



Catalytic Synthesis of Isopropyl Benzene from Di isopropyl Benzene using Triflic Acid Catalyst at Room Temperature

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ABSTRACT

The significance of isopropyl benzene has made isopropylation reactions the most widely studied using a wide range of catalysts such as Lewis acids (metal halides) i.e. aluminum chloride, and inorganic acids (Bronsted acids) i.e. sulphuric acid, hydrofluoric acid, supported phosphoric acid, and zeolite. Therefore, in order to produce higher yield of isopropyl benzene from di isopropyl benzenes which are the results of the above isopropylation processes, a series of isomerization and trans alkylation reactions of *p*- and *m*-di isopropyl benzenes in the presence of trifluoromethanesulphonic acid (Triflic acid) as catalyst with different molar ratios 1:1, 1:3 and 1:6 of catalyst to each isomer were carried out in liquid phase under atmospheric pressure and room temperature. The results shows that the isomerization and trans alkylation reactions gives higher yield of cumene (46 mol%) at 1:1 molar ratio with both isomers. When the molar ratio of isomer to benzene increases, the conversion of di isopropyl benzene isomers and the yield of cumene also increase.

Key words: Isopropyl Benzene, Triflic Acid, GLC Analysis, Trans alkylation and Isomerization

INTRODUCTION

Cumene (CAS no. 98-82-8; C₉H₁₂) 2-phenylpropane, isopropylbenzene, 1-methylethyl-benzene is a volatile, colorless liquid at room temperature with a characteristic sharp, penetrating, aromatic odor. It is nearly insoluble in water but is soluble in alcohol and many other organic solvents. Structurally, cumene is a member of the alkyl aromatic family of hydrocarbons, which also includes toluene (methylbenzene) and ethyl benzene. Isopropylbenzene is a naturally occurring substance present in coal tar and petroleum, insoluble in water, but is soluble in many organic solvents. It is used as a feedback for the production of Phenol and its byproduct acetone. It is also used as a solvent for fats and raisins. It is a constituent of crude oil and refined fuels. It is a flammable colorless liquid that has a boiling point of 152 °C. Nearly all the cumene that is produced as a pure compound on an industrial scale is converted to cumene hydro peroxide, which is an intermediate in the synthesis of other industrially important chemicals, primarily phenol and acetone [1].

Cumene is a naturally occurring constituent of crude oil and may be released to the environment from a number of anthropogenic sources, including processed hydrocarbon fuels. Crude oils typically contain approximately 0.1 wt% of cumene, but concentrations as high as 1.0 wt% have been reported. Measurements of various grades of petrol revealed that cumene concentrations range from 0.14 to 0.51 vol% and that the average cumene concentration was 0.3 vol%. Premium diesel fuel contains 0.86 wt% of cumene; furnace oil (no. 2) contains 0.60 wt%. Several technological changes have occurred in the petroleum refining industry with the aim of improving the performance of these processes, which highlights the development of catalysts that provide higher activity and selectivity in the conversion of oil derived products with high aggregate value [2-5]. Trifluoromethanesulphonic acid, also known as Triflic acid, TFMS, TFSA, HOTf or TfOH, is a sulfonic acid with the chemical formula CF₃SO₃H. It is one of the strongest acids. Triflic acid is mainly used in research as a catalyst for esterification.[1-2] It is a hygroscopic, colorless, slightly viscous liquid which is soluble in polar solvents [6-7].

Gas-liquid partition chromatography was first used by James and Martin in 1952 for the separation and analysis of mixtures of volatile fatty acids. Gas Chromatography as a convenient method for the separation and analysis of gases and volatile materials has been accepted extensively in the field of chemistry. Chromatographic methods have

the advantages that the separating equipment itself is simpler, the operation is easier and it is considerably less time-consuming. The main uses of chromatography in the laboratory are : (a) as an analytical method for identifying the constituents of a mixture qualitatively and determining them quantitatively, (b) as a research method for determining certain physical quantities, such as partition, coefficients and adsorption isotherms, Gas Chromatography 107 (c) as a preparative procedure for isolating components from mixtures. As an analytical method, chromatography has been accepted extensively during recent years. Chromatography has most of the advantages of the physical methods of separation. It is carried out in such a manner that no constituents of the mixture are lost and no new substances are formed by chemical reactions. Consequently, if a substance has been isolated by that method, it is almost certainly present in the original sample [8]. Transalkylation is a chemical reaction involving the transfer of an alkyl group from one organic compound to another. The reaction is most commonly used for the transfer of methyl groups between benzene rings and is widely used in the petrochemical industry to manufacture p-xylene, styrene, and other aromatic compounds. Motivation for using transalkylation reactions is based on a difference in production and demand for benzene, toluene, and xylenes. Transalkylation can convert toluene, which is overproduced, into benzene and xylene, which are under-produced. Zeolites are often used as catalysts in transalkylation reactions.

In most of the above processes, several competing side reactions take place to greater or lesser extent depending on the conditions of alkylation, and the greater difficulty of trans alkylating of higher substituted isopropylbenzene such as diisopropylbenzene (isomers, triisopropylbenzenes (TIPB) isomers and tetraisopropylbenzene (TetIPB) isomers. During the alkylation, about 7-10% of the above polyisopropylbenzenes referred to as high-boiling point residue is unavoidably obtained as byproduct which mainly contains 50-60% DIPS (ortho-, meta-, and para-). It is not possible to recycle these products to the alkylation reactors. Transalkylation of DIPS isomers with benzene are an effective way for utilizing this byproduct and increasing the cumene yield again. Therefore, it was of some interest to investigate the efficiency and catalytic behavior of Triflic acid as catalyst for cumene synthesis with a higher yield from DIPS isomers (p-, and m-) by isomerization and transalkylation reactions at room temperature.

MATERIALS AND METHODS

p-DIPS and m-DIPS were used directly without further purification. Benzene was purified using the standard method, and dried prior to use over sodium wire. Hexane which was used as a solvent for GLC analysis was high grade and spectroscopically pure. Its purity and benzene purity was checked by GLC. Talc acid was a commercial sample purified by double distillation (B.P. 68-70°C) under dry nitrogen at reduced pressure immediately prior to use.

ANALYTICAL PROCEDURES

A Varian CP 3400 Gas Chromatograph, equipped with a CP-Sil 5 column (60-m length x 0.32-mm ID) and a FID detector was used to quantify the products in liquid samples. Peaks were identified by retention time matching with known standards. Isomerization and transalkylation reactions were carried out in a closed system with continuous stirring under nitrogen atmospheric pressure and room temperature.

RESULTS AND DISCUSSIONS

Transalkylation reaction of DIPB (p-, and m- isomers) to cumene is of industrial interest as some low value products can be converted to cumene, which is in higher demand and higher value. While the aluminum chloride catalyst enables the reaction to be carried out at 80-100°C temperature, there are inherent problems with this catalyst such as, complex formation with polyisopropylated products, short catalyst life, require large amount of catalyst, it is not recycled, problem in disposing the waste catalyst complex, and polluting problems. Using solid catalysts there are also inherent problems such as rapid catalyst deactivation, poor transalkylation capabilities, and energy consumption is high since the transalkylation reaction carried out at 200-240°C and high pressure.

A lot of research work has been carried out on transalkylation of DIPS isomers with benzene using many kinds of zeolites at high temperatures and pressures, but commercial use of these zeolites could not be made, mainly due to its fast deactivation. However no reports were available in the literature, for the use of triflic acid as catalyst for the transalkylation of DIPS isomers with benzene. Therefore, the objective of the study reported in this work was to test the activity and the efficiency of triflic acid as catalyst for the transalkylation of DIPB (p-, and m- isomers) with benzene in order to obtain higher yield of cumene. The activity of the catalyst was evaluated in terms of mole percent of DIPS isomers converted and mole percent yield of cumene formed. We have investigated the effect of various molar ratios of isomer to benzene to catalyst (i.e. 1:1:1, 1:3:1, and 1:6:1 respectively).

Transalkylation of p-DIPB isomer with Benzene:

Reactions of p-DIPS isomer, benzene and triflic acid with different molar ratios of 1:1:1, 1:3:1 and 1:6:1 respectively at room temperature caused mainly rapid isomerization as well as transalkylation to cumene at the first half an hour.

Then there was rapid transalkylation and little disproportionation to mainly cumene and TIPS as shown in figures (1,2, and 3). When the mole percentage values of benzene and p-DIPB were normalized, it was observed that the conversion of p-isomer (77.5 mol%) and the mole percent of benzene remained (22.5 mol%) after 0.5 h with 1:1 molar ratio. The conversion of p-isomer gradually increased until approximately 4 h to reach about (82 mol %). The same trend was found with 1:3 and 1:6 molar ratio, but the rates of isomerization and transalkylation were slower.

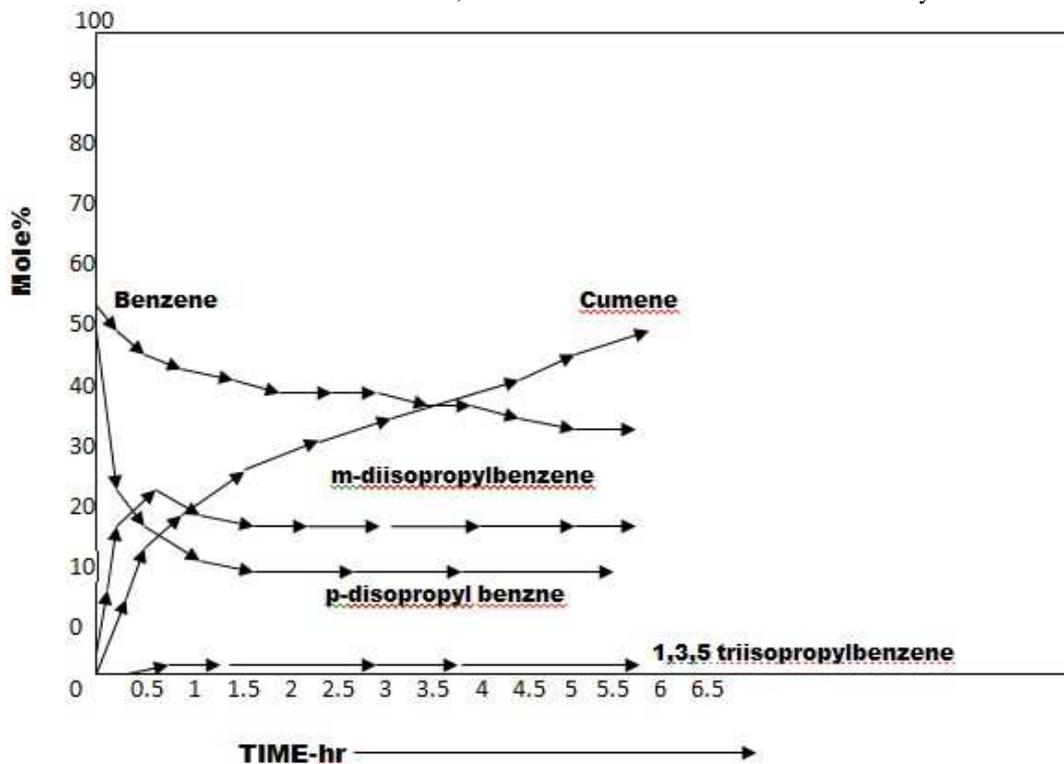


Fig.1 Product distribution from isomerisation and transalkylation of p-DIPB isomer with benzene (1:1) in presence of triflic acid catalyst at room temperature

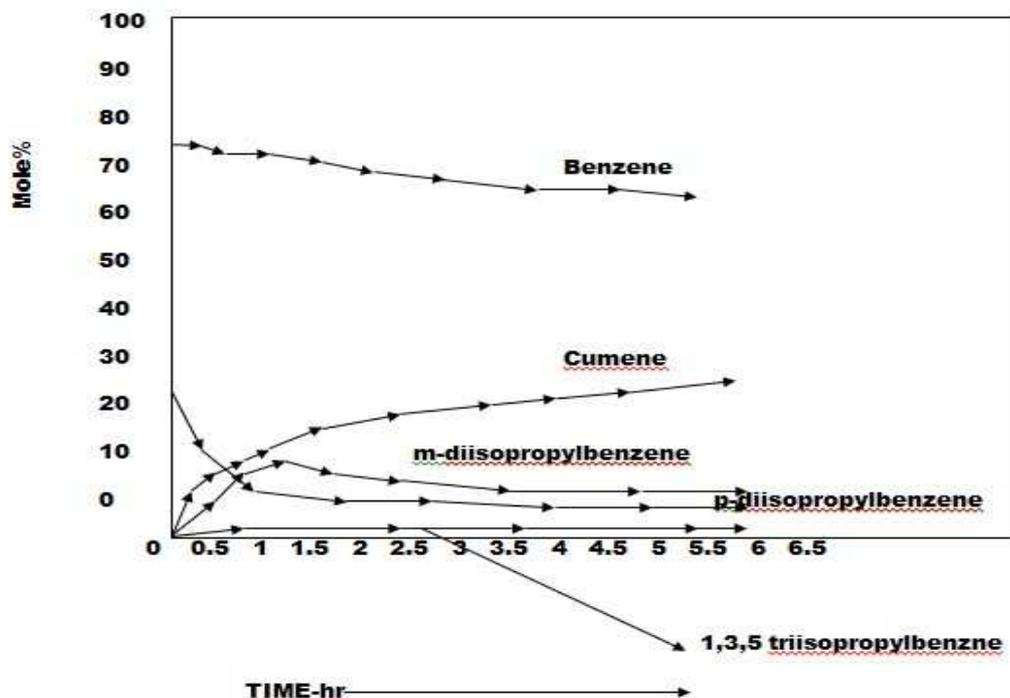


Fig.2 Product distribution from isomerisation and transalkylation of p-DIPB isomer with benzene (1:3) in presence of triflic acid catalyst at room temperature

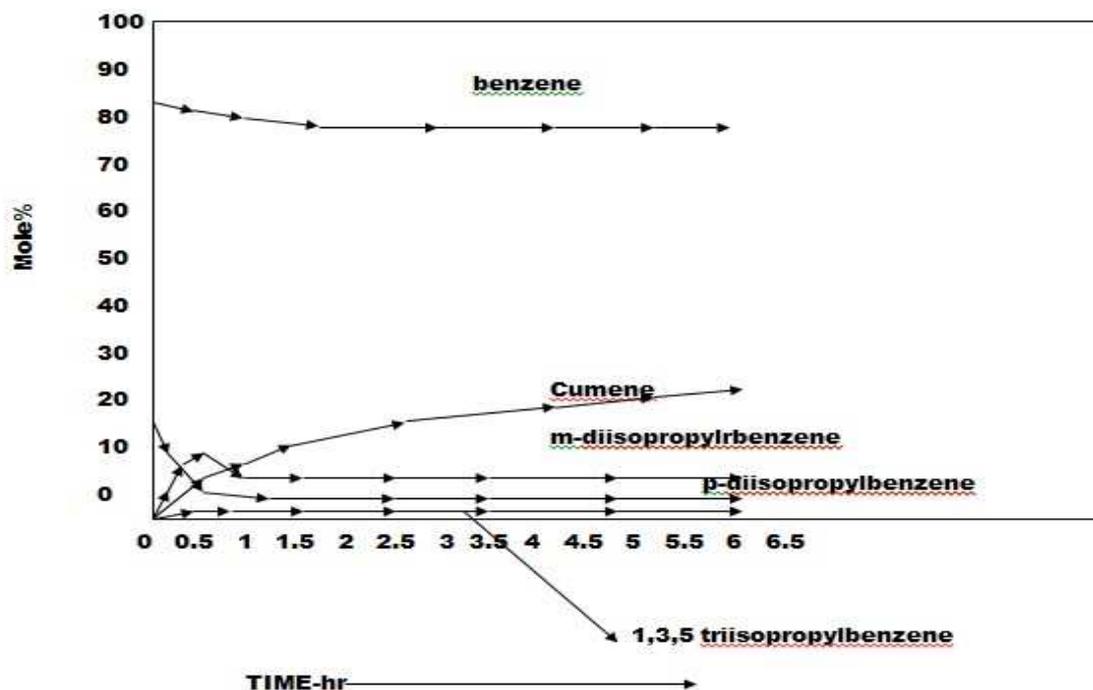


Fig.3 Product distribution from isomerisation and transalkylation of p-DIPB isomer with benzene (1:6) in presence of triflic acid catalyst at room temperature

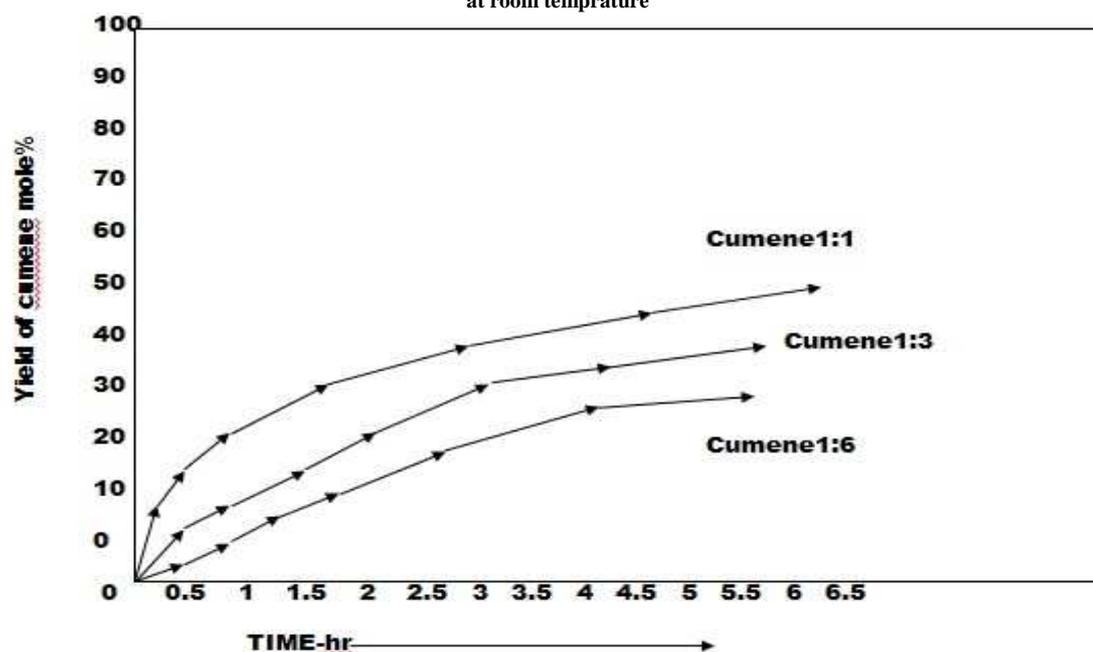
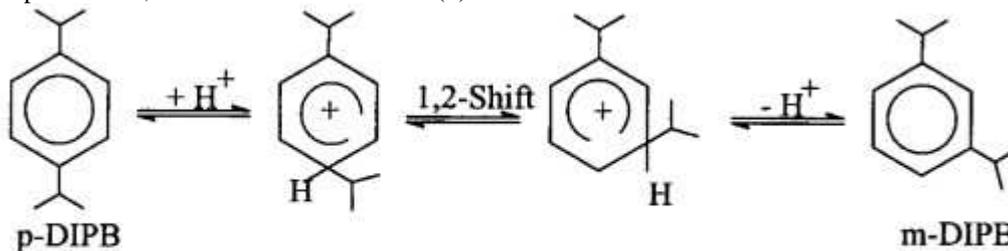


Fig.4 Yield of cumene from isomerisation and transalkylation of p-DIPB isomer with benzene (1:1, 1:3 and 1:6 molar ratio) in presence of triflic acid catalyst at room temperature

It can be seen from the figures (1,2 and 3) that p-isomer gave predominantly m-isomer during the early stages of the reaction as expected of 1,2-shift mechanism scheme(1).



(Scheme1)

Fig.5

It is interesting that m-isomer is the only product of isomerization reaction with a very little trace of o-isomer. The absence of o-DIPB, it might have been predicted on steric grounds. The rate of transalkylation, after 0.5 h is faster than the rate of isomerization. The formation of cumene is possible either by transalkylation reaction between DIPB isomers and benzene or dealkylation of DIPB isomers as shown in reactions (1) and (2) respectively.

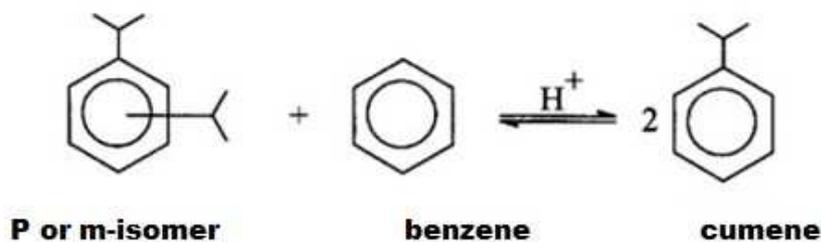


Fig.6

(1)

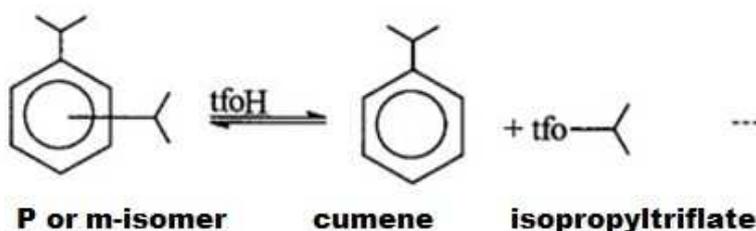


Fig.7

(2)

The formation of TIPB is possible by very little disproportionation of DIPB isomers as shown in reaction (3).

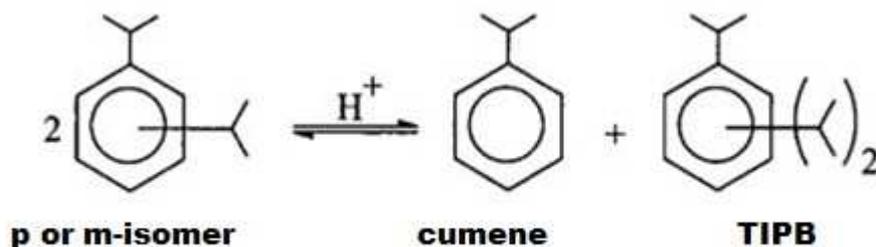


Fig.8

(3)

Transalkylation of m-DIPB isomer with Benzene

meta-Diisopropylbenzene (m-DIPB) is a chemical intermediate for the preparation of stabilizers, polymers, synthetic lubricants, hydro peroxides, and a variety of other products. Reactions of DIPB include side chain modification by oxidation, dehydrogenation, and bromination. Ring substitution reactions include nitration, sulfonation, bromination, and acetylation.

The same trends were observed when m-DIPB isomer used under similar conditions as shown in figures (5,6 and 7). It can be seen that the rate of isomerization and transalkylation of m-isomer are slower than that found with p-isomer, but both gave mainly cumene. This was expected because of the thermodynamically more stable m-isomer. When the mole percentage values of benzene and m-DIPB normalized, the conversion of m-isomer (67 mol%) with 1:1 molar ratio after 0.5 h. This value continues to rise throughout the reaction to reach (70 mol%) after 4 h. It can also be seen from figures that there is a marked increase in the conversion to cumene with an increase in the molar ratio of isomer to benzene. The maximum yield of about (46 mol%) was observed at 1:1 molar ratio while (18 mol%) with 1:6 molar ratio after 6 h of the reaction as shown in fig. (8).

The activity of triflic acid was similar to that found in our previous studies such as alkylation of benzene with ethene, isopropylation of benzene with propene, isomerization and disproportionation of diethyl benzene isomers, and isomerization and transalkylation of diethyl benzene isomers.

CONCLUSIONS

The following conclusions can be drawn from this work; The isomerization and transalkylation reactions gave higher yield of cumene (46 mol%) at 1:1 molar ratio with both isomers. - When the molar ratio of isomer to benzene increases, the conversion of DIPB isomers and the yield of cumene increases.

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