

## Catalytic Isomerization of Tetralin

Dual-functioning catalysts having acidic and dehydrogenating activities are used in many petroleum processing operations. The reactions occurring over these catalysts are isomerization, dehydrogenation, cyclization, hydrogenolysis, and cracking. Recently we used the reactions of *n*-butylbenzene to clarify the roles of the acid and platinum components of reforming catalysts in these reactions (1). We found that cyclization of alkylbenzenes over acidic catalysts was a self-alkylation process involving carbonium ion intermediates. The stability of the intermediate carbonium ion determined whether cyclization forms five- or six-membered rings. The acid-catalyzed cyclization produced almost exclusively five-membered rings from *n*-butylbenzene. Platinum-catalyzed cyclization occurred by a different mechanism. Rates of cyclization of *n*-butylbenzene to five- and six-membered rings over platinum-silica gel catalyst were about equal at around 400°C temperature.

This determination of acid and dehydrocyclization activities and our mechanistic interpretations were based on the assumption that once formed, five- or six-membered products of dehydrocyclization do not isomerize to each other. The experiment described here justifies this assumption.

### EXPERIMENTAL

We reacted tetralin over four different catalysts, representing wide variations in acid and dehydrocyclization activities. The catalysts were alumina (American Cyanamid Aeroextrudate 9999), silica-alumina (Socony Mobil white TCC beads cracking catalyst, with a BET nitrogen surface area of 426 m<sup>2</sup>/g), 2% platinum impregnated on Davison desiccant grade silica gel (800 m<sup>2</sup>/g BET surface area), and 2% platinum impregnated on Socony Mobil white TCC beads. Catalyst preparation and activation procedures were discussed earlier (1).

Reaction conditions were 371°C temperature, an LHSV of 6.8, atmospheric total pressure, and an H<sub>2</sub> diluent flow of 34.2 ml/min. In each experiment 0.35 g (between 0.5 ml and 0.6 ml) catalyst was used. Catalysts were pretreated first for 1½ hr in dry air at 480°C followed by 1 hr in dry H<sub>2</sub> at 565°C. The experiments were 30 min long. Conversion figures were based on analyses of reaction effluent samples (taken at 20 min onstream times) and liquid products (collected between 5 min and 30 min). We used a 91.5 m long, 0.508-mm ID stainless steel capillary gas chromatographic column filled with Ucon LB-550-X polypropylene glycol. Identification of minor products is tentative, based on gas chromatographic retention times.

The feed was Eastman Organic Chemical "P-550" 1,2,3,4-tetrahydronaphthalene. Purity (by gas chromatography) was 99.5 mole %. Analyses were corrected for feed impurities. To avoid plugging by naphthalene over the two platinum-containing catalysts, in Experiments 3 and 4 the above feed was diluted with 3 volume parts of benzene. In these experiments, the initial hydrogen-to-tetralin mole ratio was 13.2 to 1, and initial tetralin, benzene, and hydrogen partial pressures were 0.054, 0.246, and 0.70. Naturally, conversions to benzene (and toluene) in Experiments 3 and 4 could not be determined.

### RESULTS AND DISCUSSION

Reaction product analyses are shown in Table 1. Isomerization of tetralin to methylindans or methylindenes was in the same order of magnitude as ring opening to *n*-butylbenzene, phenylbutenes, and phenylbutadienes. This relationship suggests that tetralin isomerization to methylindans might proceed through phenylbutene intermediates. As expected, the two platinum-containing catalysts converted tetralin to naphthalene. The conversion level probably

TABLE 1  
REACTIONS OF TETRALIN OVER DIFFERENT CATALYSTS AT 371°C

Catalyst:	Alumina	Silica-alumina	2% Platinum on silica gel	2% Platinum on silica-alumina
Experiment No.:	1	2	3	4
Feed:	a	a	b	b
Conversions, moles/100 moles of tetralin feed				
Unreacted tetralin	99.74	97.10	0.54	0.68
Naphthalene	0.06	0.64	99.40	99.00
1-Methylindan	—	0.19	—	—
2-Methylindan	—	0.29	0.01	0.14
1-Methylindene	—	—	0.01	—
<i>n</i> -Butylbenzene	0.02	0.02	—	—
Phenylbutenes	—	0.14	—	0.06
Benzene	—	0.08	<i>c</i>	<i>c</i>
Toluene	—	0.04	<i>c</i>	<i>c</i>
Ethylbenzene	—	—	0.02	0.02
<i>n</i> -Propylbenzene	—	—	0.01	0.04
Other <sup>d</sup>	0.18	1.50	0.01	0.03

<sup>a</sup> The feed was Eastman Organic Chemical "P-550" 1,2,3,4-tetrahydronaphthalene. Purity (by gas chromatography) was 99.5 mole %. Analyses were corrected for feed impurities. Initial hydrogen-to-tetralin mole ratio was 3.3 to 1. Initial tetralin partial pressure was 0.23 atm.

<sup>b</sup> To avoid plugging, the above feed was diluted with 3 volume parts of benzene. Initial hydrogen-to-tetralin mole ratio was 13.2 to 1. Initial tetralin, benzene, and hydrogen partial pressures were 0.54, 0.246, and 0.70 atm.

<sup>c</sup> Undetermined.

<sup>d</sup> Includes phenylbutadienes.

corresponds to the tetralin  $\rightleftharpoons$  naphthalene equilibrium. Dehydrogenation rates over alumina and silica-alumina are very slow, silica-alumina being about an order of magnitude more active in this respect than alumina.

#### CONCLUSION

Isomerization of tetralin to methylindan over alumina, silica-alumina, platinum-on-alumina, and platinum-on-silica-alumina catalysts at 371°C is extremely slow. In the reactions of *n*-butylbenzene, the distribution of dehydrogenation products (i.e.,

naphthalene and methylindan) is therefore not influenced by such isomerization. Thus, the naphthalene-methylindan distributions in the reaction product of *n*-butylbenzene represent primary reaction paths.

#### REFERENCE

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