JOURNAL OF CATALYSIS 9, 336–357 (1967)

Reactions of *n*-Butylbenzene over Supported Platinum Catalysts

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Received July 31, 1967; revised September 25, 1967

n-Butylbenzene was reacted over a series of catalysts covering a wide range of acidic and dehydrogenation activities (Pt-SiO_2, Pt-SiO_2-Al_2O_3, Pt-Al_2O_3, and SiO_2-Al_2O_3). All the basic reforming reactions—dehydrogenation, cyclization, isomerization, and cracking—were observed. The acid- and metal-catalyzed processes were distinguished, thus establishing the relative importance of each. There are two cyclization mechanisms: one catalyzed by acid sites, the other by the Pt metal. Over Pt-SiO_2, only the Pt-catalyzed reaction occurs. Cyclization by this mechanism produces nearly equal amounts of five- and six-membered ring products (i.e., methylindan and naphthalene). Over Pt-SiO_2-Al_2O_3, the acid-catalyzed cyclization mechanism predominates, which produces only methylindan, leading to a very much higher methylindan/naphthalene product ratio over Pt-SiO_2-Al_2O_3 than over Pt-SiO_2 (22.6 versus 1.46). Isomerization might proceed by three mechanisms: Over nonacidic Pt-SiO_2, *sec*-butylbenzene is formed via cyclic intermediates and a noncarbonium-ion-type 1-2 methyl shift forms isobutylbenzene. Acid-catalyzed isomerization occurs over SiO_2-Al_2O_3 and Pt-SiO_2-Al_2O_3. On Pt-SiO_2, fragmentation proceeds exclusively by Pt-catalyzed hydrogenolysis. In this reaction the different side chain bonds have about equal scission probabilities. Over Pt-SiO_2-Al_2O_3 and Pt-Al_2O_3, both Pt-catalyzed hydrogenolysis and acid-catalyzed cracking occur. It has been believed that the role of the Pt in dual-functional reforming catalysts was primarily the dehydrogenation of saturated hydrocarbons. This work shows that Pt metal has considerable dehydrocyclization and isomerization activity as well.

Dual-functional catalysts exhibiting acidic and dehydrogenating activities are used in catalytic reforming. The reactions occurring over these catalysts are isomerization, dehydrogenation, cyclization, hydrogenolysis, and cracking. We wanted to clarify the roles of the acidic and metallic components of reforming catalysts in these reactions. *n*-Butylbenzene serves as a particularly good model compound to elucidate the reaction mechanisms.

EXPERIMENTAL

Hydrocarbon Feed

Phillips 66 research grade *n*-butylbenzene was used in all of the experiments. Its purity (by gas chromatography) was over 99.8%. Impurities (in mole percent) were toluene, 0.0010; ethylbenzene, 0.0015; *n*-propylbenzene, 0.0016; *sec*-butylbenzene, 0.0143; cymenes, 0.0400; other, 0.0600.

Catalysts

Platinum on silica gel. Fifty-two grams of Davison desiccant-grade silica gel (800 m^2/g BET surface area) was impregnated with a solution of 42 ml of H_2PtCl_6. The solution contained 1.04 g of platinum. The impregnated catalyst was dried in a vacuum oven at 105°C in nitrogen to constant weight, then calcined in air for 3 hr at 450°C. The finished catalyst contained 2% platinum by weight. Its density was 0.82 g/ml.

Platinum on alumina. We used a commercial reforming catalyst containing 0.75% Pt. The platinum surface area, determined by CO chemisorption according to the procedure of Hughes, Houston, and

Sieg (*1*), was 25 μmole CO/g of catalyst. Catalyst density was 0.46 g/ml.

Platinum on silica-alumina. The catalyst was prepared in a process similar to the one we used in the preparation of platinum on silica gel. The catalyst contained 2% platinum. The silica-alumina was a 450 m^2/g BET surface area Socony Mobil white TCC bead cracking catalyst. It contained 10% alumina. The platinum surface area was 66 μmole CO/g of catalyst. Catalyst density was 0.678 g/ml.

Silica-alumina. Silica-alumina was a Socony Mobil white TCC bead cracking catalyst. Its density was 0.635 g/ml.

Procedure

The fixed-bed reactor was a 6.35-mm OD stainless steel tube. We mixed ½ ml, 60-100 mesh size catalyst samples with ½ ml, 100-200 mesh size Alundum. Reaction conditions were atmospheric total pressure, hydrogen diluent, hydrogen-to-butylbenzene molar ratio at about 3, temperatures between 316° and 482°C, and liquid hourly space velocities (LHSV) between 4 and 37. We kept conversions at a low level to avoid secondary reactions. The experiments were between 22 and 85 min long. Liquid products were condensed in an acetone–dry ice cooled condenser. Collection of the liquid samples started 10–40 min after the experiments were started. Liquid samples were handled at dry ice temperature before being analyzed. Reaction effluent samples were taken at various intervals during the experiments. A Beckman sampling valve was used for reaction effluent sampling.

Five additional experiments were made with 1-methyl-2-ethylbenzene feed at 390°C temperature. The procedure and the reaction conditions were the same as with the *n*-butylbenzene feed.

Analytical Procedure

Total reaction effluent samples were analyzed with a temperature-programmed silicon elastomer gas chromatography column. Gaseous reaction products were determined from these reaction effluent sample analyses. However, the resolution of some of the aromatic reaction products was incomplete. Hence liquid products were further analyzed with two high-resolution and high-sensitivity capillary gas-chromatographic columns. Retention times of the different hydrocarbons and column operating conditions are shown in Table 1. The retention times of most alkylbenzenes and styrenes, indan, indene, the decalins, tetralin, and naphthalene were determined by using standards (supplied by API or the Phillips Petroleum Company). Determination of the retention times of the dimethylethylbenzene and diethylbenzene isomers was described by Baumann and Csicsery (*2*). Retention times for the 1-phenyl-1-butenes, 1-methylindan, and 1-methylindene were determined as described in the above reference. No reliable boiling point data existed for the 1-phenyl-2-butenes and 3-methylindene. Two peaks with nearly constant area ratios to the 1-phenyl-1-butenes were tentatively identified as the *cis*- and *trans*-1-phenyl-2-butenes. Similarly, the identification of 3-methylindene was based on its constant ratio with 1-methylindene.

Capillary column gas chromatography of the reaction products obtained over the more acidic catalysts showed a number of unidentified small peaks. Retention times of these compounds were (on the temperature-programmed capillary column): 4.07, 4.26, 4.90, 4.92, 4.97, 5.14, 5.46, 5.77, 5.80, 5.95, and 6.28. Most of these compounds are isomeric methylindans, methylindenes, and the two 1-phenylbutadiene isomers (5.77 may be the retention time of one of the latter).

Several of the liquid products were also analyzed by low-voltage mass spectroscopy. The ionizing potential was 8.0 V, and the repeller potential was 3.0 V, giving an actual ionizing potential of 9.5 V. MS analyses showed more methylindenes (or phenylbutadienes) than the gas-chromatographic analyses. This also suggested that the unidentified compounds in the gas-chromatographic analyses were isomeric methylindenes and phenylbutadienes.

n-Butylbenzene conversions are shown in Table 2.

TABLE 1

RELATIVE GAS-CHROMATOGRAPHIC RETENTION TIMES

	Gas-chromatographic column		
Hydrocarbon	Temperature-programmed capillary[a]	Isothermal capilary[b]	Silicone elastomer[c]
Benzene	0.66	0.54	0.66
Toluene	1.000	1.000	1.00
Ethylbenzene	1.55	1.69	1.32
ortho-Xylene	1.91	2.18	—
meta-Xylene	1.67	1.83	—
para-Xylene	1.64	1.80	—
Styrene	2.11	2.42	—
n-Propylbenzene	2.35	2.83	1.61
Isopropylbenzene	2.02	2.32	—
1-Methyl-2-ethylbenzene	2.72	3.42	—
1-Methyl-3-ethylbenzene	2.48	3.00	—
1,2,3-Trimethylbenzene	3.42	4.57	—
1,2,4-Trimethylbenzene	2.98	3.82	—
1,3,5-Trimethylbenzene	2.69	3.36	—
α-Methylstyrene	3.04	3.87	—
trans-β-Methylstyrene	—	5.47	—
ortho-Methylstyrene	3.26	4.24	—
meta-Methylstyrene	3.31	—	—
para-Methylstyrene	3.44	—	—
Indan	3.63	5.19	—
Indene	4.27	6.61	—
n-Butylbenzene	3.60	4.98	1.90
sec-Butylbenzene	2.90	3.73	1.77
Isobutylbenzene	2.86	3.68	1.77
tert-Butylbenzene	2.70	—	—
1-Methyl-2-*n*-propylbenzene	3.78	—	—
1-Methyl-3-*n*-propylbenzene	3.53	—	—
1-Methyl-4-*n*-propylbenzene	3.57	—	—
1-Methyl-2-isopropylbenzene	3.36	—	—
1-Methyl-3-isopropylbenzene	3.09	4.25	—
1-Methyl-4-isopropylbenzene	3.15	—	—
1,2-Diethylbenzene	3.68	4.80	—
1,3-Diethylbenzene	3.47	4.71	—
1,4-Diethylbenzene	3.57	4.96	—
1,2-Dimethyl-3-ethylbenzene	4.50	7.26	—
1,2-Dimethyl-4-ethylbenzene	4.14	6.20	—
1,3-Dimethyl-2-ethylbenzene	4.21	6.46	—
1,3-Dimethyl-4-ethylbenzene	4.06	6.00	—
1,3-Dimethyl-5-ethylbenzene	3.75	5.20	—
1,4-Dimethyl-2-ethylbenzene	3.98	5.80	—
1,2,3,4-Tetramethylbenzene	5.35	—	—
1,2,3,5-Tetramethylbenzene	4.90	—	—
1,2,4,5-Tetramethylbenzene	4.77	—	—

TABLE 1 (*Continued*)

Hydrocarbon	Gas-chromatographic column: Temperature-programmed capillary[a]	Isothermal capillary[b]	Silicone elastomer[c]
n-Butylcyclohexane	2.48	—	—
cis-1-Phenyl-1-butene	4.14	6.41	—
trans-1-Phenyl-1-butene	5.05	8.95	2.18
cis-1-Phenyl-2-butene[d]	4.23	6.22	2.08
trans-1-Phenyl-2-butene[d]	4.06	5.98	1.86
2,4-Dimethylstyrene	—	8.00	—
2,5-Dimethylstyrene	—	7.63	—
2,6-Dimethylstyrene	—	6.60	—
1-Methylindan	4.18	6.61	2.02
1-Methylindene	5.66	11.74	—
3-Methylindene[d]	4.47	7.43	—
trans-Decalin	—	4.20	—
cis-Decalin	—	5.54	—
Tetralin	5.58	10.92	—
Naphthalene	6.67	17.1	2.26
1-Methylnaphthalene	—	—	2.46
2-Methylnaphthalene	—	23.6	2.42

[a] A 91.5-m long, 0.508-mm ID stainless steel capillary column filled with Ucon LB-550-X polypropylene glycol. It was temperature-programmed between 60–130°C at 1°C/min heating rate in a Perkin-Elmer Model 800 gas-chromatographic apparatus.

[b] A column similar to the one above, operated isothermally at 130°C in an F and M Model 810 gas-chromatographic apparatus.

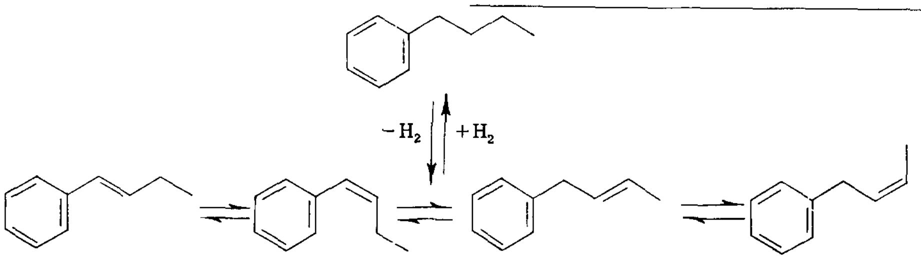
[c] A 6.56-m long, 4.75-mm OD copper column with silicon elastomer liquid phase. It was temperature-programmed between 76–215°C at 4.7°C/min heating rate in a Research Specialties gas-chromatographic apparatus.

[d] Tentatively identified.

RESULTS

Dehydrogenation

The products of the dehydrogenation of n-butylbenzene are 1-phenylbutenes:



Over the platinum-on-silica gel and platinum-on-alumina catalysts, dehydrogenation conversions are limited by equilibrium within the temperature range studied. The n-butylbenzene $\rightleftarrows$ 1 phenylbutene equilibrium is unknown. We expect close similarity between this equilibrium and that of the n-propylbenzene $\rightleftarrows$ 1-phenylpropene equilibrium. Equilibrium constants calculated for the n-propylbenzene $\rightleftarrows$ *trans*-1-phenyl-1-propene + H_2 reaction from Rossini's data (*3*) are very close to the experimentally obtained

TABLE 2
REACTIONS OF n-BUTYLBENZENE OVER DIFFERENT CATALYSTS

Catalyst:	Platinum (2%) on silica gel								Pt (0.75%)-Al_2O_3	Platinum (2%) on silica-alumina			Silica-alumina	
Experiment:	6	7	8	9	10	11	12	13	14	15	16	17	18	19
H_2: n-Butylbenzene mole ratio:	3.06	3.46	3.04	3.04	3.06	3.44	3.05	3.05	3.44	3.44	3.05	3.05	3.05	3.05
Reaction temperature (°C):	316	316	371	371	371	371	427	482	371	371	427	482	427	482
LHSV:	9	4	36.2	18.1	9.0	4	9	9	8	8	9	9	9	9
Residence time (sec):	0.33	0.67	0.07	0.15	0.30	0.6	0.27	0.25	0.31	0.31	0.27	0.25	0.27	0.25
Products (Moles Per 100 Moles of Feed)														
Methane	—	—	—	—	—	—	0.91	2.10	0.54	0.46	0.42	1.89	—	0.53
Ethane	0.05	0.07	0.17	0.26	0.77	0.73	1.57	3.85	0.57	0.19	0.39	1.16	—	—
Propane, propylene	0.32	0.39	0.34	0.49	0.72	1.14	1.07	1.48	0.87	0.69	0.82	1.32	—	0.41
n-Butane	0.05	0.10	0.13	0.16	0.25	0.44	0.58	0.67	1.50	0.25	0.36	0.36	0.11	
Isobutane	—	—	—	—	—	—	—	0.02	—	0.03	0.01	0.01	0.03	0.20
Butenes	—	—	—	—	—	—	—	0.02	—	—	—	0.07	1.43	7.34
1-Phenylbutenes	0.044	0.054	0.356	0.332	0.360	0.408	1.994	4.178	0.395	0.332	1.854	2.422	—	—
1-Methylindan	0.282	0.579	1.275	2.008	3.301	6.064	8.035	8.079	2.123	5.004	7.276	6.469	0.152	0.771
Methylindenes	0.008	0.012	0.102	0.127	0.269	0.405	2.894	8.391	0.207	0.324	2.379	4.198	—	0.059
Naphthalene	0.095	0.202	0.864	1.322	2.440	4.420	11.866	28.785	1.287	0.235	0.917	1.456	—	0.023
n-Butylcyclohexane	0.744	0.642	0.026	0.013	0.011	0.015	0.001	—	0.012	0.006	0.002	0.011	0.001	0.002
sec-butylbenzene	0.030	0.023	0.045	0.053	0.101	0.193	0.364	0.507	0.099	0.310	0.731	0.325	0.052	0.081
Isobutylbenzene	0.042	0.050	0.074	0.097	0.159	0.241	0.313	0.352	0.117	0.434	0.536	0.142	0.006	0.025
1-Methyl-2-isopropylbenzene	—	—	—	—	0.006	0.045	—	0.043	—	—	0.135	0.354	—	—
1-Methyl-2-n-propylbenzene	—	—	—	—	—	—	—	—	—	—	0.033	0.105	—	—
1,2-Diethylbenzene	—	—	—	—	—	—	—	—	—	—	—	0.039	—	—
Benzene	0.06	0.02	0.14	0.17	0.26	0.45	0.61	0.95	1.57	0.50	0.63	1.31	1.92	7.94
Toluene	0.15	0.22	0.30	0.38	0.60	.93	1.12	1.63	0.53	0.19	0.28	0.62	0.01	0.15
Ethylbenzene	0.06	0.09	0.17	0.27	0.43	0.65	1.37	2.88	0.44	0.15	0.26	0.39	0.005	0.05
n-Propylbenzene	0.07	0.13	0.17	0.24	0.40	0.59	1.02	1.57	0.41	0.10	0.17	0.18	0.003	0.01
Other	—	0.002	0.008	0.012	0.03	0.10	0.34	1.90	0.05	0.87	2.47	4.55	0.02	0.46
Total n-Butylbenzene converted (Mole %)	1.59	2.02	3.53	5.02	8.37	14.51	29.93	59.27	7.24	8.46	17.67	22.57	2.17	9.57

TABLE 3
Dehydrogenation Equilibrium Constants

	Temperature (°C)			
	316°	371°	427°	482°
n-Butylbenzene $\rightleftarrows$ *trans*-1-phenyl-1-butene + H_2 (experimental)	0.00023	0.002	0.012	0.052
n-Propylbenzene $\rightleftarrows$ *trans*-1-phenyl-1-propene + H_2 (calculated)	0.00017	0.00115	0.0075	0.0304

equilibrium constants for the n-butylbenzene reaction (Table 3). The two log K versus $1/T$ curves are parallel (Fig. 1).

Equilibrium distributions of the different 1-phenylbutene isomers will be discussed elsewhere.

Over platinum-on-silica-alumina catalyst, dehydrogenation conversions are lower than over platinum on silica gel (Table 4).

Some of the 1-phenylbutenes could isomerize to olefins with a different skeleton over the strongly acidic silica-alumina support; however, the total amount of unidentified "other" products (3.85%) in Experiment 17 is too low to account for the decreased level of 1-phenylbutenes. Platinum apparently has lower dehydrogenation activity on silica-alumina support than on silica gel or alumina.

We did not observe any dehydrogenation over silica-alumina. If phenylbutenes were formed, they quantitatively reacted further by other reactions.

TABLE 4
Effects of Support on Dehydrogenation Conversions

Catalyst	1-Phenylbutenes, % of butylbenzene plus 1-phenylbutenes	
	427°C	482°C
Platinum on silica-alumina	2.2	3.0
Platinum on silica gel	2.8	9.0

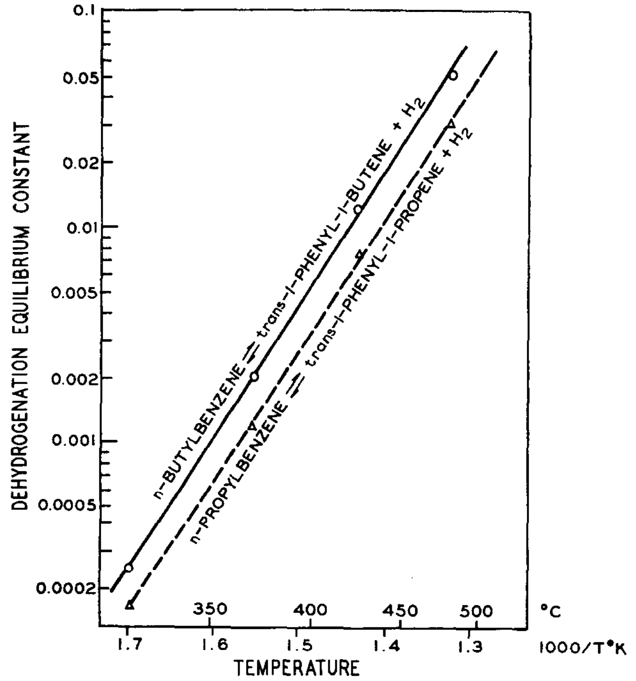
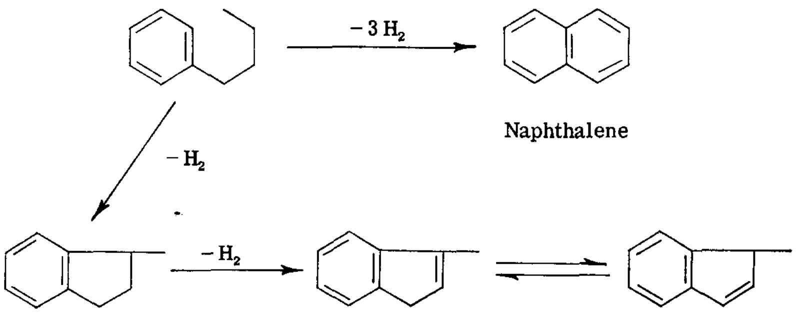


Fig. 1. Dehydrogenation equilibria of alkylbenzenes.

Dehydrocyclization

Dehydrocyclization produces 1-methylindan, methylindenes, and naphthalene.



Naphthalene

1-Methylindan 1-Methylindene 3-Methylindene

Tetralin and decalins were not observed in any of the experiments. Between 0.02% and 0.1% tetralin and less than 0.001% decalins were expected if these compounds were in equilibrium with the naphthalene formed [equilibrium conversions calculated from the data of Egan (*4*)].

There are two essential differences between cyclizations to naphthalene and methylindan. The first reaction forms a six-membered ring and involves the addition of a primary carbon atom to the aromatic ring. Formation of methylindan (and methylindenes) creates a five-membered ring and involves the addition of a secondary carbon atom to the aromatic ring.

The nature of these two different cyclization processes might be clarified by comparisons of the reactions of *n*-butylbenzene with those of *n*-propylbenzene and 1-methyl-2-ethylbenzene. The cyclization of *n*-propylbenzene to indan forms a five-membered ring, and this involves the attachment of a primary carbon atom to the aromatic ring. This reaction, and the cyclization of 1-methyl-2-ethylbenzene, was studied by Shephard and Rooney (*5*). In Shephard and Rooney's experiments, product distributions were essentially similar over platinum-on-alumina and platinum-on-silica-gel catalysts. The methylethylbenzene/*n*-propylbenzene cyclization rate ratio in Shephard and Rooney's experiments was about 1.6. In our experiments, the methylethylbenzene/*n*-butylbenzene to methylindan cyclization rate ratio over platinum on silica gel was 1.8 (Table 5). Thus, cyclization rates of *n*-propylbenzene to indan and *n*-butylbenzene to methylindan are essentially the same over platinum on silica gel. This indicates that the positions of the carbon atom involved in the cyclization step (primary versus

TABLE 5

DEHYDROCYCLIZATION OF 1-METHYL-2-ETHYLBENZENE AT 399°C TEMPERATURE, ATMOSPHERIC TOTAL PRESSURE, AND AT A HYDROGEN-TO-HYDROCARBON MOLE RATIO OF 3

Catalyst:	Platinum-on-silica gel			Pt-SiO_2-Al_2O_3	Pt-Al_2O_3
Experiment No.:	20	21	22	23	24
Residence time (sec):	0.29	0.58	1.14	0.29	0.29
Dehydrocyclization products (Mole %)					
Indan	11.36	17.25	20.35	3.95	4.60
Indene	0.59	0.89	1.10	0.24	0.28
n-Propylbenzene	1.73	5.18	6.63	0.12	0.22
First-order cyclization rate constants (Sec^{-1})	0.508	0.458	0.231	0.141	0.181

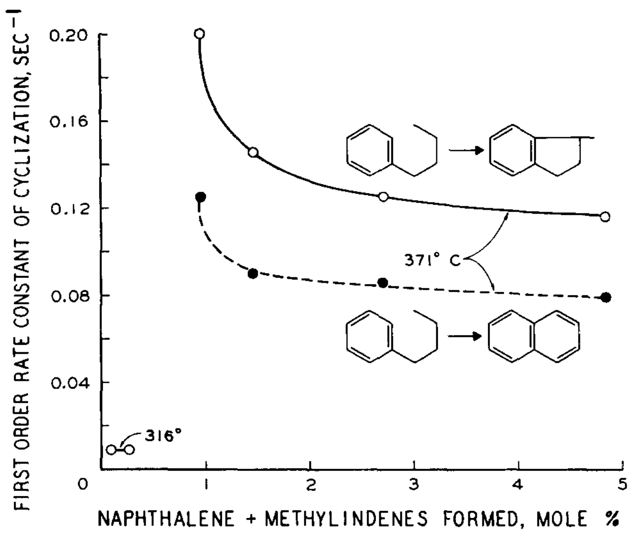


Fig. 2. Dehydrocyclization of *n*-butylbenzene over 2% platinum-on-silica-gel catalyst. Cyclization to methylindan and methylindenes, solid lines; cyclization to naphthalene, dashed line.

secondary) *do not influence* the rate of reaction. Carbonium ions are not involved in this type of cyclization over platinum on silica gel.

First-order rate constants for the dehydrocyclization reaction over platinum on silica gel are plotted against the concentration of bicyclic aromatics formed on Fig. 2. The rate constant decreases with increasing level of naphthalene and methylindene concentration. This suggests that the rate of cyclization might be inhibited

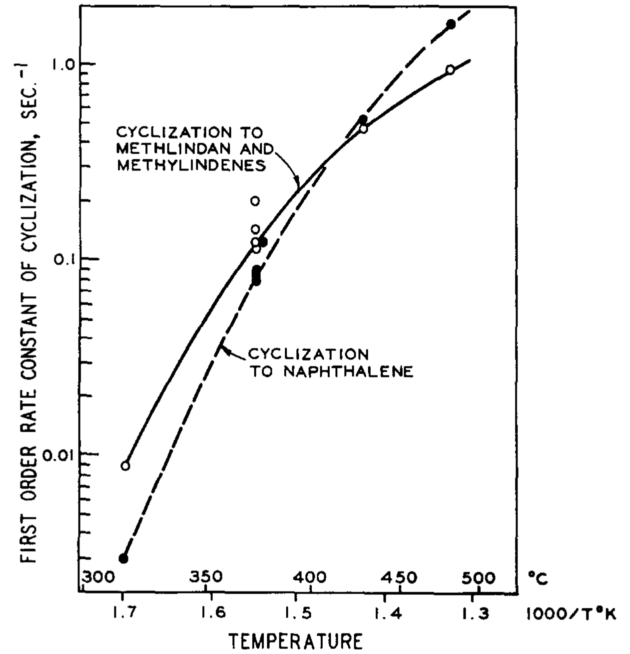


Fig. 3. Dehydrocyclization of *n*-butylbenzene over 2% platinum-on-silica-gel catalyst. The effect of temperature on cyclization.

TABLE 6
DEHYDROCYCLIZATION PRODUCT DISTRIBUTIONS OF *n*-BUTYLBENZENE OVER DIFFERENT CATALYSTS

Catalysts	LHSV	(Methylindan + methylindenes) / Naphthalene 316°	371°	427°	482°	Methylindenes, % of methylindane + methylindenes 316°	371°	427°	482°	1-Methylindene / 3-Methylindene 316°	371°	427°	482°
2% Platinum on silica gel	36	—	1.60	—	—	—	7.4	—	—	—	9	—	—
	18	—	1.61	—	—	—	6.0	—	—	—	11	—	—
	9	3.05	1.46	0.92	0.57	2.7	7.5	27.5	51	—	14	10	8
	4	2.92	1.47	—	—	2.0	6.3	—	—	11	9	—	—
0.75% Platinum on alumina	8	—	1.81	—	—	—	8.9	—	—	—	33	—	—
2% Platinum on silica-alumina	9	—	22.6	10.5	7.3	—	6.1	24.6	39.4	—	11	8	9
Silica-alumina	9	—	—	∞	36	—	—	—	7.1	—	—	—	28

by (bicyclic) product desorption. In a similar reaction, the dehydrogenation rate was controlled by the rate of product desorption (*6*).

Rate constants are plotted against the reaction temperature on Fig. 3. The activation energy of the dehydrocyclization forming naphthalene is about 8-9 kcal higher than that forming methylindan and methylindenes. This value is in good agreement with the results of Kasanski and Liberman (*7*).

The (methylindan plus methylindenes)/naphthalene ratio does not change with changing space velocity (Table 6). The ratio decreases with increasing temperature (Fig. 4). The methylindenes as percent of the sum of methylindan and methylindenes increase with temperature but do not change with space velocity (Table 6). The methylindan ⇄ methylindene equilibrium is not known. The observed ratios probably represent equilibria. The 1-methylindene/3-methylindene ratio is not affected by either temperature, space velocity, or catalyst on-stream time. The ratio is about 10:1 (Table 6).

Dehydrocyclization selectivities are very different over platinum on silica-alumina compared to platinum on silica gel (Table 7 and Fig. 5). The methylindan/naphthalene ratios are about an order of magnitude higher over the platinum on silica-alumina than over platinum on silica gel. Rate constants for cyclization to six-membered rings are 11-26 times higher over the silica-gel-supported platinum catalyst than over platinum on silica-alumina (Table 7). Apparently, the silica-alumina support decreases the six-membered ring dehydrocyclization activity of the platinum metal.

Over platinum on silica-alumina, rates of dehydrocyclization to five-membered rings

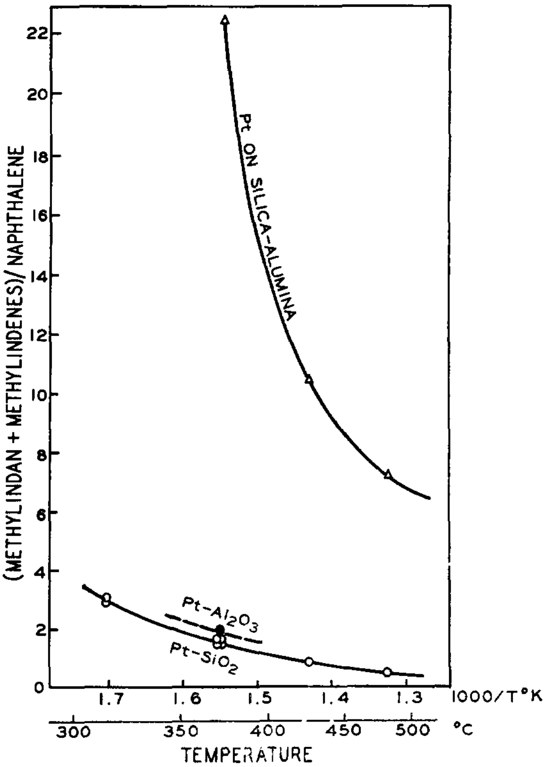


FIG. 4. Cyclization of *n*-butylbenzene. Methylindan/naphthalene ratios.

TABLE 7

Dehydrocyclization Rate Constants of n-Butylbenzene over Different Catalysts at 1 atm Total Pressure and with a Hydrogen-to-Hydrocarbon Mole Ratio of 3:1

Catalyst	Temperature (°C)	LHSV	First-order cyclization rate constants k_5 To Methylindan and methylindenes	 k_6 To naphthalene	k_5/k_6
2% Platinum on silica gel	316°	9	0.009	0.003	3.05
	—	4	0.009	0.003	2.92
	371°	36.2	0.200	0.125	1.59
	—	18.1	0.146	0.090	1.61
	—	9	0.125	0.086	1.46
	—	4	0.116	0.079	1.46
	427°	9	0.475	0.515	0.92
	482°	9	0.958	1.670	0.57
0.75% Platinum on alumina	371°	8	0.078	0.043	1.81
2% Platinum on silica-alumina	371°	8	0.179	0.008	22.6
	427°	9	0.388	0.037	10.5
	482°	9	0.477	0.065	7.3
Silica-alumina	427°	9	0.006	—	∞
	482°	9	0.035	0.001	36

are similar to those of platinum on silica gel (Table 7). However, the reaction over platinum on silica-alumina has a significantly lower apparent activation energy than over platinum on silica gel (Figs. 3 and 5).

Five-membered rings may be formed by two dehydrocyclization mechanisms over platinum on silica-alumina. One mechanism is similar to the one observed with platinum on silica gel. It is catalyzed by the platinum metal. When supported by silica-alumina, platinum probably has low activity for dehydrocyclization to six-membered rings. Therefore, lower rates are expected for the platinum-catalyzed de-

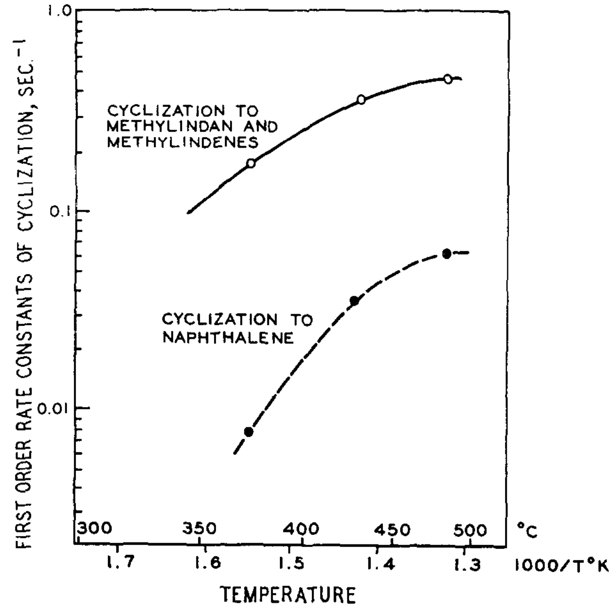
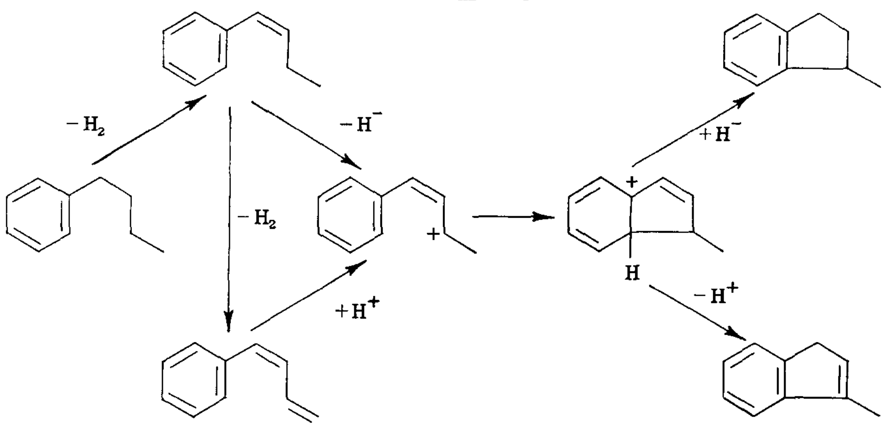
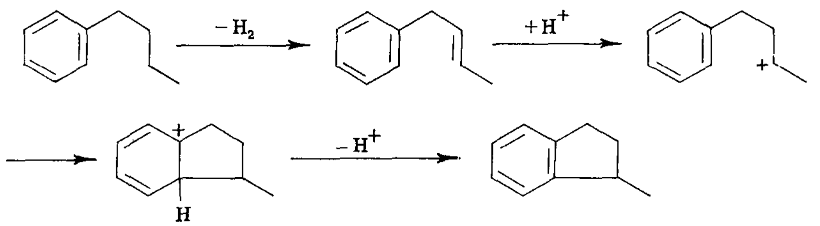


Fig. 5. Dehydrocyclization of n-butylbenzene over 2% platinum-on-silica-alumina catalyst.

hydrocyclization to five-membered rings also. Acid-catalyzed self-alkylation is a second possible cyclization mechanism. Dehydrogenation produces phenylbutenes and phenylbutadiene. A phenylallyl cation may be produced by proton addition to phenylbutadiene or by hydride ion removal from phenylbutene. Ring closure proceeds by the formation of a bond between the electron-deficient γ-carbon atom of the side chain and an ortho position of the aromatic ring. The bicyclic carbonium ion is stabilized by hydride ion addition (forming methylindan) or by proton removal (forming methylindene).



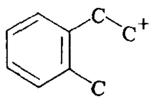
Proton addition to *cis*-1-phenyl-2-butene is another possible reaction path. Cyclization of the carbonium ion $C_6H_5CH_2CH_2$-^+CH-CH_3, followed by proton loss, gives 1-methylindene).



Silica-alumina is a strong acid able to catalyze reactions with carbonium ion intermediates. Over platinum on silica-alumina, most of the cyclization of *n*-butylbenzene to methylindan probably proceeds by this mechanism. Naphthalene cannot be formed from *n*-butylbenzene by such a mechanism. This reaction would involve a very unstable primary carbonium ion: C_6H_5-CH_2-CH_2-CH_2-CH_2^+. Also, this carbonium ion lacks the strong resonance stabilization of the phenylallyl system.

Among the olefin isomers, *cis*-1-phenyl-1-butene has the most advantageous configuration for cyclization. This isomer was present in less than equilibrium concentration among the 1-phenylbutenes. Preferential cyclization of this isomer explains this phenomenon. Naphthalene might isomerize over platinum-on-silica-alumina catalyst to methylindan. However, at the conditions of our experiments (an H_2 partial pressure of only 0.75 atm), such an isomerization must be negligible. We may conclude that acid-catalyzed self-alkylation is responsible for the high methylindan/naphthalene ratio over platinum on silica-alumina.

The acid-catalyzed self-alkylation of *n*-butylbenzene over silica-alumina may be compared with that of 1-methyl-2-ethylbenzene. In the case of the methylethylbenzene, the two possible carbonium ion intermediates are primary.



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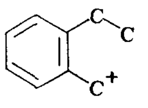


Resonance would stabilize only the second one (i.e., the benzylic carbonium ion). Hence, the acid-catalyzed cyclization might contribute less to the total cyclization than in the case of *n*-butylbenzene, where a secondary carbonium ion is involved. Cyclization of 1-methyl-2-ethylbenzene to indan is indeed faster over platinum on silica gel than over platinum on silica-alumina (Table 5). Over platinum on silica gel, methylethylbenzene has a higher cyclization rate constant than *n*-butylbenzene. Over platinum on silica-alumina we observe the opposite (Table 8).

TABLE 8
DEHYDROCYCLIZATION RATE CONSTANTS

First-order cyclization rate constants at 399°C	Pt-SiO_2	Pt-SiO_2-Al_2O_3
1-Methyl-2-ethylbenzene → indan	0.51	0.14
n-Butylbenzene → methylindan	0.28	0.26
n-Butylbenzene → naphthalene	0.20	0.016

The butylbenzene data were determined graphically from Figs. 3 and 5.

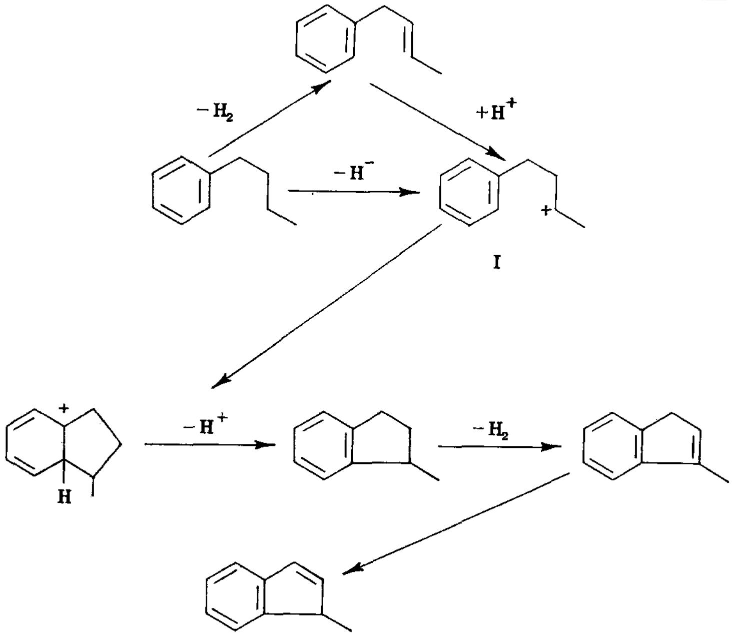
This observation also supports the theory of two mechanisms. Over platinum on silica gel, the cyclization of methylethylbenzene to indan and the cyclization of *n*-butylbenzene to methylindan proceeds by the platinum-metal-catalyzed mechanism. *n*-Butylbenzene cyclizes to methylindan over platinum on silica-alumina predominantly by an acid-catalyzed self-alkylation mechanism. The contribution of the acid-catalyzed mechanism to the cyclization of 1-methyl-2-ethylbenzene might be significant but not as great as in the case of the *n*-butylbenzene, where a secondary carbonium ion is involved.

Dehydrocyclization rates over the platinum-alumina catalyst (0.75% platinum) are lower than over platinum on silica gel (2% platinum). The ratio of dehydrocyclization to five-membered rings, to dehydrocyclization to naphthalene (k_5/k_6, Table 7) over platinum-alumina is slightly higher than over platinum on silica gel but substantially lower than over platinum on silica-alumina (1.81, 1.46, and 22.6, respectively). Acid-catalyzed cyclization (so important over platinum on silica-alumina) contributes only to a minor extent to the formation of methylindan over platinum on alumina. About four-fifths of the methylindan is formed by the platinum-catalyzed route.

Another indication of the acid-catalyzed cyclization process over the platinum-on-alumina catalyst is the relative increase of *n*-butylbenzene cyclization rate compared to the rate of cyclization of 1-methyl-2-ethylbenzene. The ratio of the cyclization rate of methylethylbenzene to the cyclization of *n*-butylbenzene to methylindan and methylindenes over platinum on silica gel is 1.8. Over platinum on alumina, the ratio is about 1.1 (methylethylbenzene value extrapolated). That is, the rate of *n*-butylbenzene cyclization to five-membered rings over the platinum on alumina is relatively higher than over the neutral platinum on silica gel catalyst.

Over silica-alumina cracking catalyst, the rate of dehydrocyclization to naphthalene is practically zero. Dehydrocyclization to five-membered rings is very slow. At 427°C the rate of dehydrocyclization to five-membered rings over platinum on silica-alumina is about 70 times faster than over silica-alumina (Table 7). Dehydrocyclization over the silica-alumina cracking catalyst most probably proceeds by an acidic mechanism (i.e., through phenylbutene and phenylbutyl carbonium ion intermediates). The rate-limiting step is probably the slow formation of the phenylbutene. No methylindenes are observed at 427°C. At 482°C the methylindenes/methylindan ratio is 0.08. The equilibrium ratio is about 1. The 1-methylindene/3-methylindene ratio is 29, far above the equilibrium value of about 10. Rates of the methylindan $\rightleftarrows$ methylindene dehydrogenation and the 1-methylindene $\rightleftarrows$ 3-methylindene isomerization are very much slower over silica-alumina than over the platinum-containing catalysts. The methylindan plus methylindenes fraction contains an excess of methylindan relative to the equilibrium.

The primary cyclization product over silica-alumina is apparently methylindan (and not methylindene). Similarly, the primary product of the dehydrogenation of methylindan is 1-methylindene (and not 3-methylindene). The dehydrocyclization path over silica-alumina may be reconstructed:



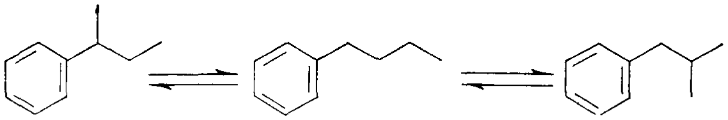
Phenylbutene may be formed by thermal dehydrogenation. Proton addition gives carbonium ion (I). Hydride ion removal from *n*-butylbenzene may also form I. Ring closure of (I), and subsequent loss of a proton, forms 1-methylindan. This may dehydrogenate to 1-methylindene. 3-Methylindene may be formed in a subsequent double-bond isomerization step.

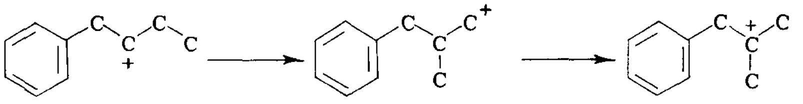
Isomerization

Isobutylbenzene and *sec*-butylbenzene are produced by skeletal isomerization of the alkyl side chain of *n*-butylbenzene. First-order isomerization rate constants of *n*-butylbenzene are summarized in Table 9. A cationic (acid-catalyzed) reaction will produce both isomers. Over acidic molybdenum-alumina catalysts at 484°C, Covini and Pines (*8*) observed that nearly equal amounts of *sec*-butylbenzene and isobutylbenzene were formed from *n*-butylbenzene. Roberts and his co-workers (*9*) observed that aluminum chloride catalyzed the isomerization of *n*-butylbenzene to a 2:1 mixture of isobutylbenzene and *sec*-butylbenzene. Both isomers are formed over silica-alumina. The reactions probably involve carbonium ion intermediates. Methyl migration produces isobutylbenzene.

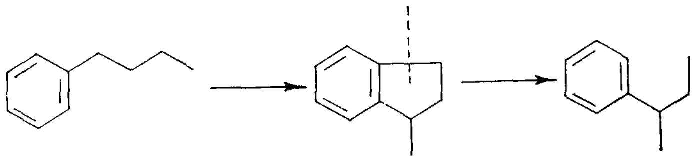
sec-Butylbenzene may be formed by either phenyl or ethyl migration. Methyl migration is less favored than phenyl or ethyl migration. *sec*-Butylbenzene-to-isobutylbenzene ratios at 427° and 482°C temperatures are 8.7 and 3.2.

sec-Butylbenzene and isobutylbenzene are formed over the neutral platinum on silica gel catalyst also. Reaction mecha-





nisms are different here than over silica-alumina. *sec*-Butylbenzene is probably formed from methylindan by ring opening.



The ratio of methylindan (plus methylindenes) to *sec*-butylbenzene is constant within experimental error over wide ranges of temperature and space velocity (Table 10).

The *sec*-butylbenzene/isobutylbenzene ratio increases with increasing temperature. (This ratio decreased over silica-alumina!) The ratio does not change with changing space velocity.

Isobutylbenzene cannot be formed by ring cleavage of any of the primary cyclization products of *n*-butylbenzene. Variations of the *sec*-butylbenzene/isobutylbenzene ratio suggest also that these two compounds are formed by two different mechanisms. Isobutylbenzene is probably formed by a methyl shift. 1–2-Methyl shifts have been recently described by

TABLE 9

Isomerization Rate Constants of *n*-Butylbenzene over Different Catalysts at 1 atm Total Pressure and with a Hydrogen-to-Hydrocarbon Mole Ratio of 3:1

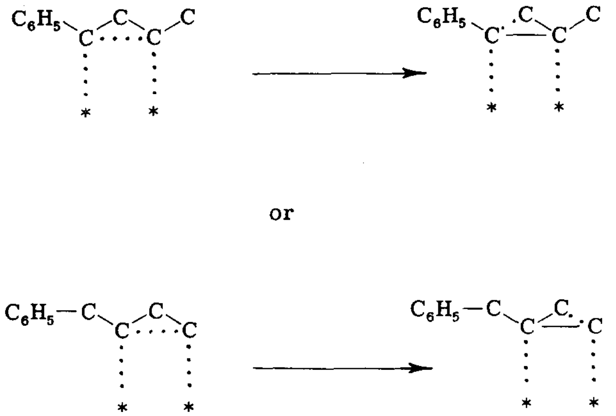
Catalyst	Temp. (°C)	To *sec*-butylbenzene	To isobutylbenzene	To methyl-*n*-propylbenzene and *o*-cymene
2% Platinum on silica gel	316°	0.0009	0.0013	—
	371°	0.0035	0.0056	0.0002
	427°	0.0158	0.0136	—
	482°	0.0295	0.0205	0.0025
0.75% Platinum on alumina	371°	0.0033	0.0039	—
2% Platinum on silica-alumina	371°	0.0104	0.0146	—
	427°	0.0294	0.0216	0.0068
Silica-alumina	427°	0.0020	—	—
	482°	0.0034	0.0011	—

TABLE 10

Isomerization Product Ratios over Platinum on Silica Gel

	Temperature (°C)						
	316°	371°				427°	482°
LHSV	4	36	18	9	4	9	9
$\frac{\textit{sec}\text{-Butylbenzene}}{\text{Isobutylbenzene}}$	0.4	0.6	0.6	0.6	0.8	1.16	1.14
$\frac{\textit{sec}\text{-Butylbenzene}}{\text{Methylindan plus methylindenes}}$	0.040	0.033	0.025	0.028	0.030	0.033	0.031

Anderson and Avery (*10*) and by Barron, Maire, Muller, and Gault (*11*). The reaction proceeds through α–γ-diabsorbed intermediates over platinum deposited on neutral supports. The reaction does not involve carbonium ion intermediates. If the *n*-butylbenzene ⇄ isobutylbenzene reaction proceeds by this platinum metal-catalyzed isomerization, the following steps would be involved:



Some *sec*-butylbenzene may be formed by this route also.

Isomerization to *sec*-butylbenzene and isobutylbenzene over platinum on silica-alumina is faster than over any of the other catalysts tested. The *sec*-butylbenzene/isobutylbenzene ratio increases with increasing temperature (Table 11).

TABLE 11
Isomerization Product Ratios over Platinum on Silica-Alumina

Temperature (°C):	371°	427°	482°
sec-Butylbenzene/ isobutylbenzene:	0.7	1.4	2.3

Isobutylbenzene may be formed through the two different reaction paths: the acid-catalyzed and the platinum-catalyzed processes.

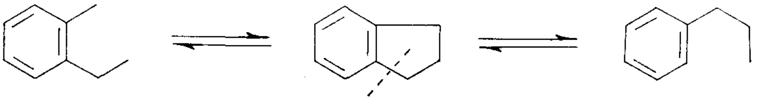
sec-Butylbenzene could be formed by either the acid-catalyzed reaction or through a methylindan intermediate (as occurs over platinum on silica gel). On platinum-silica gel, where *sec*-butylbenzene is formed only through methylindan intermediate, the *sec*-butylbenzene/methylindan + methylindene) ratio is nearly constant (about 0.03). These ratios vary from 0.03 to 0.08 over platinum on silica-alumina because two other reactions affect the *sec*-butylbenzene level. *sec*-Butylbenzene levels could increase due to contributions from the acid-catalyzed mechanism. The *sec*-butylbenzene level could decrease due to excessive cracking. (*sec*-butylbenzene would dealkylate much faster over a silica-alumina supported catalyst than *n*-butylbenzene.)

Isomerization rates decrease with decreasing catalyst on-stream times. The decrease was particularly great at 482°C, the highest temperature studied (Table 12). Isomerization may also be retarded by some of the reaction products (perhaps methylindenes). This retardation is more pronounced at higher temperatures. The

TABLE 12
Effects of On-Stream Time on Isomerization

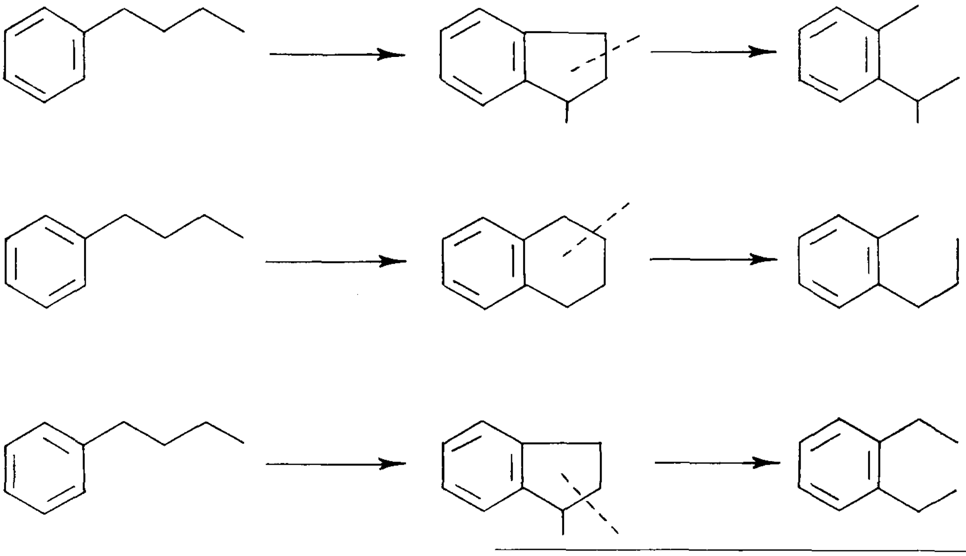
	Temperature (°C)		
	371°	427°	482°
sec-Butylbenzene + isobutylbenzene at 20-min on-stream time	0.92	1.62	0.68
sec-Butylbenzene + isobutylbenzene at 65-min on-stream time	0.87	1.12	0.35

rate of isomerization is lower at 482°C than at 371°C. Methylindene concentration in the reaction product at 482°C is 4.2% versus only 0.32% at 371°C temperature. A similar mechanism was proposed by Shephard and Rooney for the 1-methyl-2-ethylbenzene ⇄ *n*-propylbenzene isomerization (*5*).



Both acid- and platinum-catalyzed mechanisms may contribute to the overall isomerization over platinum (0.75%) on alumina. The rates may be compared with those observed over the neutral platinum (2%) on silica gel catalyst. If there were only platinum-catalyzed isomerization, the two rates would be in proportion to the dehydrogenation activities (or Pt contents) of the two catalysts. However, relatively higher isomerization rates are observed over platinum-alumina (0.003 to *sec*-butylbenzene and 0.0039 to isobutylbenzene) than over platinum on silica (0.0035 and 0.0056). This relatively higher isomerization rate over platinum on alumina suggests contributions from the acid-catalyzed mechanism.

Small amounts of 1-methyl-2-isopropylbenzene, 1-methyl-2-*n*-propylbenzene, and 1,2-diethylbenzene are produced over most of the catalysts tested. These compounds may be formed by sequential cyclization and ring-opening steps.



All types of isomerization conversions decrease with increasing catalyst on-stream times over all the catalysts tested.

Fragmentation Reactions

There are two types of fragmentation reactions: cracking and hydrogenolysis. In cracking, one of the products is an olefin. A molecule of hydrogen is added in hydrogenolysis, and no olefin is formed. However, differentiating between the two reactions is not always simple. In the presence of hydrogen over a hydrogenating catalyst, the olefinic products of cracking could be completely saturated; or vice versa, the paraffinic products of hydrogenolysis may be dehydrogenated.

Only cracking is observed over silica-alumina. Cracking rates over this catalyst are high; 83–88% of the overall *n*-butylbenzene reaction is cracking. Most of the scission occurs between the phenyl ring and the α-carbon atom (Table 13). Benzene and butenes are produced. Butenes/benzene

TABLE 13

FRAGMENTATION OF *n*-BUTYLBENZENE—DISTRIBUTION OF PRODUCTS, AS PERCENTS OF TOTAL FRAGMENTATION

	Catalyst:	Platinum on silica gel								$Pt\text{-}Al_2O_3$	Pt on silica-alumina			Silica-alumina	
	Temperature (°C):	316°		371°				427°	482°	371°	371°	427°	482°	427°	482°
	LHSV:	9	4	36	18	9	4	9	9	8	8	9	9	9	9
	Experiment:	6	7	8	9	10	11	12	13	14	15	16	17	18	19
Position	Products of fragmentation														
Phenyl–α	Benzene + butane, butenes	18	4	18	16	15	17	15	14	53	53	47	52	99.1	97.5
α–β	Toluene + propane, propylene	44	48	38	36	36	35	27	23	18	20	21	25	0.5	1.8
β–γ	Ethylbenzene, styrene + ethane, ethylene	18	20	22	25	25	25	33	41	15	16	19	16	0.25	0.6
γ–δ	*n*-Propylbenzene + methane	20	28	22	23	24	23	24	22	14	11	13	7	0.15	0.1
Total fragmentation products (Mole % of *n*-butylbenzene)		0.34	0.46	0.78	1.06	1.69	2.62	4.12	7.03	2.95	0.94	1.34	2.50	1.94	8.15

mole ratios are about 0.9 (Table 2). Most of the butenes (and butanes) do not readsorb and crack further to lower hydrocarbons. Only a small fraction of the butenes is hydrogenated. The main product of hydrogenation is isobutane (Table 2). Normal olefins may be converted to isoparaffins over acidic catalysts. The reaction is commonly known as "hydroisomerization" (*12*).

Hydrogenolysis reactions over platinum on silica gel produce benzene plus butane, toluene plus propane, ethylbenzene plus ethane, and n-propylbenzene plus methane. Hydrogenolysis rates are between one-third and one-fourth of the overall cyclization rate. The reaction is not selective. At lower temperatures (316–371°C), hydrogenolysis between the first and second carbon of the butyl side chain (producing toluene plus propane) is the most prevailing (Table 13). At higher temperatures (427–482°C) cleavage between the second and third carbon atoms of the butyl side chain (producing ethylbenzene plus ethane) becomes more important. Through the whole temperature range studied, hydrogenolysis between the ring and the α-carbon atom is the least important of the different types of scissions possible (Fig. 6).

At longer residence times (at higher conversion levels), hydrogenolysis rates are more retarded than cyclization rates (Fig. 7). Hydrogenolysis-to-total cyclization molar ratios decrease from 0.35 to 0.24 with the LHSV changing from 36 to 4.

Retardation of hydrogenolysis is probably caused by bicyclic aromatics (naphthalene and methylindenes).

The distribution of different types of

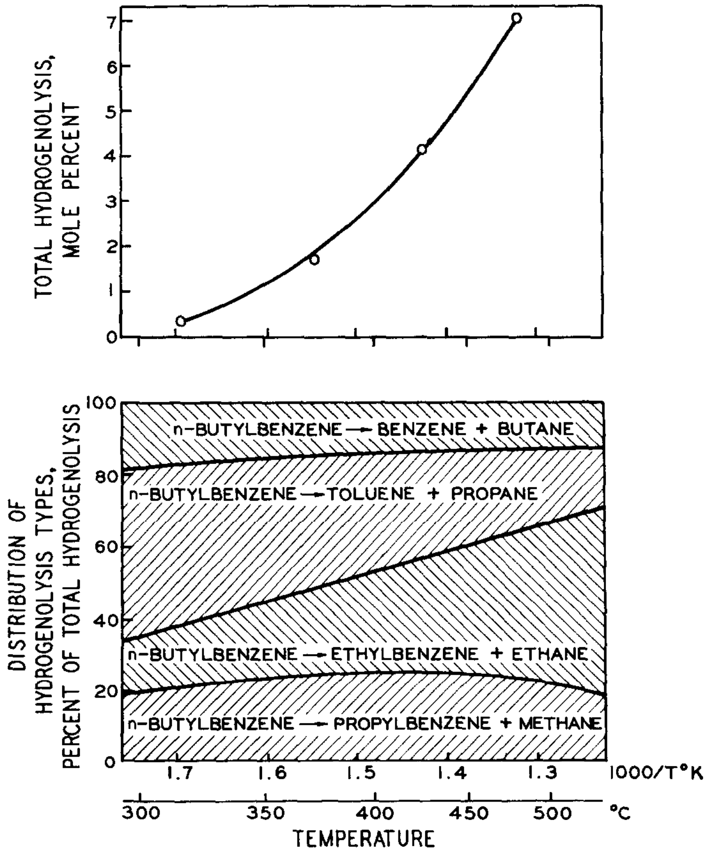


FIG. 6. Hydrogenolysis of n-butylbenzene over platinum-on-silica catalyst at a H_2 to feed mole ratio of 3 and a LHSV of 9.

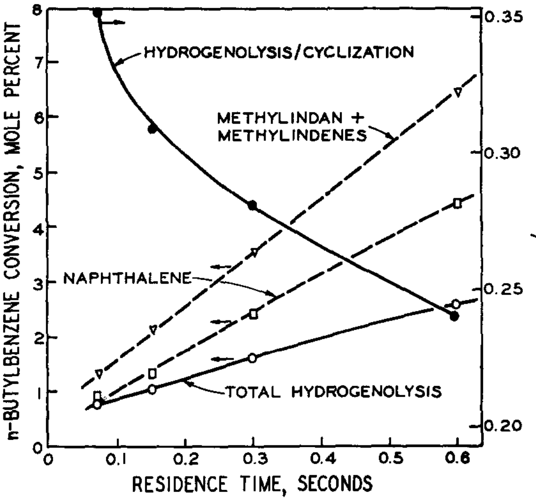


FIG. 7. Reactions of *n*-butylbenzene over platinum on silica gel at 371°C temperature at a H_2:feed mole ratio of 3.

hydrogenolysis reactions is unaffected by changing residence times (Table 13). Secondary hydrogenolysis is very limited. The paraffin product of hydrogenolysis—once it leaves the catalyst—does not readsorb and react further. In most of our experiments, *n*-butane/benzene mole ratios are about 0.95.

Over platinum on silica-alumina, acid-catalyzed cracking and platinum-catalyzed hydrogenolysis reactions proceed simultaneously. The different contributions from the two types of fragmentation determine the distribution of the scission products (Table 13). About one-half of the fragmentation occurs between the aromatic ring and the α-carbon atom. Over platinum on silica gel, this is the least frequent position of hydrogenolysis. Benzene and a C_4 olefin may be produced in cracking. However, most of the olefins are subsequently hydrogenated on platinum sites. Over the platinum on silica-alumina catalyst, concentrations of benzene plus butanes and *n*-propylbenzene plus methane do not match each other (Table 2). There is an abundance of methane relative to *n*-propylbenzene, and less butanes are found than benzene. Butane/benzene ratios are 0.56 and 0.59 at 371° and 427°C temperatures. At 482°C the butane/benzene ratio is only 0.34. Part of the butanes initially formed may be readsorbed later and crack further.

Contributions of the acid-catalyzed cracking and platinum-catalyzed hydrogenolysis may be determined separately. Fission between the β–γ and γ–δ carbon atoms proceeds predominantly via the platinum-catalyzed hydrogenolysis. (On silica-alumina cracking catalyst, cracking at these positions is below 0.06%, Table 13). Hydrogenolysis selectivities may be similar over platinum-on-silica-alumina and platinum-on-silica-gel catalysts. From the hydrogenolysis patterns observed over platinum on silica gel (where acid-catalyzed cracking is absent), one may calculate hydrogenolysis of the phenyl–α and α–β bonds. The total extent of hydrogenolysis over Pt on silica-alumina may be estimated. At 371° and 427°C, hydrogenolysis may be responsible for about 55% of the total fragmentation (0.51 mole % and 0.75 mole %). At 482°C, hydrogenolysis is about 0.92 mole %, only 37% of total fragmentation. Platinum supported on the silica-alumina has only one-third to one-eighth of the hydrogenolysis activity of platinum supported by neutral silica gel.

Hydrogenolysis and cracking rates increase with increasing temperature (Table 2).

Over platinum on alumina, the rates of

hydrogenolysis and cracking are high, similar to the rates of cyclization. The distribution of the products of fragmentation reactions is similar to that observed over the platinum on silica-alumina catalyst. Fission between the aromatic ring and the α-carbon atom of the side chain is the predominant reaction (Table 13). Relative rates for hydrogenolysis and cracking were determined in a manner similar to that used for platinum on silica-alumina. Hydrogenolysis-to-cracking ratios are probably 59:41. It is interesting that cyclization over platinum on alumina follows the pattern of the neutral platinum on silica gel, while cracking is similar to that observed over platinum on silica-alumina. However, on platinum on alumina, only a small fraction of the butenes cracks further down to smaller fragments. Butane/benzene ratios are 0.9 and 0.95 at 20 min and 65 min catalyst on-stream times over platinum on alumina (versus 0.56 and 0.62 over platinum on silica-alumina).

Other Reactions

Small amounts of *n*-butylcyclohexane are formed over all the catalysts tested (Table 2).

Higher molecular weight hydrocarbons may be formed by acid-catalyzed transalkylation reactions over platinum on silica-alumina. Mass-spectrometric analysis shows C_{11} alkylbenzenes (0.2%), dimethylindans and dimethylindenes (0.4%), methylnaphthalenes (0.1%), and traces of dimethylnaphthalenes in the product of the 482°C experiment.

The possible reactions of *n*-butylbenzene are summarized in Fig. 8.

SUMMARY

Dehydrocyclization. There are at least two different dehydrocyclization processes over supported platinum catalysts. Cyclization over acidic catalysts is a self-alkylation process involving carbonium ion intermediates. The stability of the intermediate carbonium ion determines whether cyclization forms five- or six-membered rings. The acid-catalyzed cyclization produces almost exclusively five-membered rings from *n*-butylbenzene.

Platinum metal catalyzes cyclization by a different mechanism. Between 371° and 427°C at atmospheric pressure and at an H_2-to-hydrocarbon mole ratio of 3, the platinum-metal-catalyzed rates of cyclization to five- and six-membered rings are about equal. Over dual-functional catalysts (e.g., platinum on acidic supports), acid- and platinum-catalyzed cyclizations may proceed simultaneously.

Isomerization. Platinum metal catalyzes at least two types of isomerization processes. One of these involves cyclic intermediates; the other is a 1–2 methyl shift, involving α–γ diadsorbed intermediates.

Acid-catalyzed isomerization, involving carbonium ions, occurs over platinum on silica-alumina and silica-alumina. By dehydrogenating *n*-butylbenzene to phenylbutenes, platinum facilitates the formation of carbonium ions and thus increases the rate of isomerization.

Fragmentation: Hydrogenolysis and cracking. Fragmentation of *n*-butylbenzene over silica-alumina occurs exclusively by cracking. The reaction is very selective. Cracking of the bond between the aromatic ring and the side chain occurs more than 100 times more frequently than cracking of all the other bonds combined.

Hydrogenolysis occurs over platinum on neutral supports. Scission of the different side-chain bonds have about equal probability.

Dehydrogenation. Dehydrogenation conversions are equilibrium-limited over platinum on silica and platinum on alumina. Dehydrogenation rate is substantially lower over platinum on silica-alumina than over the other platinum catalysts. Silica-alumina does not catalyze dehydrogenation.

Interaction between platinum and the acid sites. When platinum is impregnated on silica-alumina, both the specific activities of platinum (dehydrocyclization, dehydrogenation, and hydrogenolysis) and the acidity of the silica- alumina decrease. This mutual activity loss suggests an interaction between platinum and the acid sites of the support. A similar interaction

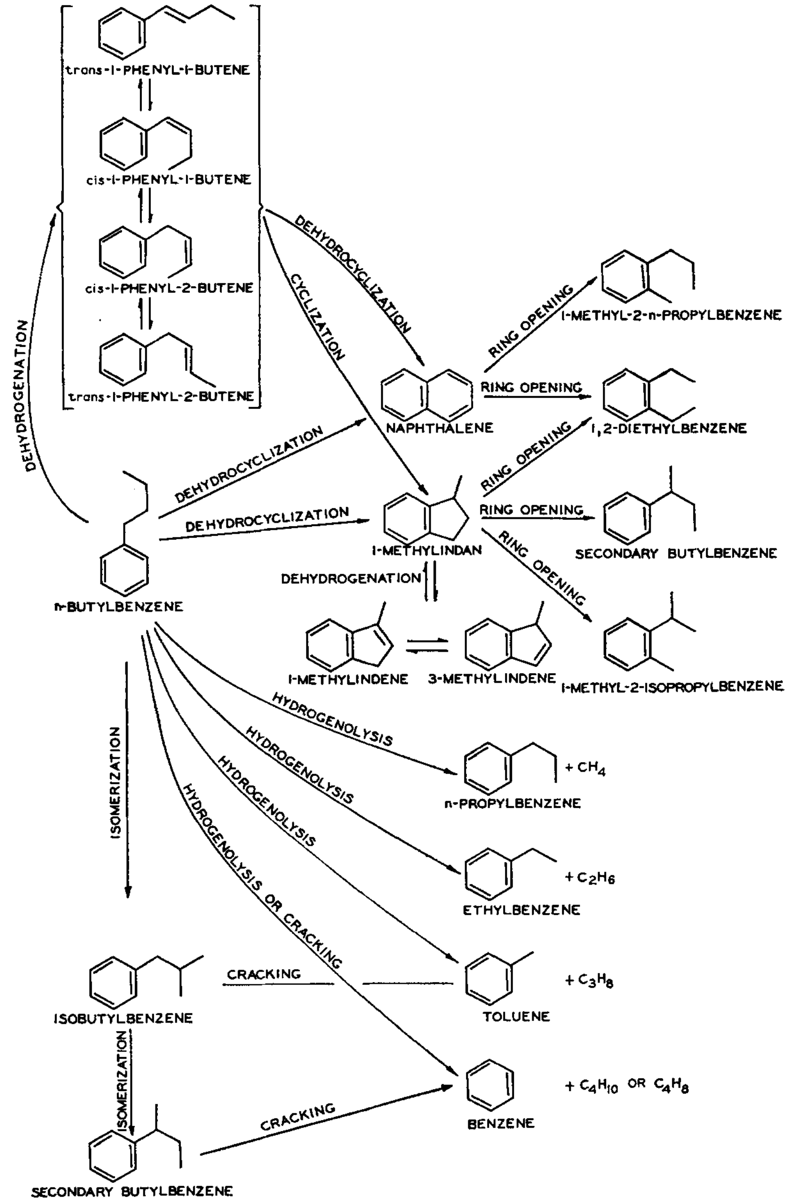


Fig. 8. Catalytic reactions of *n*-butylbenzene.

between the acid sites of silica-alumina and nickel has been recently described by Langlois, Sullivan, and Egan (*13*).

Acknowledgments

The author thanks Chevron Research Company for permission to publish this work and Dr. G. E. Langlois for stimulating discussions in the course of this work.

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