

## Low temperature transalkylation of *o*-diethylbenzene with benzene to ethylbenzene using triflic acid as a catalyst

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### Abstract

The catalytic performance of trifluoromethanesulphonic acid (triflic acid) has been investigated for synthesis of ethylbenzene (EB) by transalkylation of *o*-diethylbenzene (DEB) with benzene (B). Different mole ratios of benzene to the isomer (1:1, 3:1 and 6:1) were used at atmospheric pressure and low temperatures (15–35 °C). Ethylbenzene was the main product of the transalkylation. From isomerization reactions, the products were *o*-diethylbenzene isomers (*meta*- and *para*-), and from disproportionation reactions, 1,3,5-triethylbenzene was also obtained. In the case of 1:1 mole ratio of benzene to the isomer, yield of ethylbenzene of 49 mol% was obtained after 6 h of reaction at 35 °C. This decreased, at the same temperature, to 25 and 8 mol% for 3:1 and 6:1 mole ratios, respectively. A decrease in the temperature to 25 and 15 °C (with 1:1 mole ratio), caused the yield of ethylbenzene to decrease to 43 and 32 mol%, respectively. Similar trends were observed with 3:1 and 6:1 ratios. The conversion of *o*-diethylbenzene to ethylbenzene and ethylated benzenes appeared to depend strongly on mole ratio of benzene/diethylbenzene at a given temperature. The study has shown that the triflic acid is active as a catalyst for the reaction. It exhibited high yield of ethylbenzene from *o*-diethylbenzene at low temperatures and atmospheric pressure.

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### 1. Introduction

Ethylbenzene is an important chemical intermediate that is almost exclusively used in manufacture of styrene. Recently, there has been increase in research interest towards improving its production processes and especially designing new catalysts for the reaction [1]. In most of the liquid and gas phase processes for the production of ethylbenzene, several competing side reactions take place, causing the formation of polyalkylates, depending on conditions of the alkylation and the difficulty for the transalkylation of higher substituted ethylbenzenes such as diethylbenzene (DEB) isomers (*ortho*-, *meta*- and *para*-), triethylbenzene (TEB) and tetraethylben-

zene (TetEB) isomers. During the alkylation, about 5–10% polyalkylated benzenes are formed which mainly contain DEB isomers (total 50–60%). The amounts of these byproducts have increased due to increase in the production of ethylbenzene. Its overall world demand increased at an average annual rate of 4.3% from 1998 to 2003, to about 25 million metric tons. To increase the overall efficiency of the ethylbenzene (EB) process, some plants have a separate reactor facility to transalkylate DEB isomers with benzene (B) to EB. These processes have some technological problems due to difficulty of recycling with associated economic and environmental challenges.

Transalkylation of *o*-DEB isomer with B is an effective way for utilizing the byproducts and increasing the EB yields. This approach has been extensively studied and several zeolitic and non-zeolitic catalysts have been proposed [2–5].

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Zeolitic material is especially suitable for controlling the product distribution due to the bulky bimolecular intermediate species involved in the reaction [6,7]. Recently, an effective  $\beta$ -zeolite-based catalyst for liquid phase alkylation has been proposed. The catalyst has been shown to possess high yield, low rate of deactivation and absence of corrosive side products [8]. In another report, the reaction was studied over faujasite Y catalysts and the relevance of the B to DEB ratio was emphasized. Increase in the ratio from 1:1 to 5:1 increased the selectivity to DEB to more than 90% [9]. While non-zeolitic catalysts such as aluminum catalyst enables the reaction to be carried out at temperatures of 80–100 °C, there are inherent problems such as complex formation with polyethylated benzenes, short catalyst life, requirement of large amount of catalyst and threat to environment due to difficulty in disposing the waste catalyst complex. There are also inherent problems, using solid catalysts, such as rapid catalyst deactivation and poor transalkylation capabilities.

Liquid phase reaction with trifluoromethanesulphonic acid (triflic acid) as a catalyst offers possibility of high yield at lower temperatures. Roberts and Roengsumran [10] and Olah et al. [11] have reported earlier works on this class of catalysts. Recently, our group has demonstrated the potential of the use of triflic acid as catalyst for isomerization and disproportionation of DEB isomers [12–14]. However, apart from these, no report is available in the literature on the use of triflic acid as a catalyst for the transalkylation of *o*-DEB with B. The use of triflic acid as a catalyst has shown some promise in the alkylation of benzene with ethylene and with propylene to produce ethylbenzene and isopropylbenzene, respectively [15]. It was also tested in isomerization, disproportionation and transalkylation of alkylated benzenes at room temperature and atmospheric pressure [16]. In this paper, we report the performance of triflic acid as a catalyst for transalkylation of *o*-DEB with benzene at low temperatures (15–35 °C) and mole ratios of B to *o*-DEB to catalyst of 1:1:1, 3:1:1 and 6:1:1 for transalkylation of *o*-diethylbenzene and benzene to ethylbenzene. It has been found that the catalyst performed better than some catalysts in the literature.

## 2. Experimental

Benzene was purified according to a method reported in the literature [17] and dried prior to use. Trifluoromethanesulphonic acid catalyst was a commercial sample (Aldrich Co. Ltd.;  $d = 1.696$ ), which was purified by double distillation (b.p. 68–70 °C, 20 mm Hg) under dry nitrogen at reduced pressure. *o*-DEB was obtained from Fluka with a purity of 97% and was used directly without further purification. High grade and spectroscopically pure hexane was used as a solvent for gas–liquid chromatography (GLC). The transalkylation reactions were performed in a close liquid-batch reactor. The reactor was continuously stirred under dry nitrogen at atmospheric pressure over the temperature range of

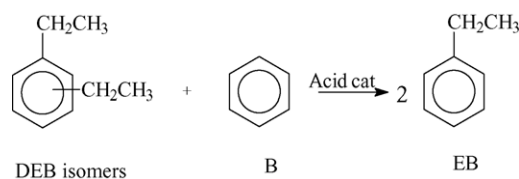
15–35 °C. The reactor was equipped with a PID temperature controller.

Gas–liquid chromatography analysis of the product mixtures obtained from transalkylation reactions were performed quantitatively on a Varian 3400 chromatograph fitted with a flame ionization detector (FID) and a 60 m long  $\times$  0.32 mm internal diameter capillary column (phase DBI, film thickness of 1  $\mu$ m). The instrument was calibrated by External Standardization method using standard mixtures of B, EB, *o*-, *p*- and *m*-DEB; 1,3,5-TEB and 1,2,4,5-TetEB. The progress of the transalkylation reactions using this system was monitored by GLC analysis. Aliquots were withdrawn every 30 min over the time of reaction, quenched in water and extracted with hexane.

## 3. Results and discussion

The ethylation of benzene to ethylbenzene using Friedel–Crafts or solid acid catalysts leads to mixture of polyethylated products especially diethylbenzene isomers (*ortho*-, *meta*- and *para*-), but also exhibiting tri-, tetra-, penta- and hexaethylbenzene. The DEB isomers could be used for production of EB by transalkylation with benzene. This reaction is industrially of interest as some of the low valued products like DEB isomers can be converted to their monosubstituted homologues, which are of higher value. The generalized transalkylation reaction scheme for DEB isomers with benzene can be represented by Scheme 1. This is by both Bronsted and Lewis acid catalysts. The classic Friedel–Crafts transalkylation mechanism over a Bronsted acid catalyst is given in Scheme 2. The transalkylation reaction is very often accompanied by isomerization of starting DEB isomer to thermodynamically more stable isomers, and also by disproportionation to EB and TEB isomers.

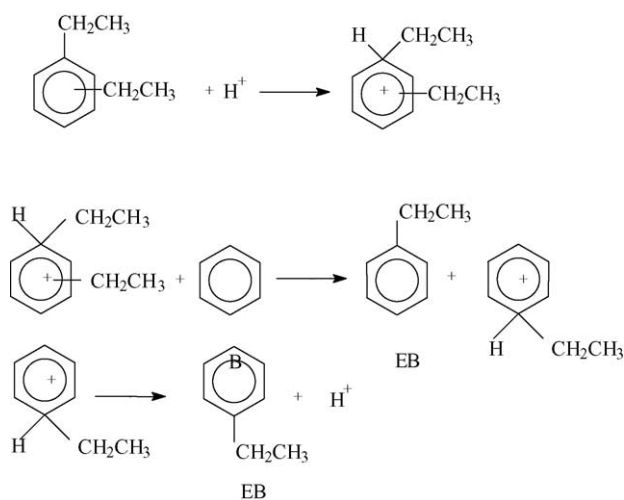
Mixing anhydrous triflic acid catalyst with B and *o*-DEB in the mole ratios: 1:1, 3:1 and 6:1 at different temperatures of 15, 25 and 35 °C exhibits mainly transalkylation to EB as well as isomerization to *p*- and *m*-DEB and to a lesser extent disproportionation to EB and 1,3,5-TEB. Table 1 shows benzene and *o*-DEB conversions and products selectivities for different *o*-DEB/benzene ratios, at different temperatures after 2 h of reaction. Fig. 1 displays a sample of the product distribution with 3:1 mole ratio at 35 °C. Analysis of all reaction mixtures (reactants and products) showed that after 15 min about 8.5 mol% of *o*-DEB and 1.3 mol% of B has been converted into EB (5.6 mol%), *m*-DEB (3.7 mol%), *p*-DEB



Scheme 1.

Table 1  
Benzene conversions and products selectivities at different *o*-diethylbenzene/benzene/catalyst ratios and different temperatures

	Ratios								
	1:1:1			3:1:1			6:1:1		
	15 °C	25 °C	35 °C	15 °C	25 °C	35 °C	15 °C	25 °C	35 °C
Conversion (%)									
Benzene	9.9	14.7	18.8	4.0	5.6	9.6	1.9	3.1	1.6
<i>o</i> -DEB	46.8	48.2	49.4	14.9	19.6	22.9	4.6	7.0	10.1
Selectivity (%)									
EB	53.3	50.7	70.2	59.8	61.9	69.2	49.2	53.6	58.8
<i>p</i> -DEB	11.6	9.9	8.8	5.8	5.6	5.5	1.5	2.1	2.6
<i>m</i> -DEB	30.0	35.3	19.1	30.7	27.4	22.2	46.2	43.3	37.7
TEB	5.1	4.2	1.9	3.7	5.2	3.1	3.1	1.0	0.9



(0.3 mol%) and 1,3,5-DEB isomer (0.2 mol%). The conversion of *o*-DEB gradually increased until approximately 6 h, with corresponding increase of selectivity to EB. The selectivity to *m*-DEB decreased from 38% at 25 min to 20% at 6 h. Selectivity to *p*-DEB and 1,3,5-TEB exhibited different

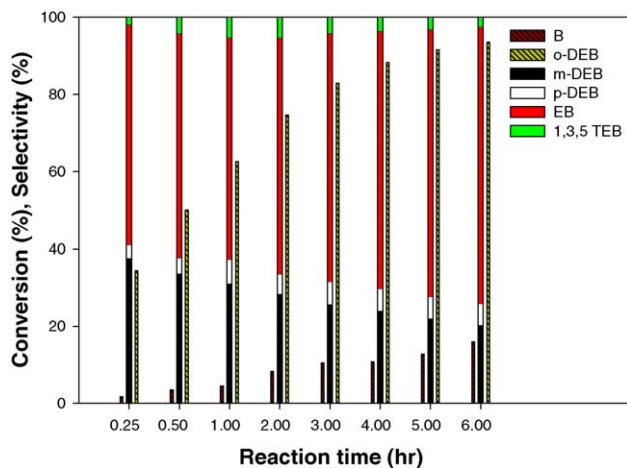


Fig. 1. Benzene and *o*-diethylbenzene conversions and products selectivities profile at 35 °C and B:*o*-DEB ratio of 3:1.

degrees of variations. Similar trends were obtained with 1:1 and 6:1 at different temperatures. The results indicate that the formation of EB resulted from transalkylation of *o*-DEB with benzene either by disproportionation or by dealkylation of *o*-DEB. During the disproportionation reaction, two moles of *o*-DEB react to form 1 mole of EB and 1 mole of 1,3,5-TEB isomer as shown in reaction (1), while during dealkylation reaction, 1 mole of *o*-DEB produces 1 mole of EB and 1 mole of ethyl triflate as shown in reaction (2). However, the presence of the catalyst could change the significance of one reaction compared with others thereby modifying the products distributions.

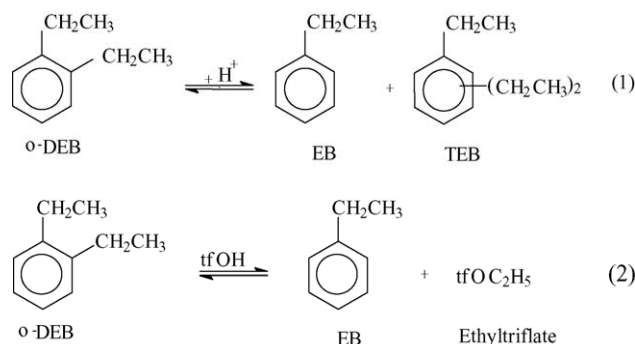


Fig. 2 shows the effect of variation of mole ratio of B to *o*-DEB and temperature on the conversion of *o*-DEB. There is increase in the conversion of *o*-DEB with a decrease in the mole ratio of B to *o*-DEB and with an increase in temperature. At lower ratio (1:1), the effect of temperature on the conversion was not strong. The use of benzene in excess against the *o*-DEB lowered the conversion of *o*-DEB and decreased the yield of EB. Fig. 3 depicts the effects of the mole ratios on the performance of the catalyst for the temperature of 15, 25 and 35 °C. The yield of EB after 5 h reached a maximum of 49 mol% with 1:1 mole ratio at 35 °C. This gradually decreased to 7 mol% with increase of mole ratio to 6:1. Similar trends were obtained at temperatures 15 and 25 °C. At 15 °C with B to *o*-DEB mole ratio of 1:1, the yield of EB was 30 mol% after 5 h and this decreased to 3 mol% when the ratio increased to 6:1. While at 25 °C with mole ratio 1:1, the yield of EB obtained was 41 mol% but at mole ratio of 6:1 it decreased to 5 mol%. Similar relationship was

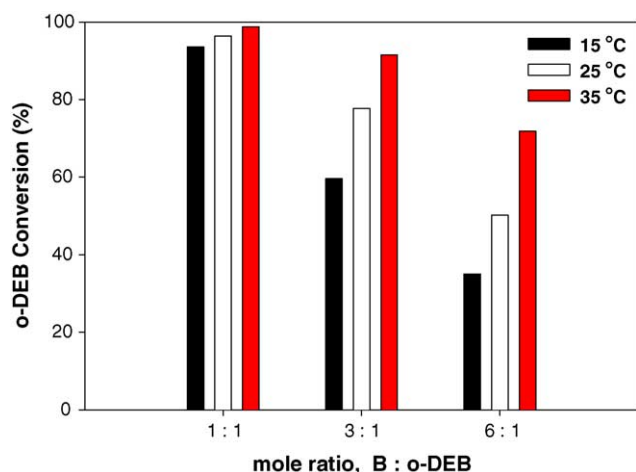


Fig. 2. Effect of B:o-DEB mole ratio on o-DEB conversions at different temperatures after 5 h.

observed when the same reaction was conducted on  $\beta$ -zeolite catalyst tested at 270 °C [8]. The increase in concentration of benzene in the feed makes it to be in excess. This makes the benzene to have weak effect on the conversions of o-DEB especially at high temperatures. The increase in the amount of B has stronger effect on the yield of EB than on conversions in the concentration range explored. The EB appeared to be a primary product, exhibiting high selectivity even at low benzene conversions. The selectivity may decrease if EB is disproportionated to DEBs and B.

Alternatively, Figs. 2 and 3 may elucidate the influence of temperature on the reaction for different ratios. The differences in the total conversions among the three temperatures are markedly large. From Fig. 2, the effect of temperature could be observed. As the temperature increased from 15 to 35 °C the conversion of o-DEB increased markedly from 35.0 to 71.8 mol% after 5 h of reaction for ratio of 3:1. The maximum conversion of 98.8 mol% was obtained at a 1:1 mole

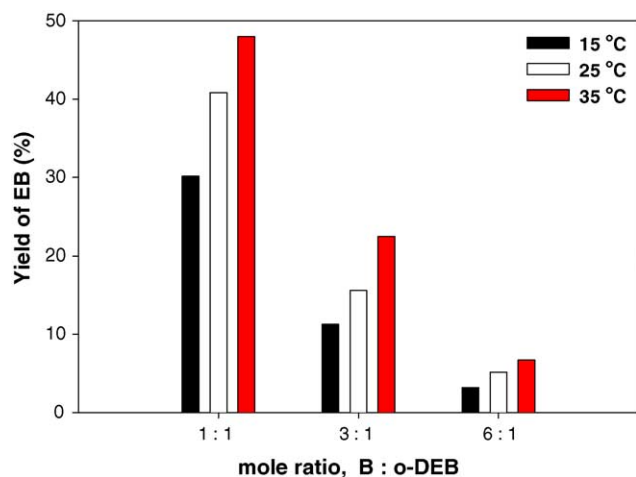


Fig. 3. Effect of B:o-DEB mole ratio on the EB yields at different temperatures after 5 h.

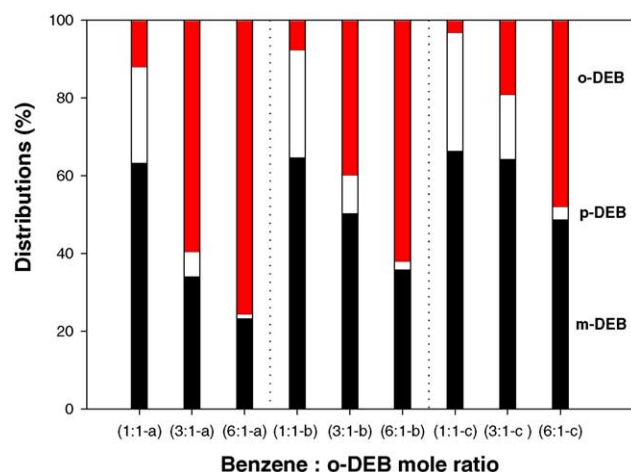


Fig. 4. Normalized diethylbenzene isomers distributions for different B:o-DEB mole ratios and reaction temperatures (a) -15 °C, (b) -25 °C and (c) -35 °C after 5 h.

ratio after 2 h of reaction, whereas the value was 72.0 mol% with 6:1 mole ratio. Typical results of the yield of EB after 5 h of the reaction time are shown in Fig. 3. A yield of EB (30 mol%) with 1:1 mole ratio of B to o-DEB was 10 times of that with 6:1 mole ratio at the same temperature (15 °C). Similar trend was observed when the temperature raised to 35 °C. The yield of EB (30 mol%) with 1:1 mole ratio increased to 49 mol% as the temperature increased from 15 to 35 °C, whereas with 6:1 mol ratio the increase was from 3 to 7 mol%. This shows that the effect of increase in temperature on EB yield is limited by excess amount of B thereby exhibiting insignificant change at the highest ratio.

When the mole percentage values of DEB isomers were normalized, the o-DEB under different conditions gave predominantly m-isomer as expected of 1,2-shift mechanism as shown in Fig. 4. The normalized mole percent values for o-, p- and m-DEB shows that isomerization of o-DEB competes with disproportionation and thermodynamically more stable m-isomer increases with corresponding increase in the amount of o-DEB isomers. For instance, the composition of DEB isomers with a mole ratio 1:1 at 35 °C is 3 mol% (ortho-), 66.5 mol% (meta-) and 30.5 mol% (para-) after 5 h of the reaction time. The figure shows relative distribution of the DEB isomers. The amount of m-DEB dominates at low B:o-DEB ratio irrespective of reaction temperature. As the ratio increased, m- and p-DEB decreased while the amount of o-DEB increased at all temperatures. The increase in o-DEB corresponds with the decrease in conversion as shown in Fig. 2. At 35 °C and ratio of 6:1, about equal amounts of m- and o-DEB were observed. The dominance of m-DEB at lower ratio suggests the prevalence of isomerization reaction in addition to other reactions. In various results obtained by Bolton et al. [16] on the study of the isomerization of o-DEB using zeolitic catalyst at 170 °C, the normalized mol% values of o-, m- and p-DEB after 7 h of the reaction time were 78.4, 18.7 and 2.9 mol%, respectively. The equilibrium composition in solution of isomers under the

Table 2  
Equilibrium mixtures of DEB isomers with some acidic catalysts

Catalyst	Temperature (°C)	Normalized DEB isomers distribution (%)		
		<i>ortho</i>	<i>meta</i>	<i>para</i>
AlCl <sub>3</sub> -HCl [11]	25	4.0	79.0	17.0
Zeolite-Y [16]	170	6.0	63.0	31.0
Triflic acid <sup>a</sup>	15	11.9	63.4	24.7
Triflic acid <sup>a</sup>	25	5.7	73.7	20.6
Triflic acid <sup>a</sup>	35	3.2	66.5	30.47

<sup>a</sup> This work.

same condition after 100 h was 6.0, 63.4 and 30.5 mol%, respectively. The normalized equilibrium mixture of DEB isomers using different catalysts and variable temperatures are compared in Table 2. The normalized DEB isomer distribution obtained from this work falls in the ranges of those obtained with different classes of catalysts at higher temperatures.

The yield of EB change with reaction time was plotted using the data obtained in individual runs with different reaction times at temperatures 15, 25 and 35 °C with 1:1, 3:1 and 6:1 mole ratio of B to *o*-DEB as shown in Fig. 5. When the reaction time increased with increasing temperature and decreasing mole ratio of B to *o*-EB, the onset of transalkylation occurred almost immediately and after about 15 min, the yield of EB was already greater than 16 mol% with the three mole ratios and temperatures. It exhibited yield higher than 22 mol% after 1 h. When the product distribution became almost constant, the highest yield of EB obtained (49 mol%) with 1:1 mole ratio at 35 °C after 6 h is shown in the figure. With 6:1 mole ratio the initial rate of formation of EB was much slower than that of 1:1. The figure also shows that up to about 1 h, the yield of EB was greater than 1.2 mol%. The yield increased at slow rate to reach a maximum value of 8 mol% with 6:1 mole ratio at 35 °C.

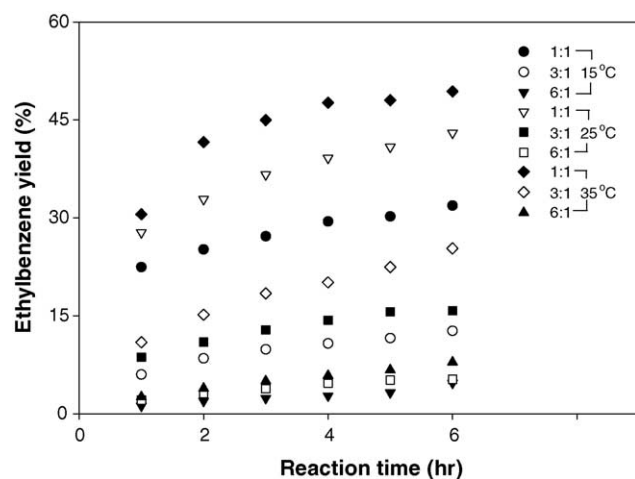


Fig. 5. Ethylbenzene yields profiles for different B:*o*-DEB mole ratios and reaction temperatures.

## 4. Conclusions

It has been shown that triflic acid is active in transalkylation of diethylbenzene and benzene to ethylbenzene. The reaction of *o*-DEB with B gave EB yield as high as 49 mol% with 1:1 mole ratio at 35 °C. When the mole ratio of *o*-DEB to B was decreased, while the reaction time and the temperature increased, the degree of conversion of *o*-DEB and the yield of EB increased. The results obtained have shown that the triflic acid is active catalyst for the transalkylation of *o*-DEB with benzene to produce high yield of EB at room temperature and atmospheric pressure. The activity is comparable with or better than other solid acid catalysts in the literature.

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