Isomerization and Transmethylation over Platinum-on-Silica Catalyst

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The reactions of 1-methyl-2-ethylbenzene and *n*-heptane over platinum on silica gel catalyst were studied in a continuous flow system.

Isomerization over platinum on the neutral silica support proceeded through cyclic intermediates. 1-Methyl-2-ethylbenzene gave *n*-propylbenzene, and *n*-heptane was isomerized to 3-methylhexane in this way.

Small amounts of dimethylbenzenes, cymenes, methyl-*n*-propylbenzenes, and diethylbenzenes were formed from methylethylbenzene in a new type of transmethylation. The reaction probably involved methyl radicals and may be considered as the reverse reaction of hydrogenolysis.

INTRODUCTION

The conversion of methylethylbenzene to *n*-propylbenzene via cyclic intermediates represents a new type of isomerization first observed by Shephard and Rooney (*1*). More recently, Anderson and Avery (*2*) reported on isomerization of butanes and pentanes on metal films, while Barron *et al.* (*3*) experienced isomerization of hexanes on platinum films and on supported platinum catalysts. The latter authors reported isomerization with platinum on alumina at temperatures lower (230°C) than those generally regarded as necessary for acid catalysis by the support.

We have studied the conversion of methylethylbenzene and of *n*-heptane in a continuous flow unit, wherein the partial pressure of the hydrocarbon reactant, its space velocity, and the hydrogen-to-hydrocarbon mole ratio are kept constant. Reaction kinetics, therefore, may be studied under controlled conditions.

We have tested catalysts comprising platinum on both neutral (SiO₂) and acidic (Al₂O₃) supports in order to distinguish between types of mechanism. Radiotracer experiments using 1,3-dimethylcyclopentane have also been carried out to lend further confirmation of the mechanisms proposed.

EXPERIMENTAL

1-Methyl-2-ethylbenzene experiments. 1-Methyl-2-ethylbenzene was purchased from Columbia Organic Chemicals Company, Columbia, South Carolina. Purity, as measured by gas-liquid chromatography (GLC) was 99.8 mole % 1-methyl-2-ethylbenzene, 0.15% 1-methyl-3-ethylbenzene, and 0.08% xylenes and other light hydrocarbons. Sulfur content was 0.3 ppm.

The continuous flow tubular reactor consisted of a 50-cm long, ¼-inch OD stainless steel tube. Five-tenths ml of 100/200 mesh catalyst was charged to the reactor; and experiments were carried out at 400°C, atmospheric pressure, and a hydrogen-to-hydrocarbon molar dilution ratio of 3. Liquid feed rate was varied to obtain different conversion levels. Reaction products were collected in an acetone–dry ice trap. Reaction periods were 75–160 min long. A Beckman chromatographic sample valve was located immediately below the reactor, where it was held at 232°C for use in direct reaction effluent sampling.

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Liquid product analyses were carried out in a 300-ft long, 0.02-inch ID capillary column packed with Ucon LB 550-X polypropylene glycol. A Perkin-Elmer Model 800 gas chromatograph was used.

Reaction effluent samples were analyzed over a 21.5-ft long, $\frac{3}{16}$-inch OD column filled with silicon elastomer on firebrick. Ethane, propane, and the alkyl aromatics were well resolved by this column. Indan and indene were eluted as one peak. Indan/indene ratios were determined from the capillary column liquid product analyses.

n-Heptane experiments. n-Heptane was purchased from the Phillips Petroleum Company and was mixed with m-xylene at a ratio of 4:1 for purposes of providing a nearly constant aromatics content in the reaction mixture. This feed was desulfided over a sulfur-free cobalt-molybdenum catalyst and was found to contain less than 1 ppm sulfur. Reactant composition was 79.9 mole % n-heptane, 19.7% xylene, 0.29% isomeric heptane, and 0.10% toluene.

The continuous flow tubular reactor was as above with a 0.125-g 24 to 28 mesh size catalyst charge diluted 10:1 with Alundum of the same mesh size. Experiments were carried out at 482°C temperature, 18 atm pressure, at a 6:1 hydrogen-to-hydrocarbon molar ratio, and 10 cc/hr feed rate. Analyses were carried out by reaction effluent sampling as above with the aid of a Beckman process chromatograph. A three-column analysis provided nearly complete separation of all reaction components. These chromatographic columns consisted of (1) 7-ft by $\frac{3}{16}$-inch OD 20% squalane on firebrick; (2) 20-ft by $\frac{3}{16}$-inch OD 1.5% squalane on Pelletex; (3) 20-ft by $\frac{3}{16}$-inch OD 20% Tergitol NP-35 on firebrick.

Radiotracer experiments were carried out using methyl-1-C^{14}-1,3-dimethylcyclopentane obtained from Nuclear Research Chemicals, Inc., Orlando, Florida. The tracer was added continuously at the head of the reactor by syringe at a rate of 0.25 ml/hr of 0.1 mC/ml specific activity material, while the n-heptane plus m-xylene mixture was fed as usual. A Nuclear-Chicago radiotracer chromatographic detection system was employed on the chromatographic effluent.

Catalysts. The platinum-on-silica-gel catalyst was prepared from Davison desiccant-grade silica gel (BET surface area = 800 m²/g). The silica gel was impregnated at room temperature with H_2PtCl_6 solution. The catalyst was first kept at room temperature for 16 hr then dried at 105°C in vacuum and calcined in air at 450°C for 3 hr.

The platinum-on-alumina catalyst employed for comparative purposes was a commercial platinum-halogen-alumina preparation with approximately 0.8 wt % each of platinum and halogen.

Before the methylethylbenzene experiments, the catalysts were reduced in situ 2 hr each at 200°, 315°, and 400°C in 1 atm of hydrogen. When more than one experiment was made on the same platinum-on-silica sample, the catalyst was regenerated with a 1:1 air-nitrogen mixture at 480°C. Regeneration cycles were ½ to 1 hr long and were followed by 2-3 hr treatments with hydrogen at 400°C. Catalyst activities increased slightly after the first regeneration but decreased 30% overall between the first and fourth regenerations (Table 1, Runs 1, 2, and 5).

A 4-hr reduction in hydrogen at 482°C preceded the experiments with n-heptane. Catalysts were not regenerated during the experiments.

DISCUSSION

1-Methyl-2-Ethylbenzene

Dehydrocyclization to produce indan is the main reaction of 1-methyl-2-ethylbenzene over platinum on silica. The rate of this reaction decreased with increasing contact time (Fig. 1). There are two possible causes:

(1) Desorption limitation by one of the products (e.g., indene). Such a kinetic scheme in which the reaction rate corresponded to the rate of desorption of a dehydrocyclization product was proposed by Sinfelt et al. (4).

(2) Limitation by the methylethylbenzene ⇌ indan equilibrium. Data on this equilib-

TABLE 1

REACTIONS OF 1-METHYL-2-ETHYLBENZENE OVER PLATINUM ON HIGH SURFACE AREA
(800 M²/G) DAVISON SILICA GEL CATALYST[a]

Catalyst:		2% Platinum on silica gel				
Experimental No.:		1	2	5	3	4
LHSV:		8	8	8	3.6	2
Feed partial pressure (atm):		0.25	0.25	0.25	0.23[b]	0.25
Number of previous catalyst regenerations:		0	1	4	2	3
Length of run (min):		85	85	76	85	160
Liquid sample collected (min):		40–80	40–80	40–75	44–82	70–155
Reaction mix sampling time (min):		65	65	65	80	145
Reactions	Products (mole %)					
Dehydrocyclization	Indan	14.21	15.88	11.36	17.25	20.35
	Indene	0.66	0.65	0.59	0.89	1.10
	n-Propylbenzene	3.33	3.51	1.73	5.18	6.63
	Total dehydrocyclization	18.20	20.04	13.68	23.32	28.08
Hydrogenolysis	o-Xylene + CH₄	0.75	0.64	0.42	1.09	1.28
	Ethylbenzene + CH₄	0.59	0.50	0.30	0.82	1.02
	Toluene	1.18	0.82	0.52	1.33	1.49
	Ethane	1.18	0.82	0.53	0.84	1.45
	Benzene	0.20	0.16	0.08	0.27	0.37
	Propane	0.11	0.09	0.03	0.17	0.22
Dehydrogenation	o-Methylstyrene	0.05	0.05	0.08	0.09	0.08
Isomerization	1-Methyl-3-ethylbenzene	0.02	0.01	0.05	0.10	0.16
Methyl transfer	Dimethylethylbenzene	—	—	0.02	0.06	0.04
	Cymenes	—	—	0.02	0.03	0.01
	Methyl-n-propylbenzenes	0.02	—	0.02	—	—
	Diethylbenzenes	—	0.01	—	0.02	0.05
	Cumene	—	—	0.0015	0.044	0.06
n-Propylbenzene, % of equilibrium with 1-methyl-2-ethylbenzene[c]		16.3	17.4	8.0	26.5	35.9
Indan/indene		22	24	19	19	19
Deethylation/aromatic demethylation (toluene/ethylbenzene)		2	1.6	1.7	1.6	1.5
Aliphatic/aromatic demethylation (o-xylene/ethylbenzene)		1.3	1.3	1.4	1.3	1.3

[a] Reaction conditions, 400°C temp., atmospheric total pressure, and a H₂-to-feed mole ratio of 3.

[b] H₂-to-feed mole ratio was 3.34.

[c] Equilibrium n-propylbenzene/1-methyl-2-ethylbenzene ratio at 400°C = 0.33.

rium are unavailable. The reverse reaction of indan ring splitting may give either 1-methyl-2-ethylbenzene or n-propylbenzene. At 400°C, equilibrium conversion of 1-methyl-2-ethylbenzene to n-propylbenzene is 24.8% (4). Conversion to n-propylbenzene, however, was one-third or less of this value even at the lowest space velocity (Fig. 1). If the rate were limited by the methylethylbenzene ⇌ indan equilibrium, then n-propylbenzene formation would have continued to increase. On the other hand, if the rates are limited by desorption

of one of the reaction products, the rate of n-propylbenzene formation would decrease in a similar manner to the conversion to indan and indene. This is what we observed. The rate of dehydrocyclization of alkylbenzenes may have been limited by the desorption of one of the reaction products, most probably indene.

Three types of hydrogenolysis reactions were observed with methylethylbenzene. The products obtained by breaking different C–C bonds were toluene + ethane,
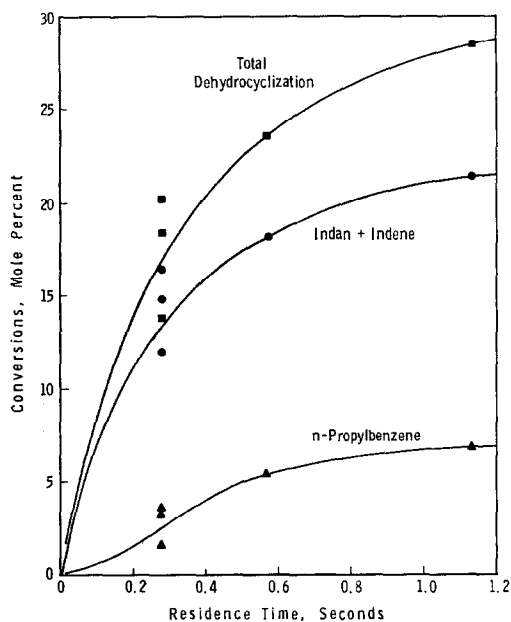
FIG. 1. Dehydrocyclization of 1-methyl-2-ethylbenzene over 2% Pt on SiO₂ catalyst at 400°C temperature.

ortho-xylene + methane, and ethylbenzene + methane (Table 1 and Fig. 2). Hydrogenolysis rates decreased also with increasing residence time. This decrease was similar to the decrease in dehydrocyclization rates. Hydrogenolysis rates also may have been limited by desorption of indene. Equilibrium conversion for the hydrogenolysis reactions would be over 99.9% (5). The conversions observed were very far from this value. Relative conversions of the different hydrogenolysis reactions did not change with the space velocity. The ratio of deethylation to demethylation (giving ethylbenzene) was between 1.5 and 2 at all conversion levels. Similarly, the ratio of demethylation to ethylbenzene to demethylation to *ortho*-xylene was 1.3. Propane and benzene were most probably formed by hydrogenolysis of *n*-propylbenzene.
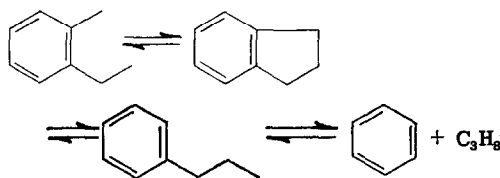
Small amounts of dimethylethylbenzene, cymene, methyl-*n*-propylbenzene, and diethylbenzene were also formed over the platinum-silica gel catalyst. The combined amount of these products was about 0.1% (Table 1). Over acid catalysts, transethylation is faster than transmethylation (6). We did not observe any transethylation in our reaction. Transmethylation over acid catalysts was very selective; methyl groups were transferred only to ring carbon atoms. Transmethylation over the neutral platinum silica gel catalyst was not selective. Methyl groups were added to practically any position on methylethylbenzene with equal probability. The reaction probably proceeds via methyl radicals
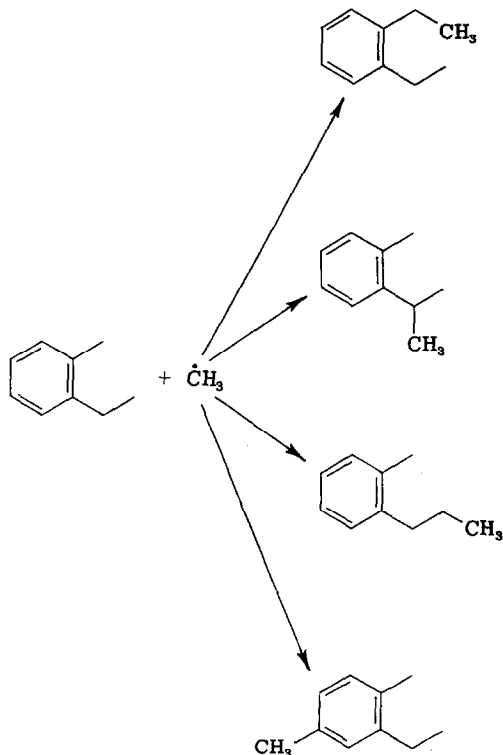
Dehydrogenation to *o*-methylstyrene was limited by the methylethylbenzene–methylstyrene equilibrium (Table 1). Conversion at all space velocities was about 0.08%. Similarly, the indan–indene equilibrium was instantly established. The indan–indene ratio was about 20.
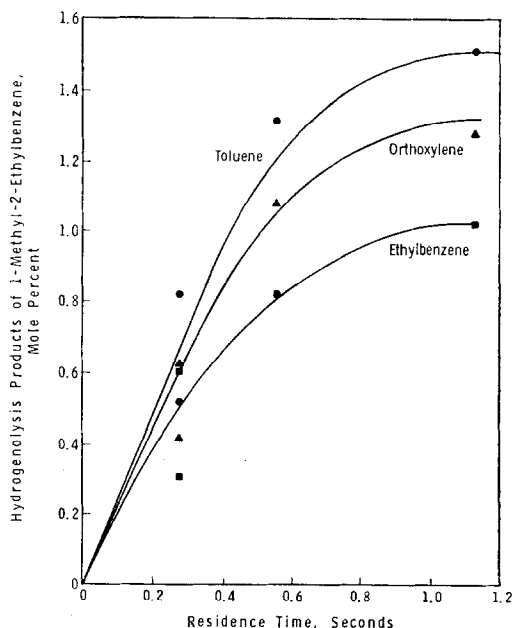
FIG. 2. Hydrogenolysis of 1-methyl-2-ethyl-benzene over 2% Pt on SiO₂ catalyst at 400°C temperature, atmospheric total pressure, and at a H₂/HC mole ratio of 3.

The reaction rates of 1-methyl-2-ethyl-benzene over 2% platinum-on-silica-gel catalyst are given in Table 2.

(3-MHx) can be formed from n-heptane only through 2-methylhexane (2-MHx) intermediate:
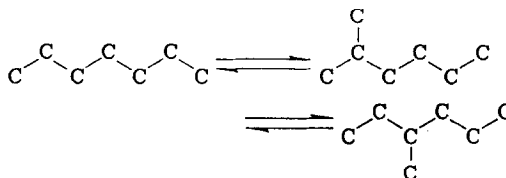
The formation of 2,3-dimethylpentane (2,-3-DMP) and 3-ethylpentane (3-EtP) would be still subsequent steps. However, independent gas chromatographic analyses of our reaction products have proven these to be present in minor amounts. If the reaction proceeds by an acidic mechanism, the (3-MHx + 2,3-DMP + 3-EtP)/2-MHx ratio may only increase with increasing conversion, up to an equilibrium maximum of 2.0 (5).

However, the (3-MHx + 2,3-DPM + 3-EtP)/2-MHx ratios were higher over the platinum-silica catalyst at a lower conversion (6.2%) than over the platinum-alumina catalyst at a higher conversion level (13.1%). Thus, isomerization of n-heptane over the platinum-silica catalyst

TABLE 2
1-METHYL-2-ETHYLBENZENE OVER 2% PLATINUM ON SILICA GEL

Reciprocal space velocity:	0.125		0.38	0.50
Number of catalyst regenerations before run:	1	4	2	3
	Reaction rates (g methylethylbenzene/ml catalyst/hr)			
Total dehydrocyclization	1.43	0.98	0.75	0.50
Total hydrogenolysis	0.14	0.09	0.103	0.067
Dehydrogenation	—	0.0057	0.0029	0.0014

n-Heptane

Isomerization via dehydrocyclization and ring opening was also observed in the reactions of paraffins over platinum-containing catalyst. n-Heptane was dehydrogenated over 2% platinum-on-neutral-silica-gel and 0.8% platinum-on-halogenated-alumina catalysts. The distribution of C₇ isomers in the reaction products was as given in Table 3.

In an acidic mechanism 3-methylhexane

cannot proceed with the same (acid-catalyzed, carbonium-ion-type) mechanism as over the Pt-Al₂O₃ catalyst.

Cyclization to methylcyclohexane or dimethylcyclopentane followed by ring splitting can give the relatively higher ratios of (3-MHx + 2,3-DMP + 3-EtP)/2-MHx over the neutral Pt-SiO₂ catalyst. Small amounts of methylcyclohexane and dimethylcyclopentane isomers were, in fact, observed in the reaction product

TABLE 3
n-HEPTANE ISOMERIZATION PRODUCTS

Product component	Conversion (mole %) over	
	2% Pt-SiO₂ (Neutral)	0.8% Pt-Al₂O₃ (Acidic)
2-Methylhexane	0.87	4.67
3-Methylhexane + 2,3-dimethylpentane + 3-ethylpentane[a]	5.18	8.15
2,4-Dimethylpentane	0.12	0.30
Toluene	7.05	2.55
3-Methylhexane, etc./2-Methylhexane	6.0	1.7

[a] These components not resolved from one another.

chromatogram. These reaction intermediates, once formed, would be subject to hydrogenolysis at any point in the ring structure, forming the original or other heptane isomers.

That such ring hydrogenolysis is brought about in a nonstereospecific way is demonstrated by the following radio tracer experiment. Methyl-1-C^{14}-1,3-dimethylcyclopentane was added to the n-heptane feed in an

TABLE 4
PRODUCT DISTRIBUTION FROM
1,3-DIMETHYLCYCLOPENTANE
(METHYL-1-C^{14})

Product component	Mole percent
Methane + Ethane	8.5
Propane	3.6
Isobutane + n-Butane	3.9
Isopentane + n-Pentane	1.3
Methylcyclopentane	0.5
2-Methylhexane	3.7
3-Methylhexane	1.5
n-Hexane	2.4
2,4-Dimethylpentane (2,4-DMP)	10.3
2-Methylhexane (2-MHx)	22.8
3-Methylhexane (3-MHx)	22.7
n-Heptane	0
Dimethylcyclopentanes	10.0
Toluene	8.8

amount comprising 2.5% by volume. Table 4 presents the product distribution of radioactive components derived from the original radioactive dimethylcyclopentane over the Pt-SiO₂ catalyst. The radioactive products indicate initial ring opening followed by further breakage of carbon–carbon bonds so that a wide variety of

components resulted. There was no n-heptane. None would be expected, since n-heptane cannot be formed directly by opening of the 1,3-dimethylcyclopentane ring. A surprising amount (8.8%) of toluene was formed, however. The mechanism may have involved formation of a methylhexene (or methylhexane) by ring opening of 1,3-dimethylcyclopentane. Toluene would then be formed by dehydrocyclization of the methylhexene (or methylhexane).

The product distribution particularly of interest here is the nearly exact 1:2:2 ratio of 2,4-DMP:2-MHx:3-MHx. This and the absence of n-heptane, would be expected from statistical breakage of the carbon–carbon bonds in the 1,3-dimethylcyclopentane molecule. Similar results were obtained by Barron and his co-workers on 0.2% platinum on alumina (3).

In view of the nonpreferential carbon–carbon bond breakage indicated in the above radiotracer experiment, a statistical probability of formation of isomeric heptanes from n-heptane over a nonacidic platinum on silica may be postulated. Cycloparaffin structures directly obtainable by ring closure of n-heptane are ethylcyclopentane, methylcyclohexane, and 1,2-dimethylcyclopentane. It was assumed that their formation was equally probable. Figure 3 indicates the statistical probability of branched heptane formation from reopening of these ring structures. The ratio of 5.2 calculated for (3-MHx + 2,3-DMP + 3-EtP)/2-MHx is not far from the experimentally observed value of 6.0. Actually, the only source of 2-MHx by direct ring opening is the methylcyclo-
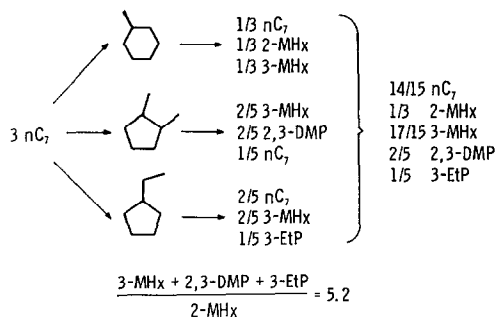
$$\frac{\text{3-MHx} + \text{2,3-DMP} + \text{3-EtP}}{\text{2-MHx}} = 5.2$$

FIG. 3. Formation of isoheptanes from n-heptane on Pt-on-SiO$_2$ catalyst—statistical probabilities.

hexane molecule. Since this reaction also receives competition from the dehydrogenation to toluene, the actual ratio would be expected to be higher than the 5.2 predicted.

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