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Kinetics of phenol alkylation with *tert*-butyl alcohol using sulfonic acid functional ionic liquid catalysts

Pandian Elavarasan, Kishore Kondamudi, Sreedevi Upadhyayula*

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

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ABSTRACT

N-methyl imidazole, pyridine and triethylamine based Bronsted acidic ionic liquids with sulfonic acid ($-SO_3H$) functionality were obtained using 1,4-butane sultone. They were tested in a batch reactor for catalytic activity in the *tert*-butylation of phenol with *tert*-butyl alcohol (TBA). The reaction time, reaction temperature and reactant mole ratio were optimized. Among the three ionic liquids, triethylammonium based sulfonic acid functionalized ionic liquid was found to be the most promising and gave the highest phenol conversion. A maximum phenol conversion of 86% with 57.6% selectivity to 4-*tert*-butylphenol (4-TBP) was achieved at a temperature of 70 °C at a low ionic liquid to phenol ratio. The catalyst retained its activity even after 5 recycles. A kinetic model was developed for the reaction mechanism based on the product distribution and the kinetic parameters were estimated. The activation energy for ionic liquid catalyzed alkylation of phenol was found to be 11.13 kcal/mol in the temperature range of 50–90 °C. Negative activation energy was observed for 2-*tert*-butylphenol (2-TBP) to 2,4-di-*tert*-butylphenol (2,4-DTBP) and the extended Arrhenius equation was used to interpret this trend.

1. Introduction

Alkylation of phenol with *tert*-butyl alcohol yields butylated phenols which find use as raw materials in the production of antioxidants, phenolic resins, agrochemicals, rubber chemicals, printing ink, varnish, surface coatings, fungicides, ultraviolet absorbers, petroleum additives and heat stabilizers for polymeric materials [1–9]. Both homogenous and heterogeneous catalysts have been reported in the *tert*-butylation of phenol which include Lewis acid, $AlCl_3$ and BF_3 [10], Bronsted acids such as H_3PO_3, H_2SO_4, HF and $HClO_3$ [11], cation exchanged resins [7], zeolites [2,7], mesoporous materials [3,9], heteropoly acids [9], super critical and near critical water [5]. The major drawbacks of liquid acid catalysts include their hazardous, corrosive nature and tedious work-up involved in the separation of these catalysts from the reaction mixture. The solid acid catalysts have the problem of rapid deactivation due to coke formation due to pore blocking and also spent catalyst disposal problems. The cation-exchanged resins show good performance but are thermally unstable and fouling of resin is still a major issue.

In recent years, room-temperature ionic liquids (RTILs) have growing potential applications as environmentally benign alternative reaction media for both solvent and organic transformations [12–14]. The advantages of ionic liquids are negligible vapor pressure, thermal stability and good recoverability and recyclability [15,16]. The literature includes very few reports in the use of ionic liquids as catalysts in the alkylation of phenol with *tert*-butyl alcohol. Recently, Shen et al. reported high phenol conversion and 2,4-DTBP selectivity in the *tert*-butylation of phenol using Lewis acidic functionalized ionic liquid [bmim]PF_6 [7,8]. The major disadvantage of using Lewis acidic ionic liquids is the decomposition of IL forming hydrofluoric acid. Gui et al. compared various task specific imidazolium salts [6]. By tethering an alkane sulfonic group to the cation, they prepared Bronsted acid functionalized ionic liquids and achieved higher phenol conversion and selectivity to 2,4-DTBP in the *tert*-butylation of phenol. However, the drawback of imidazolium salts is that they are toxic due to the presence of imidazolium cation [17]. Henceforth, there is a need to develop environmentally benign catalysts which facilitate high phenol conversion and desired product selectivity along with easy recoverability and recyclability. Also, detailed kinetic investigations on promising ionic liquid catalysts are still scarce in the literature. Hence, the present work reports the preparation and characterization of sulfonic acid Bronsted acidic functionalized ionic liquids using low cost chemicals of triethylamine, pyridine and 1-methyl imidazole. These three different compounds were chosen, on the basis of literature reports [12–16] on compounds which can give lower viscosity ionic liquids, to study the effect of the anion in this alkylation reaction. The relative acidity of these

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* Corresponding author at: Department of Chemical Engineering, Indian Institute of Technology Delhi, I-209, Hauz Khas, New Delhi 110016, India.
Tel.: +91 11 26591083; fax: +91 11 26581120.
E-mail address: sreedevi@chemical.iitd.ac.in (S. Upadhyayula).

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functionalized ionic liquids measured by Hammett function, confirms that their acidity is almost equal to sulfuric acid [18]. Detailed kinetic investigations of phenol alkylation with TBA using the best of the prepared catalysts are also reported here.

2. Experimental

2.1. Materials and reagents

All the experiments were conducted using commercially available solvent and chemicals, used without further purification. N-methylimidazole, pyridine, triethylamine and 1,4-butane sultone were purchased from Sigma–Aldrich Chemicals Pvt. Ltd., India. Phenol and *tert*-butyl alcohol were purchased from Merck & CDH, New Delhi, India.

2.2. Preparation of ionic liquids

Sulfonic acid functionalized Bronsted acidic ionic liquids were prepared in the laboratory adopting the literature procedure [19,20]. N-methylimidazole was mixed with 1,4-butane sultone by stirring at 40–80 °C for about 24 h. After solidification, the zwitterion mass was washed three times using ethyl ether and dried under vacuum. Stoichiometric amount of sulfuric acid is added to the zwitterions and the mixture was stirred at 80 °C for 8 h to obtain the ionic liquid. Similar, procedure was adopted in the preparation of triethylamine and pyridine ionic liquids. The structures of the ionic liquids are presented in Fig. 1.

The prepared ionic liquids were characterized using NMR techniques and the results are as follows:

IL-1 (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate): ^{1}H NMR (D_2O, 400 MHz): δ (ppm) 1.16 (t, 9H, J = 6.8 Hz), 1.65 (m, 4H), 2.58 (t, 2H, J = 7.1 Hz), 3.13 (t, 2H, J = 8.0 Hz), 3.19 (m, 6H, J = 6.9 Hz); ^{13}C NMR (D_2O, 100 MHz): δ (ppm) 8.00, 20.69, 22.76, 51.04, 23.87, 56.65.

IL-2 (1-(4-sulfonic acid) butyl pyridinium hydrogen sulfate): ^{1}H NMR (DMSO, 400 MHz): δ (ppm) 1.58 (t, 2H), 2.01 (t, 2H), 2.62 (t, 2H, J = 7.5 Hz), 4.63 (t, 2H, J = 7.3 Hz), 8.15 (t, 2H, J = 7.6 Hz), 8.60 (t, 1H, J = 7.4 Hz), 9.09 (d, 2H, J = 7.0 Hz): ^{13}C NMR (D2O, 100 MHz): δ (ppm) 22.16, 30.60, 51.16, 61.21, 128.99, 145.66, 146.41.

IL-3 (1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate): ^{1}H NMR (D_2O, 400 MHz): δ (ppm) 1.55 (t, 2H), 1.87 (t, 2H), 2.59 (t, 2H, J = 7.9 Hz), 3.84 (s, 3H), 4.17 (t, 2H, J = 6.9 Hz), 7.7089 (d,1H), 9.15 (d,1H), 10.30 (s,1H); ^{13}C NMR (D_2O, 100 MHz): δ (ppm) 22.28, 29.31, 36.58, 49.28, 51.24, 123.15, 124.48, 137.48.

2.3. Activity testing

The alkylation experiments were carried out in a sealed glass tube under autogeneous pressure. A typical batch contains 10 mmol each of phenol, *tert*-butyl alcohol and ionic liquid stirred at 800 rpm for 8 h. At the end of the reaction, the mixture was cooled and the products were extracted by toluene. A qualitative product analysis was conducted using GC–MS and quantitative analyses were conducted by separating the product mixture in a CHROMSORB-WHP (2 m × 3.175 mm × 2 mm) column and flame ionization detector in a NUCON GC supplied by M/s AIMIL India Ltd.

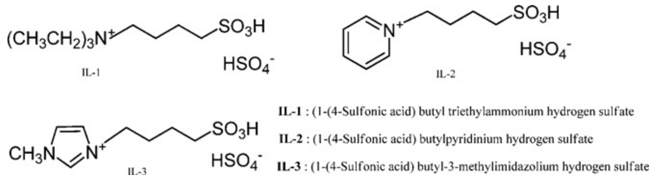

Fig. 1. Structure of ionic liquids.

3. Results and discussion

3.1. Comparison of activity of the three ionic liquids

The three ionic liquids were found to be thermally stable well above the reaction temperatures. Thermal decomposition temperatures of IL-1, IL-2 and IL-3 were observed to be 325.4 °C, 324.8 °C and 366.9 °C respectively when tested in a TA instruments TGA model SDT Q600 at a heating rate of 10 K min^{-1} under nitrogen atmosphere.

The activity of the prepared ionic liquid catalysts in this reaction was compared with solid and liquid acid catalysts reported in literature, as shown in Table 1. From the table, it can be observed that the product distribution using the ionic liquid catalysts ranges from *ortho* and *para tert*-butyl phenol (2-TBP and 4-TBP) to dialkylated products 2,4-DTBP and 2,6-DTBP. No *meta*-TBP or ethers are observed even when the phenol conversion is high. Also, no oligomers were observed in the product. It is evident that all the three ionic liquids gave high phenol conversion and good selectivity to the desired products, 2-TBP and 2,4-DTBP at 70 °C compared to other catalysts. Although the [bmim] PF_6 ionic liquid shows a marginally higher conversion, yet, it has the disadvantage of forming HF during reaction. Ionic liquid catalyst, [hmim] 1,4-$(CH_2)_4SO_3$]HSO_4 also shows good conversion of phenol at 70 °C and 2:1 TBA to phenol ratio, but comparatively lower than the conversion obtained using IL-1 even at higher catalyst to phenol mole ratio (1.5:1). When similar catalyst to phenol mole ratio (1:1) was used, the conversion using [hmim] 1,4-$(CH_2)_4SO_3$]HSO_4 is lower compared to that obtained using all the three prepared ILs. Among the three ionic liquids, IL-1 (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate) gave the maximum conversion and good selectivity to 2,4-DTBP (2,4-di-*tert*-butylphenol) at the given temperature. Hence, detailed kinetic investigations were conducted using IL-1 catalyst, which is also the cheapest of the prepared catalysts [17].

3.2. Effect of reaction time on phenol conversion

Fig. 2 shows the effect of reaction time on conversion of phenol at 70 °C using 1:1 molar ratio of phenol to TBA and 1:1 molar ratio of phenol to IL-1 (N-(4-sulfonic acid) butyl triethylammonium

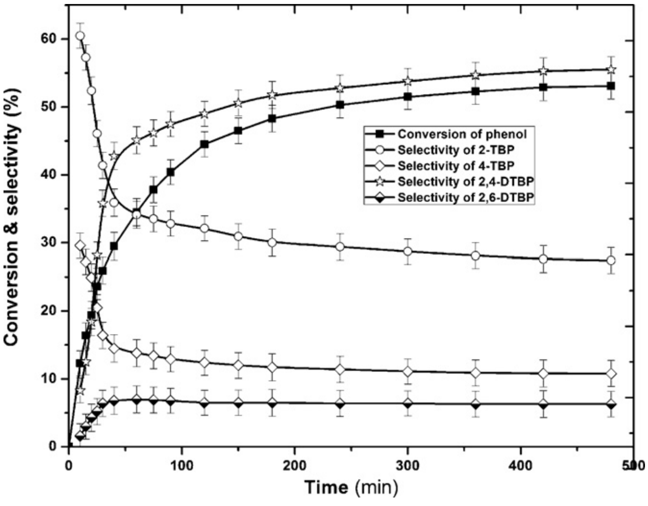

Fig. 2. Effect of reaction time on phenol conversion and product selectivity. Reaction conditions: phenol (10 mmol):TBA:IL-1 (1:1:1) mole ratio at 70 °C.

Table 1
Comparison of catalyst performances in the alkylation of phenol with TBA.

Catalyst	Reactant to catalyst ratio (phenol:IL)	Reactant mole ratio (TBA:phenol)	Temperature (°C)	Conversion of phenol (%)	Selectivity (%)			
					2-TBP	4-TBP	2,4-DTBP	2,6-DTBP
IL-1[a]	1:1	2:1	70	84.5	23.8	10.2	57.6	7.4
IL-2[a]	1:1	2:1	70	79.6	25.7	9.7	57.0	7.6
IL-3[a]	1:1	2:1	70	78.2	23.2	12.7	55.1	8.9
[bmim]PF_6 [7]	2:1	2:1	70	91.5	13.1	9.4	74.9	2.6
	1:1	2:1	60	71.2	12.8	30.1	56.4	0.7
[hmim]1,4-$(CH_2)_4SO_3$]HSO_4 [6]	1:1.5	2:1	70	80.3	25.8	9.0	60.2	5.1
	1:1	2:1	70	75.6	28.8	10.96	56.7	4.2
TPA/ZrO_2 [9][b]	–	6:10	80	60.0	3.6	96.4	–	–
USY [2][c]	–	6:10	70	52.7	63.0	23.0	13.1	–
Mordenite [2][d]	–	6:10	60	44.8	48.1	49.1	2.8	–
TPA/MCM-41 [8][e]	–	2:1	70	44.8	29.0	49.0	21.2	–

[a] Reaction conditions: phenol to ionic liquid ratio = 1:1; stirrer speed = 800 rpm; reaction time: 8 h.
[b] 250 mg catalyst, reaction time: 1 h.
[c] 200 mg catalyst, reaction time: 3 h.
[d] 200 mg catalyst, reaction time: 8 h.
[e] 12-Tungstophoaphoric acid, 282 mg catalyst, reaction time: 4 h.

hydrogen sulfate). The conversion of phenol increased with reaction time up to about 6 h and selective yield of 2,4-DTBP reached equilibrium after 6 h similar to the observations of Gui et al. [6] and Shen et al. [7] in similar reaction systems. Initially, the selectivity to mono-alkylated (2-TBP and 4-TBP) products was high and then decreased with time as the selectivity towards di-alkylated products increased. The maximum conversion of phenol reached 54.5% and selectivity to 2,4-DTBP reached 58.6% respectively.

3.3. *Effect of reaction temperature*

The effect of reaction temperature on phenol conversion and product selectivity was checked in the range of 50–90 °C and are shown in Fig. 3. At temperatures lower than 50 °C, mass transfer resistances occur due to increased viscosity of the ionic liquid as observed experimentally. At temperatures higher than 90 °C, oligomerization and polymerization of butene, which is released in situ during the reaction following *tert*-butyl alcohol dehydration, becomes dominant. This observation is similar to that reported in literature by Subramanian et al. for this reaction over solid acid catalysts [21]. From Fig. 3, it is evident that the conversion of phenol increases with temperature up to 70 °C and further increase in temperature does not significantly affect the conversion. Hence, the optimum temperature for this reaction is 70 °C. The selectivity to 2,4-DTBP and 2,6-DTBP, decreases beyond 70 °C while the selectivity to 2-TBP and 4-TBP increases. This may be attributed to dealkylation of the di-alkylated products at higher temperatures and also due to lower amount of solvated butene gas available in the reaction mixture as observed during experiments. The maximum selectivity to 2,4-DTBP is 58% at the highest phenol conversion.

3.4. *Effect of reactant mole ratio on phenol conversion*

Fig. 4 shows the influence of TBA to phenol feed mole ratio on phenol conversion and desired product selectivity. The experiments were conducted varying the feed mole ratio of TBA and phenol from 0.5 to 3 at 70 °C with a constant phenol to IL mole ratio of 1:1. From Fig. 4, it can be observed that as the TBA to phenol feed mole ratio increases, the conversion of phenol and selectivity to 2,4-DTBP and 2,6-DTBP increases up to a mole ratio of 2 and then decreases. However, the experimental observations also show that the selectivity to the monalkylated products decreases up to a mole ratio of 2 ratio and then increases. This can be attributed to the dilution of ionic liquids by TBA resulting in lowering of acidity leading to suppression of the di-alkylated product formation and increase

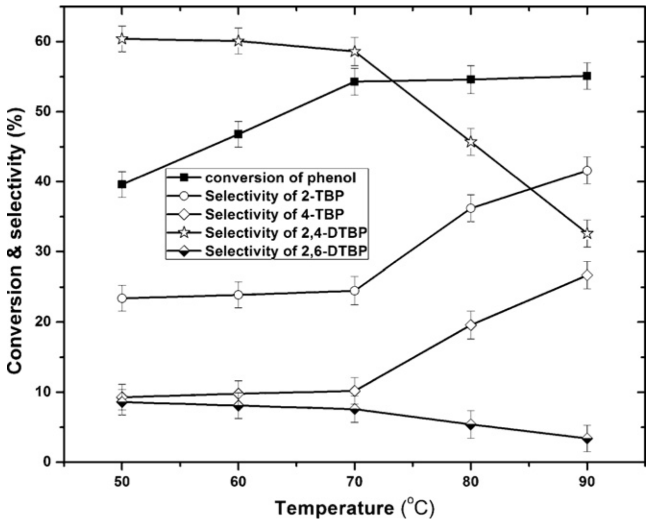

Fig. 3. Effect of reaction temperature on phenol conversion and product selectivity. Reaction conditions: phenol (10 mmol):TBA:IL-1 (1:1:1) molar ratio, 8 h.

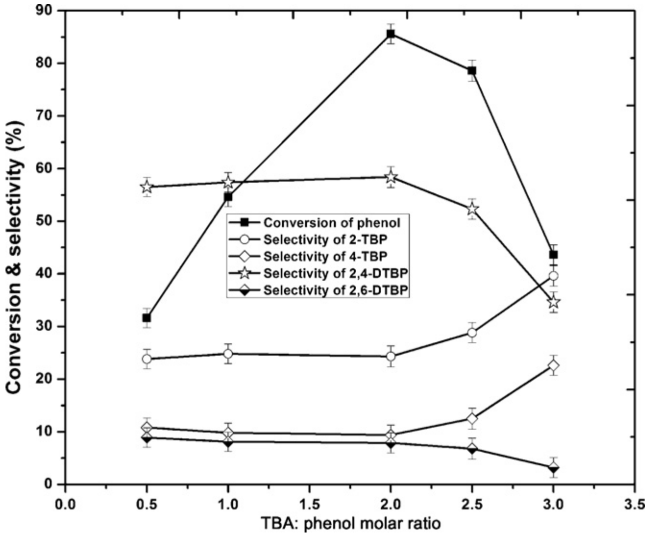

Fig. 4. Effect of reactant mole ratio on phenol conversion and product selectivity. Reaction conditions: phenol (10 mmol):IL-1 (1:1) molar ratio at 70 °C, 8 h.

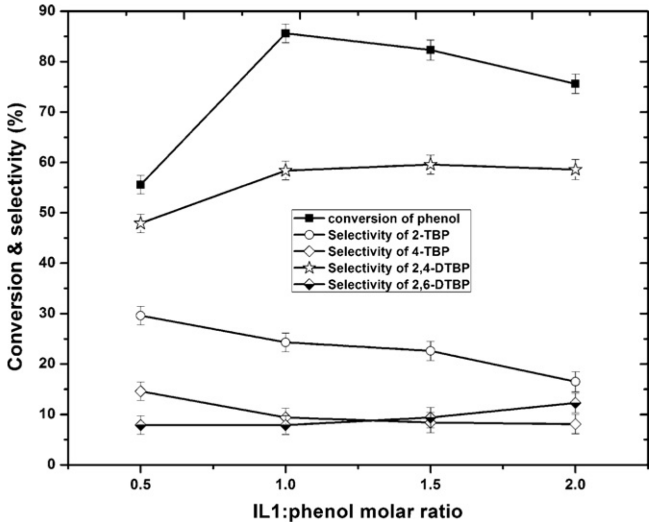

Fig. 5. Effect of ionic liquid mole ratio on phenol conversion and product selectivity. Reaction conditions: phenol (10 mmol):TBA (1:2) molar ratio at 70 °C, 8 h.

in monoalkylated product. Similar observation was reported by Gui et al. who investigated this alkylation reaction using Bronsted acidic imidazolium salts as catalysts [6]. The highest phenol conversion, in this study, was observed at TBA to phenol feed mole ratio of 2:1 at 70 °C and this was chosen as optimum for further investigations.

3.5. Effect of ionic liquid to phenol mole ratio

The effect of ionic liquid to phenol mole ratio is shown in Fig. 5. The amount of phenol taken was 10 mmol and the ionic liquid was varied as 5, 10, 15 and 20 mmol so that the ratio of ionic liquid (IL-1) to phenol was varied from 0.5 to 2. The temperature was maintained constant during all these experiments at 70 °C and phenol to TBA feed mole ratio was maintained constant at 1:2. It is observed that as the ionic liquid to phenol ratio increases, the conversion of phenol increases up to a mole ratio of 1:1 after which it decreases. The selectivity to di-alkylated products, however, increased or at least remained constant after reaching a maximum at 1:1. The mono-alkylated products, 2-TBP and 4-TBP decreased with increase in this mole ratio due to their conversion to di-alkylated products which is attributed to the increased acidity of the reaction mixture due to the higher amount of IL. Gui et al. [6] and Shen et al. [7,8] also found changes in the product distribution in this alkylation reaction using various quantities of liquid catalysts and attributed it to the varied acidity of the reaction mixture. The selectivity to 2,4-DTBP reached 58% at 1:1 of ionic liquid and phenol mole ratio and almost remained constant with further increase in ionic liquid in the feed. Hence, this ratio was taken to be the optimum to study the reaction kinetics.

Table 2
Recyclability of ionic liquids.

Experimental run	Conversion of phenol (%)	Selectivity (%)			
		2-TBP	4-TBP	2,4-DTBP	2,6-DTBP
Fresh catalysts	84.5	23.8	10.2	57.6	7.4
Recycle 1	84.3	24.4	11.0	57.4	7.1
Recycle 2	82.6	23.7	10.9	58.5	7.6
Recycle 3	84.1	23.7	10.6	58.9	7.3
Recycle 4	83.7	23.6	10.4	58.4	7.1
Recycle 5	81.9	23.9	10.1	57.8	7.2

Reaction conditions: phenol:TBA:IL-1 = 1:2:1 molar ratio at 70 °C for 8 h.

3.6. Recyclability of ionic liquid catalyst

In order to examine the recoverability and recyclability of the ionic liquid, after the reaction, the ionic liquid was extracted with toluene (5× 3 ml) and dried under vacuum for 5 h. After vacuum drying, the IL-1 was assessed with H NMR spectroscopy, which showed no traces of reactants or products. IL-1 was repeatedly used 5 times without significant decrease in phenol conversion and desired product selectivity as shown in Table 2.

3.7. Reaction mechanism

Based on the product distribution obtained from experimental results, detailed reaction mechanism has been proposed and shown in Fig. 6. It was observed that the TBA instantaneously dehydrates to iso-butylene gas in the reaction mixture at 70 °C. The in situ produced iso-butylene gas in the reactor, maintained at autogeneous pressure, reacts through C-alkylation of phenol and forms the *ortho* and *para* alkylated products. No oligomer products were observed in the chosen range of reaction conditions. On these highly acidic catalysts, realkylation of mono-alkylated products to di-alkylated products was observed. 2,4-DTBP was the major product. Some amount of tri-alkylated product was also observed only when the amount of ionic liquid in the reaction mixture is increased.

4. Kinetic modeling

The kinetic runs were carried out at five different temperatures, namely 323, 333, 343, 353 and 363 K under autogeneous pressure. Table 3 shows the phenol conversion and product distribution at various temperatures.

The system can be described by the following reactions:

Alkylation of phenol

$$P + \mathrm{TBA} \xrightarrow{k_1} \text{2-TBP} + \text{4-TBP} + 2 \times W \tag{1}$$

tert-Butyl phenol isomerization

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

Table 3
Product percentage yields in alkylation of phenol with TBA in IL-1 at various temperatures.

Temperature (°C)	Conversion of phenol (%)	Yield (%)						
		Phenol	TBA	2-TBP	4-TBP	2,4-DTBP	2,6-DTBP	Water
50	67.6	10	27	6	2	14	2	40
60	72.4	6	21	6	3	16	2	46
70	83.7	5	20	8	3	16	2	46
80	85.3	4	24	9	7	13	1	43
90	83.9	5	28	12	7	9	1	39

Reaction condition: phenol:TBA:IL-1 = 1:2:1 molar ratio, autogeneous pressure.

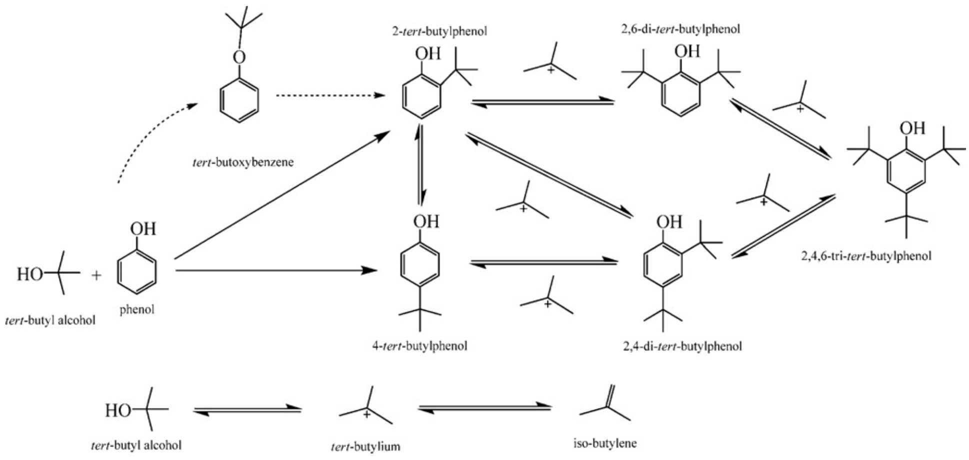

Fig. 6. Possible reaction mechanism for alkylation of phenol with *tert*-butyl alcohol using ionic liquid catalyst.

Alkylation of 2-*tert*-butyl phenol

$$2\text{-TBP} + \text{TBA} \underset{k_5}{\overset{k_4}{\rightleftharpoons}} 2,4\text{-DTBP} + W \tag{3}$$

$$2\text{-TBP} + \text{TBA} \underset{k_7}{\overset{k_6}{\rightleftharpoons}} 2,6\text{-DTBP} + W \tag{4}$$

Alkylation of 4-*tert*-butyl phenol

$$4\text{-TBP} + \text{TBA} \underset{k_9}{\overset{k_8}{\rightleftharpoons}} 2,4\text{-DTBP} + W \tag{5}$$

Based on the product distribution, the following assumptions were made:

1. Formation of iso-butene gas is negligible due to its instantaneous reaction.
2. *tert*-Butylation of phenol (Eq. (1)) is considered as irreversible reaction.
3. Reactions (2)–(5) are considered as reversible.
4. Isomerization of mono-alkylated product (reaction (2)) is only considered.

4.1. Batch reaction kinetic model

A second order rate equation was developed based on the reaction mechanism formulated from the product distribution for this reaction [22]. The rates of formation of products can be expressed as follows:

Rate of alkylation of phenol

$$\frac{dC_p}{dt} = -k_1 C_p C_{\text{TBA}} \tag{6}$$

Rate of conversion of *tert*-butyl alcohol

$$\frac{dC_{\text{TBA}}}{dt} = -k_1 C_p C_{\text{TBA}} - k_4 C_{\text{2-TBP}} C_{\text{TBA}} + k_5 C_{\text{2,4-DTBP}} C_W - k_6 C_{\text{2-TBP}} C_{\text{TBA}} + k_7 C_{\text{2,6-DTBP}} C_W - k_8 C_{\text{4-TBP}} C_{\text{TBA}} + k_9 C_{\text{2,4-DTBP}} C_W \tag{7}$$

Rate of formation of 2-TBP

$$\frac{dC_{\text{2-TBP}}}{dt} = k_1 C_p C_{\text{TBA}} - k_2 C_{\text{2-TBP}} + k_3 C_{\text{4-TBP}} + k_4 C_{\text{2-TBP}} C_{\text{TBA}} - k_5 C_{\text{2,4-DTBP}} C_W + k_6 C_{\text{2-TBP}} C_{\text{TBA}} - k_7 C_{\text{2,6-DTBP}} C_W \tag{8}$$

Rate of formation of 4-TBP

$$\frac{dC_{\text{4-TBP}}}{dt} = k_1 C_p C_{\text{TBA}} + k_2 C_{\text{2-TBP}} - k_3 C_{\text{4-TBP}} - k_8 C_{\text{4-TBP}} C_{\text{TBA}} + k_9 C_{\text{2,4-DTBP}} C_W \tag{9}$$

Rate of formation of 2,4-DTBP

$$\frac{dC_{\text{2,4-DTBP}}}{dt} = k_4 C_{\text{2-TBP}} C_{\text{TBA}} - k_5 C_{\text{2,4-DTBP}} C_W + k_8 C_{\text{4-TBP}} C_{\text{TBA}} - k_9 C_{\text{2,4-DTBP}} C_W \tag{10}$$

Rate of formation of 2,6-DTBP

$$\frac{dC_{\text{2,6-DTBP}}}{dt} = -k_2 C_{\text{2-TBP}} + k_3 C_{\text{4-TBP}} + k_6 C_{\text{2-TBP}} C_{\text{TBA}} - k_7 C_{\text{2,4-DTBP}} C_W \tag{11}$$

Rate of formation of water

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

where C is the concentration of respective components in mol/L, t is the batch reaction time in s and k is the rate constant of respective reaction in L/mol s. A nonlinear regression algorithm was used to estimate the kinetic parameters [23]. The optimum values of the parameters were estimated by minimizing the objective function given by

$$f = \sum_{i=1}^{n} [(C_{pred})_i - (C_{\exp})_i]^2 \tag{13}$$

The estimated rate constants, activation energies and pre-exponential factors are shown in Table 4. The standard error between predicted and estimated was 10^{-5} using Eq. (13). The experimental and predicted phenol and TBA conversions and products from Eq. (6)–(12) at 243 K temperature were plotted in Fig. 7. It shows that the proposed reaction mechanism predicts the alkylation values comparable with the experimental ones.

The kinetic rate constants evaluated at various temperatures were used to determine the activation energy and frequency factor using Arrhenius relationships as shown in Table 4. The Arrhenius plot for conversion of phenol is shown in Fig. 8 from which the energy of activation was obtained as 8.83 kcal/mol in the temperature range of 50–90 °C (323–363 K). The activation energy values for

Table 4
Estimated second-order rate constants, apparent activation energies and pre-exponential factors for alkylation reaction of phenol with *tert*-butyl alcohol in IL-1 catalyst.

Temperature (°C)	Rate constants (L/mol s)								
	$k_1 \times 10^5$	$k_2 \times 10^4$	$k_3 \times 10^5$	$k_4 \times 10^5$	$k_5 \times 10^5$	$k_6 \times 10^5$	$k_7 \times 10^5$	$k_8 \times 10^5$	$k_9 \times 10^5$
90	1.06	0.78	1.60	0.73	0.31	9.03	24.83	4.84	0.91
80	1.39	1.39	3.11	1.82	0.53	5.11	11.39	8.56	1.55
70	1.79	1.83	3.44	2.04	1.17	2.20	4.18	17.67	1.74
60	2.99	4.75	6.64	3.94	3.00	3.95	11.62	116.62	50.15
50	4.84	7.75	10.41	6.02	3.68	15.43	166.64	159.47	72.58
Activation energy (E_a) (kcal/mol)	8.83	13.55	10.51	11.64	15.54	–	–	22.34	28.32
Pre-exponential factor	8.77	1.03×10^5	205.41	606.01	0.94×10^5	–	–	4.6×10^{10}	69.6×10^{12}

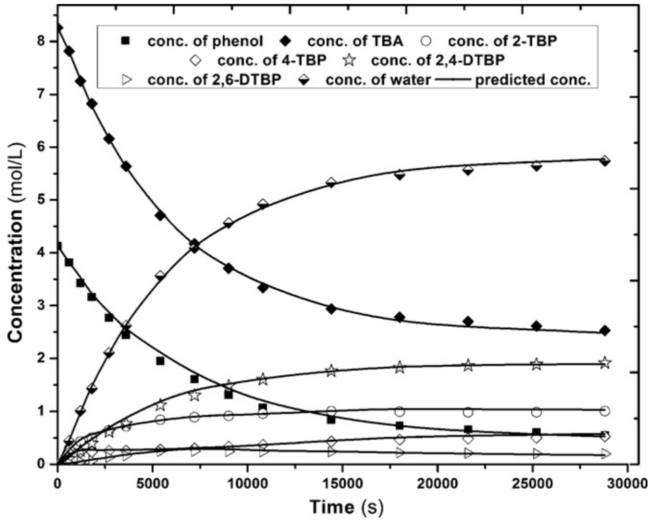

Fig. 7. Comparison of experimental and predicted concentrations for alkylation of phenol with *tert*-butyl alcohol using ionic liquid catalyst at 70 °C.

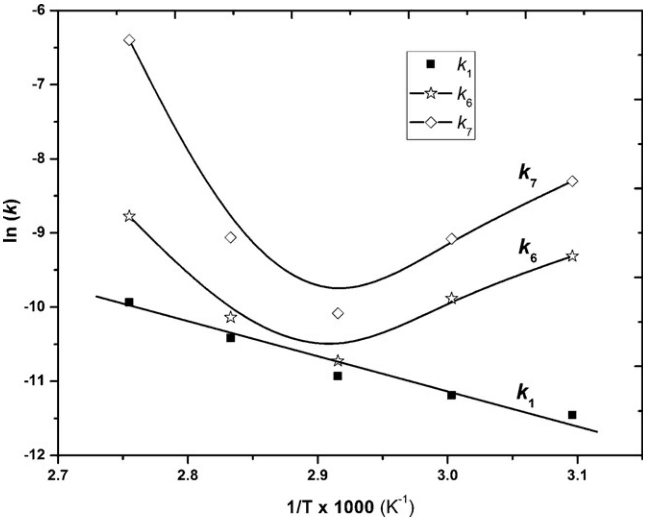

Fig. 8. Arrhenius plot for alkylation of phenol with *tert*-butyl alcohol using ionic liquid catalyst (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate).

various reactions compare well with the values of similar reactions using near-critical water and clay based catalysts by other investigators. Activation energy for alkylation over coal and fly ash of 8.9 kcal/mol in the temperature ranges of 40–70 °C, however, good recyclability was not achieved with these catalysts [4]. Activation energy of 18.53 kcal/mol clay-based catalysts in the temperature ranges of 40–70 °C [24]. Activation energy for alkylation of phenol was reported to be 28 and 20 kcal/mol in the temperature range of 250–300 °C, for *ortho* and *para* alkylated products respectively [5]. As compared to other batch alkylations of phenol, activation energy is low using ionic liquids and also shows that reaction is intrinsically kinetically controlled. The plots for the rate constant k_6 and k_7 shows a curvature, this deviation from the Arrhenius relation is attributed to mass transfer resistances at low temperature and also the solvolysis effect in the reaction [25–27]. In order to incorporate these effects, a modified empirical form of Arrhenius equation is applied as given below:

$$\ln k = A + B\left(\frac{1}{T} - \frac{1}{T_0}\right) + \varepsilon \tag{14}$$

$$\ln k = \ln\left(\frac{kT}{h}\right) - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \tag{15}$$

$$E_a = -RB \tag{16a}$$

$$\Delta H = -R(B + T_0) \tag{16b}$$

$$\Delta S = R\left(A - \ln\left(\frac{k_B T_0}{h}\right) + \frac{\Delta H}{RT}\right) \tag{16c}$$

The empirical Arrhenius equation for the temperature dependent rate constant and its interpretation by the transition state theory using the parameters *A* and *B* was reported in literature for similar reactions [27]. The empirical Arrhenius equation given by the

Table 5
Estimated parameters in the empirical Arrhenius equation with $T_0 = 70\,°\mathrm{C}$.

	Reaction rate constant								
	k_1	k_2	k_3	k_4	k_5	k_6	k_7	k_8	k_9
A	−10.58	−8.03	−9.85	−10.40	−11.00	−9.73	−8.39	−7.70	−9.03
$B \times 10^{-3}$	−4.44	−6.82	−5.29	−5.86	−7.82	−0.78	−4.19	−11.23	−14.25
E_a (kcal/mol)	8.82	13.55	10.50	11.64	15.53	1.54	8.32	22.32	28.31
ΔH (kcal/mol)	8.13	12.86	9.81	10.94	14.84	0.85	7.62	21.63	27.61
ΔS (cal/K mol)	−56.16	−37.34	−49.82	−47.62	−37.44	−75.69	−53.29	−11.11	3.70

Table 6
Estimated parameters in extended Arrhenius equation with $T_0 = 70\,^{\circ}\mathrm{C}$.

	Reaction rate constant	
	k_6	k_7
A'	−10.34	−9.43
$B' \times 10^{-3}$	−6.14	−13.31
$C' \times 10^{-7}$	5.16	8.77
ΔC_p (cal/K mol)	0.84	1.43
ΔH (kcal/mol)	11.48	25.67
ΔS (cal/K mol)	−46.15	−3.57

linear relationship with the error function 'ε' in Eqs. (14) and (15) interprets the reaction rate constant in terms of transition state theory. Linear regression analysis was used to estimate the parameters A and B, activation energy, enthalpy of activation and entropy of activation calculated from Eq. (16) and valid only in an interval around the temperature T_0 (K). Most kinetic data can adequately be described by the empirical Arrhenius equation. In this case, the enthalpy and entropy of activation given in Table 5 suggests that the extended Arrhenius equation needs to be used to interpret the kinetics better. The extended Arrhenius equation:

$$\ln k = A' + B'\left(\frac{1}{T} - \frac{1}{T_0}\right) + C'\left(\frac{1}{T} - \frac{1}{T_0}\right)^2 + \varepsilon \tag{17}$$

$$\Delta C_p = R\left(\frac{C'}{T_0^2} - 1\right) \tag{18a}$$

$$\Delta H = -R(B' + T_0) \tag{18b}$$

$$\Delta S = R\left(A' - \ln\left(\frac{k_B T_0}{h}\right) + \frac{\Delta H}{RT}\right) \tag{18c}$$

The extended Arrhenius equation is in the form of second order quadratic expression (17). Non-linear regression analysis was used to solve for parameters A', B' and C' with the error estimate in the range of 10^{-5}. The activation parameters, enthalpy change and the entropy change were calculated from Eq. (18) and the values are given in Table 6. The rate constant for the main reaction of phenol alkylation is 1.79×10^{-5} L/mol s at the optimum temperature.

5. Conclusion

The alkylation of phenol with *tert*-butyl alcohol was carried out in a batch reactor using laboratory prepared ionic liquid catalysts. These ionic liquid catalysts were found to be promising in the *tert*-butylation of phenol with *tert*-butyl alcohol when compared to all the literature reports with respect to better phenol conversion and 2,4-DTBP selectivity. Among the three ILs, N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate was found to be the best catalyst. It gave the highest phenol conversion of 84.5% and 2,4-DTBP selectivity of 57.6% at an optimum reaction temperature of 70 °C, 2:1 TBA to phenol mole ratio and 1:1 ionic liquid to phenol mole ratio. The ionic liquid is easy recoverable and could be recycled five times without significant loss of activity. The activation energy for this reaction using this catalyst was found to be 8.82 kcal/mol and agrees well with activation energy of similar reactions over similar catalysts. The enthalpy of activation (8.13 kcal/mol) and entropy of activation (56.16 kcal/mol) were estimated using the extended Arrhenius equation.

Nomenclature

2-TBP	2-*tert*-butylphenol
4-TBP	4-*tert*-butylphenol
2,4-DTBP	2,4-di-*tert*-butylphenol
2,6-DTBP	2,6-di-*tert*-butylphenol
2,4,6-DTBP	2,4,6-tri-*tert*-butylphenol
E_a	Activation energy (kcal/mol)
C_{exp}	Experimental concentration (mol/L)
C_{TBA}	Concentration of *tert*-butyl alcohol (mol/L)
$C_{\mathrm{2\text{-}TBP}}$	Concentration of 2-*tert*-butylphenol (mol/L)
$C_{\mathrm{4\text{-}TBP}}$	Concentration of 4-*tert*-butylphenol (mol/L)
$C_{\mathrm{2,4\text{-}DTBP}}$	Concentration of 2,4-di-*tert*-butylphenol (mol/L)
$C_{\mathrm{2,6\text{-}DTBP}}$	Concentration of 2,6-di-*tert*-butylphenol (mol/L)
C_p	Concentration of phenol (mol/L)
C_{pred}	Predicted concentration (mol/L)
C_W	Concentration of water (mol/L)
k_1–k_9	Second order rate constant (L/mol s)
A', B' and C'	Parameters in expansion of Arsenics equation
ΔC_p	Activation parameter (kcal/K mol)
ΔH	Enthalpy of activation (kcal/mol)
ΔS	Entropy of activation (cal/K mol)
A and B	Parameters in the empirical Arrhenius equation
ε	Error function
k_B	Boltzmann's constant
h	Planck's constant
IL	Ionic liquid
IL-1	N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate
IL-2	1-(4-sulfonic acid) butylpyridinium hydrogen sulfate
IL-3	1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate
TBA	*tert*-Butyl alcohol
W	water
T	Reaction temperature (K)
T_0	Reference temperature within interval of the reaction temperature (K)

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