



# Mechanistic insights into solvent induced alkylation of *p*-cresol with *tert*-butyl alcohol using Brønsted acidic ionic liquids

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## ABSTRACT

In this work, a combination of density functional theory (DFT) and ab initio methods were used to develop a molecular level understanding of the alkylation of *p*-cresol with *tert*-butyl alcohol using Bronsted acidic ionic liquids (ILs) as catalysts. Commonly used triethylammonium based Bronsted acidic ILs were synthesized and their catalytic activity in the alkylation of *p*-cresol were investigated. Theoretical molecular simulation mimicking the experimental conditions was used to explain the conversion of *p*-cresol and selectivity to the alkylated products. The experimentally obtained product selectivity was correlated with the theoretically calculated atom reactivity based on superdelocalizability parameter and the charge distribution. Effect of these parameters in the neutral as well as ionic pathway mechanism in presence of ionic liquid and water solvent mixture were investigated. The mechanism is confirmed from thermochemical energy values that the direct O-alkylation leading to the kinetically controlled ether product predominates at lower temperature (343 K) and shorter reaction time. Whereas, the thermodynamically controlled *ortho* C-alkylated product, 2-TBC, predominates at higher temperature and longer reaction time. Solvent was also found to affect the product selectivity either at the C- or O- sites. With the formation of water as a side product in the course of the alkylation reaction, the dielectric constant of the reaction media increased. Hence, rearrangement of the *tert*-butyl carbocation in O-alkylated product in presence of the combined IL and water media leads to the formation of C-alkylated products.

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## 1. Introduction

Alkylation reactions of aromatics like *p*-cresol with alcohols using acidic catalysts have been researched because of their wide spread commercial applications and the ease of use of alcohols instead of alkenes [1]. The *tert*-butylated products of *p*-cresol are used as antioxidants in polymers, in technical oils, edible oils and fat-containing foods, light protection agents, UV-absorbers, rubber and paint industry, as well as in cosmetics and pharmaceutical industry [2–5]. Homogeneous corrosive acids like H<sub>2</sub>SO<sub>4</sub>, HClO<sub>3</sub> and HF, Lewis acids like AlCl<sub>3</sub>, BF<sub>3</sub>, heteropoly acids, cation-exchange resins, Y-Zeolites and solid acidic materials have been reported as efficient catalysts for this alkylation reaction [6–12]. These suffer from the disadvantage of corrosive nature of the acids and low selectivity to desired products. The solid acids have the

disadvantage of rapid deactivation because of pore blocking due to coke formation. The cation-exchange resins are not thermally stable enough to be used industrially. Recently, several researchers reported Bronsted acidic IL catalysts under homogeneous phase mild reaction conditions in batch reactor process yielding more than 80% of *p*-cresol conversion [13–15]. With negligible vapor pressure, ease of separation, excellent thermal stability and almost complete recoverability, room temperature ILs seem to be attractive solution for most of these acid catalyzed alkylation reactions [16–23]. Recently, Wang et al. have investigated the acidic effect towards the C–H and C=O bonds activation using DFT studies [24–26]. However, detailed mechanistic investigation of the acid-catalyzed alkylation reaction mechanism involving ILs are scanty [27–29]. Henceforth, detailed theoretical and experimental investigations are needed to elucidate their catalytic nature as well as the effect as solvents in such reactions.

Triethylamine based Bronsted acidic ILs have been reported earlier to be highly efficient catalysts for this alkylation reaction [14]. In this present study, *p*-cresol was considered as a model aromatic compound and *tert*-butyl alcohol as a model alkylating agent, to investigate the effect of ILs on this type of alkyla-

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## Nomenclature

IL	ionic liquid
RTIL	room temperature IL
IL-HSO <sub>4</sub>	1-(4-sulfonic acid) triethylammonium hydrogen sulfate
IL-CF <sub>3</sub> SO <sub>3</sub>	1-(4-sulfonic acid) triethylammonium trifluoromethane sulfonate
IL-PTS	1-(4-sulfonic acid) triethylammonium 4-methylbenzenesulfonate
IL-CH <sub>3</sub> SO <sub>3</sub>	1-(4-sulfonic acid) triethylammonium methane sulfonate
TBA	<i>tert</i> -butyl alcohol
2-TBC	2- <i>tert</i> -butyl- <i>p</i> -cresol
TBCE	<i>tert</i> -butyl- <i>p</i> -cresol ether
2, 6-DTBC	2, 4-di- <i>tert</i> -butyl- <i>p</i> -cresol
T	temperature, K

tion mechanism. Based on the product distribution obtained from the experimental results, two different pathways were investigated. The neutral pathway mechanism involving the gas phase molecules. The charged pathway approach shows the effect of solvent in the mechanism. The catalytic activity of different functionalized ILs were investigated using a combined DFT and ab initio study on the IL structures. Structural parameters, charge distribution and orbital energies were estimated to understand the effect of acidity and product distribution in alkylation reaction.

## 2. Experimental

### 2.1. Chemicals

Triethylamine and 1,4-butane sultone were purchased from Sigma Aldrich Chemicals Pvt. Ltd, India. Trifluoromethane sulfonic acid, methanesulfonic acid, sulfuric acid and *p*-toluene sulfonic acid were purchased from Merck, India. The other reactants, *p*-cresol and *tert*-butyl alcohol, were purchased from Ranbaxy Ltd., New Delhi, India. These chemicals were used as received without any further purification.

### 2.2. Catalyst preparation

The Bronsted acidic ILs as shown in Fig. 1 were prepared following the procedure mentioned in literature [30,31]. In a typical IL preparation procedure, triethylamine was mixed with 1,4-butane-sultone and stirred at 333–353 K for 12–24 h. The solidified zwitterionic mass was washed three times with diethyl ether and then dried under reduced pressure (393 K, 0.01 Torr). Stoichiometric amount of sulfuric acid, trifluoromethane sulfonic acid, *para*-toluene sulfonic acid and methane sulfonic acid was then added to the precursor zwitterion to obtain four different ILs. The mixture was stirred at 353 K for 5 h to obtain the IL. Finally, the obtained ILs were dried under reduced pressure (393 K, 0.01 Torr).

### 2.3. Catalyst characterization

The acidity of the ionic liquids was measured using Fourier transformed infra-red (FTIR) spectroscopy with pyridine as a probe molecule. Pyridine was dried prior to use with KOH and 4 Å molecular sieves overnight and finally by distillation. All the IL samples were dried under reduced pressure (0.01 Torr). The IL samples were mixed with pyridine at IL: pyridine mole ratio of 1:5 and the spectra

were collected using Nicolet-6700 FTIR spectrometer at a resolution of 4 cm<sup>-1</sup> and 32 scans per spectrum.

### 2.4. Catalytic activity study

The activity testing of these IL catalysts, in this reaction, was carried out in a 2 mL Borosil glass reactor and equipped with a magnetic stirrer under autogenous pressure. A typical batch consisted of 10 mmol each of *p*-cresol, TBA and ILs. Reaction temperature was maintained at 343 K and reaction mixture was stirred for 3 h. A qualitative product analysis and quantitative analyses were conducted with a NUCON GC supplied by AIMIL India Ltd. using a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column with flame ionization detector. The carbon balance and the aromatic ring balance were checked to be 99.2 and 97.8% respectively.

## 3. Computational methods

Geometry optimization of different structures was performed using the DFT calculations using B3LYP hybrid functional and 6-31 G (d) basis set which was reported to be the best reliable computational level to treat these type of aromatic ring containing structures by Miklis et al. [32]. A vibrational analysis was also performed for each geometry optimized structure of the reactants, products and intermediate to check the absence of negative frequency, which in turn, confirmed the structure to be minimum. A zero point energy (ZPE) correction with a correction factor of 0.9804 was also used in the energy values obtained from frequency analysis on the basis of the method used. The stabilization energy ( $\Delta E$ ) of the IL was calculated as the difference between the energy of the IL subtracted from the sum of energies of the pure cation and anion as mentioned in the following equation:

$$\Delta E (\text{kcalmol}^{-1}) = \{E_{IL} - (E_C + E_A)\} \times 627.503$$

Where,  $E_{IL}$ ,  $E_C$  and  $E_A$  are the Gibbs free energy values of the IL, cation and anion of the IL respectively in Hartree. A full natural bond order (NBO) analysis was also performed using the same level of theory to obtain the charge distribution in the ILs as well as in the reactants and the products. The initial structure of all the ILs was started from the all Trans conformer. The gas-phase reactants, products and intermediate geometries were optimized in vacuum. For all the geometry optimizations including solvent effects, a combined average dielectric constant of 20 and a probe radius ( $r_0$ ) of 1.4 Å was chosen for IL and water mixture formed during the course of the reaction [33]. The solvent phase energies of all of these species were obtained using the polarization continuum model. Frontier molecular orbital analysis was also performed using MP2 method with 6-311G(++) (d, p) basis set. All these calculations were performed using Gaussian 09 program [19].

## 4. Results & discussion

### 4.1. Role of ILs

The IL behaves as solvent as well as catalyst in this alkylation reaction. Dehydration of TBA occurs mainly in presence of the Bronsted acidic IL to produce the electrophilic tertiary carbocation. Also, the ILs play an important role in the transfer of the carbocation to the aromatic ring. To further investigate the role of the ILs in this reaction, the structural parameters as well as the stabilization energy values were compared.

#### 4.1.1. Characterization of the ILs

FTIR spectra of the ILs using Pyridine as a probe are shown in Fig. 2. Pyridine has two characteristic peaks in the region of

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