

## Kinetics of Transalkylation of Diisopropylbenzenes with Benzene

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### ABSTRACT

Transalkylation is an important class of reaction to utilize low value by-products of alkylation reactions. Diisopropylbenzenes (DIPBs) are such by-products formed during the production of cumene by isopropylation of benzene. In the present work, the DIPBs were utilized to produce value-added chemical like cumene by transalkylation with benzene. Transalkylation reactions were carried out in the vapor phase over commercial H-mordenite catalyst in a fixed-bed down-flow laboratory scale reactor. The influences of various process parameters such as temperature, space-time, and benzene-to-DIPB mole ratio on conversion were studied. The experiments were carried out to choose the zone in which the mass transfer effects were negligible. A detailed literature review was made establish a suitable mechanism to explain the course of the reaction.

**Key words:** Transalkylation; Diisopropylbenzene; Cumene; H-mordenite; Kinetics.

### INTRODUCTION

Transalkylation is an important class of reaction to convert low value polyalkylated by-products to commercially more important chemical intermediates or end products. Transalkylation is the reaction between two similar or dissimilar molecules involving transfer of an alkyl group. This reaction is commercially very interesting as some of the low valued polyalkylated byproducts can be converted to their monosubstituted or disubstituted homologues from dialkylated and trialkylated byproducts respectively, which are in higher demand and of higher value.

For example, xylenes are the key raw materials for polyesters, plasticizers and engineering plastics. The major sources of these aromatic hydrocarbons, the reforming and pyrolysis gasoline, contains appreciable amount of toluene and trimethylbenzenes (TMB). A convenient way to increase xylenes production is to transform less valuable toluene and TMB by catalytic transalkylation. This transformation was carried out over various types of zeolite catalyst like H-beta, H-mordenite, H-omega, Y, NaHY; molecular sieves like SAPO-5, transition metals Substituted aluminophosphate; and hybrid heteropoly acid/zeolite catalysts. [1-6]

Ethyl benzene on the other hand is commercially important intermediate for the manufacture of styrene which is an important monomer in the production of synthetic rubber, plastics and resins. The worlds more than 90% of ethyl benzene demand is met through benzene ethylation. However, benzene ethylation is usually accompanied by the formation of large amount diethylbenzenes isomers. Many processes were developed to convert diethylbenzenes isomers byproduct to increase the yield of ethylbenzene by transalkylation with benzene over various types of zeolite catalyst like  $\beta$ -zeolite, faujasite Y, beta, Y etc. [7-9]

Yet another example of transalkylation reaction is the selective synthesis of 4-alkyl- or 4,4'-dialkyl biphenyls or naphthalenes. These compounds find many applications as valuable industrial intermediates to produce thermotropic liquid crystals or heat-resistant polymers. The direct alkylation of biphenyls or naphthalenes with alcohols (methanol and ethanol) gives rise to undesirable product distribution. However, transalkylation of these compounds with polyalkylbenzenes (byproducts of alkylation reaction) was found to be highly shape selective as it proceeds through an extremely bulky transition state. Recently this approach was used for selective transmethylation [10], transethylation [11] and transisopropylation [12] of biphenyl and naphthalene.

Cumene is an important intermediate for the production of phenol and acetone. Conventionally it is produced by isopropylation of benzene. However, during the isopropylation of benzene to cumene, 5-10 wt% diisopropylbenzene (DIPB) isomers are produced as by-product. These isomers are diverted to the fuel pool in many commercial plants. This results in additional raw material consumption affecting the economy of the whole process. The one way of utilizing DIPBs is to produce valuable chemicals such as cymenes, by transalkylating with toluene [13-16] in a separate

transalkylation reactor. Cymenes are important starting materials for the production of a range of intermediates and end products, such as cresols, fragrances, pharmaceuticals, herbicides, heat transfer media, etc. Another way of utilizing DIPBs is to produce cumene by transalkylation with benzene [15-16]. In this case, the DIPBs (or heavy fractions) can be separated from alkylated product stream by conventional methods and recycled to produce cumene either in the same alkylation reactor or in a separate transalkylation reactor.

Only a few studies were reported in open literature on transalkylation of DIPB with benzene. For example, Suresh et al. [15] studied this reaction under liquid phase conditions over sulfate-treated superacidic zirconia catalyst in the temperature range of 175-225 °C. It was also reported the use of large pore zeolites (H-mordenite, La-H-Y, and H-beta) for this reaction under liquid phase condition in the temperature range of 170-210 °C both in atmospheric and high pressure condition (25 kg/cm<sup>2</sup>) [16]. Many processes were also developed using various types of zeolite catalyst for transformation of DIPB to cumene using pure isomers of DIPB or their mixture or cumene bottoms under liquid phase conditions and at high pressure [17-26]. However, detail kinetic study for such an important system is not reported in open literature under vapour phase conditions at atmospheric pressure using zeolite catalyst. Considering the importance of the system; the detail kinetic study was carried out under vapour phase conditions at atmospheric pressure over commercial H-mordenite catalyst using mixture of DIPB isomers (2:1: *m*:- *p*-) as the feed (since an industrial cumene bottom fraction consist of these isomers).

It is well known to catalyze the alkylation of aromatics with a variety of conventional Friedel Crafts catalysts. These materials are highly corrosive to process equipment, create operational problems, and are often difficult to dispose of in an environmentally acceptable manner. Therefore, nowadays these catalysts are being replaced by Zeolites and zeolite-like materials which are shown to be promising catalysts for conversion of alkylaromatics due to their high activity, selectivity, environmental safety and avoidance of corrosion. Present study is thus carried out using protonic form of mordenite (H-M) catalyst.

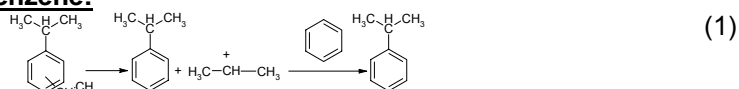
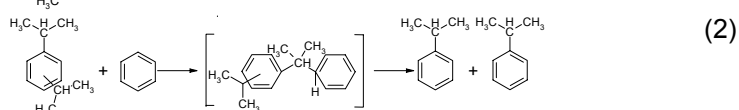
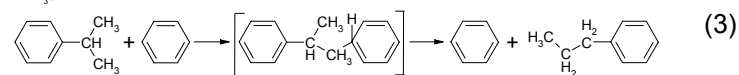
## EXPERIMENTAL

**Materials.** Benzene (≥99.7%) of GR grade was procured from Merck (India) Ltd., Mumbai, India. Diisopropylbenzenes (98%), 2: 1 mixture of *m*- and *p*-isomer, was obtained from Acros Organics, New Jersey, USA. H-mordenite in the form of 1/16 inch extrudate was obtained from Sud-Chemie India Pvt. Ltd., Baroda, India.

**Experimental Setup.** The catalytic experiments were carried out in a fixed-bed, continuous down-flow cylindrical stainless steel (SS 316) tubular laboratory scale reactor (0.014m i.d. and 0.16m in length). The reactor was fitted with a preheater in the upstream and a condenser at its outlet. The reactor was heated electrically from outside and insulated to prevent heat loss. The temperature of the reactor and preheater was measured by a thermocouple placed in a thermowell placed at the centre of the respective parts of the setup.

**Procedure.** In a typical run, about 0.0035 kg of catalyst was loaded into the reactor and supported by inert beads on either side of the bed. The catalyst was activated 'in situ' for 2 h in an atmosphere of nitrogen before the experimental runs were started. The benzene-DIPB mixture was introduced with the help of a metering pump and vaporized in the pre-heater before contacting the catalyst. The reactant vapors along with nitrogen entered the reactor from the top. The product vapors, along with un-reacted reactants, were condensed in the condenser and the liquid samples collected.

**Products Analysis.** The liquid samples collected from the condenser were analyzed in a gas-liquid chromatography (GLC) using a 2 m×3 mm stainless steel column packed with 10% OV-17 on Chromosorb W (80/100). A Chemito Model 8610 GC interfaced with a Shimadzu C-R6A Chromatopac data processor was used for the analysis. The column temperature was programmed with an initial temperature at 100 °C, increased at 10 °C/min to 250 °C. Nitrogen was used as the carrier gas with a flow rate of 15 cm<sup>3</sup>/min. An injector temperature of 150 °C was used during the analysis. An FID detector was used at the temperature of 300 °C. The material balance was checked and it was >98%.

**Transalkylation of DIPB with benzene:**SN<sup>1</sup> MechanismSN<sup>2</sup> Mechanism**Cumene-*n*-PB isomerisation:****Scheme 1.****RESULTS AND DISCUSSION**

Transalkylation of 2:1 mixture of *m*- and *p*-DIPB with benzene to produce cumene was carried out over H-mordenite catalyst. The *n*-propylbenzene (*n*-PB) was obtained as the byproduct.

**Reaction Mechanism.** The DIPB undergo transalkylation with benzene to produce cumene. The cumene formed in the reaction may also undergo isomerisation forming *n*-PB. Two mechanisms (Scheme 1) are generally used to describe transalkylation/ disproportionation types of reactions over zeolite catalysts: (1) SN<sup>1</sup> mechanism in which alkyl carbenium ions were supposed as intermediate (2) SN<sup>2</sup> mechanism involving bimolecular intermediates, in which two aromatic rings are bridged by a C-atom of the alkyl group.

The various parameters can affect the relative proportion of the two mechanisms. As for example, disproportionation of *n*-PB over various zeolites (USY, beta, mordenite, ZSM-5) shows that reaction mechanism depends on the internal pore structures of zeolites [27]. The preference for *n,n*-propylbenzene (*n,n*-PB) formation decreases in the order of USY > beta > mordenite > ZSM-5. The ZSM-5 has inadequate internal pore space required for the formation of biphenylmethane intermediates as in the SN<sup>2</sup> mechanism. Therefore reaction proceeds via SN<sup>1</sup> mechanism that results statistical distribution of *n,n*-PB and *n,i*-PB.

Sometimes stability of carbenium ions determines the mechanism of the reaction. For example, for xylene transformation over zeolite Y, transalkylation can not proceed through SN<sup>1</sup> mechanism as it leads to the formation of unstable methenium ions [28].

Conversion of 1- and 2-methylnaphthalene over zeolites with different pore widths viz. HZSM-5 (0.54 × 0.56 nm), HZSM-12 (0.57 × 0.61 nm), and HY (0.74 nm) shows that transalkylation is the major reaction, besides isomerisation, on HY catalyst. On zeolite HZSM-12 and HZSM-5, there is virtually no transalkylation for both 1-methylnaphthalene and 2-methylnaphthalene although the zeolite is active in isomerization. This may be due to the fact that the voids inside HZSM-12 and HZSM-5 are not spacious enough to accommodate the very bulky transition states required for the bimolecular transalkylation reactions of naphthalene derivatives [29].

**Table 2. Effect of Benzene-to-DIPB Mole Ratio on Conversion and Products Selectivity.<sup>a</sup>**

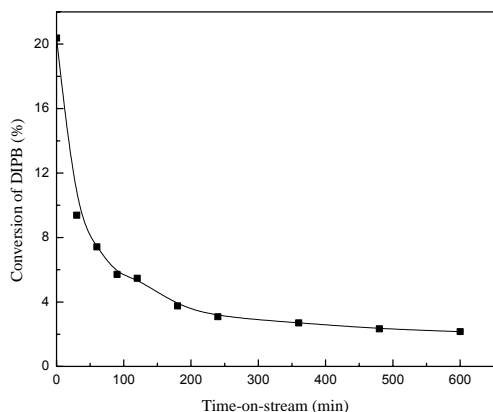
Benzene-to-DIPB mole ratio	Conversion (%) of DIPBs	Selectivity (%)	
		cumene	<i>n</i> -PB
4.0	1.16	100	0
5.0	2.25	100	0
6.5	4.69	94.9	5.1
8.6	4.73	95.3	4.7
12.2	6.59	96.3	3.7
19.3	9.24	95.9	4.1

<sup>a</sup> **Conditions:** pressure = 1 atm; temperature = 493 K; space-time = 19.7 h. kg catalyst/kmol; nitrogen-to-feed mole ratio = 0.5.

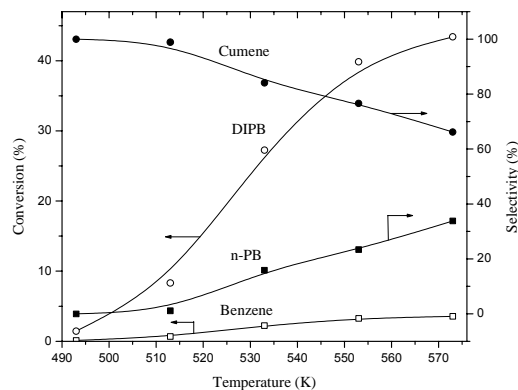
**Table 1. Effect of Space-Time on Conversion and Products Selectivity.<sup>a</sup>**

Space-time, h. kg catalyst/kmol	Conversion (%)		Selectivity (%)	
	Benzene	DIPB	cumene	<i>n</i> -PB
11.26	0.12	1.44	100	0
14.07	0.33	3.98	100	0
18.76	0.54	6.59	99.1	0.9
28.15	0.77	9.39	98.4	1.6
56.30	2.67	15.50	96.3	3.7

<sup>a</sup> **Conditions:** pressure = 1 atm; temperature = 493 K; benzene-to-DIPB mole ratio = 12.2; nitrogen-to-feed mole ratio = 0.5.



**Fig. 1. Effect of time-on-stream on conversion of DIPBs.** Conditions: pressure = 1 atm; space-time = 28.15 h. kg catalyst/kmol; benzene-to-DIPB mole ratio = 12.2; nitrogen-to-feed mole ratio = 0.5.



**Fig. 2. Effect of temperature on conversion and products selectivity.** Conditions: pressure = 1 atm; space-time = 11.26 h. kg catalyst/kmol; benzene-to-DIPB mole ratio = 12.2; nitrogen-to-feed mole ratio = 0.5.

During a study of cumene interaction with labeled benzene over medium pore H-ZSM-11 using  $^{13}\text{C}$  MAS NMR technique, the transalkylation and disproportionation reactions are not observed whereas this reaction proceeds over large pore mordenite. This can be explained by the space restrictions for the formation reaction intermediate in medium pore zeolites. The same experimental technique was also used to prove the existence of the intermolecular  $\text{SN}^2$  mechanism during the ethylbenzene transformations over mordenite catalysts [30].

In order to find out the cumene-*n*-PB isomerisation mechanism (intra or intermolecular) over H-ZSM-11; two experiments were carried out using in situ tracing MAS NMR techniques. (1) cumene labeled with  $^{13}\text{C}$  in the aromatic ring and (2) benzene labeled with  $^{13}\text{C}$  in the aromatic ring [30]. In both experiment, a benzene-*n*-PB aromatic ring label transfer was observed. This confirmed unambiguously the intermolecular character of cumene isomerization. In order to prove whether the reaction proceeds through monomolecular  $\text{SN}^1$  or bimolecular  $\text{SN}^2$  mechanism, again two experiments were conducted using cumene labeled with  $^{13}\text{C}$  in the alkyl chain at (1)  $\alpha$ - (2)  $\beta$ -position [30]. The  $^{13}\text{C}$  label was observed to transfer into  $\beta$ -position of *n*-PB in case of starting  $\alpha$ - $^{13}\text{C}$  cumene and into  $\alpha$ - and  $\gamma$ -positions in the case of starting  $\beta$ - $^{13}\text{C}$  cumene. This proves the bimolecular  $\text{SN}^2$  mechanism of cumene-*n*-PB isomerisation.

**Time-on-stream behavior of the catalyst.** The stability of commercial H-mordenite was tested for about 10 hrs time-on-streams at 493 K under atmospheric pressure. The activity of the catalyst was found to decrease with time-on-stream as shown in the Fig. 1. The conversion of DIPB falls from about 20% to about 3% after 10 hrs time-on-stream as observed from the figure. The deactivation of the H-mordenite catalyst is largely due to the formation of coke on pores of the zeolite structure and its faster deactivation is attributed to its high acidity and monodimensional nature of pore structure [31]. Coke is formed preferentially on the strongest acid sites and causes their deactivation. The presence of one coke molecule in a channel makes all the acid sites of this channel inaccessible to the reactant from the end at which the molecule is located that results faster deactivation of the mordenite catalyst. However, the catalyst can be simply reactivated by hot benzene flush when necessary or the reactivation might also be accomplished by burn-off of carbonaceous deposits [32]. The conversion and selectivity of products reported in the subsequent experiments are therefore based on 30 min time-on-streams.

**Effect of space-time on conversion and products selectivity.** The effect of space-time on conversion of benzene and DIPB and products distribution is shown in Table 1. As it is observed from the table, the conversion of both benzene and DIPB increases with increase in space-time as expected. However, the selectivity of cumene was observed to decrease with increase in space-time whereas the selectivity of *n*-PB increases with space-time. With increase in space-time isomerisation of cumene to *n*-PB increases that result lower selectivity of cumene at higher space-time.

**Table 3. Effect of External Diffusional Resistance on Conversion of DIPB<sup>a</sup>**

Space-time (h. kg catalyst/kmol)	Conversion (%) of DIPB	
	b	c
11.26	1.40	1.44
18.76	6.62	6.59
28.15	9.45	9.39

<sup>a</sup> **Conditions:** pressure = 1 atm; temperature = 493 K; benzene-to-DIPB mole ratio = 12.2; nitrogen-to-feed mole ratio = 0.5. b = 0.0025 kg of catalyst. c = 0.0035 kg of catalyst.

**Table 4. Effect of Intraparticle Diffusion on Conversion of DIPB<sup>a</sup>**

Partical size, d <sub>p</sub>	Conversion (%) of DIPB at space-time (h. kg catalyst/kmol) of		
	11.26	18.76	28.15
0.5	1.35	6.63	9.37
1.0	1.41	6.55	9.35
1.5	1.44	6.59	9.39

<sup>a</sup> **Conditions:** pressure = 1 atm; temperature = 493 K; benzene-to-DIPB mole ratio = 12.2; nitrogen-to-feed mole ratio = 0.5.

**Effect of benzene-to-DIPB mole ratio on conversion and products selectivity.** The effect of benzene-to-DIPB mole ratio on DIPB conversion and products selectivity was studied by varying the benzene-to-DIPB mole ratio from 4 to 19.3 as shown in Table 2. The conversion of DIPB was found to increase with increase in benzene-to-DIPB mole ratio. The selectivity of cumene was however found to be higher at lower mole ratio.

**Effect of Temperature on Conversion and Products Selectivity.** The effect of temperature on conversion of benzene and DIPB and product distribution was studied in the temperature range of 493-573 K under otherwise identical experimental conditions as shown in the Fig. 2. As it is observed from the figure, the conversion of benzene and DIPB increases with increase in temperature as expected. The selectivity of cumene was observed to decrease with increase in temperature whereas opposite trend was observed for *n*-PB. At higher temperatures, isomerisation of cumene to *n*-PB increases, thereby decreasing the selectivity of cumene and increasing the selectivity of *n*-PB. During the alkylation of benzene with propylene over HZSM-5 catalysts, *n*-PB becomes a major product (36% selectivity) at 300°C and at temperatures below 250°C; cumene isomerization is not a favorable reaction since there is a wide departure from the thermodynamic equilibrium ratios calculated for PBs [33]. The contamination of the *n*-PB isomer in cumene product purification has a profound impact on the economics of the cumene manufacturing process. The minimization of isomer byproduct yield to the lowest acceptable level is therefore growing need for this process. It is therefore desirable to carry out the reaction at temperature below 240°C. A small amount of C<sub>9-11</sub> was observed to form above 533 K and found to increase with temperature. However, the total amount of these compounds remains less than 0.5wt% even at 300°C and therefore not included in the results of Fig. 2.

**Mass transfer considerations.** For any kinetic study, it is important that the mass transfer resistances be negligible during the reaction. To estimate the external diffusional effects, experiments were carried out at constant space-time and catalyst size, but with varying feed rates. The results of Table 3 indicate that the conversion of DIPB for both the series at constant *W/F* are independent of feed rate. Therefore, the external mass transfer resistance is negligible.

Experiments were also conducted to test the intraparticle diffusional limitations by varying the catalyst particle size while keeping space-time constant. The experimental data obtained are presented in Table 4. The results showed that there was no change in conversion of DIPB with catalyst size indicating negligible intraparticle mass transfer resistance in the particle size range studied. The particle sizes employed in the kinetic study were within the intraparticle diffusion free range. In zeolite-catalyzed reactions, two types of diffusion processes are involved: (i) micropore diffusion inside the zeolite crystal and (ii) macropore diffusion between the zeolite crystals within the catalyst pellets. The above experiments for mass transfer resistances confirms only the absence of diffusion in the macropores. The resistance due to micropore could not be evaluated, as it requires a modification of the synthesis conditions of the zeolite that affect the micropore size of the crystals, which would subsequently affect the diffusional characteristics.

## COLCLUSIONS

The commercial H-mordenite catalyst was successfully used to transalkylate DIPB with benzene to cumene under vapour phase conditions at atmospheric pressure. Significant amount of *n*-PB was



observed to form above 513 K by isomerisation of cumene. The catalyst was found to deactivate with time-on-stream due to the formation of coke on pores of the zeolite structure. The conversion of DIPB increases with increase in space-time, benzene-DIPB mole ratio, and temperature. The selectivity of cumene increases with decrease in space-time and reactor temperature. The mass transfer effects were found to be negligible. A detailed review was reported on mechanism of transalkylation and isomerisation reaction.

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