Kinetics and Mechanisms of Transalkylation and Disproportionation of *meta*-Diethylbenzene by Triflic Acid Catalyst

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ABSTRACT: The kinetics of transalkylation and isomerization of *meta*-diethylbenzene in the presence of benzene using triflic acid as a catalyst has been investigated. High catalytic activity of the triflic acid catalyst was observed in homogeneous liquid-phase reactions. On the basis of the product distribution obtained, transalkylation, disproportionation, and isomerization reactions have been considered and the main product of the reaction was ethylbenzene. These reactions are conducted in a closed liquid batch reactor with continuous stirring under dry nitrogen and atmospheric pressure over the temperature range of 288–308 K. The main transalkylation, disproportionation, and isomerization reactions occurred simultaneously and were considered as elementary reactions. The apparent activation energy of the transalkylation reaction was found to be 35.5 kJ/mol, while that of disproportionation reaction was 42.3 kJ/mol. The reproducibility of the experimental product distribution occurred with an average relative error of $\pm 2\%$. © 2003 Wiley Periodicals, Inc. Int J Chem Kinet 35: 555–563, 2003

INTRODUCTION

Dialkylbenzenes include xylene, diethylbenzene, and diisopropylbenzene which are very important raw materials for many intermediates of commodity petrochemicals and valuable fine chemicals such as monomers for engineering plastics, polyesters, intermediates for detergents, pharmaceuticals, agricultural products, and explosives [1]. In 1995, 13.66 billion pounds of ethylbenzene (EB) was produced in the United States, which ranked 19th among all chemicals produced in the United States, representing an increase of 27% from the 1994 production volume of 10.76 billion pounds. In 1998, the global operating rate of EB was 83%. The operating rate for facilities in North America averaged 90%, in Western Europe 85% and in Asia 84%. Japan accounted for about 50% of the Asian EB demand in 1998. Overall EB demand for the world increased at an average annual rate of 4.3% from 1998 to 2003, resulting in global EB demand of nearly 25 million metric tons. In 2003 consumption is expected to grow the fastest in the Middle East and

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South America. Almost all of the EB produced in the world is used in the manufacture of styrene.

Transalkylation and disproportionation are the two major practical processes for the utilization of aromatics. They are coined as "alkyl group transfer reactions." The catalytic rearrangement of alkyl groups present in alkyl aromatic hydrocarbons to provide one or more products suitable for use in the petroleum and chemical industries has heretofore been effected by a wide variety of catalysts [1-8]. Such processes are commonly used in conversion of diethylbenzene (DEB), which yields EB, isomers of DEB (ortho-, para-, and meta-), triethylbenzene, and tetraethylbenzene. Current EB production processes are based on commercial catalysts that are effective above 473 K. Developing new catalysts that work at lower temperatures will increase the operational and economical benefits of these processes.

Acidic halides such as aluminum chloride, aluminum bromide, boron trifluoride-hydrogen fluoride mixtures, etc. have been used in the rearrangement of alkyl benzenes to provide valuable intermediates that find utility in the synthesis of rubber, plastic, fibers, and dyes. Triflic acid, owing to its catalyst stability, which is far superior to that of other acids, and its resistance to oxidation and reduction reactions, is particularly a valuable reactant and solvent. It does not split off fluorine ions, even in the presence of strong nucleophiles. Triflic acid has been used in the plastic industry as an oligomerization-polymerization catalyst, as well as for the production of electrically conductive polymers. Also it has been used as a protonization catalyst in the fuel industry besides its utilization in the pharmaceutical, sugar, and vitamins industries. In addition to triflic acid and its derivatives, in the form of acid halides, anhydrides and esters are also used. Mixed anhydrides formed from triflic acid are extremely strong Friedel-Crafts alkylating agents. The salts of triflic acids are used in microelectronics, polymer membrane technology, and in preparative organic synthesis.

Transalkylation reaction for the synthesis of EB is usually carried out on an industrial scale, employing aluminum chloride or trifluoroboron at 100°C or zeolite catalysts at temperatures higher than 200°C. The transalkylation of DEB with benzene has also been investigated over superacidic catalyst, such as Nafion-H [9]. The major reactions include isomerization and transalkylation with their relative contributions controlled by the nature of the catalyst and the reaction conditions. Considerable efforts have been aimed at the isomerization and disproportionation of DEB isomers in the absence and presence of benzene to produce EB using trifluromethanesulphonic acid catalyst [10,11].

Streitweisere and Reif [12] investigated the kinetics of transalkylation of radiolabeled and optically labeled EB in benzene with a gallium tribromide-hydrogen bromide catalyst. Moore and Wolf [13] have demonstrated from a study of disproportionation and isomerization reactions of ethylbenzene-1-¹⁴C in AlBr₃-HBr that para alkylation is dominant followed by an intramolecular 1,2-shift of an ethyl group to give the thermodynamically most stable isomer. Bakoss et al. [14] have measured the rates of disproportionation of EB and *m*-DEB using triffic acid as catalyst at room temperature and indicated that the EB disproportionates very rapidly, whereas m-DEB reacts at a conveniently measurable rate and the reactions obey firstorder kinetics. Al-Zahrani et al. [15] have studied the kinetics of transalkylation and isomerization of o-DEB in the presence of benzene using trifluoromethanesulphonic acid as a catalyst. Power law type model has been tested for the main transalkylation and disproportionation reactions, while the isomerization reactions followed a first-order mechanisms. The apparent activation energy of the transalkylation reaction was found to be 50 kJ/mol, while that of disproportionation reaction was 29 kJ/mol. Recently Cavani et al. [16] investigated the transalkylation of DEB with benzene over β -zeolite in the liquid phase over temperature ranges of 513–573 K. These authors confirmed that EB was formed via the direct reaction of DEB transalkylation with benzene.

The aim of the present work is to develop a kinetic model for the transalkylation, disproportionation, and isomerization of *m*-DEB using triflic acid catalyst. The model will be used to understand the physiochemical nature of the process and to interpret the experimental results via developing rate equations for the transalkylation of *m*-DEB with benzene, and disproportionation of DEB and isomerization reactions.

EXPERIMENTAL

Materials

The materials used in this reaction include benzene, *m*-DEB, trifluoromethanesulphonic acid (triflic acid) as reactants and hexane as a solvent. Benzene was obtained from Sigma with purity of 99.9%. It was also purified according to the standard method and dried prior to use over sodium wire. Triflic acid was a commercial sample obtained from Fluka Chemie with purity of 98% and density of 1.696 gm/cm³. The acid was purified by double distillation under dry nitrogen at reduced pressure immediately before use. Hexane (HPLC grade) was used as solvent for reaction product

extraction and was obtained from Fluka. *m*-DEB was also obtained from Fluka with a purity of 97% and was used directly without further purification. The physical and chemical properties of triflic acid, *m*-DEB, and EB are listed in Table I.

Reaction System

The reaction was performed in a closed liquid batch reactor with continuous stirring under dry nitrogen environment and atmospheric pressure over the temperature range of 15–35°C. The batch reactor was equipped with a PID temperature controller to monitor the reaction temperature. The reaction procedure involved first flushing the reactor with nitrogen, and then introducing weighted sample according to the required ratio of m-DEB, benzene, and catalyst. The reaction mixture was heated to the chosen temperature under continuous stirring. The reaction continued for 6 h. The analysis of the reaction mixture was carried out using a Varian 3400 chromatograph equipped with a 60 m \times 0.32 mm id capillary column (phase DBI, film thickness of 1 µm) and a flame ionization detector. The instrument was calibrated by external standardization method using standard mixture of benzene, ethylbenzene, m-, p-, and o-DEB, 1,3,5-triethylbenzene, and 1,2,4,5tetraethylbenzene. The ratios of m-DEB to benzene (B) and to catalysts (i.e., m-DEB/B/catalyst) ranged from 1:1:1 to 1:6:1 at a pressure of 1 atm. In all the different experiments, the products distributions were followed by analyzing samples of the organic layer at 0.5-h intervals after quenching with deionized water and extracting with hexane.

Triflic acid			
Formula and structure	CF ₃ SO ₃ H		
Molecular weight	150.08 gm/mol		
Appearance at 20°C	Colorless to yellowish liquid, pungent		
Density	1.7 g/cm^{3}		
Boiling point	162°C		
Neutralization equivalent	149-151.5 (min. 99%)		
(content)			
<i>meta</i> -Diethylbenzene (<i>m</i> -DEB)			
Formula and structure	$C_6H_4(C_2H_5)_2$		
Appearance	Colorless limpid liquid		
Boiling point (°C)	181.1		
Melting point (°C)	-84.2		
Ethylbenzene (EB)			
Boiling point (°C)	136.2		
Melting point (°C)	-95.0		

Table IChemical and Physical Properties ofReactants, Products, and Catalyst

RESULTS AND DISCUSSION

m-DEB reacted with benzene in the presence of triflic acid catalyst. Triflic acid has a great advantage of providing a homogeneous medium of high acidity and is much more easily handled than the Friedel-Crafts catalytic system [14]. The reaction proceeds via rapid transalkylation to EB and disproportionation to triethylbenzene as well as isomerization to o- and p-DEB. Figure 1 shows conversion of *m*-DEB at three different temperatures versus reaction time. Obviously increasing the reaction time will increase the *m*-DEB conversion. After 6 h of reaction time 30% of *m*-DEB at 15° C, 50% at 25°C, and 60% at 35°C were converted. During the reaction time, small amounts of triethylbenzene were found among the reaction products. This indicates that a part of *m*-DEB undergoes the disproportionation reaction (R2) to EB and triethylbenzene. P-DEB and o-DEB isomers were also found among the reaction products [23].

In accordance with the product distribution obtained, the system can be described with the following reactions:

Transalkylation of *m*-DEB with benzene (R1):



Disproportionation of *m*-DEB (R2):



Isomerization reactions to *o*- (R3) and *p*-DEB (R4):





Figure 1 The conversion of *m*-DEB vs. reaction time at *m*-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.



(R4)

Isomerization reactions of *o*- and *p*-DEB (R5):



(R5)

In the kinetic model developed here, the transalkylation, disproportionation, and isomerization reactions are treated as elementary reactions. The rate of transalkylation reaction is expressed in the following form:

$$r_1 = k_{f1} C_{m\text{-}\text{DEB}} C_{\text{B}} - k_{b1} C_{\text{EB}}^2 \tag{1}$$

while the rate of disproportionation reaction of *m*-DEB is given by

$$r_2 = k_{f2}C_{m-\text{DEB}}^2 - k_{b2}C_{\text{EB}}C_{\text{TEB}}$$
(2)

and the isomerization reactions are expressed by

$$r_3 = k_{f3}C_{m-\text{DEB}} - k_{b3}C_{o-\text{DEB}}$$
 (3)

$$r_4 = k_{f4}C_{m\text{-DEB}} - k_{b4}C_{p\text{-DEB}}$$
(4)

$$r_5 = k_{f5}C_{o\text{-DEB}} - k_{b5}C_{p\text{-DEB}} \tag{5}$$

Based on the given kinetic scheme, the components mass balance equations are shown below in the differential form:

Consumption rate of *m*-DEB:

$$\frac{\mathrm{d}C_{m\text{-}\mathrm{DEB}}}{\mathrm{d}t} = -r_1 - 2r_2 - r_3 - r_4 \tag{6}$$

Consumption rate of benzene:

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{d}t} = -r_1 \tag{7}$$

Formation rate of ethylbenzene:

$$\frac{\mathrm{d}C_{\mathrm{EB}}}{\mathrm{d}t} = 2r_1 + r_2 \tag{8}$$

Formation rate of *o*-DEB:

$$\frac{\mathrm{d}C_{o\text{-DEB}}}{\mathrm{d}t} = r_3 - r_5 \tag{9}$$



Figure 2 The EB concentration vs. reaction time at *m*-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.

Formation rate of *p*-DEB:

$$\frac{\mathrm{d}C_{p\text{-DEB}}}{\mathrm{d}t} = r_4 + r_5 \tag{10}$$

Formation rate of triethylbenzene (TEB):

$$\frac{\mathrm{d}C_{\mathrm{TEB}}}{\mathrm{d}t} = r_2 \tag{11}$$

The direct transalkylations from p- or o-DEB are neglected reactions in this work. Other reactions like

disproportionation of *p*- or *o*-DEB are also neglected because of the small concentrations reported here for both *p*- and *o*-DEB and also to avoid complexity of the reaction network.

The kinetic model for this batch reaction system is in the form of ordinary differential equations (i.e., Eqs. 5–11). The integral form of the above differential equations was used to determine the kinetic parameters because of high *m*-DEB conversion obtained in this work. The objective is to determine the kinetic parameters listed on the rate equations of the kinetic schemes, which will be used to predict the *m*-DEB and benzene



Figure 3 The o-DEB concentration vs. reaction time at m-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.



Figure 4 The *p*-DEB concentration vs. reaction time at *m*-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.

conversions and EB and other product selectivities and yield. Therefore, the problem requires a combination of nonlinear differential equation solver and nonlinear regression analysis technique. For this objective, a computer program was developed to solve the problem, which combined an integrator such as the Runge–Kutta method with the least-square approximation technique to solve for the best fitting kinetic parameters. More than 30 experimental data points at each temperature have been used to determine these kinetic parameters, which require the solution of the above six nonlinear differential equations simultaneously for these parameters to be obtained.

The simulation results reveal that the rate of backward reactions for the transalkylation and disproportionation steps are small compared to the forward reactions and therefore can be neglected. These results are in agreement with the recent findings reported



Figure 5 The TEB concentration vs. reaction time at *m*-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.

	Product Distribution (mol%; at $t = 4$ h)				
Compound	T = 288 K	T = 298 K	T = 308 K		
EB	12.6	24.2	25.7		
o-DEB	0.3	0.60	0.7		
p-DEB	1.3	3.61	3.7		
TEB	0.98	2.45	2.6		
Unreacted <i>m</i> -DEB	34.5	27.4	23.4		
Unreacted benzene	46.5	41.6	41.0		
Total	96.2%	99.86%	97.1%		

 Table II
 Example of Measured Product Distribution

 (mol%) at m-DEB/B/Catalyst 1:1:1 (Molar Ratio) at Three

 Different Temperatures

by Ngandjui et al. [17]. The kinetic expression reaction obeys first-order with respect to m-DEB and benzene, while the rate of the disproportionation reaction obeys second-order kinetics over the studied range. The kinetic parameters for the above reaction scheme are listed in Table I. Bakoss [14] reported that the disproportionation of DEB obeys first-order kinetics.

For all of the kinetic parameters listed above the Arrhenius form was substituted before starting the simulation. For the main transalkylation reaction the reaction rate constants has the following Arrhenius expression:

$$k_{f1} = 3.6602 \times 10^4 \times \exp\left(\frac{-4270}{T}\right)$$
 (12)

For the main disproportionation reaction the rate constant is given by the formula

$$k_{f2} = 2.02371 \times 10^5 \times \exp\left(\frac{-4967}{T}\right)$$
 (13)

The forward and backward rate constants for the isomerization reactions [i.e. reactions (3)-(5)] are given below:

$$k_{f3} = 2.1445 \times 10^5 \times \exp\left(\frac{-4441}{T}\right)$$
 (14)

$$k_{b3} = 5.2402 \times 10^3 \times \exp\left(\frac{-2231}{T}\right)$$
 (15)

$$k_{f4} = 6.71987 \times 10^6 \times \exp\left(\frac{-5472}{T}\right)$$
 (16)

$$k_{b4} = 1.74726 \times 10^1 \times \exp\left(\frac{-1092}{T}\right)$$
 (17)

$$k_{f5} = 2.73633 \times 10^5 \times \exp\left(\frac{-4017}{T}\right)$$
 (18)

$$k_{b5} = 4.39459 \times 10^1 \times \exp\left(\frac{-1455}{T}\right)$$
 (19)

Figures 2 and 3 show the model predictions (solid lines) along with the experimental values (symbols) for EB and TEB, respectively, versus reaction time at ratio 1:1:1 and temperatures of 288, 298, and 308 K. These figures indicate that the kinetic model predicts fairly well the number of moles with time. Increasing the temperature will lead to an increase in both EB and



Figure 6 The *m*-DEB conversion vs. EB selectivity at DEB/B/catalyst 1:1:1 (molar ratio) and T = 298 K.



Figure 7 The benzene concentration vs. reaction time at *m*-DEB/B/catalyst 1:1:1 (molar ratio) at three different temperatures.

TEB. The selectivity for EB almost doubled when the temperature increased from 288 to 298 K, while it was increased only by 10% when the temperature increased further from 288 to 308 K. Figures 4 and 5 show the mole predictions along with the experimental data for mol% of *o*-DEB and *p*-DEB respectively. The mol% of *o*-DEB varied between 0 and 0.6%, while that of *p*-DEB varied between 0 and 5%. These figures indicated that the isomerization reactions are small compared to the transalkylation reaction and these results are in agreement with the results obtained by Cavani et al. [16]. An example for the measured molar distribution of the products with time is shown in Table II.

Figure 6 shows the *m*-DEB conversion versus the EB selectivity at 288 K. When the conversion increases from 0 to 55%, the selectivity drops only from 84 to 78%, which indicates that increasing the conversion

is accompanied with a slight drop in EB selectivity. Figure 7 shows the model predictions of mol% for benzene along with the experimental values versus reaction time at ratio 1:1:1 and the above-mentioned temperatures. Higher temperature leads to higher conversion of benzene. The conversion of benzene increases with increasing the reaction time.

Most of the studies reported in the literature on aromatics transalkylation were conducted in the gaseous phase over zeolite catalysts; however, few studies were conducted in the liquid phase. The activation energies for such reactions are listed in Table III. From the results illustrated in Table III it can be observed that the activation energy calculated in this work falls in the range of the ones reported in several publications for DEB or toluene transalkylation in both liquid and gaseous phases.

Table IIIComparison of Activation Energies for Transalkylation and Disproportionation Over Different CatalyticSystems

Authors [Ref.]	Reaction	Phase	Catalyst	Activation Energy (kJ/mol)
Ngandjui et al. [17]	Transalkylation of DEB-BZ	Liquid	Y(Si/Al = 13.8)	81
Corma et al. [18]	Transalkylation of aromatics	Gaseous	HYD-3(Si/Al = 12.8)	107
Betrame et al. [19]	Transalkylation of toulene	Gaseous	USY-3 (Si/Al = 12) Various zeolite	85.8
Dooley et al. [20]	Transalkylation of toulene	Gaseous	Y	87 ± 10
Bhaskar and Do [21]	Disproportionation of toluene	Gaseous	HZSM-5	100-121
Nayak and Riekert [22]	Disproportionation of toluene	Gaseous	Pentasil (Si/Al $=$ 36)	53
Bakoss et al. [14]	Disproportionation of <i>m</i> -DEB	Liquid	Triflic acid	66 ± 2
Al-Zahrani et al. [15]	Transalkylation of <i>o</i> -DEB	Liquid	Triflic acid	50
Cavani et al. [16]	Transalkylation of DEB	Liquid	β-Zeolite	130
This work	Transalkylation of <i>m</i> -DEB	Liquid	Triflic acid	35.5

CONCLUSIONS

Adequate kinetic models describing the transalkylation, disproportionation, and isomerization of *m*-DEB over triflic catalyst were derived. Experiments over a wide variety of experimental conditions were performed in a liquid batch reactor with continuous stirring under dry nitrogen and atmospheric pressure over the temperature range of 288–308 K and kinetic parameters were estimated. The predicted conversion and product selectivities were found to agree well with the experimental data. In addition, such catalytic systems were found to be highly stable with a very good activity under lower reaction temperature environments.

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