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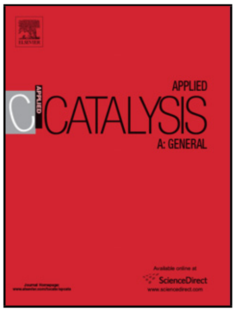

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Author: Tanmoy Patra Salahuddin Ahamad Sreedevi
Upadhyayula

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Highly efficient alkylation of phenol with *tert*-butyl alcohol using environmentally benign Bronsted acidic ionic liquids

Tanmoy Patra, Salahuddin Ahamad, Sreedevi Upadhyayula*

Department of Chemical Engineering, Indian Institute of Technology Delhi, Hauz Khas,
New Delhi–110016, India.

*Corresponding author. Tel. No.: +91-11-26591083, fax: +91-11-26591120,
E-mail: sreedevi@chemical.iitd.ac.in

Graphical abstract

Highlights

- Phenol alkylation using Bronsted acidic ionic liquids as catalyst
- Kinetics study on phenol alkylation using synthesized ionic liquids
- High phenol conversion (94.2%) obtained at 80 °C within 2 hours of reaction time
- DFT studies to correlate acidity and catalytic activity trends of the ionic liquids
- Estimation of activation energy (34.8 kJ mol^{-1}) from kinetic modeling

ABSTRACT

A series of SO_3-H functionalized environmentally benign Bronsted acidic ionic liquids were prepared using triethylamine, 1-methyl imidazole, pyridine, diethanolamine, 1, 4–butane sultone and methane sulfonic acid as the starting materials. These synthesized ionic liquid catalysts were characterized using spectroscopic tools like ^{1}H NMR, ^{13}C NMR. The catalytic activity of the synthesized ionic liquids was investigated in *tert*-butylation of phenol with *tert*-butyl alcohol. The effect of kinetic parameters like reaction time, reaction temperature, reactant mole ratio, reactant to catalyst mole ratio, on the conversion of phenol and selectivity to 2-*tert*-butyl-phenol and 2,4-di-*tert*-butyl-phenol were investigated. Phenol conversion upto 94.2% was achieved at temperature as low as 80°C and low alcohol to phenol molar ratio of 2:1, ionic liquid to phenol ratio of 1:1 and reaction time of 2 hours. The catalyst was found to retain its activity even after 8 recycles and was completely recoverable. The plausible reaction mechanism was formulated based on product distribution. The kinetic data was found to agree well with classical phenomenological models and the kinetic parameters were estimated. The experimental results were further validated by Density Functional Theory (DFT) optimizations of the ionic liquid structures performed at the B3LYP/6-311G** level using Gaussian 09 package.

Keywords: Ionic liquids; Alkylation; phenol; *tert*-butyl alcohol; *tert*-butylation; 2,4-di-*tert*-butyl phenol; Density Functional Theory

1. Introduction

Alkylation of phenol with *tert*-butyl alcohol (TBA) is an industrially important Friedel-Crafts reaction for the production of the fine chemicals, mainly 2-*tert*-butyl-phenol (2-TBP) and 2, 4-di-*tert*-butyl-phenol (2, 4-DTBP) [1]. All the products of this reaction are important lipophilic phenols used in the production of antioxidants in food industry. These *tert*-butylated phenols are also used as additives in jet fuels, petroleum products, cosmetics, pharmaceuticals, rubber manufacturing, varnishes, printing inks and also as polymerization inhibitors, UV absorbers, antiseptic and embalming fluids [1-12]. Several investigations on the *tert*-butylation of phenol using both homogeneous and heterogeneous catalysts, Lewis acids like $AlCl_3$ and BF_3 [2], Bronsted acids like HF, H_3PO_4, H_2SO_4, and $HClO_3$ [3], mesoporous materials [4, 5], near critical as well as super critical water [6], cation-exchange resins [7], zeolites [7, 8], heteropoly acids [5], solid sulfanilic acids [9] are reported till date. However, most of the homogeneous liquid acid catalysts are environmentally hazardous due to their corrosive nature. The solid acids have the disadvantages of rapid deactivation by coking and pore blocking as well as solid waste disposal problem. The cation-exchange resins are not thermally stable to be used in industry [10]. Hence, the need for greener routes using environmentally benign catalysts is recognized by many researchers. During the last two decades, ionic liquids, with their tremendous potential both as solvents and catalysts have evolved immensely as a solution to most of the problems involving catalytic reactions. Room temperature ionic liquid (RTIL) catalysts, with negligible vapor pressure, ease of separation from reaction products, excellent thermal stability and almost complete recyclability, have been considered to be a solution for most of the above mentioned problems [11-20]. However, reports on alkylation of phenol with TBA using ionic liquid catalysts are scanty [13-20]. Moreover, Density Functional Theory (DFT) studies on correlating the properties of ionic liquids in catalytic reactions are almost negligible. Shen et al. reported imidazole based Lewis acidic ionic liquid, [bmim] PF_6 in catalyzing the alkylation of phenol with TBA [13, 14]. However, these Lewis acidic ionic liquids produce corrosive acids. Gui et al. reported a set of imidazole based Bronsted acidic ionic liquids with SO_3-H as the active functional group. This process is, however, not viable for large scale alkylated phenols production because of the inherent toxicity of these ionic liquids due to the presence of the imidazole ring [18]. Elavarasan et al. reported a set of SO_3-H functionalized Bronsted acidic ionic liquids with 86% phenol conversion [20] and Liao et al. made an effort to correlate the activities of the Bronsted acidic ionic liquids using DFT optimizations of the structures in Gaussian 09 [21]. In the present study, we report highly energy efficient 94.2% conversion of phenol using environmentally benign SO_3-H functionalized room temperature ionic liquids in alkylation of phenol with TBA. DFT calculations were used to correlate the experimental acidity trends of these ionic liquids and hence, to explain their high catalytic activity in this reaction. Further those results were used to validate the effect of acidity and functionality variation on the alkylation mechanism.

The effect of kinetic parameters like reaction time, temperature, reactant mole ratio, catalyst to reactant mole ratio on phenol conversion were investigated and these parameters were optimized in a batch reactor. Based on the product distribution, a reaction mechanism was proposed for the alkylation of phenols using functionalized ionic liquid catalysts. The kinetic data was fitted to various models reported in literature [20] and the best fit model was used to estimate the kinetic parameters. The activation energy was finally calculated using the Arrhenius equation.

2. Experimental

2.1. Chemicals

A series of Bronsted acidic ionic liquids with SO_3-H functionality were synthesized following the procedure outlined in literature [20, 22-24]. 1-methyl imidazole was purchased from Sigma Aldrich Chemicals Pvt. Ltd., UK. Triethylamine, pyridine and diethanolamine were purchased from Spectrochem Chemicals, India. 1, 4–butane sultone was purchased from Sigma Aldrich Chemicals Pvt. Ltd, Germany. Phenol and TBA were purchased from Merck Chemicals Pvt. Ltd, Mumbai, India.

2.2. Synthesis of ionic liquids

As a general methodology for ionic liquid preparation, the individual amine was mixed with 1, 4-butane-sultone and stirred at 60-80°C for 12-18 hours. Resultant zwitterionic solid was washed three times with diethyl ether and then dried under vacuum (120°C, 0.01 Torr). Finally, equivalent amount of methane sulfonic acid was added to the solidified zwitterionic mass and stirred at 80°C for 4-7 hours to obtain the ionic liquid. The structures of the synthesized ionic liquids are shown in **Fig. 1**. All the chemicals were research grade and were used without further purification unless otherwise stated.

2.3. Characterization of synthesized ionic liquids

The prepared ILs were characterized by ^{1}H NMR and ^{13}C NMR spectroscopy using Bruker ARX-300 spectrometer. Thermo gravimetric analysis (TGA) was performed using a TG 209 F3 Tarsus instrument. UV-Visible spectra were recorded on a Shimadzu UV-2450 instrument.

2.3.1. Characterization of ionic liquids by NMR

IL-1 [N-(4-sulfonic acid) butyl triethylammonium methane sulfonate]: ^{1}H NMR (D_2O, 300 MHz): ∂ (ppm) 0.953 (t, 9H), 1.501 (m, 4H), 2.475 (s, 3H), 2.644 (t, 2H), 2.888 (t, 2H), 2.967 (q, 6H), ∂(ppm)=4.80 [Solvent peak (D_2O)]; **^{13}C NMR** (D_2O, 75 MHz): δ(ppm) 4.301, 17.552, 18.975, 36.151, 47.677, 50.244, 53.600.

IL-2 [1-(4-sulfonic acid) butylimidazolium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 1.542 (m, 2H), 1.879 (m, 2H), 2.125 (s, 1H), 2.416 (s, 3H), 3.856 (s, 3H), 4.186 (t, 2H), 4.293 (t, 2H), 7.713 (d, 1H), 7.778 (d, 1H), 9.148 (s, 1H), δ (ppm)= 2.508 [Solvent peak (DMSO)]; **^{13}C NMR** (DMSO, 75 MHz): δ (ppm) 21.065, 28.065, 30.274, 35.318, 48.044, 49.982, 121.895, 123.206, 136.209, δ (ppm)= 39.006 [Solvent peak (DMSO)].

IL-3 [1-(4-sulfonic acid) butylpyridinium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): δ (ppm) 1.615 (m, 2H), 2.022 (m, 2H), 2.281 (s, 1H), 2.580 (s, 3H), 2.603 (t, 2H), 4.677 (t, 2H), 8.169 (t, 2H), 8.613 (t, 1H), 9.096 (d, 2H), δ (ppm)= 2.511 [Solvent peak (DMSO)]; **^{13}C NMR** (DMSO, 75 MHz) : δ (ppm) 20.5389, 28.9577, 49.6571, 60.7467, 75.6754, 127.9776, 143.8474, 145.3695, δ (ppm)= 38.2471 [Solvent peak (DMSO)].

IL-4 [N, N-bis(2-hydroxyethyl)-(4-sulfonic acid)-1-aminium methane sulfonate]: ^{1}H NMR (DMSO, 300 MHz): ∂(ppm) 1.640 (m, 2H), 1.733 (m, 2H), 2.410 (s, 3H), 3.020 (m, 1H), 3.160 (m, 1H), 3.221 (t, 2H), 3.301 (t, 2H), 3.658 (t, 2H), 3.742 (t, 4H), 3.933 (broad m, 4H), ∂

(ppm)= 2.513 [Solvent peak (DMSO)]; **^{13}C NMR** (DMSO, 75 MHz): δ (ppm) 21.790, 22.396, 49.280, 53.338, 55.913, 57.993, 63.651, δ (ppm)= 39.510 [Solvent peak (DMSO)].

2.3.2. Thermo Gravimetric Analysis of ionic liquids

The thermal decomposition temperatures of the ILs were obtained using TG 209 F3 Tarsus at a heating rate of 10 K/min, under nitrogen atmosphere. Thermal decomposition temperature of IL-1, IL-2, IL-3 and IL-4 were observed at 312ºC, 324.8ºC, 366.9ºC and 326ºC respectively.

2.3.3. Acidity of ionic liquids

To compare the Bronsted acidity of different ionic liquids, UV-Visible spectroscopy was used as mentioned in literature [25-30]. As a general methodology 4-nitro aniline (pK_a value of 0.99) was chosen as a basic indicator to abstract proton from the Bronsted acidic ionic liquids in water. The variation in acidity was evaluated in terms of the measurable ratio of the unprotonated and protonated indicator concentration ratio, $[B]_{aq}/ [BH^+]_{aq}$. The Hammett function (H_0) was then calculated using equation 1 as shown below:

$$H_0 = pK(B)_{aq} + \log([B]_{aq}/[BH^+]_{aq}) \tag{1}$$

Where, $pK(B)_{aq}$ is the pK_a value of the indicator in aqueous solution. The terms $[BH^+]_{aq}$ and $[B]_{aq}$ are protonated and unprotonated indicator molar concentrations in the solvents respectively. The blank solution of 4-nitro aniline in water showed absorbance maxima at 381 nm. **Fig. 2a** shows the absorbance of IL-1 solution at different concentrations. The Hammett function of the other ionic liquids prepared in the laboratory was also found by similar procedure, and the results are shown in the **Fig. 2b**. From the figure, it is clear that the four ionic liquids possess strong acidity which is very important for this acid-catalyzed reaction.

2.3.4. Catalytic testing

A series of activity tests using these laboratory synthesized ionic liquids were carried out in a 3 mL polytetrafluoroethylene (PTFE) sealed *Borosil* glass reactor under autogeneous pressure placed on a magnetic stirrer. In a typical batch run, 1 mmol each of phenol, TBA and ionic liquid were taken in the reactor and stirred for 5 hours at 80ºC. The product mixture was analyzed both using a NUCON GC supplied by AIMIL India Ltd. equipped with a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column and flame ionization detector (FID). The carbon balance was checked and found to be more than 99.9% while ring balance was obtained to be more than 97.9%.

2.3.5. Computational methods

MATLAB 8.4 software version was used to perform the optimization in the kinetic modeling. The DFT studies were performed using Gaussian 09 software [31]. Geometry optimizations of different ionic liquids were performed at the B3LYP level using the 6–311++G (d, p) basis set. A vibrational analysis was also performed for each optimized structure to check the absence of negative frequency which, in turn, confirms the structure to be an energy minimum. The basis set superposition errors (BSSEs) were confirmed to be negligible by the counterpoise method [32, 33]. Chemcraft software was used to calculate the optimized structural parameters (http://www.chemcraftprog.com/). The initial structure of all the ionic liquids was started from the all Trans conformer. The stabilization energy (ΔE) was calculated as the difference between the energy of the ionic liquid subtracted from the sum of energies of the pure cation and anion as shown in equation 2:

$$\Delta E\ (kJ\ mol^{-1}) = [E_{IL}(atomic\ unit) - (E_C + E_A)(atomic\ unit)] * 2622.9901 \qquad (2)$$

3. Results & Discussion

3.1. Comparison of activity of the four ionic liquid catalysts

A comparative study of the activity of the prepared ionic liquids with that of the already available catalysts was performed in this reaction [29]. From **Table 1**, it is obvious that all the ionic liquid catalysts gave high phenol conversion at 80°C temperature. The selectivity to 2-TBP and 2, 4-DTBP was higher as compared to the other products compared to literature reports in all cases. Interestingly, IL-2 and IL-3 showed higher selectivity towards the 2, 6-di-*tert*-butyl phenol (2, 6-DTBP) in comparison to IL-1 and IL-4. The reason can be attributed to the sterically hindered transition state in the formation of the di-*ortho* substituted phenol, 2, 6-DTBP. Both IL-1 and IL-4 consisting of bulky alkyl chains do not favor the transition state geometry and hence, less selectivity to 2, 6-DTBP. In case of IL-2 and IL-3 the selectivity towards 2, 6-DTBP was obtained to be as high as 36.5% and 41.6% respectively. Among the four ionic liquid catalysts, IL-1 gave 94.2% phenol conversion at 80°C reaction temperature and phenol: TBA: IL mole ratio of 1:2:1 within 2 hours of reaction time. These reactions were repeated at least five times and the results were found to be similar. The TOF of IL-1 was observed to be highest at 1.543 min^{-1}. IL-1 was found to be the most promising catalyst as well as least toxic [30]. Hence, IL-1 was chosen for further detailed kinetic evaluation. The improved efficiency of this ionic liquid as compared to those with similar functionality, reported in prior art [20], can be attributed to the solubility factor imparted by the methane sulfonate anion of IL-1. The presence of this anion resulted in improved solubility of TBA leading to more reaction with IL-1 to form IL-esters. The product distribution obtained during the detailed kinetic study helped us to understand the reaction mechanism.

3.2. Effect of reaction time on phenol conversion

To investigate the effect of reaction time on phenol conversion and the selectivity to 2-TBP and 2, 4-DTBP, a series of reactions were conducted at different temperatures and different reactant mole ratios. The results are summarized in **Fig. 3a**. It is evident from the figure that most of the phenol conversion was obtained within the first 2 hours of the reaction and, thereafter, reached steady state. The maximum conversion of phenol was observed to be 94.2%, while the selectivity to 2-TBP and 2, 4-DTBP reached 24.3% and 52.9% respectively after 2 hours. Beyond two hours, the conversion of phenol reached steady state. At 30 minutes reaction time, the selectivity to 2-TBP was 43.9% and beyond that selectivity to 2, 4-DTBP increased. The selectivity to the other dialkylated product, 2, 6-DTBP also increased slowly up to 13.5% after 5 hours of reaction time. This significantly lower selectivity towards 2, 6-DTBP can be attributed to the sterically hindered reaction mechanism of C-alkylation at both the *ortho* positions of phenol. Thus, the formation of 2, 6-DTBP is less likely for this type of ionic liquids and hence, selectivity is less [20]. Also, no significant ether product was observed during the reaction steps. This means that the mechanism proceeds via alkylation at *ortho* position followed by *tert*-butylation at the *para* position.

3.3. Effect of reaction temperature

A series of reactions were conducted in the temperature range of 40°C to 120°C using different reactant mole ratios for 5 hours. The conversion of phenol decreased significantly beyond 100°C since the dealkylation reaction becomes prominent as reported by earlier researchers [20, 35-36]. Higher temperatures also lead to dehydration of TBA followed by oligomerization, which in turn, suppresses dialkylated product selectivity [37]. At lower temperature, the extent of reactions were restricted by mass transfer limitations due to the increased viscosities of the ionic liquid which was also observed by Gu et al. [34]. **Fig. 3b** summarizes the results obtained for the alkylation reaction conducted in the temperature range of 50°C to 100°C up to 2 hours of reaction time and 1:2:1 phenol: TBA: IL-1 mole ratio. With increase in temperature from 50°C to 80°C, the conversion of phenol increased from 40.4% to 94.2%. Beyond 80°C, there is a decrease in phenol conversion which may be attributed to the vaporization of TBA whose boiling point is 82°C. At 60ºC, IL-1: phenol mole ratio of 1:1 and TBA: phenol mole ratio of 2:1, the selectivity to 2, 4-DTBP is high (65.5%) and with the increase in temperature, the selectivity to 2, 4-DTBP decreased up to 52.9% at 80ºC. This decrease in selectivity to 2, 4-DTBP can be attributed to the decreasing concentration of *tert*-butyl cation which is more stable at lower reaction temperatures. The conversion of phenol reached a maximum at reaction temperature of 80°C with moderate selectivity to 2, 4-DTBP of 52.9%. Hence, considering higher phenol conversion and moderate selectivity to the desired main product, the reaction temperature of 80°C was taken as optimum for further kinetic investigations.

3.4. Effect of TBA to phenol mole ratio

The effect of increase in reactant mole ratio (TBA to phenol) from 0.5 to 4 was investigated keeping the temperature at 80°C and IL to phenol mole ratio at 1:1. The results are shown in **Fig. 3c**. The TBA to phenol mole ratio of 2:1 gave the highest phenol conversion beyond which the conversion of phenol decreased due to dilution of the catalyst by TBA and also due to formation of oligomers. As the amount of TBA increased, at a constant IL-1 to phenol molar ratio, the conversion of phenol and selectivity to 2-TBP also increased. While the selectivity to 2, 4-DTBP decreased gradually with the increase in amount of TBA. This trend in product selectivity indicates that increased amount of TBA concentration leads to dilution of the acidity of the ionic liquid catalysts [20, 35]. Thus, the dealkylation becomes predominant and conversion to *ortho* substituted phenol, 2-TBP increases in this kinetically controlled reaction regime. The reaction mechanism proceeds via C-alkylation, favoring the *ortho* substituted phenol. Hence, considering the phenol conversion as well as product selectivity, the optimum TBA to phenol mole ratio is 2:1 at a constant IL-1 to phenol molar ratio of 1:1, temperature of 80°C and a reaction time of 2 hours.

3.5. Effect of catalyst to phenol mole ratio

The effect of increase in IL-1 to phenol mole ratio from 0.5 to 5 on the phenol conversion and product selectivity was investigated at 80°C keeping TBA to phenol molar ratio constant at 2:1. **Fig. 3d** shows a gradual increase in phenol conversion as the amount of IL to phenol mole ratio to 1:1. Thereafter, phenol conversion remained almost constant. The selectivity to 2-TBP and 2, 4-DTBP showed opposite trends with increased amount of IL-1 to phenol molar ratio. The selectivity to 2-TBP increased from 19.4% to 58.6% as IL-1 to phenol molar ratio increased from 0.5 to 5, while the selectivity to 2, 4-DTBP decreased from 66.4% to 16.4%. The decreased selectivity towards dialkylated products can be attributed to the increased amount of IL-1 in the reaction mixture which does not favor the sterically hindered dialkylation reaction step [34]. Since, the conversion of phenol was highest at IL-1 to phenol molar ratio 1:1, it was considered to be the optimum catalyst to reactant molar ratio at 80°C within 2 hours of reaction time.

3.6. Recyclability of ionic liquid

The recyclability of these prepared ionic liquid catalysts was found to be high when compared to ionic liquids reported [20] in literature for similar reactions. The residual trace amount of products of the alkylation reactions were separated from the ionic liquids by extracting with toluene (5 × 3mL). The resultant layer of the catalyst was washed with diethyl ether (5 × 3mL) and then dried under vacuum (10 mm of Hg) for 4-5 hours at 125°C. The purity of the recovered ionic liquid catalysts was checked by comparing with ^{1}H NMR, ^{13}C NMR, etc. as well as thin layer chromatography of the pure ionic liquid showing negligible amounts of products and unconverted reactants. No significant amount of oligomerized products were formed at 80ºC. The other unreacted reactants or products were highly soluble in the washing solvents used. Hence, the ionic liquids showed high recyclability. The results of the recycle experiments conducted using

IL-1 are summarized in **Table 2**. IL-1 was found to maintain significant activity even after 8 recycles.

3.7. Effect of acidity on phenol conversion

Fig. 2b shows the Hammett acidity function (H_0) values of the synthesized ionic liquids. From the figure it is evident that the order of acidity of the ionic liquids is IL-4>IL-1>IL-2>IL-3. DFT studies on the ionic liquid structures were performed to correlate the acidity trend. The ionic liquid structures were first geometrically optimized to a minimum using Gaussian 09 program as shown in **Fig. 4**. Then, the different structural parameters as well as the thermochemical energy values were calculated and used to explain the acidity of the ionic liquids. The optimized structural parameters are summarized in **Table 3**. The structural parameters for the ionic liquids were compared with literature [18] reported ionic liquid, 1-methyl-3-(butyl-4-sulfonate) imidazolium hydrogen sulfate (IL-0), having similar functionality with those reported in this study used in similar type of reactions. The structural parameters for IL-0 were used to compare the experimental and theoretical acidity values of the ionic liquids as also reported by Liu et al. [21]. There are two parameters controlling the acidity of the ionic liquids: (i) the interaction between the cationic species of the ionic liquids with the anion (expressed in terms of stabilization energy) and (ii) the hydrogen bonding capability between the anionic O atoms and the cationic acidic proton of O-H bond [21]. Thus, the acidity trend in ionic liquids cannot be directly correlated with the cationic O-H bond distances. The acidic O-H bond lengths in the cationic part are in the order of IL-0>IL-3>IL-2>IL-1>IL-4. Again, the stabilization energies of the ionic liquids are in the order of IL-0>IL-2>IL-3>IL-1>IL-4. Hence, the cation and anion are loosely bound in IL-4 or IL-1 than in IL-0, IL-2 or IL-3. The distance between anion and the cation in terms of hydrogen bonding are in the order of IL-4>IL-1>IL-2>IL-3>IL-0, exactly in the opposite order of the acidic O-H bond distances. Thus, when the hydrogen bonding is weak, the stabilization energy is also low and the ion pair is loosely bound. Hence, the acidic proton of SO_3-H group will be more active and more will be the acidity of the corresponding ionic liquid. The relative acidity trend from these DFT calculations can be summarized as IL-4>IL-1>IL-2>IL-3, which is in agreement with the experimental results. Surprisingly, IL-4 with the shortest cationic O-H bond distance has the strongest acidity because of the other two dominating parameters. Hence, it is obvious that both IL-1 and IL-4, with their strong acidity as compared to IL-2, IL-3 and IL-0, proved to be promising catalysts in this alkylation reaction. **Table 1** shows increase in phenol conversion with acidity for IL-1, IL-2 and IL-3. However, IL-4 with the highest acidity shows lower phenol conversion which may be attributed to its increased viscosity due to the presence of -OH groups increasing the H-bonding capability. IL-1 with its optimum acidity and viscosity showed higher catalytic activity in the reaction.

3.8. Kinetic modeling

Kinetic runs were conducted at four different temperatures, from 60°C to 100°C at 10°C interval. At each temperature, the product samples were collected at regular time intervals. In all these runs, the TBA to phenol mole ratio was kept at 2:1 and the phenol to catalyst mole ratio was 1:1. The *tri* substituted product (*2, 4, 6*-tri-*tert*-butyl phenol) was detected in very small amounts compared to other isomers. Since, no ether product was obtained, the conversion of *tert*-butyl phenol ether (TBPE) to 2-TBP was not considered in the model. In accordance with the product distribution, a reaction mechanism was proposed as shown in **Fig. 5**. Based on this mechanism, the system can be described by the following reaction scheme as shown in between equations 3 to 9:

Conversion of phenol:

$$P+TBA \xrightarrow{\mathrm{k_1}} 2\text{-}TBP+4\text{-}TBP+TBPE+3*W \qquad (3)$$

Isomerization of monoalkylated phenols:

$$2\text{-}TBP \underset{k_3}{\overset{k_2}{\rightleftharpoons}} 4\text{-}TBP \tag{4}$$

Alkylation of 2-TBP:

$$2\text{-}TBP+TBA \underset{k_5}{\overset{k_4}{\rightleftharpoons}} 2,4\text{-}DTBP+W \tag{5}$$

$$2\text{-}TBP+TBA \underset{k_7}{\overset{k_6}{\rightleftharpoons}} 2,6\text{-}DTBP+W \tag{6}$$

Alkylation of 4-TBP:

$$4\text{-}TBP+TBA \underset{k_9}{\overset{k_8}{\rightleftharpoons}} 2,4\text{-}DTBP+W \tag{7}$$

Isomerization of dialkylated phenols:

$$2,6\text{-}DTBP \underset{k_{11}}{\overset{k_{10}}{\rightleftharpoons}} 2,4\text{-}DTBP \tag{8}$$

Conversion of ether to 2-TBP:

$$TBPE \xrightarrow{k_{12}} 2\text{-}TBP \tag{9}$$

Model parameters were estimated by minimizing the objective function, as shown in equation 10, which is the sum of squares of errors between the predicted and measured values for all the state variables for a dynamic run:

$$f = \sum_{i=1}^{n} \sum_{j=1}^{m} (x_{ij} - x_{0,ij})^2 \tag{10}$$

Where, x is computed value, x_0 is observed value, n is total number of state variables and m is total number of observations.

The program requires the input data in six main steps described as follows:

- Model equations (Given in Sec. 3.8.1).
- Number of model parameters (k_1 to k_{11}).
- Initial, lower and upper bounds of the parameters.
- Starting, final and sampling times for experimental data.
- Number of state variables (There are 7 state variables starting from C_P (conc. of phenol) to C_W (conc. of water).
- Experimental measurements of state variables.

3.8.1 Batch reactor kinetic model

The rate equations considered in the kinetic model for all the individual reactions involved in the alkylation are as follows (equations 11 to 17):

Alkylation of phenol:

$$\frac{dC_P}{dt} = -k_1 * C_P * C_{TBA} \tag{11}$$

Rate of conversion of TBA:

$$\frac{dC_{TBA}}{dt} = -k_1 * C_P * C_{TBA} - k_4 * C_{2-TBP} * C_{TBA} + k_5 * C_{2,4-DTBP} * C_W - k_6 * C_{2-TBP} * C_{TBA} + k_7 * C_{2,6-DTBP} * C_W - k_8 * C_{4-TBP} * C_{TBA} + k_9 * C_{2,4-DTBP} * C_W \tag{12}$$

Rate of formation of 2-TBP:

$$\frac{dC_{2-TBP}}{dt} = -k_1 * C_P * C_{TBA} - k_2 * C_{2-TBP} * C_{2-TBP} + k_3 * C_{4-TBP} * C_{4-TBP} - k_4 * C_{2-TBP} * C_{TBA} + k_5 * C_{2,4-DTBP} * C_W - k_6 * C_{2-TBP} * C_{TBA} + k_7 * C_{2,6-DTBP} * C_W \tag{13}$$

Rate of formation of 4-TBP:

$$\frac{dC_{4-TBP}}{dt} = k_1 * C_P * C_{TBA} + k_2 * C_{2-TBP} * C_{2-TBP} - k_3 * C_{4-TBP} * C_{4-TBP} - k_8 * C_{4-TBP} * C_{TBA} + k_9 * C_{2,4-DTBP} * C_W \tag{14}$$

Rate of formation of 2, 4-DTBP:

$$\frac{dC_{2,4-DTBP}}{dt} = k_4 * C_{2-TBP} * C_{TBA} - k_5 * C_{2,4-DTBP} * C_W + k_8 * C_{4-TBP} * C_{TBA} - k_9 * C_{2,4-DTBP} * C_W + k_{10} * C_{2,6-DTBP} * C_{2,6-DTBP} - k_{11} * C_{2,4-DTBP} * C_{2,4-DTBP} \quad (15)$$

Rate of formation of 2, 6-DTBP:

$$\frac{dC_{2,6-DTBP}}{dt} = k_6 * C_{2-TBP} * C_{TBA} - k_7 * C_{2,6-DTBP} * C_W - k_{10} * C_{2,6-DTBP} * C_{2,6-DTBP} + k_{11} * C_{2,4-DTBP} * C_{2,4-DTBP} \quad (16)$$

Rate of formation of Water:

$$\frac{dC_W}{dt} = k_1 * C_P * C_{TBA} + k_4 * C_{2-TBP} * C_{TBA} - k_5 * C_{2,4-DTBP} * C_W + k_6 * C_{2-TBP} * C_{TBA} - k_7 * C_{2,6-DTBP} * C_W + k_8 * C_{4-TBP} * C_{TBA} - k_9 * C_{2,4-DTBP} * C_W \quad (17)$$

Where, C_P, C_{TBA}, C_{2-TBP}, C_{4-TBP}, $C_{2,4-DTBP}$, $C_{2,6-DTBP}$ and C_W are the concentrations of respective components, and k_1 to k_{11} are the second order rate constants. A comparison of experimental and predicted phenol conversion with time at 80ºC is shown in **Fig. 6a**. The predicted data fits well with the experimental measurements at five different temperatures 60ºC, 70ºC, 80ºC, 90ºC and 100ºC. The optimized parameters are summarized in the **Table 4**. The value of the activation energy and pre-exponential coefficient were obtained for each of the rate constants after plotting ln (k) vs 1/T as shown in **Fig. 6b** (shown for k_1 only).

4. Conclusions

SO_3-H functionalized room temperature Bronsted acidic ionic liquids were prepared in the laboratory using a greener approach and characterized using spectroscopic techniques. The acidity was optimized to suite the alkylation reaction chosen. A highly efficient and greener route for selective liquid phase *tert*-butylation of phenol with TBA, in room temperature ionic liquids, was systematically conducted in a batch autoclave under autogeneous pressure. The kinetic parameters like temperature, reaction time, reactant ratio, catalyst to reactant ratio were optimized. DFT studies on the ionic liquid structures were performed and from the calculated structural parameters the experimental acidity trends were correlated. The synthesized ionic liquids proved to be very efficient catalysts for this alkylation reaction. They are inexpensive, completely recoverable and recyclable. Catalytic amount of the laboratory prepared IL-1 showed very high phenol conversion, complete alcohol conversion and high dialkylated product selectivity at low temperatures. Thus, these Bronsted acidic ionic liquid catalysts show promise for the development of a continuous, environmentally benign, energy efficient and economical process route for the production of alkylated phenols. The activation energy for the ionic liquid catalyzed alkylation process was estimated to be 34.8 kJ mol^{-1} with a pre-exponential factor value of 28.7 lit. mol^{-1} min^{-1}.

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Fig. 1. Structure of ionic liquids.

Fig. 2. Relative acidity measurements using UV-Visible spectroscopy: a) Absorption spectrum of 4-nitroaniline for different concentration of IL-1 in H_2O, b) Hammett Function (acidity) of ILs in water with 4-nitroaniline as indicator (pK_a=0.99), A_{max}=381 nm.

Fig. 3. Kinetics study for alkylation of phenol with *tert*-butyl alcohol: a) Effect of reaction time on phenol conversion and product selectivity, b) Effect of reaction temperature on phenol conversion and product selectivity, c) Effect of TBA to phenol mole ratio on phenol conversion and product selectivity, d) Effect of catalyst (IL-1) to phenol mole ratio on phenol conversion and product selectivity.

Fig. 4. Optimized structure of different ionic liquids: a) Structure of IL-0, b) Structure of IL-1, c) Structure of IL-2, d) Structure of IL-3, e) Structure of IL-4.

Fig. 5. Proposed reaction mechanism involving IL-1.

Fig. 6. Kinetic parameter estimation from kinetic modeling: a) Comparison of experimental and predicted concentrations in alkylation of phenol with *tert*-butyl alcohol using IL-1 at 80ºC, b) Arrhenius plot for rate constant, k_1.

Table 1. Activity of the various catalysts in alkylation of phenol with TBA

Catalysts	Temperature (^{0}C)	Mole ratio (TBA: phenol)	Conversion (%)	% Selectivity			
				2-TBP	4-TBP	2, 4-DTBP	2, 6-DTBP
IL-1[a]	80	2:1	94.2	24.3	10.9	52.9	11.9
IL-2[a]	70	2:1	72.6	19.9	21.8	36.4	21.9
IL-2[a]	80	2:1	77.4	20.2	7.2	36.1	36.5
IL-3[a]	70	2:1	70.1	23.8	12.9	48.9	14.4
IL-3[a]	80	2:1	78.2	14.1	5.1	39.2	41.6
IL-4[a]	80	2:1	82.5	26.5	12.1	45.6	15.8
[bmim]PF$_6$ [13]	70	2:1	91.5	13.1	9.4	74.9	2.6
[hbim-SO$_3$H] HSO$_4$ [18]	70	2:1	80.3	25.8	9.0	60.2	5.1
[TEA-(CH$_2$)$_4$-SO$_3$H] HSO$_4$ [21]	70	2:1	84.5	23.8	10.2	57.6	7.4
TPA/TiO$_2$ [5][b]	80	6 :10	60.0	3.6	96.4	-	-
Mordenite [7][c]	60	6 :10	44.8	48.1	49.1	2.8	-
USY [7][d]	70	6 :10	52.7	63.0	23.0	13.1	-
RHAPhSO$_3$H [22][e]	120	1 :2	57.0	42.0	22.0	2.0	
TPA/MCM-41[14][f]	70	2 :1	44.8	29.0	49.0	21.2	-

[a] Reaction Conditions: phenol (1 mmol), TBA (1 to 2 mmol), ionic liquid (1 mmol); stirring speed= 800 rpm; reaction time: 2 h.

[b] Reaction Conditions: 250mg catalyst; reaction time: 1 h.

[c] Reaction Conditions: 200mg catalyst; reaction time: 3 h.

[d] Reaction Conditions: 200mg catalyst; reaction time: 8 h.

[e] Reaction Conditions: 50mg mass of catalyst; reaction time: 9 h.

[f] Reaction Conditions: 282mg catalyst; reaction time: 4 h.

Table 2. Recyclability of ionic liquids

Experimental Run	**% Conversion with respect to Phenol**	**% Selectivity**		
		2-TBP	**4-TBP**	**2, 4-DTBP**
Fresh Catalyst	94.2	24.3	10.9	52.9
Recycle 1	93.9	23.9	9.2	54.2
Recycle 2	93.5	23.6	9.6	53.4
Recycle 3	93.9	24.4	11.1	52.1
Recycle 4	93.0	23.7	10.1	53.0
Recycle 5	92.4	22.3	9.6	53.9
Recycle 6	91.1	21.6	9.1	54.9
Recycle 7	90.4	20.3	8.6	55.9
Recycle 8	90.1	20.2	8.1	56.9

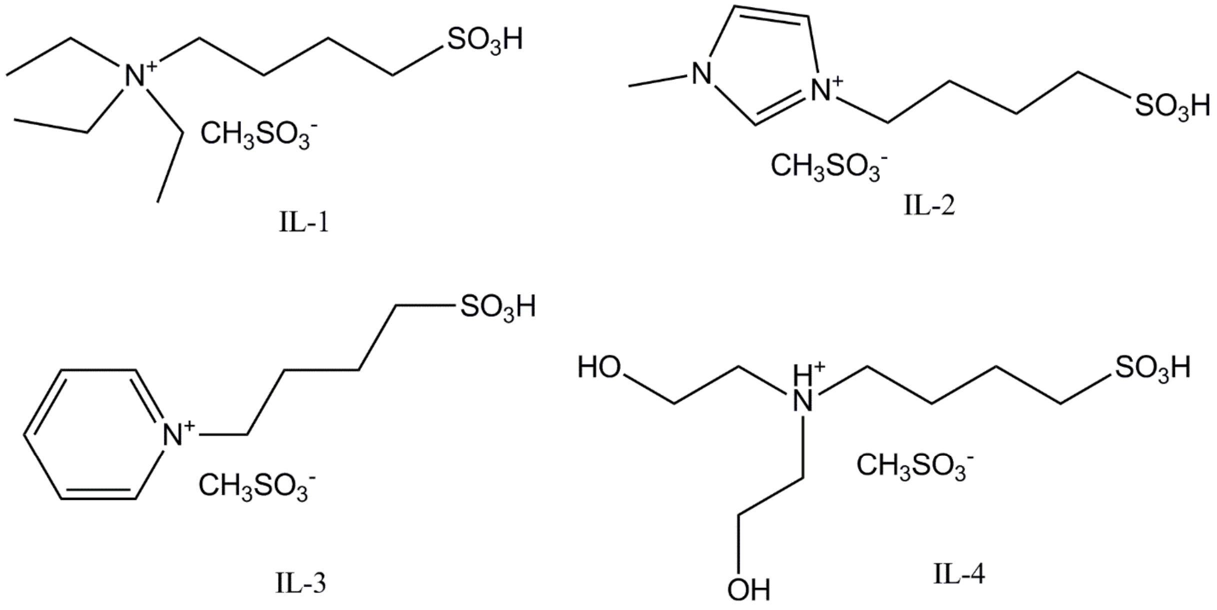
Reaction conditions: phenol (1 mmol): TBA: IL-1 (1:2:1) molar ratio; 80ºC; 2 h.

Bond type	IL-1	IL-2	IL-3	IL-4	IL-0
Cationic O-H bond distance (Å)	1.022	1.049	1.421	1.021	1.491
O-H bond distance between anionic O and cationic H (Å)	1.545	1.446	1.059	1.546	1.036
ΔE (kcal/mole)	-1447.215	-1620.129	-1541.095	-1391.998	-1728.352

Table 3. DFT Study - Structural parameters and stabilization energy values for the ionic liquids

Table 4: Kinetic parameters for alkylation of the phenol with *tert*-butyl alcohol using ionic liquid (IL-1) as a catalyst.

Rate Constant (lit. mol^{-1} min^{-1})	**Temperature (^{0}C)**					**Activation energy (E$_a$) (kJ mol^{-1})**	**Pre-exponential factor (lit. mol^{-1} min^{-1})**
	60	**70**	**80**	**90**	**100**		
k_1	0.93×10^{-4}	1.31×10^{-4}	1.91×10^{-4}	2.75×10^{-4}	3.50×10^{-4}	34.8	28.74
k_2	0.55×10^{-4}	0.73×10^{-4}	0.92×10^{-4}	1.06×10^{-4}	2.16×10^{-4}	31.5	4.8
k_3	0.27×10^{-4}	0.75×10^{-4}	1.12×10^{-4}	7.44×10^{-4}	10.79×10^{-4}	99.4	1.2×10^{11}
k_4	2.10×10^{-5}	2.93×10^{-5}	3.32×10^{-5}	3.80×10^{-5}	5.20×10^{-5}	20.0	31.7
k_5	0.1×10^{-5}	0.4×10^{-5}	0.5×10^{-5}	1.00×10^{-5}	1.20×10^{-5}	54.6	6.3×10^{2}
k_6	0.19×10^{-3}	0.34×10^{-3}	1.03×10^{-3}	1.41×10^{-3}	1.97×10^{-3}	62.7	1.6×10^{6}
k_7	0.01×10^{-2}	0.02×10^{-2}	0.025×10^{-2}	0.5×10^{-2}	3.06×10^{-2}	158.4	3.4×10^{20}
k_8	0.92×10^{-3}	1.70×10^{-3}	5.84×10^{-3}	6.07×10^{-3}	7.1×10^{-3}	55.8	6.6×10^{4}
k_9	0.75×10^{-4}	1.21×10^{-4}	2.23×10^{-4}	8.22×10^{-4}	84.34×10^{-4}	115.4	6.6×10^{13}
k_{10}	1.20×10^{-5}	2.90×10^{-5}	4.90×10^{-5}	8.30×10^{-5}	17.8×10^{-5}	67.1	4.7×10^{5}
k_{11}	0.3×10^{-5}	0.8×10^{-5}	2.5×10^{-5}	8.0×10^{-5}	10.1×10^{-5}	98.0	8.4×10^{9}



IL-1: N-(4-sulfonic acid) butyl triethylammonium methane sulfonate

IL-2: 1-(4-sulfonic acid) butylimidazolium methane sulfonate

IL-3: 1-(4-sulfobutyl) pyridinium methane sulfonate

IL-4: N, N-bis (2-hydroxyethyl)-4-sulfobutan-1-aminium methane sulfonate

Fig 1

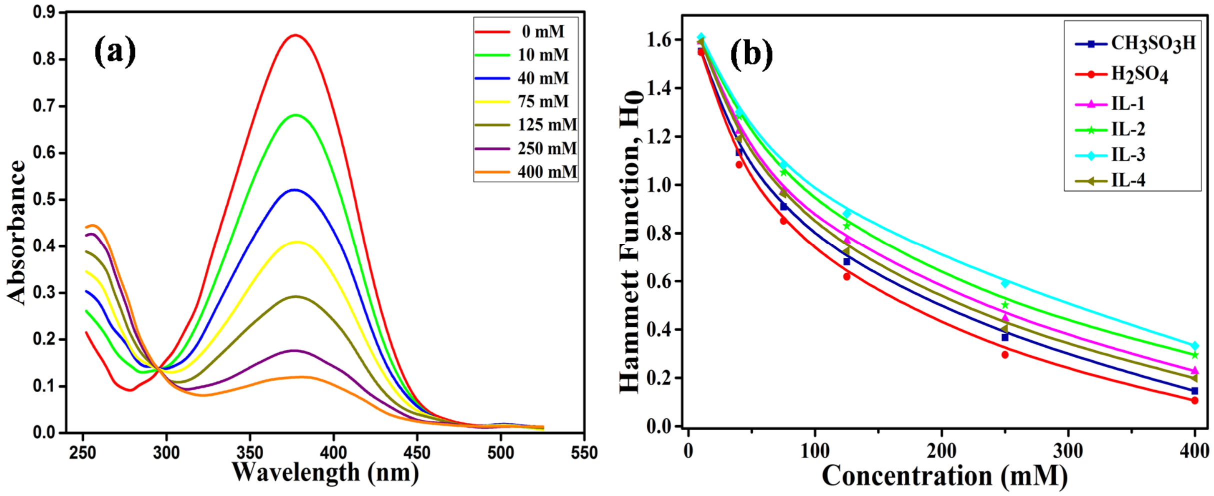


Fig 2

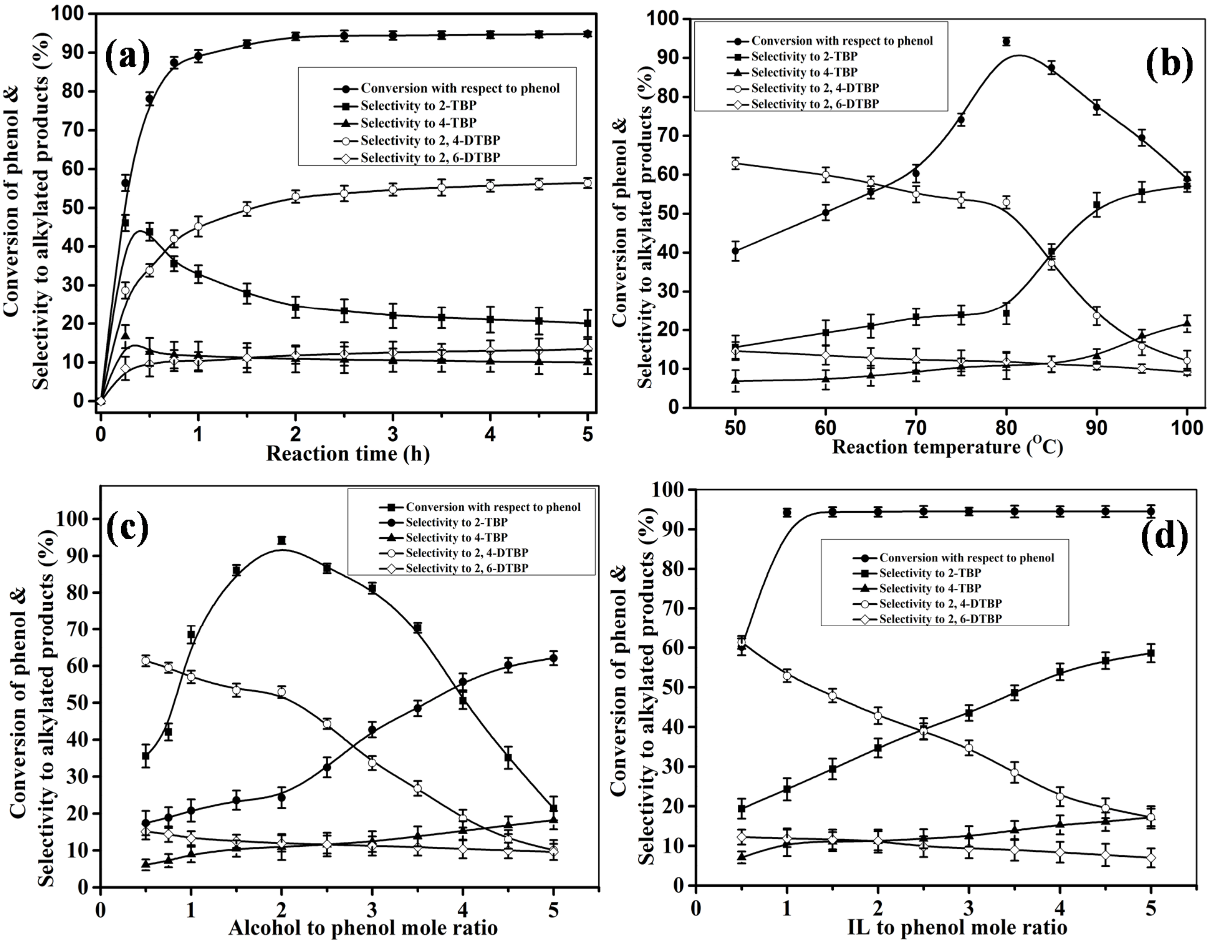

(a)
Conversion with respect to phenol
Selectivity to 2-TBP
Selectivity to 4-TBP
Selectivity to 2, 4-DTBP
Selectivity to 2, 6-DTBP
Conversion of phenol &
Selectivity to alkylated products (%)
Reaction time (h)
0
1
2
3
4
5
10
20
30
40
50
60
70
80
90
100
(b)
Reaction temperature (°C)
50
60
70
80
90
100
(c)
Alcohol to phenol mole ratio
(d)
IL to phenol mole ratio

Fig 3

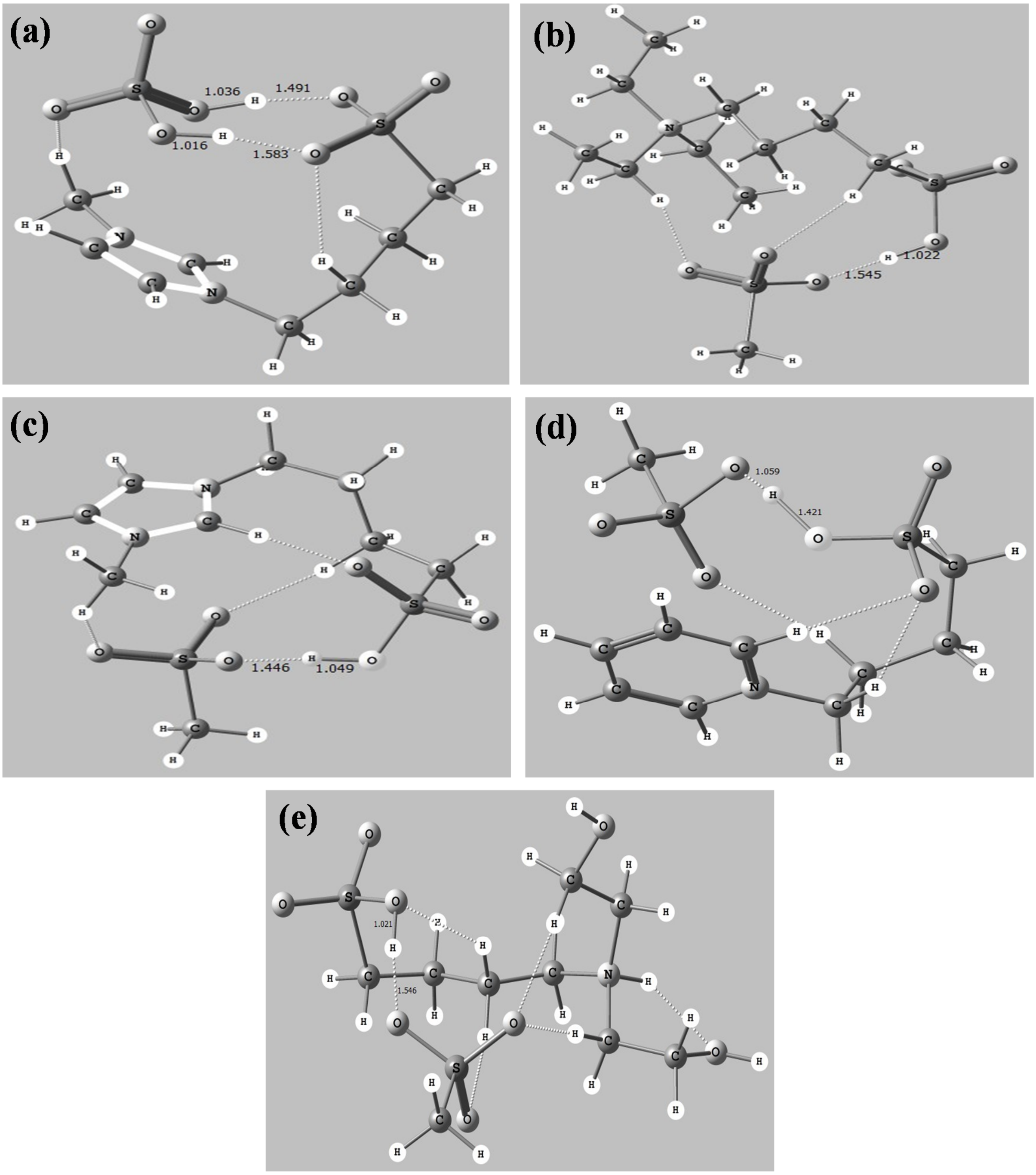

(a)
1.036
1.491
1.016
1.583
(b)
1.022
1.545
(c)
1.446
1.049
(d)
1.059
1.421
(e)
1.021
1.546

Fig 4

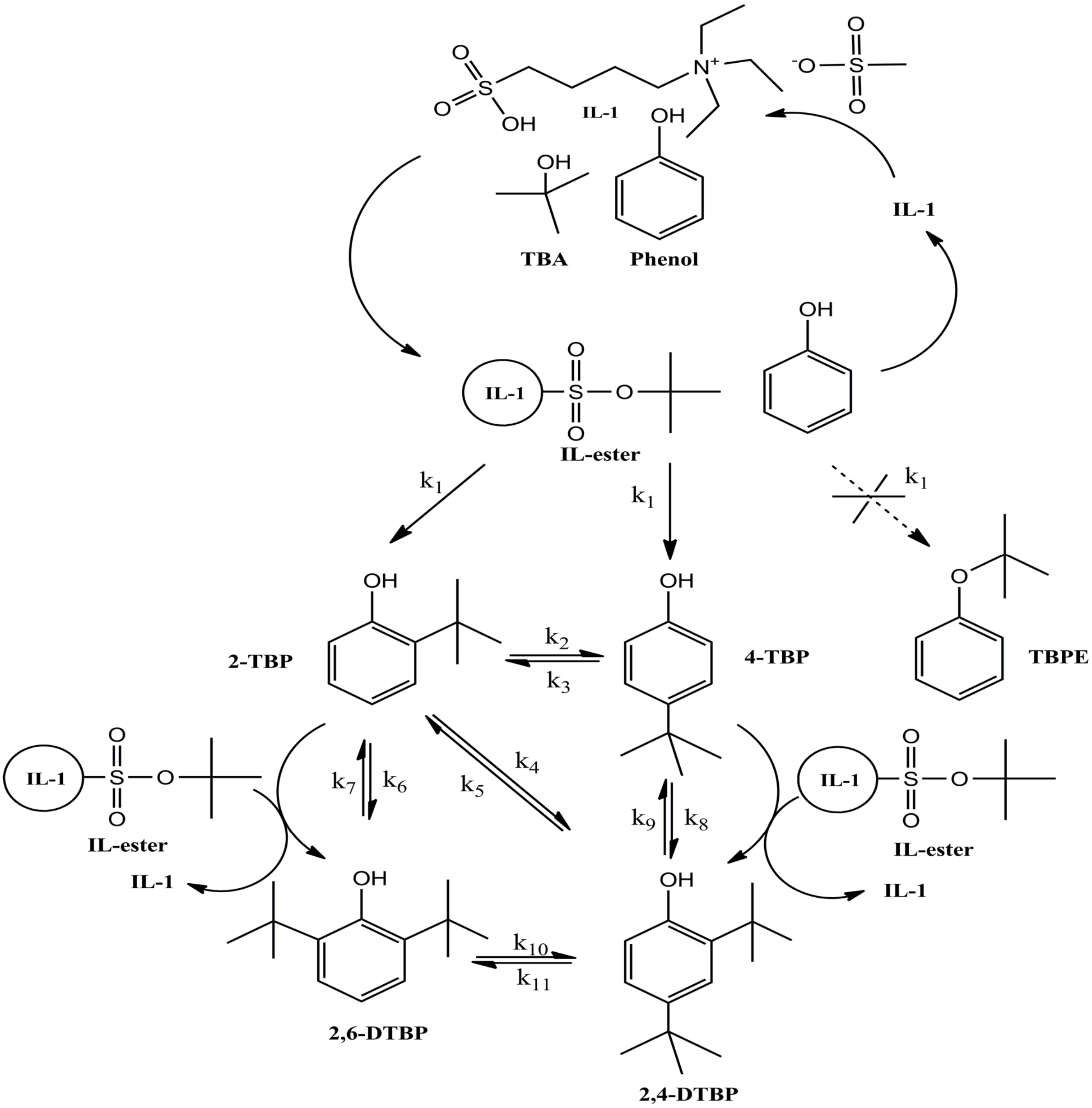

IL-1
TBA
Phenol
IL-1
IL-ester
k1
k1
k1
2-TBP
4-TBP
TBPE
k2
k3
k4
k5
k6
k7
k8
k9
k10
k11
IL-ester
IL-ester
IL-1
IL-1
2,6-DTBP
2,4-DTBP

Fig 5

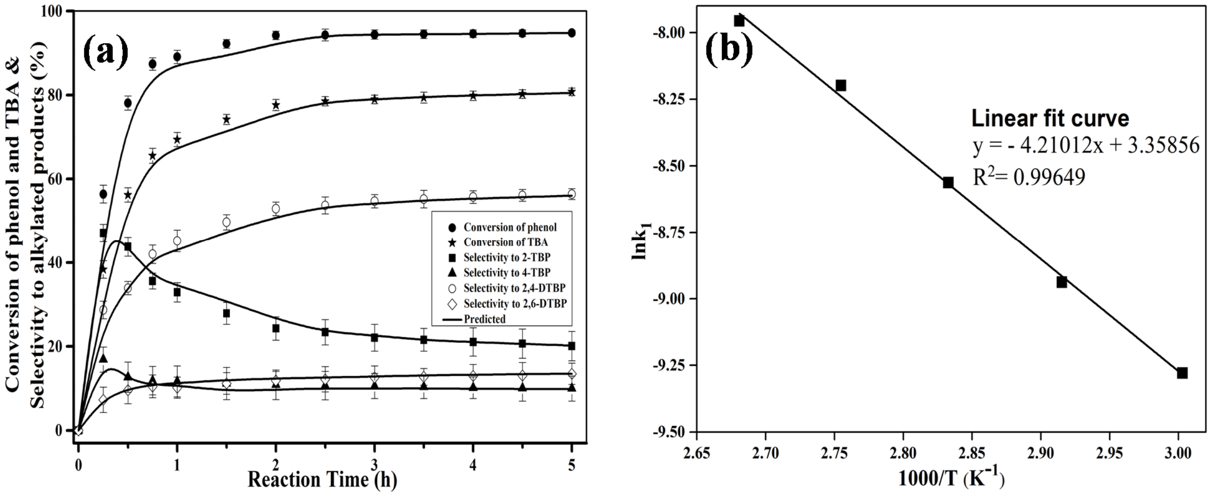

(a)
Conversion of phenol and TBA &
Selectivity to alkylated products (%)
100
80
60
40
20
0
0
1
2
3
4
5
Reaction Time (h)
Conversion of phenol
Conversion of TBA
Selectivity to 2-TBP
Selectivity to 4-TBP
Selectivity to 2,4-DTBP
Selectivity to 2,6-DTBP
Predicted
(b)
lnk1
-8.00
-8.25
-8.50
-8.75
-9.00
-9.25
-9.50
2.65
2.70
2.75
2.80
2.85
2.90
2.95
3.00
1000/T (K-1)
Linear fit curve
y = - 4.21012x + 3.35856
R2= 0.99649

Fig 6