



Alkylation of *p*-cresol with *tert*-butyl alcohol using benign Bronsted acidic ionic liquid catalyst

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ABSTRACT

Novel and environmentally benign Bronsted acidic ionic liquids with SO₃-H functionality were prepared using *N*-methyl imidazole, pyridine, triethylamine and 1,4-butanediol as the source chemicals. The prepared ionic liquid catalysts were characterized by NMR and their catalytic activity in *tert*-butylation of *p*-cresol with *tert*-butyl alcohol (TBA) was investigated. The effects of reaction time, reaction temperature, reactant mole ratio and the recyclability of the catalysts on the conversion of *p*-cresol and selectivity to 2-*tert*-butyl-*p*-cresol (TBC) and 2,6-di-*tert*-butyl-*p*-cresol (DTBC) called butylated hydroxytoluene (BHT) were investigated. Lower alcohol to *p*-cresol mole ratios, lower ionic liquid to *p*-cresol ratio and temperature as low as 70 °C gave 80% conversion of *p*-cresol. The catalyst activity was found to be almost completely retained even after 5 recycles. Extended Arrhenius equation was used to calculate the rate constants for this reaction.

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1. Introduction

Friedel-Crafts alkylation of aromatic compounds with alkyl halides, alcohols, alkenes or ethers as alkylating reagents is an important reaction that has been used in the production of pharmaceuticals and fine chemicals for more than a century [1]. Alkylation of *p*-cresol with *tert*-butyl alcohol (TBA) gives 2-*tert*-butyl-*p*-cresol (TBC) and 2,6-di-*tert*-butyl-*p*-cresol (DTBC) called butylated hydroxytoluene (BHT). These are used as antioxidants in food industry as well as in jet fuels, petroleum products, cosmetics, pharmaceuticals, rubber, and embalming fluid, antiseptic, polymerization inhibitor and UV absorber [2–4]. Butylated hydroxytoluene (BHT), is an important lipophilic phenol mainly used as plastics and elastomer antioxidant and petroleum additive. Investigation of both homogeneous and heterogeneous catalysts for this typical Friedel-Crafts reaction resulted in different selectivities and activities based mainly on the acidity of the catalysts used. Catalysts used for the production of alkylated *p*-cresols include Lewis acids (AlCl₃, FeCl₃ and ZnCl₂) [5], Bronsted acids (H₃PO₄, H₂SO₄, HF and HClO₄) [6], cation-exchange resins [7], mesoporous materials [8], zeolites [9], sulfated zirconia [10], heteropolyacids [11] and also supercritical and near-supercritical fluids [12]. The liquid

acid catalysts cause equipment corrosion and environmental pollution while solid acids deactivate rapidly. Although cation-exchange resins showed promise, thermal stability and fouling of the resins pose major problems for their commercialization [7].

Recently, there has been an increasing interest in developing catalytic processes with minimum environmental threats and maximum economic benefits. Room temperature ionic liquids are finding growing applications as alternative reaction media for organic transformations and separations. They possess important attributes, such as negligible vapor pressure, excellent chemical and thermal stability, potential recoverability and ease of separation of products from reactants [13–16]. Bronsted acidic ionic liquids as novel benign catalysts have been reported for similar acid-catalyzed reactions [17–19]. Alkylation of *m*-cresol with TBA in acidic ionic liquids has been reported to give selectively high yield of 2-TBC [20]. Liu et al. reported the alkylation of *p*-cresol in sulfonic acid functionalized, pyridinium based ionic liquids with 79% *p*-cresol conversion and 92% selectivity to TBC [34]. In this paper, we report a more efficient and environmentally benign alkylation reaction of *p*-cresol with TBA using SO₃-H functionalized ionic liquids. The activity of different ionic liquids in this reaction and the effects of process parameters like reaction time, temperature, reactant ratio, catalyst to reactant ratio and catalyst recyclability are investigated. The kinetic constants were evaluated and the temperature dependency of the activation energy has been analyzed and explained for this reaction. High selective yield of TBC, BHT could be obtained at optimum reaction conditions in a laboratory batch reactor.

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Nomenclature

$[I]_s$	molar concentrations of unprotonated indicator in the solution
$[IH^+]_s$	molar concentrations of protonated indicator in the solution
C_C	yield of <i>p</i> -cresol
C_{DTBC}	yield of 2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol
C_{TBA}	yield of <i>tert</i> -butyl alcohol
C_{TBC}	yield of 2- <i>tert</i> -butyl- <i>p</i> -cresol
C_W	yield of water
E_a	activation energy, kcal/mol
k_1, k_2 and k_3	second-order rate constant, L/mol s
A', B' and C'	parameters in expansion of Arrhenius equation
ΔC_p	activation parameter, kcal/K mol
ΔH	enthalpy of activation, kcal
ΔS	entropy of activation, cal
A and B	parameters in empirical Arrhenius equation
ε	error function
k_B	Boltzmann's constant
h	Planck's constant
BHT	butylated hydroxytoluene
DTBC	2,6-di- <i>tert</i> -butyl- <i>p</i> -cresol
H_0	Hammett function
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
IL-4	1-(3-sulfonic acid) propyl pyridinium toluenesulfonate
IL-5	1-(4-sulfonic acid) butyl pyridinium toluenesulfonate
T	temperature, K
T_0	reference temperature used in the extended Arrhenius equation, K
RTIL	room temperature ionic liquid
TBA	<i>tert</i> -butyl alcohol
TBC	2- <i>tert</i> -butyl- <i>p</i> -cresol
TBCE	<i>tert</i> -butyl- <i>p</i> -cresol ether
TGA	thermogravimetric analysis
x_{exp}	experimental yield
x_{pred}	predicted yield

2. Experimental

2.1. Catalyst preparation

SO₃H-functionalized Brønsted acidic ionic liquids were prepared in the laboratory following the procedure outlined in literature [21–23]. N-methyl imidazole, pyridine, triethylamine and 1,4-butane sultone were purchased from Sigma Aldrich Chemicals Pvt. Ltd., India. *p*-cresol and *tert*-butanol were purchased from Ranbaxy Ltd., New Delhi, India. In a typical ionic liquid preparation procedure, N-methyl imidazole was mixed with 1,4-butane sultone stirring at 40–80 °C for 12–24 h. After solidification, the zwitterions mass was washed three times with ethyl ether and then dried under vacuum (120 °C, 0.01 Torr). Stoichiometric amount of sulfuric acid was then added to the precursor zwitterions. The mixture was stirred at 80 °C for 8 h to obtain the ionic liquid. The structures of the prepared ionic liquid are shown in Fig. 1. All the chemicals

were research grade and were used without further purification unless otherwise stated.

2.2. Catalyst characterization

The ILs were characterized by ¹H and ¹³C NMR spectroscopy using Bruker ARX-400 spectrometer. The thermal stability data for the ILs was obtained by TGA at a heating rate of 10 K/min under nitrogen. UV–vis spectra were obtained on a Perkin-Elmer instrument.

2.2.1. Identification of ionic liquids by NMR and ESI-MS

IL-1 (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate): ¹H NMR (D₂O, 400 MHz): δ (ppm) 1.1625 (t, 9H), 1.6599 (m, 4H), 2.5862 (t, 2H), 3.1376 (t, 2H), 3.1995 (m, 6H); ¹³C NMR (D₂O, 100 MHz): δ (ppm) 8.0002, 20.6977, 22.7652, 51.0469, 23.8737, 56.6530. ESI-MS Positive Mass Peaks (m/z): 86.09, 103.13, 157.17, 239.15. Thermal decomposition of ionic liquid 1 observed to be 325.4 °C.

IL-2 (1-(4-sulfonic acid) butylpyridinium hydrogen sulfate): ¹H NMR (DMSO, 400 MHz): δ (ppm) 1.5883 (t, 2H), 2.0126 (t, 2H), 2.6204 (t, 2H), 4.6336 (t, 2H), 8.1578 (t, 2H), 8.6059 (t, 1H), 9.0961 (d, 2H); ¹³C NMR (D₂O, 100 MHz): δ (ppm) 22.1620, 30.6026, 51.1654, 61.2132, 128.9924, 145.6609, 146.4140. ESI-MS Positive Mass Peaks (m/z): 55.05, 80.05, 137.02, 216.06. Thermal decomposition of ionic liquid 2 observed to be 324.8 °C.

IL-3 (1-(4-sulfonic acid) butyl-3-methylimidazolium hydrogen sulfate): ¹H NMR (D₂O, 400 MHz): δ (ppm) 1.5542 (t, 2H), 1.8759 (t, 2H), 2.5957 (t, 2H), 3.8486 (s, 3H), 4.1791 (t, 2H), 7.7089 (d, 1H), 9.1533 (d, 1H), 10.3077 (s, 1H); ¹³C NMR (D₂O, 100 MHz): δ (ppm) 22.2840, 29.3126, 36.5853, 49.2827, 51.2456, 123.1597, 124.4810, 137.4818. ESI-MS Positive Mass Peaks (m/z): 55.05, 83.06, 137.11, 219.08. Thermal decomposition of ionic liquid 3 observed to be 366.9 °C.

2.2.2. Acidity of ionic liquids

Several researchers [24–28] showed that spectroscopic techniques are extremely useful to evaluate the Brønsted acidity of ionic liquids. In this technique, basic indicator is used to trap the dissociative proton and then determine the Hammett acidity function. In the present work, 4-nitroaniline ($pK_a = 0.99$) was used as indicator to trap the dissociative proton in H₂O, using similar procedure described by Liu et al. [20]. The protonation extent of uncharged indicator bases (I) in a solution was evaluated in terms of the measurable ratio $[I]_s/[IH^+]_s$. Then Hammett function (H_0) was calculated as

$$H_0 = pK(I)_{aq} + \log \left(\frac{[I]_s}{[IH^+]_s} \right)$$

where $pK(I)_{aq}$ is the pK_a value of the indicator in an aqueous solution. $[IH^+]_s$ and $[I]_s$ are the molar concentrations of the protonated and unprotonated forms of the indicator in the solvents, respectively.

The maximum absorbance of the blank solution (indicator in H₂O) was observed at 380 nm. Fig. 2 shows the absorbance of IL-1 solution at different concentrations. Similar procedure was followed for all three ionic liquids, to calculate the Hammett function and the results are shown in Fig. 3. From the figure, it is clear that the three ionic liquids possess strong acidity which is an important characteristic for this acid-catalyzed.

2.3. Activity testing

The activity testing of the ionic liquids as catalysts in this reaction was carried out in a 30 ml stainless steel autoclave lined with

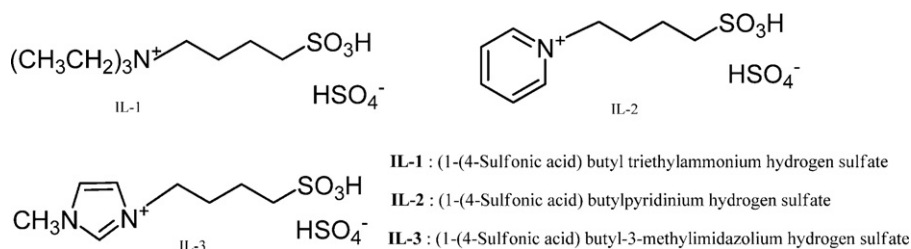
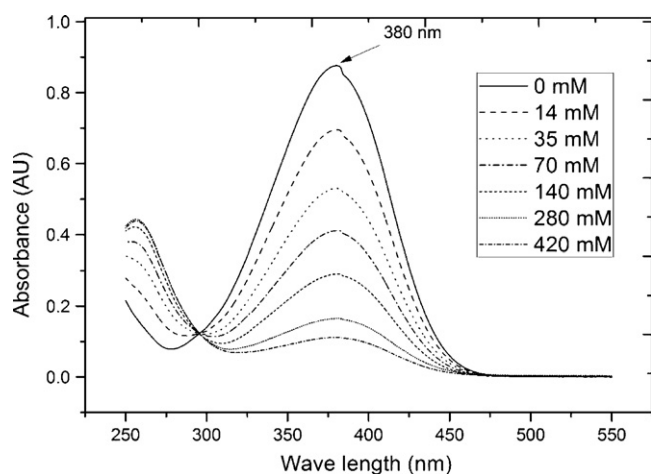


Fig. 1. Structure of ionic liquids.

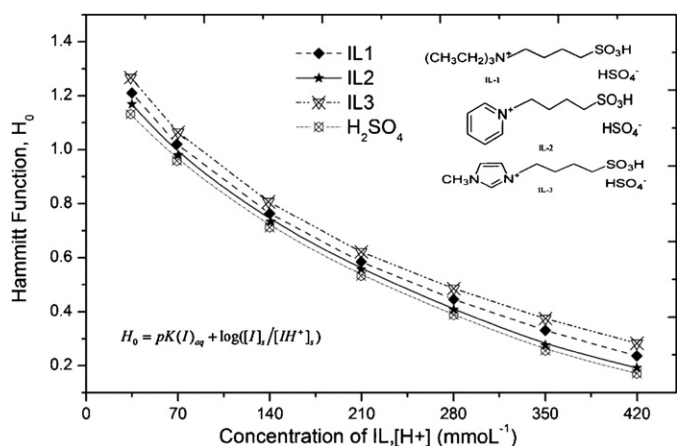
Fig. 2. Absorption spectra of 4-nitroaniline for various concentrations of IL-1 in H₂O.

a Teflon bomb and equipped with a magnetic stirrer under auto-geneous pressure. A typical batch consisted of 10 mmol each of *p*-cresol, TBA and ionic liquid. Reaction temperature was maintained at 70 °C and reaction mixture was stirred for 8 h. A qualitative product analysis was conducted with a GC–MS 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 and flame ionization detector.

3. Results and discussion

3.1. Comparison of activity of the three ionic liquid catalysts

The activity of the prepared ionic liquid catalysts was compared with that of other solid acid catalysts in this reaction [29] and

Fig. 3. Hammett functions (acidity) of ionic liquids in water with 4-nitroaniline as indicator ($pK_a = 0.99$), $A_{\text{max}} = 380$ nm, by UV-spectroscopy.

shown in Table 1. From the table, it is clear that all ionic liquid catalysts gave high *p*-cresol conversion at a temperature as low as 70 °C. Among the three ionic liquid catalysts, N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate gave 90% TBC selectivity at the given reaction conditions. Detailed kinetic investigations to optimize various reaction parameters were conducted using this catalyst since it is also less toxic [30] and cost effective besides showing high product selectivity.

3.2. Effect of reaction time on *p*-cresol conversion

The influence of reaction time on conversion of *p*-cresol and the selectivity towards TBC and DTBC was investigated at different temperatures and different reactant mole ratios. Fig. 4 shows the conversion of *p*-cresol at 70 °C, 1:1 molar ratio of *p*-cresol/TBA and 1:1 molar ratio of IL-1/*p*-cresol. The alkylation of *p*-cresol with TBA in the ionic liquid shows high selectivity to TBC, 2,6-di-*tert*-butyl-3-methyl phenol (2,6-DTBC). With increase in reaction time, the conversion of *p*-cresol and selective yield of TBC increased rapidly and reached an equilibrium level after 8 h and remained almost constant thereafter. In all the cases, it was observed that 90% of *p*-cresol conversion was achieved within the first hour of the reaction time. The conversion of *p*-cresol reached 80.7%, the selectivities to TBC and DTBC reached 90.8% and 9.1%, respectively, after 8 h. The increase in the selectivity to TBC led to decrease in selectivity to DTBC with time but the combined selectivities of TBC and DTBC almost remained constant over the time period investigated.

3.3. Effect of reaction temperature

The reaction was studied at various temperatures from 40 to 90 °C, the lower limit of temperature was restricted by physical

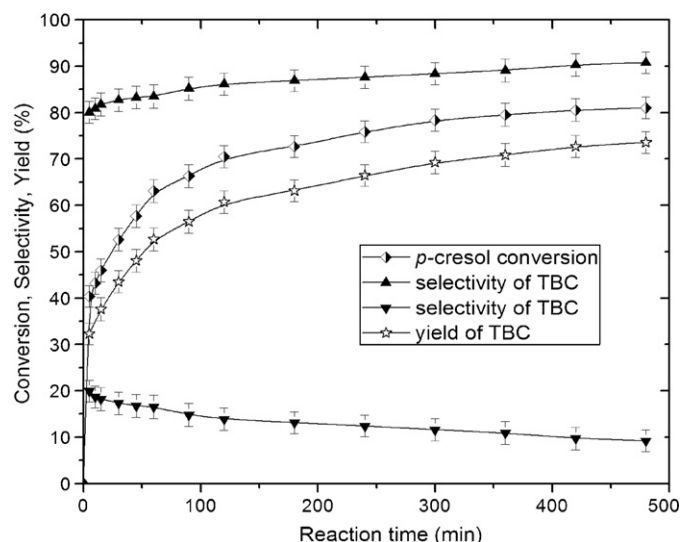
Fig. 4. Effect of reaction time on *p*-cresol conversion.

Table 1
Activity of the various catalysts for alkylation of *p*-cresol with TBA.

Catalyst	Molar ratio (TBA: <i>p</i> -cresol)	Temperature, °C	Conversion (%)	% Selectivity	
				TBC	DTBC
IL-1	1:1	70	80.7	90	9.5
IL-1	3:2	70	85	66.8	32.3
IL-2	1:1	70	78	82.7	16.9
IL-2 [34]	1:1	70	82.6	80.5	16.7
IL-2	2:1	70	84	72	27
IL-3	1:1	70	80	91	8.9
IL-4 [34]	1:1	70	70.8	70.6	3.5
IL-5 [34]	1:1	70	66.9	69.2	3.9
H ₂ SO ₄	1:1	70	68.3	71.3	1.2
TPA/TiO ₂ [29]	3:1	130	82	87	9
WO ₃ /ZrO ₂ [29]	3:1	130	70	92	7
USY [29]	3:1	130	33	73	1
Al-MCM-41[8]	2:1	90	96.2	46.3	42.2

Reaction conditions: *p*-Cresol (10 mmol), TBA (10–20 mmol), IL (10 mmol); speed = 800 rpm; reaction time = 8 h.

properties of ionic liquid, where mass transfer constraints became dominant and the upper limit of temperature was limited by the formation of unwanted oligomerization products. At the reaction conditions of our investigations, no products of iso-butene oligomerization were detected by GC–MS, which may be attributed to the lower reaction temperature [31].

Fig. 5 shows the variation of *p*-cresol conversion and alkylated product selectivities with temperature. At 40 °C the conversion of *p*-cresol is 31.4% and increased to 80.7% at 70 °C. An increase of reaction temperature above 70 °C results in decrease of *p*-cresol conversion. This can be attributed to the dealkylation of dialkylated product (DTBC) to monoalkylated product (TBC) and also, the oligomerization reaction of TBA becomes dominant over alkylation [32] along with gasification of TBA [20].

The selectivity to DTBC is high (30%) at 40 °C and as the temperature is increased, the selectivity to DTBC decreased. This decrease in selectivity to DTBC is due to the rearrangement of C-alkylated product. Devassy et al. [33] have also reported such a rearrangement over acid catalysts at high temperatures. The highest selectivity to DTBC was found to be 40% at 70 °C, IL-1: *p*-cresol mole ratio 1:1 and TBA:*p*-cresol mole ratio of 2, presumably, due to higher stability and the availability of solvated *tert*-butyl cation at lower reaction temperatures. Considering conversion and selectivities, the optimum reaction temperature is 70 °C. At this 40% conversion of *p*-cresol selectivity to TBC was found to be highest.

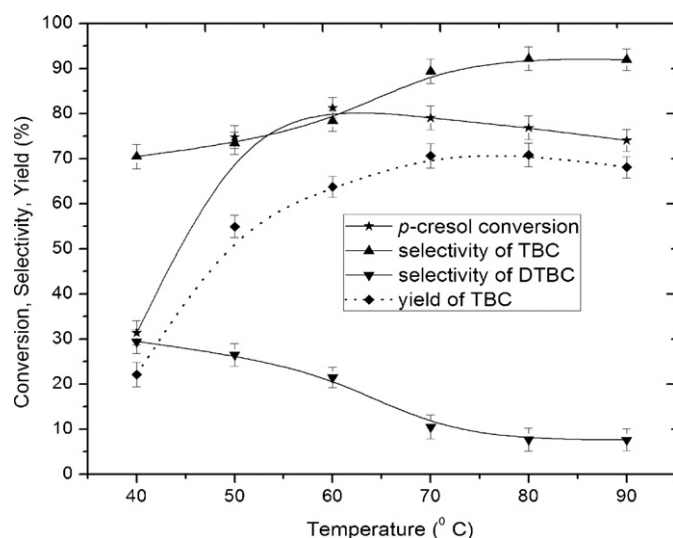


Fig. 5. Effect of temperature on *p*-cresol conversion.

3.4. Effect of molar ratio of TBA to *p*-cresol

The effect of molar ratio on *p*-cresol conversion and product selectivity was studied at 70 °C with TBA/*p*-cresol molar ratio of 0.5–3 by keeping ionic liquid/*p*-cresol molar ratio at 1:1 and the results were shown in Fig. 6. For a constant IL-1/*p*-cresol molar ratio, it was observed that as the amount of TBA increases, the conversion of *p*-cresol and yield of TBC passed through a maximum, while selectivity of TBC passed through minimum. The maximum *p*-cresol conversion was observed when equal amount of TBA is used. Conversion of *p*-cresol decreased when molar ratio of TBA and *p*-cresol was more than 1, this is because of the progressive dilution of the ionic liquid with water, which was formed during the dehydration of TBA. This affects the conversion of *p*-cresol as well as the formation of unwanted oligomerized and O-alkylated products. An optimum mole ratio of *p*-cresol to TBA was found to be 1:1 at a constant IL-1 and *p*-cresol ratio of 1:1 to obtain high conversions of *p*-cresol.

3.5. Effect of ionic liquid to *p*-cresol molar ratio

The effect of ionic liquid to *p*-cresol ratio on *p*-cresol conversion, TBC and DTBC selectivities were investigated using ionic liquid to *p*-cresol ratio from 0.5 to 2 at 70 °C and TBA and *p*-cresol molar ratio constant at 1:1, which can be shown in Fig. 7. As IL-1/*p*-cresol ratio

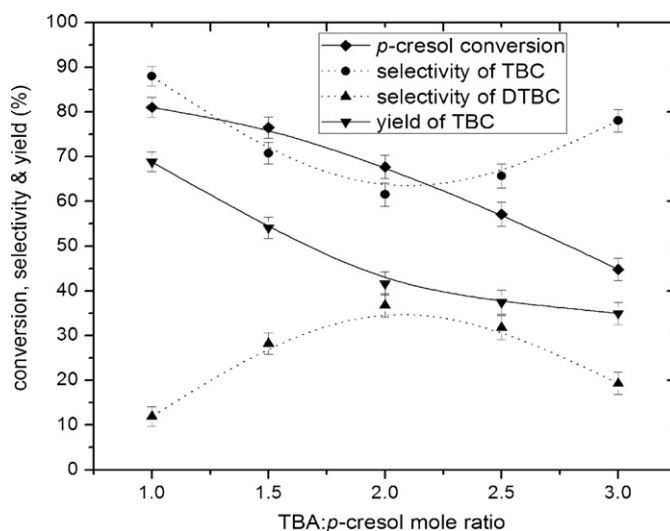


Fig. 6. Effect of reactant molar ratio on *p*-cresol conversion at fixed IL-1:*p*-cresol ratio.

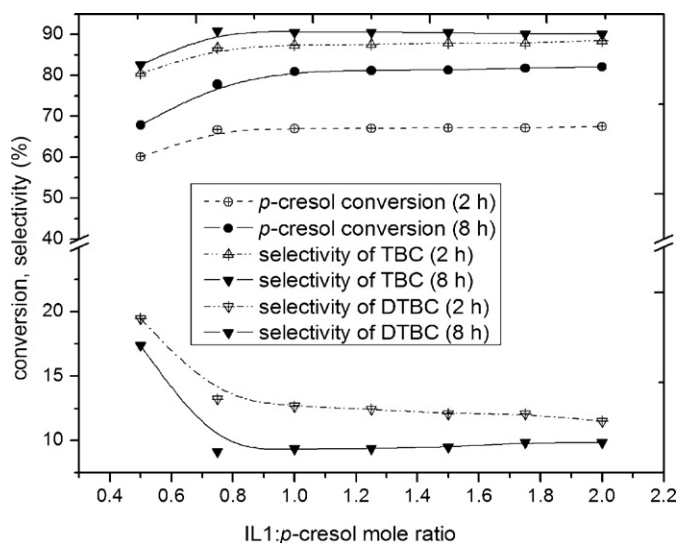


Fig. 7. Effect of amount of IL1 on *p*-cresol conversions and product selectivities.

is increased, the *p*-cresol conversion and TBC selectivity increased to maximum, thereafter *p*-cresol conversion and selectivity to TBC remained constant. This may be due to the increase in the amount catalyst, leading to increased acidity in the reaction mixture, which in turn led to higher conversion. Highest conversion of *p*-cresol and highest selectivity to TBC was achieved, when IL-1 and *p*-cresol molar ratio was maintained at 1:1.

3.6. Recoverability and recyclability of ionic liquid

In order to examine the recoverability and recyclability of the ionic liquid, the ionic liquid was extracted with toluene (5 × 3 ml) and vacuum dried for 5 h at 120 °C. After vacuum drying, the IL-1 is assessed with H NMR spectroscopy, which showed no traces of reactants or products. The results of the catalytic recycling experiment are shown in Table 2. IL-1 was repeatedly used 5 times without major loss of *p*-cresol conversion and product selectivity.

3.7. Kinetic modeling

The kinetic runs were carried out at five different temperatures 333, 343, 353, 363 and 363 K, respectively, at autogeneous pressure. Table 3 shows the final concentration of reactant and product for different temperatures. Detailed reaction mechanism of *tert*-butylation of *p*-cresol using functional ionic liquid catalyst was studied elsewhere [34]. The system can be described by the given in reactions scheme given in Fig. 8. In accordance with the product distribution and based on reaction mechanism, the kinetics model of the reaction has been taken following assumptions:

Table 2
Recyclability of ionic liquids.

S. no.	Experimental run	Conversion of <i>p</i> -cresol (%)	% Selectivity	
			TBC	DTBC
1	Fresh	80.7	90.8	9.19
2	Recycle 1	78.2	88.4	11.5
3	Recycle 2	78.9	88.5	11.3
4	Recycle 3	81.1	91.2	8.7
5	Recycle 4	78.7	88.5	11.5
6	Recycle 5	77.9	88.1	11.8

Reaction conditions: *p*-Cresol (10 mmol):TBA:IL-1 (1:1:1) molar ratio; 70 °C; 8 h.

1. Formation of *tert*-butylium/iso-butene gas is negligible due to fast conversion of TBA.
2. The amount of TBA and water calculated from mass balance of the major products.
3. *tert*-butylation of *p*-cresol is considered as irreversible.
4. 2-TBC to 2,6-DTBC reaction is considered as reversible.
5. There is no consideration of intermediate formations (O-alkylation).

3.8. Batch reaction kinetic model

The mechanism of the reaction is detailed in Fig. 8. From this reaction mechanism, a second-order rate equation is formulated [35]. The rate of formation of different components can be expressed as follows:

Alkylation of *p*-cresol

$$\frac{dC_C}{dt} = -k_1 C_C C_{TBA} \quad (1)$$

Rate of conversion of *tert*-butyl alcohol

$$\frac{dC_{TBA}}{dt} = -k_1 C_C C_{TBA} - k_2 C_{TBC} C_{TBA} + k_3 C_{DTBC} C_W \quad (2)$$

Rate of formation of 2-TBC

$$\frac{dC_{TBC}}{dt} = k_1 C_C C_{TBA} - k_2 C_{TBC} C_{TBA} + k_3 C_{DTBC} \quad (3)$$

Rate of formation of 2,6-DTBC

$$\frac{dC_{DTBC}}{dt} = k_2 C_{TBC} C_{TBA} - k_3 C_{DTBC} C_W \quad (4)$$

Rate of formation of water

$$\frac{dC_W}{dt} = k_1 C_C C_{TBA} + k_2 C_{TBC} C_{TBA} - k_3 C_{DTBC} C_W \quad (5)$$

where *C* is the concentration of respective components in mol L⁻¹, *t* is the batch reaction time in s, *k* is the rate constant of respective reaction in L mol⁻¹ s⁻¹. A non-linear regression algorithm was used for parameter estimation for above batch model Eqs. (1–5). A software for parameter estimation in dynamic models reported [36], similar algorithms followed here. The optimum values of the parameters were estimated by minimizing the objective function given by

$$f = \sum_{i=1}^n [(x_{pred})_i - (x_{exp})_i]^2 \quad (6)$$

Batch reaction rate constants were optimized shown in Table 4. The standard error of estimated for the rate reaction from concentration of reactant and products was 10⁻⁵ by Eq. (8). The experimental and the predicted concentrations of reactants and products were plotted in Fig. 9 at 70 °C. It shows that the proposed reaction

Table 3
Percentage yield of reactant and products in alkylation of *p*-cresol with TBA in IL-1 with various temperatures.

Temperature, °C	Conversion of <i>p</i> -cresol	% Yield				
		<i>p</i> -Cresol	TBA	2-TBC	2,6-DTBC	Water
50	74.8	37.6	26.8	51.6	10.8	73.2
60	81.3	25.1	18.6	68.4	6.5	81.4
70	79.1	16.2	7.7	75.3	8.5	92.3
80	78.9	11.8	2.6	79.0	9.2	97.4
90	77.1	10.9	3.0	83.0	7.0	97.0

Reaction conditions: *p*-Cresol (10 mmol):TBA:IL-1 (1:1:0.75) molar ratio, autogeneous pressure.

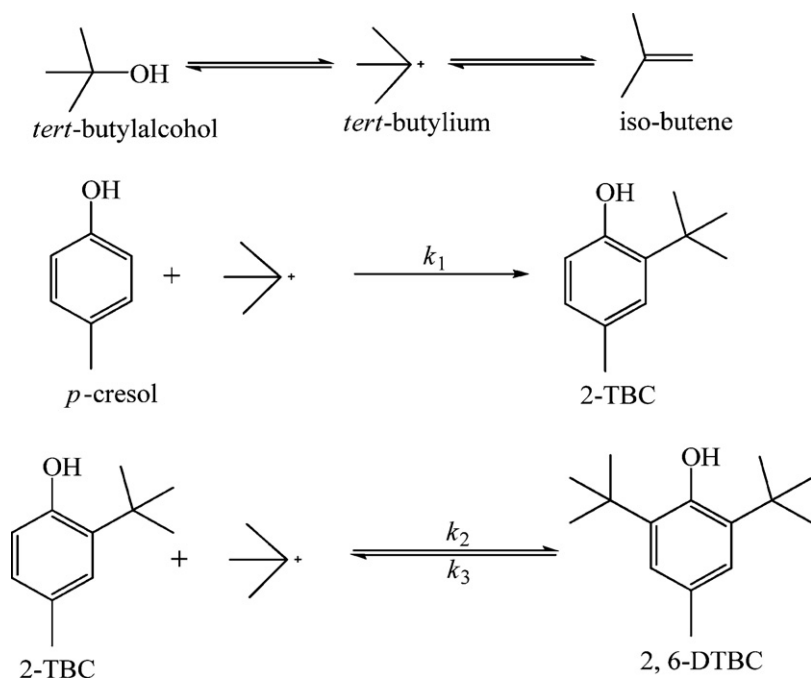


Fig. 8. Possible reaction mechanism for alkylation of *p*-cresol with *tert*-butyl alcohol in ionic liquid.

rate expression predicts the alkylation values comparable with the experimental ones.

Evaluated kinetic rate constants at various temperatures were used to determine the activation energy and frequency factor using Arrhenius relationships as shown in Fig. 10. The activation energy and frequency factor from Fig. 10 are calculated to be 15.63 kcal/mol and 2.65×10^7 in the temperature range 50–90 °C, respectively. The alkylation of *p*-cresol using sulfuric acid as catalyst was conducted in the same batch reactor in the temperature range of 70–90 °C. Activation energy for alkylation was calculated to be 10.36 kcal/mol in the temperature range of 70–90 °C, respectively. The activation energy values for various reactions compare well with the values for similar reactions in near-critical water, cation-exchanged resins and sulfated zirconia reported in literature. Activation energy for alkylation of *p*-cresol in near critical water was 29 kcal/mol in the temperature range of 250–300 °C [37]. Activation energy for this reaction over sulfated zirconia was reported as 5.5 kcal/mol in the temperature ranges of 30–120 °C [10]. Activation energy of 23.2 kcal/mol was reported over cation-exchanged resins in the temperature ranges of 34–70 °C [38]. As compared to the batch alkylation of *p*-cresol over many catalysts, the activation energy using ionic liquid is low showing that the reaction is intrinsically kinetic controlled. The plots for the rate constant k_2 and k_3 show a curvature, this deviation from the Arrhenius relation is attributed

Table 4

Optimized parameters of second-order rate constants, apparent activation energies and pre-exponential factors for alkylation of *p*-cresol with *tert*-butyl alcohol in IL-1 catalyst.

Temperature, °C	Rate constant (L/mol s)		
	$k_1 (\times 10^{-5})$	$k_2 (\times 10^{-5})$	$k_3 (\times 10^{-5})$
90	1.16	91.71	165.08
80	2.74	7.16	14.31
70	3.52	0.64	0.76
60	11.52	3.51	1.21
50	16.16	11.37	7.34
Activation energy (E_a), kcal/mol	15.64	–	–
Pre-exponential factor	4.4×10^5	–	–

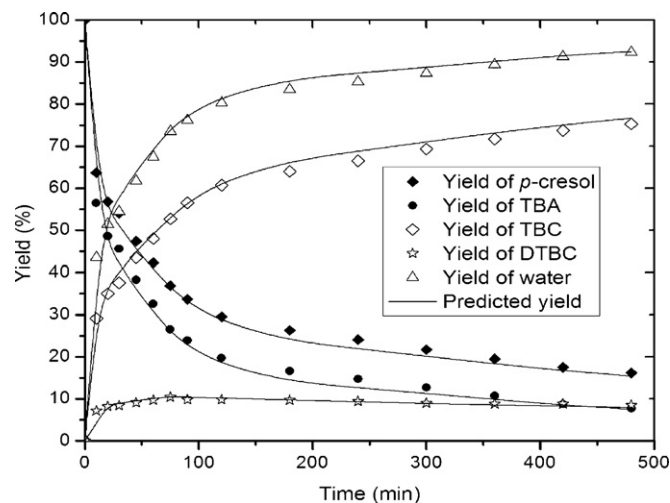


Fig. 9. Comparison of experimental and predicted product yields for alkylation of *p*-cresol with *tert*-butyl alcohol using ionic liquids at 70 °C.

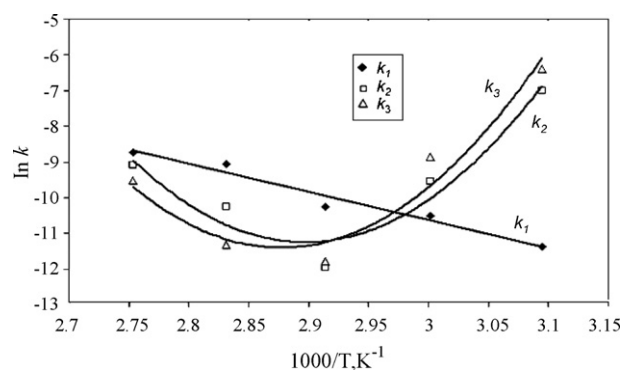


Fig. 10. Arrhenius plot for alkylation of *p*-cresol with *tert*-butyl alcohol using ionic liquid catalyst (N-(4-sulfonic acid) butyl triethylammonium hydrogen sulfate).

Table 5
Estimated parameters in empirical Arrhenius equation with $T_0 = 70^\circ\text{C}$.

Reaction rate constants	k_1	k_2	k_3
A	-9.62	-9.86	-10.7
B (10^3)	7.87	-6.13	-10.61
E_a , kcal/mol	15.64	-12.18	-21.07
ΔH , kcal	-14.95	-12.87	-21.77
ΔS , cal	-34.37	-115.94	-142.28

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

Reaction rate constant	k_2	k_3
A'	-11.18	-11.2
B' ($\times 10^3$)	-5.53	-1.05
C' ($\times 10^8$)	1.12	1.12
ΔC_p , kcal/K mol	1.82	1.83
ΔH , kcal	10.26	1.38
ΔS , cal	-51.34	-77.28

to heat and mass transfer resistances at low temperature and also the solvolysis effect in the reaction [39–41]. In order to interpret these effects on the reaction, a modified empirical form of Arrhenius equation is applied as given below

$$\ln k = A + B \left(\frac{1}{T} - \frac{1}{T_0} \right) + \varepsilon \quad (7)$$

$$\ln k = \ln \left(\frac{kT}{h} \right) - \frac{\Delta H}{RT} + \frac{\Delta S}{R} \quad (8)$$

$$E_a = -RB \quad (9a)$$

$$\Delta H = -R(B + T_0) \quad (9b)$$

$$\Delta S = R \left(A - \ln \left(\frac{k_B T_0}{h} \right) + \frac{\Delta H}{RT} \right) \quad (9c)$$

The empirical Arrhenius equation for the temperature dependent rate constant was reported in literature for similar reactions [41]. The empirical Arrhenius equation given by the linear relationship with the error function ' ε ' in Eqs. (7) and (8) interprets the reaction rate constant in terms of transition state theory with A and B valid only in an interval around the temperature T_0 (K). Linear regression analysis was used to estimate the parameters A , B , activation energy, enthalpy of activation and entropy of activation calculated from Eq. (9). The parameters, enthalpy of activation and entropy change during activation are valid only in the transition state theory and the values are given in Table 5.

Extended Arrhenius equation

$$\ln k = A' + B' \left(\frac{1}{T} - \frac{1}{T_0} \right) + C' \left(\frac{1}{T} - \frac{1}{T_0} \right)^2 + \varepsilon \quad (10)$$

$$\Delta C_p = R \left(\frac{C'}{T_0^2} - 1 \right) \quad (11a)$$

$$\Delta H = -R(B' + T_0) \quad (11b)$$

$$\Delta S = R \left(A' - \ln \left(\frac{k_B T_0}{h} \right) + \frac{\Delta H}{RT} \right) \quad (11c)$$

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 suggest that the extended Arrhenius equation needs to be used to interpret the kinetics better. The extended Arrhenius equation is in the form of second-order quadratic expression (10). Non-linear regression analysis is used to solve for parameters A' , B' and C' with the error estimate in the range of 10^{-5} . The activation parameter, enthalpy change and the entropy change were calculated from Eq. (11c) and the values are given in Table 6.

4. Conclusion

Selective liquid phase *tert*-butylation of *p*-cresol with TBA in room temperature ionic liquid has been systematically carried out at different reaction conditions in a batch autoclave under auto-geneous pressure. The $\text{SO}_3\text{-H}$ functionalized room temperature Brønsted acidic ionic liquid, prepared in the laboratory, are inexpensive and contain no halogen atoms such as fluorine and chlorine. These ILs are completely recoverable and recyclable in this alkylation reaction. The ILs can be directly reused after removal of water under vacuum. Catalytic amount of the laboratory prepared IL-1 achieved high *p*-cresol conversion, complete alcohol conversion and high product selectivity at low temperatures. Thus, these Brønsted acidic ionic liquid catalysts show promise for the development of a continuous and environmentally benign, energy efficient and economical process route for the production of TBC and BHT. The kinetics of the reaction are well interpreted using the extended Arrhenius equation. The experimental yields of the products match well with model predicted yields suggesting that the reaction rate model is appropriate.

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