

Shape-Selective Reactions with Zeolite Catalysts

VII. Alkylation and Disproportionation of Cumene to Produce Diisopropylbenzene

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Cumene disproportionates to diisopropylbenzenes (DIPB) and benzene over Mobil ZSM-12 zeolite catalyst. In addition, cumene is alkylated with propylene to give DIPB with high selectivity. With cumene alkylation, *para*-DIPB is favored (65–80%), with 20–30% *meta* and 0–5% *ortho* isomers also being produced. This is in direct contrast to thermodynamic considerations, where *meta*-DIPB is the favored isomer. © 1989 Academic Press, Inc.

INTRODUCTION

Previous reports in this series describe the alkylation of benzene with propylene to produce cumene (1). The major by-products observed are diisopropylbenzene (DIPB) isomers. At temperatures higher than 275°C, *n*-propylbenzene (*n*-PrBz) is also produced.

Diisopropylbenzenes are useful chemical intermediates. Oxidation of the *meta* or *para* isomers produces the corresponding dihydroperoxides which are used as initiators for various free radical reactions (2). These dihydroperoxides are also intermediates for production of resorcinol and hydroquinone, respectively, and acetone, by an acid-catalyzed rearrangement (3, 4). *Meta*- and *para*-DIPB also may be dehydrogenated to produce the corresponding diisopropenylbenzenes, used as monomers for preparation of an impressive number of new polymers and copolymers (5).

EXPERIMENTAL

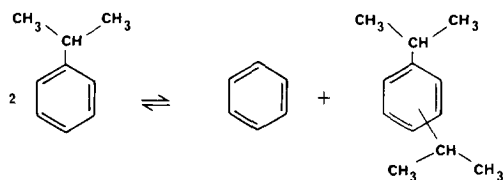
Materials. High-purity cumene was passed through alumina before use and propylene containing traces of propane was used without further treatment.

Catalyst. Procedures for synthesis of ZSM-12 catalysts have been described (6).

All catalysts were converted to the acid forms by initial calcination, followed by ion exchange with an ammonium salt and heating to expel ammonia. The catalysts were calcined in nitrogen followed by air, at 500°C, for about 1 h before use.

Apparatus. Equipment was constructed of stainless steel including a 1.5-cm i.d. × 53-cm down-flow reactor. Four to eight g of catalyst were positioned in the electrically heated fixed-bed reactor, which contained three centered thermocouples within the bed. The highest temperature in the bed is recorded. Cumene was delivered by a metering pump to a vaporizer and mixed with propylene, the latter at rates determined by a mass flow meter. The vapor from the reactor was passed through cold water condensers and the remaining gas volume was measured by a dry gas tower with a mercury-sealed float. A silica-gel g.c. column was used to analyze gases and a 5% SP-1200/5% Supelcoport column was used for the organic liquid. All equipment was automated to permit continuous, unattended operation.

Definitions. Weight hourly space velocity (WHSV): weight of reactor feed per unit weight of catalyst per hour. Selectivity to products; weight of each product obtained divided by the weight of starting materials consumed, normalized to 100%. Conver-



SCHEME 1

sion: Weight of starting material consumed divided by weight of starting material.

RESULTS AND DISCUSSION

Cumene disproportionation (Scheme 1). Table 1 shows the results of passing cumene over ZSM-12 catalyst at 3480 kPa (500 psig) pressure, in the 150–250°C. temperature range. Cumene conversion increased from 3 to 45% with increases in temperature. Benzene selectivity remained virtually constant, around 35%. However, diisopropylbenzene selectivity increased from 24 to 61% with increasing temperature, at the expense of propylene oligomers. In addition, the ratio of *para/meta* DIPB isomers changed roughly from 2/1 to 1/2 as temperature increased. The presence

TABLE 1

Cumene Disproportionation over HZSM-12,
SiO₂/Al₂O₃ = 180 (mole ratio)

Temp (°C)	150	200	250
Conversion (Wt%)			
Cumene	2.9	13.2	45.1
Selectivity to products (Wt%)			
Benzene	36.5	33.6	34.2
DIPB			
<i>para</i>	14.4	26.9	21.5
<i>meta</i>	9.4	31.6	38.9
<i>ortho</i>	0	0.7	0.5
Tot. DIPB	23.8	59.2	60.9
<i>n</i> -PrBz	4.1	0.7	0.7
Other	35.6	6.5	4.2
DIPB isomers			
<i>para</i>	60.5	45.5	35.3
<i>meta</i>	39.5	53.3	63.9
<i>ortho</i>	0	1.2	0.8

Note. DIPB = diisopropylbenzene; *n*-PrBz = *n*-propylbenzene; Other = propylene oligomer. Conditions: pressure 3480 kPa; WHSV, cumene 5.2.

TABLE 2

Alkylation of Cumene With Propylene over
HZSM-12, SiO₂/Al₂O₃ = 250 (mole ratio)

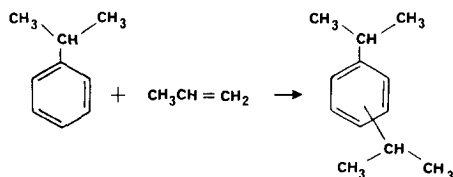
Temp. (°C)	175	185	200	225
Conversion (wt%)				
cumene	7.5	15.2	13.4	22.5
propylene	27.8	44.6	42.3	76.0
Selectivity to products (wt%)				
<i>p</i> -DIPB	78.4	70.2	74.7	66.3
<i>m</i> -DIPB	19.3	21.3	20.7	28.9
<i>o</i> -DIPB	0.8	1.9	1.4	0.5
Other Aroms.	1.5	6.6	3.2	4.3

Note. DIPB = diisopropylbenzene. Conditions: pressure, atm; cumene/C₃H₆, WHSV 10.5/1.3, mole ratio 2.8/1.

of *n*-propylbenzene, 3–5% selectivity, at low temperature (150°C) and conversion (3%) is a surprise since much lower values were observed during alkylation (see below). At low temperature, 150°C, propylene oligomers, 35% selectivity, are a major product which suggests that cumene dealkylation occurred to give free propylene that subsequently reacted with itself to produce oligomers.

At 200–250°C, the highest conversions to DIPB are observed, Table 1. For a commercial process, the benzene would need to be recycled repeatedly to produce more starting cumene. Disproportionation may be practical only at a location where large volumes of cumene are produced.

Alkylation of cumene with propylene (Scheme 2). ZSM-12 catalyst was used for the alkylation reaction at 175–225°C and atmospheric pressure, Table 2. Excellent selectivity to DIPB (94–99%) was observed at moderate conversion (15–25%) of cumene. Propylene oligomerization, cracking, and aromatization reactions increased with temperature from about 1 to 6% but dimin-



SCHEME 2

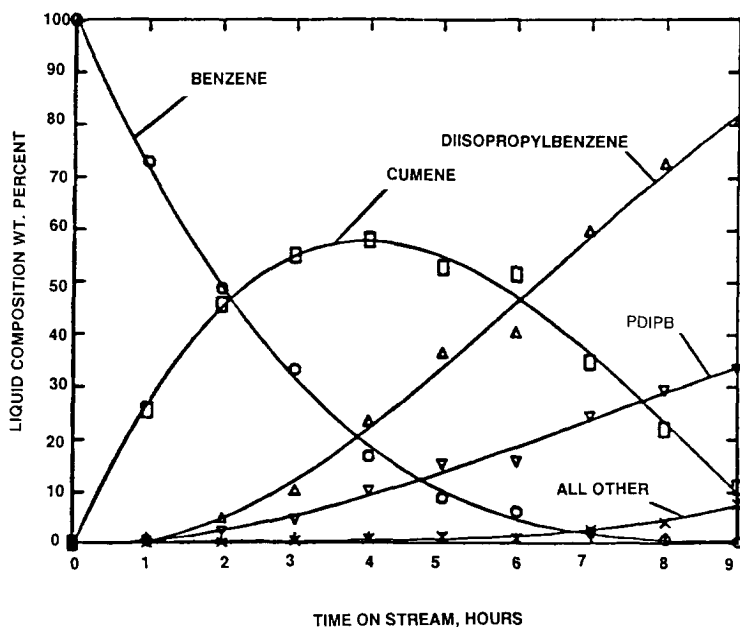


FIG. 1. Alkylation of benzene with propylene—HZSM-12 Catalyst, batch reaction, continuous propylene addition, conditions: temperature 225–250°C, pressure 2785–4525 kPa

ished with time on stream. *Para*-DIPB is the dominant isomer but decreases with temperature as the *meta*-DIPB isomer increases from about 20 to 30% at 225°C.

In a similar manner, cumene was alkylated with propylene over ZSM-12 at 3480 kPa pressure. DIPB selectivity ranged from 82–85%, approximately a 14% reduction compared with the atmospheric pressure results above. Propylene conversion was higher (83–97%) compared with experiments at atmospheric pressure (28–82%). Higher selectivities to the C7–C10+ aromatic and propylene oligomer/cracking by-products (1–4%) account for the difference. This by-product increase with an increase in pressure may be due to a change from a gaseous to a liquid phase in the catalyst bed. The distribution of DIPB isomers was remarkably constant throughout the entire temperature range.

Dialkylation of benzene with propylene over ZSM-12. Since cumene is also prepared from benzene and propylene, it was of interest to determine whether DIPB could be prepared directly and efficiently

from these raw materials in one step. Seven g of powdered ZSM-12 catalyst was suspended in 100 ml of liquid benzene in a stirred autoclave held at 225–250°C and 2785–4523 kPa pressure. Liquid propylene was pumped into the autoclave at an initial rate of 20 cm³/h, diminishing to about half this rate as the reaction proceeded. Liquid samples were withdrawn every hour for analysis.

Results show the classical, successive reaction pathway characterized by a steady, decreasing benzene concentration, then intermediate cumene building to a maximum, followed by DIPB's rapidly increasing during the remainder of the run, Fig. 1. This technique shows some promise for production of DIPB directly from benzene and propylene in a batch-type operation.

DIPB isomer distribution. A large amount of *para* isomer is produced in the DIPB product (69–80%) by alkylation of cumene with propylene over ZSM-12, Table 2. The calculated thermodynamic equilibrium value is only 32.5% *para* at 100°C (1) and the trend indicates a decrease at

higher temperatures. The high *para* isomer selectivity observed with ZSM-12 is a shape-selective effect where reactions occur within the zeolite pores. The *para* isomer has the smallest minimum dimension and will diffuse out of the pores much more rapidly than the larger *ortho* and *meta* isomers, analogously to the corresponding methyl and ethyl substituted analogs in ZSM-5 (9).

When ZSM-12 was suspended in benzene and propylene was added over a 9-h period (Fig. 1) a situation more closely resembling a homogeneous solution reaction was obtained. The final *para* isomer content was about 40%. With a dilute aluminum chloride catalyst in liquid cumene, a 63/29.5/4.5 *para/meta/ortho* distribution for DIPB was observed (8). After tripling the concentration of aluminum chloride, also an isomerizing catalyst, the distribution observed was 40/63/4. This suggests formation of the *para* isomer initially followed by isomerization to *meta* over a higher concentration of catalyst sites. Products of the analogous ZSM-12 catalyzed reaction in an autoclave are continually exposed to the zeolite catalyst for a long period of time. The *para/meta/ortho* ratio of DIPB changed from 51.3/47.8/0 after 1 h to 41.3/58.2/.05 after 9 h of reaction. The *para* isomer was favored initially but was exposed to surface acidity of the catalyst for many hours. Isomerization reactions occurred and the isomer mixture more nearly approached thermody-

namic equilibrium concentrations, favoring *meta*.

The large pore openings of ZSM-12 (12-oxygen ring channels) (7) are ideal for alkylation of benzene analogues with propylene to produce the corresponding isopropyl derivatives. This work indicates high potential for commercial production of *meta* and *para* diisopropylbenzene.

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