1/T$ gave good straight lines. Apparent activation energies calculated from the slopes are given in Table 5. For the isomerization reaction, $E_a = 16.9$; for the disproportionation reaction, $E_a = 13.6$ kcal/mole.

DISCUSSION

Reaction Products

From an analysis of the product composition, the intra- and intermolecular methyl transfer reactions are in accord with a single methyl shift per reaction step. For the intramolecular isomerization reaction, a shift of a methyl group in 1,3,5-trimethylbenzene should lead to the formation of 1,2,4-trimethylbenzene, which is experimentally observed. For the intermolecular disproportionation reaction, a transfer of a methyl group from one mesitylene molecule to another should lead to the formation of *m*-xylene and 1,2,3,5-tetramethylbenzene, which is also experimentally observed.

In addition to these primary products, secondary isomerization products are also formed, but to a lesser extent. Since the rate of the intramolecular isomerization reaction was found to be much faster than the rate of the intermolecular reaction for the primary reactions, it is most probable that intramolecular isomerization is also the principal path of the secondary reactions.

Detailed examination of secondary product distributions reveals two interesting observations, viz: (a) the degree of secondary isomerization of 1,2,3,5-tetramethylbenzene (leading to 1,2,4,5- and 1,2,3,4-) is about 10–15 times greater than that of 1,2,4-trimethylbenzene (leading to 1,2,3-) and; (b) the ratio of 1,2,4,5- to 1,2,3,4-products is about 3:1. The first fact is in line with the generally greater reactivity of substituted alkylbenzenes due to activation of the aromatic nucleus (*10*). The second fact involves the relative migration of the 1- vs 5-position methyl group in 1,2,3,5-tetramethylbenzene; the 1-position methyl is apparently more labile, which may be due to the activating influence of the other methyl groups.

Kinetic Model

Mamedaliev *et al.* (*3*) studied the isomerization of trimethylbenzenes over silica–alumina at higher temperatures. They found the isomerization reaction to follow first-order, and the disproportionation reaction second-order dependency in partial pressure of reactant. Because of higher conversions, their kinetic analysis included contributions from back reactions, but they did not consider inhibition terms in their correlation. In their studies on the isomerization of 1,3,5-trimethylbenzene to 1,2,4-trimethylbenzene, they obtained a value of 16.9 kcal/mole for E_a, which is identical with the value obtained in the present work.

The kinetic model which best correlates our rate data for isomerization and disproportionation is based on a Langmuir-Hinshelwood adsorption mechanism. In the general case, one has to consider three limiting rate processes, viz, adsorption, surface reaction, and desorption. Applying standard steady-state treatments (*11*), mathematical equations for the three limiting processes for primary isomerization and disproportionation reactions were derived based on the reaction sequence given in Fig. 6. Final kinetic expressions for rates of isomerization and disproportionation are shown in Table 6.

$$\mathrm{T + S} \overset{k_1}{\rightleftarrows} \mathrm{T\text{-}S} \qquad K_1 = \frac{\theta_2}{\theta_1 p_T} \qquad \text{(A1)}$$

$$\mathrm{T\text{-}S} \overset{k_2}{\rightleftarrows} \mathrm{I\text{-}S} \qquad K_2 = \frac{\theta_3}{\theta_2} \qquad \text{(A2)}$$

$$\mathrm{I\text{-}S} \overset{k_3}{\rightleftarrows} \mathrm{I + S} \qquad K_3 = \frac{\theta_3}{\theta_1 p_I} \qquad \text{(A3)}$$

$$2\,\mathrm{T\text{-}S} \overset{k_{22}}{\rightleftarrows} \mathrm{D\text{-}S + A\text{-}S} \qquad K_{22} = \frac{\theta_4\theta_5}{\theta_2^2} \qquad \text{(A4)}$$

$$\mathrm{D\text{-}S} \overset{k_4}{\rightleftarrows} \mathrm{D + S} \qquad K_4 = \frac{\theta_4}{\theta_1 p_D} \qquad \text{(A5)}$$

$$\mathrm{A\text{-}S} \overset{k_5}{\rightleftarrows} \mathrm{A + S} \qquad K_5 = \frac{\theta_5}{\theta_1 p_A} \qquad \text{(A6)}$$

FIG. 6. Reaction sequence for isomerization and disproportionation: p is partial pressure; S is surface site; T is 1,3,5-trimethylbenzene; I is 1,2,4-trimethylbenzene; D is 1,3-dimethylbenzene; A is 1,2,3,5-tetramethylbenzene; θ_1 is fraction of surface unoccupied; θ_2 is fraction of surface occupied by T; θ_3 is fraction of surface occupied by I; θ_4 is fraction of surface occupied by D; θ_5 is fraction of surface occupied by A.

Our results showed isomerization to be first order and strongly reactant inhibited. Therefore, adsorption is ruled out as the rate-controlling step. Further, disproportionation was found to be second order and also reactant inhibited, eliminating adsorption and desorption control. Accordingly, the disproportionation reaction is limited by surface reaction, i.e., reaction of adjacent adsorbed reactant molecules. That isomerization is also surface reaction controlled is evidenced by the equality of the equilibrium adsorption constant obtained from independent analyses of the isomerization and disproportionation kinetics. Additional evidence for surface reaction control derives from the variation of the $I/\bar{D}$ ration with $\bar{p}_T$. Consideration of the rate

TABLE 6

KINETIC EXPRESSIONS FOR ISOMERIZATION AND DISPROPORTIONATION[a]

	Rate-limiting process		
	Adsorption	Surface	Desorption
Slow reaction(s)	(A1)	(A2) and (A4)	(A3), (A5) and (A6)
Isomerization rate	$\frac{k_1K_ap_T}{(1+K_a)Y_a}$	$\frac{k_2K_1p_T}{Y_s}$	$\frac{k_3K_1K_2p_T}{Y_d}$
Disproportionation rate	$\frac{k_1p_T}{(1+K_a)Y_a}$	$\frac{k_{22}K_1^2p_T^2}{Y_s^2}$	$\frac{K_1(k_4k_5K_{22})^{1/2}p_T}{Y_d}$

$$\text{where: } K_a = \left(\frac{K_2}{K_3}\right)\left(\frac{K_4K_5}{K_{22}}\right)^{1/2}$$

$$Y_a = 1 + \left(\frac{K_3}{K_2} + K_3\right)p_I + K_4p_D + K_5p_A$$

$$Y_s = 1 + K_1p_T + K_3p_I + K_4p_D + K_5p_A$$

$$Y_d = 1 + \left[K_1 + K_1K_2 + K_1\left(\frac{k_5K_{22}}{k_4}\right)^{1/2} + K_1\left(\frac{k_4K_{22}}{k_5}\right)^{1/2}\right]p_T$$

[a] See Fig. 6 for definition of symbols.

equations given in Table 6 shows that for adsorption or desorption control, $I/\bar{D}$ (which is proportional to the ratio of their respective rates) should be independent of $\bar{p}_T$.

The surface reaction model dictates an inhibition term which includes reactant and products (Table 6). However, at low conversion, the product terms are negligible, provided their adsorption constants are not appreciably larger than that of the reactant. The latter situation must be true because addition of 10% tetra- product hardly affected the isomerization rates, from which we estimate that $K_5 < 2\,K_1$ for less than 10% error in the observed rate. It should be noted in this connection, that the isomerization product adsorption constant is very likely close to that of the reactant in view of chemical and structural similarities. Thus, the denominator terms in Eqs. (6) and (7) should rigorously be replaced by $[1 + K(\bar{p}_T + p_I)]$, but this makes little difference in the data analysis.

It should be mentioned that the correct kinetics for both isomerization and disproportionation are not obtained assuming a Rideal-type mechanism as the slow step in the disproportionation reaction, viz,

$$\text{T-S} + \text{T} \dashrightarrow \text{D} + \text{A-S},$$

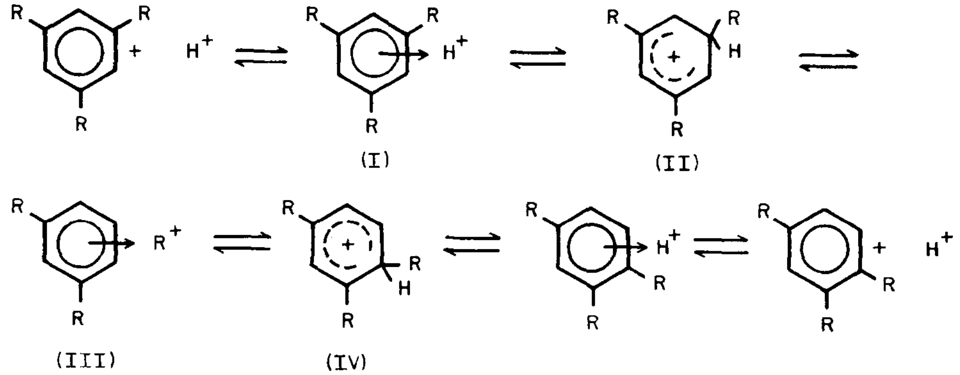
in place of Eq. (A4) in Fig. 6. It can be shown that this case leads to an I/D ratio of

$$\frac{I}{D} = \frac{k_I}{k_D}\left(\frac{1}{\bar{p}_T}\right),$$

which is to be compared with Eq. (8). The data of Fig. 5 clearly show that the correlation does not go through the origin as predicted if a Rideal reaction were operative.

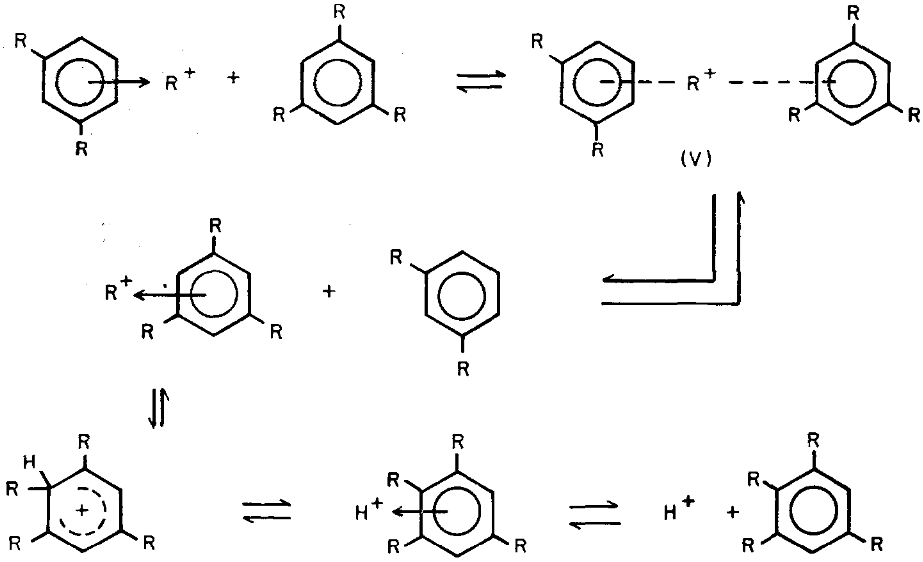
Reaction Mechanism

In the theory of electrophilic substitutions in acid-catalyzed media, carbonium-ion intermediates play an important role in the reaction (*12*). Silica–alumina exhibits the characteristics of a strong acid, containing Lewis and Bronsted acidic sites (*13*). Isomerization of butenes over silica–alumina has been shown to occur via a carbonium-ion mechanism (*14*). Pollitzer and Donaldson (*15*) have reviewed the evidence for intra- versus intermolecular transfer for isomerization of xylenes over acidic catalysts and favor the former path. Invoking these concepts, a reaction mechanism for isomerization based on carbonium-ion chemistry can be proposed:



Here R represents the methyl group. All species are assumed to be adsorbed on the catalyst surface. The proton needed to form the carbonium ion is presumably donated by surface hydroxyl groups of the silica–alumina, although unsaturated carbonaceous material could also be a source of protons, as has been recently suggested (*16*). According to the theory (*17*), a π-complex (I) is first formed, followed by a σ-complex (II). The methyl group transfer may occur directly from II to IV by a Wagner-Meerwein shift (*18*). Structure III may be considered an intermediate, wherein the methyl group is positioned between the original 1 and 2 positions in the transition state, since the methyl group migration is restricted to a single-step jump per reaction event. Deprotonation of the isomerized carbonium ion leads to the 1,2,4-trimethyl isomer.

Disproportionation has kinetically been shown to occur via bimolecular surface reaction. A plausible mechanism for this reaction would involve reaction of a carbonium ion with an adsorbed mesitylene molecule according to the sequence:



leading to the expected disproportionation products. The intermediate structure (V) has been proposed by Nelson and Broun *(12)* as the transition state in aromatic disportionation in acidic media.

Introduction of the carbonium-ion mechanism does not formally alter the kinetic analysis. Consider the simplified reaction sequence:

$$\begin{gathered} \mathrm{T} + \mathrm{S} \rightleftharpoons \mathrm{T\text{-}S} \\ \mathrm{T\text{-}S} \rightleftharpoons \mathrm{T\text{-}S}^+ \\ \mathrm{T\text{-}S}^+ \rightarrow \mathrm{I\text{-}S}_c{}^+ \rightleftharpoons \mathrm{I\text{-}S} \\ \mathrm{T\text{-}S}_c{}^+ + \mathrm{T\text{-}S} \rightarrow \mathrm{D\text{-}S} + \mathrm{A\text{-}S} \end{gathered}$$

where $\mathrm{T\text{-}S}_c{}^+$ and $\mathrm{I\text{-}S}_c{}^+$ represent the carbonium ions for feed, T, and isomer, I, respectively, and the other symbols are as defined in Fig. 6. We do not distinguish here between π- and σ-complexes for simplicity. Adsorbed T is in equilibrium with its carbonium ion as is adsorbed I. For isomerization, the rate of conversion of T carbonium ions to I carbonium ions is assumed to be the slow step in the reaction path.[*] For disproportionation, the rate of reaction between T carbonium ions and adsorbed T (since $\mathrm{T\text{-}S} \gg \mathrm{T\text{-}S}_c{}^+$) is taken to be the controlling step. Inclusion of these reactions and assumptions into the mathematical treatment described above yields the following rate expressions,

$$r_I{}^c = \frac{k_I K_c}{1 + K_c}\left(\frac{(1 + K_c)K_1\bar{p}_T}{1 + (1 + K_c)K_1\bar{p}_T}\right)$$

$$r_D{}^c = \frac{k_D K_c}{(1 + K_c)^2}\left(\frac{(1 + K_c)K_1\bar{p}_T}{1 + (1 + K_c)K_1\bar{p}_T}\right)^2$$

where K_c is the equilibrium constant for carbonium-ion formation. These equations are formally identical to the equations used in the data analysis, viz, Eqs. (6) and (7). Hence, the only difference in the carbonium-ion mechanism and the simple surface reaction model is in the interpreta-

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[*] From structural similarity (e.g., ionization potentials, heats of formation, etc.), 1,3,5- and 1,2,4-trimethylbenzene should have nearly identical energy barriers for formation of their carbonium ions. Hence, neither can be rate-determining alone, and the barrier between carbonium ions (transition state) must be largest.

tion of the constants, where now the experimental rate and adsorption constants include the carbonium-ion equilibrium constant. Hightower and Hall (*19*) reported similar results for cyclopropane isomerization

CONCLUSIONS

Reaction of 1,3,5-trimethylbenzene over a silica–alumina catalyst produced as primary products 1,2,4-tri-, 1,3,-di- and 1,2,3,5-tetramethylbenzenes. Isomerization was appreciably faster than disproportionation. Some secondary isomerization of the primary products was observed.

Both isomerization and disproportionation reactions followed the Langmuir-Hinshelwood theory for heterogeneous surface reaction with reactant inhibition. The isomerization reaction was first order and the disproportionation reaction second order in 1,3,5-trimethylbenzene. Thus, the kinetic correlation suggests an intramolecular surface reaction for isomerization and a bimolecular surface reaction for disproportionation, as predicted by theory.

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