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Alkylation of Phenol with Tert-butyl Alcohol using (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid [SBTEA][PTSA]

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ABSTRACT

Alkylation of phenol with tert-butyl Alcohol is carried out using number of acidic and solid catalyst which are not environmental friendly. Both homogenous and heterogeneous catalysts have been reported in the tert-butylation of phenol which include Lewis acid, $AlCl_3$ and BF_3 (Kirk, et al., 1978), Bronsted acids such as H_3PO_3,H_2SO_4, HF and $HClO_3$, cation exchanged resins, zeolites, mesoporous materials, heteropoly acids, super critical and near critical water have been studied. The major draw backs 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-exchange resins show good performance but are thermally unstable and fouling of resin is still a major issue.

Room-Temperature Ionic Liquids (RTILs) have growing potential applications as environmentally benign alternative reaction media for both solvent and organic transformations (Welton, et al., 1999). The advantages of ionic liquids are negligible vapour pressure, thermal stability and good recoverability and recyclability. In this paper (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid [SBTEA][PTSA] is used as catalyst as well as solvent for Alkylation of phenol with Tert-butyl Alcohol which give good results.

I. INTRODUCTION

The alkylation reaction of phenol with tert-butyl alcohol (TBA) is of both industrial importance and academic relevance. 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. 2-tert-butylphenol is an intermediate for pesticides, fragrances and other products, whereas 4-tert-butylphenol is used to make phosphate esters, fragrances, oil field chemicals and demulsifiers. 2,4-Di-tert-butylphenol is an intermediate for antioxidants and 2,6-di-tert-butylphenol is used as an antioxidant intermediate and in pharmaceuticals (Yadav, et al., 2002).

Both homogenous and heterogeneous catalysts have been reported in the tert-butylation of phenol which include Lewis acid, $AlCl_3$ and BF_3 (Kirk, et al., 1978), Bronsted acids such as H_3PO_3,H_2SO_4, HF and $HClO_3$, cation exchanged resins, zeolites, mesoporous materials, heteropoly acids, super critical and near critical water have been studied. The major draw backs 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-exchange resins show good performance but are thermally unstable and fouling of resin is still a major issue.

ILs are also known as ‘designer solvents’ since they give the opportunity to tune their specific properties for a particular need. The researchers can design a specific IL by choosing negatively charged small anions and positively charged large cations, and these specific ILs may be utilized to dissolve a certain chemical or to extract a certain material from a solution. The physical and chemical properties of ILs are varied by changing the alkyl chain length on the cation and the anion. For example, Huddleston, et al., (1998) concluded that density of ILs increases with a decrease in the alkyl chain length on the cation and an increase in the molecular weight of the anion.

II. EXPERIMENTAL DETAILS

1 Material and Reagents

Crystalline phenol and Diethyl ether were purchased from S.d fine-chem. Limited, Mumbai. Tertiary butyl alcohol was purchased from Central Drug House (P) LTD, New Delhi. 1, 4-butanesultone and p-Toulenesulfonic acid were purchased from Merck India Ltd. (Mumbai, Maharashtra, India), while Triethylamine was purchased from Thomas Baker (chemicals) Pvt. Ltd.The ionic liquid [BMIM][HSO4], [BMIM][PTSA], and [TTDP][HSO4] used in reaction were synthesised by Ms VibhutiDukhande (I.C.T, Mumbai). All other chemicals were obtained from reputed firms. They were used without further purification.

(1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid [SBTEA][PTSA]

Triethylamine was mixed with 1,4- butane sultone and stirred at 333 K for 24 h. After solidification of the mass, the product (zwitterion) was washed three times with methanol and ethyl acetate and then dried under a vacuum (353 K, 0.01 Torr). A stoichiometric amount of sulfuric acid or p-toluenesulfonic acid was added to the precursor zwitterion. The mixture was stirred at 353 K for 8 h to form the ionic liquid. The product phase was washed with solvent and dried in a Vacuum (Nie, et al., 2010).

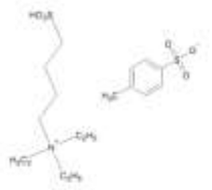

Figure 1 Structure of [SBTEA][PTSA]

III. EXPERIMENTAL SET-UP

The reactions were carried out in three necks round bottom flask with magnetic needle. The overall capacity of round bottom flask was 25 ml. It was provided with condenser and temperature thermometer to measure the temperature. The speed of agitation and temperature of reaction mixture in round bottom flask was controlled by Digital magnetic stirrer.

3.1Experimental Procedure

1. The required amount of ionic liquid is weight and added in 25 ml three necked Round bottom flask.

2. Required volume of phenol and tertiary butyl alcohol is added to Round bottom flask containing ionic liquid.
3. The reaction mixture is heated to 80°C with continuous stirring for 8 hr.
4. Reaction Sample is collected at 2 hr interval.
5. The Sample is analysed using gas chromatography.

Results and Discussions

The alkylation reaction of phenol with tertiary butyl alcohol was studied using four different ionic liquids. Different ionic liquid were 1- butyl 3-methylimidazolium para-toulenesulfonic acid ($[BMIM]^{+}PTSA^{-}$), 1-Butyl 3-Methyl Imidazolium hydrogen sulphate (BMIM [HSO_4]), Trihexyl(tetradecyl)phosphonium hydrogen sulphate.[TTDP][HSO_4], and (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid [SBTEA][PTSA]. The reaction was studied at parameters mentioned in table 3.1. No conversion of phenol was obtained when 1- butyl 3-methylimidazolium para-toulenesulfonic acid ([BMIM][PTSA], 1-Butyl 3-Methyl Imidazolium hydrogen sulphate [BMIM][HSO_4] and Trihexyl(tetradecyl)phosphonium hydrogen sulphate.[TTDP][HSO_4] ionic liquids were used as catalyst. While (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid [SBTEA][PTSA] gave good conversion so all further experiments were carried out using this ionic liquid only.

Table 3.1: Parameter studied at atmosphere pressure with their range.

Sr. No.	Parameters	Range
1	Speed of agitation	300 – 800 rpm
2	Reaction Temperature	333 – 373°K
3	Change of Concentration of Reactant.	1:2 – 1:5^{a}
4	Catalyst loading	1:0.2 – 1:1^{b}

a: ratio of moles of Phenol to TBA.

b: ratio of moles of Phenol to ILs.

3.1 Effect of speed of agitation

3.1.1 Conversion of Phenol.

The effect of speed of agitation on the conversion of phenol. The reaction was carried out at temperature of 80°C, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The agitation speed increases from 200 rpm to 800 rpm. The maximum conversion of phenol obtained at 200 rpm which is 71.2%. The maximum conversion at 200 rpm obtained due to small reaction mass of 3.462 gm. As the conversion increases by 12.82% by decreasing rpm from 500 to 200, no further experiment were carried out at rpm below 200. The results obtained were contradictory and further consideration is necessary.

3.1.2 Selectivity of products

- Selectivity of o-TBP

The effect of speed of agitation on the selectivity of o-TBP.The reaction was carried out at temperature of 80°C, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-

sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The agitation speed increases from 200 rpm to 800 rpm.With increase in time, the selectivity of o-TBP decreases. Selectivity of o-TBP decreases due to Di-alkylation of o-TBP due to enhance in mass transfer with decrease in speed of agitation. The maximum selectivity of o-TBP obtained at 800 RPM which is 44.758%.

- Selectivity of p –TBP

The effect of speed of agitation on the selectivity of p-TBP. The reaction was carried out at temperature of 80°C, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The agitation speed increases from 200 rpm to 800 rpm. The selectivity of p-TBP is decrease with respect to time at all the RPM. The minimum and maximum selectivity of p-TBP at 800 RPM and 200 RPM is 12.43% and 18% respectively. The selectivity of p-TBP decreases due to Dialkylation, which causes conversion of p-TBP to 2,4- DTBP.

- Selectivity of 2, 4-DTBP

The effect of speed of agitation on the selectivity of 2,4 DTBP. The reaction was carried out at temperature of 80°C, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The agitation speed increases from 200 rpm to 800 rpm. Selectivity of 2, 4 DTBP increases with time. The maximum selectivity of 2,4 DTBP obtained at 200 RPM while minimum selectivity obtained at 800 RPM. The maximum selectivity after 8 hr is 56.77% while minimum selectivity is 35.80%.

Conclusion

From the experiment conducted, 200 RPM considered as optimum speed of agitation because of following reasons

1. Highest conversion of phenol obtained
2. High selectivity of 2,4 DTBP
3. High Di-alkylation
4. Low selectivity of o-TBP and p-TBP.

3.2 Effect of Reaction Temperature

3.2.1 Conversion of Reactant

The effect of Temperature on the conversion of phenol.The reaction was carried out at speed of agitation of 200 rpm, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reaction temperature was varied from 60°C to 100°C. The conversion continuously increases up to 6 hr, after that rate of conversion decreases. The maximum conversion obtained after 8 hr at 80°C. While the least conversion obtained after 8 hr at 60°C. The conversion at temperature 70°C and 90°C is approximately same while at 100°C least conversion of phenol obtained due to vaporization of TBA after 80°C.

3.2.2 Selectivity of products

- Selectivity of o-TBP

The effect of reaction temperature on the selectivity of o-TBP. The reaction was carried out at speed of agitation of 200 rpm, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reaction temperature was varied from

60°C to 100°C. Increase in temperature results in decrease in the selectivity of the o-TBP. The selectivity of o-TBP after 8 hr is maximum at 60°C while minimum at 70°C. The selectivity of o-TBP continuously decreases due to Di-alkylation. The maximum selectivity of o-TBP is 59.146% while minimum selectivity is 36.62%

- Selectivity of p-TBP.

The effect of reaction temperature on the selectivity of p-TBP. The reaction was carried out at speed of agitation of 200 rpm, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reaction temperature was varied from 60°C to 100°C. Selectivity of o-TBP remains approximately constant at all temperature leaving 60°C. The maximum selectivity of p-TBP after 8 hr is 23.6%. The selectivity of p-TBP is zero for first 2 hr and then gradually increases up to 4 hr, after that it remains constant. This is due to only formation of o-TBP in first 2 hr of reaction.

- Selectivity of 2, 4- DTBP

The effect of reaction temperature on the selectivity of 2, 4 DTBP. The reaction was carried out at speed of agitation of 200 rpm, 1:2 molar ratio of phenol to Tertiary butyl alcohol and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reaction temperature was varied from 60°C to 100°C. The maximum selectivity of 2,4 DTBP obtained at 80°C, while the selectivity 17.23% at 60°C temperature.

Conclusion:

From the experimental data, 80°C considered as the optimum temperature for the system because of the following reasons

1. Highest conversion to Phenol.
2. Highest selectivity of 2,4- DTBP
3. Highest dialkylation

3.3 Effect of change in concentration of Reactant.

3.3.1 Conversion of phenol

The effect of reactant concentration on the conversion of phenol. The reaction was carried out at speed of agitation of 200 rpm, and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reactant molar ratio of phenol to tertiary butyl alcohol was varied from 1:2 to 1:5. Concentration of Tertiary butyl alcohol increases from 1:2 to 1:3, the conversion of phenol increases, but above it the concentration continuously decreases due to dilution of catalyst. Thus the maximum conversion of phenol obtained at 1:3 ratio phenol to Tertiary butyl alcohol is 68.67%.

3.3.2 Selectivity of products

- Selectivity of o-TBP

The effect of concentration of reactant concentration on the selectivity of o-TBP. The reaction was carried out at speed of agitation of 200 rpm, and 1:1 catalyst loading of Phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reactant molar ratio of Phenol to tertiary butyl alcohol was varied from 1:2 to 1:5. For the entire molar ratio it is observed that, selectivity of o-TBP decreases with the time.

This is due to di-alkylation of o-TBP to 2, 4-DTBP. The minimum selectivity of o-TBP observed at 1:3 molar ratio of Phenol to TBA, while maximum selectivity observed at 1:2 molar ratios. The selectivity at molar ratio 1:4 and 1:5 is high in first two hours, but it decreases rapidly due to di-product formation.

- Selectivity of p-TBP

The effect of reactant concentration on the selectivity of p-TBP. The reaction was carried out at speed of agitation of 200 rpm, and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reactant molar ratio of phenol to tertiary butyl alcohol was varied from 1:2 to 1:5. The selectivity of p-TBP continuously decreases with time at all the reactant concentration. It happens due to di-alkylation of mono-products. Due to less formation of p-TBP compare to o-TBP its rate of decrease in selectivity is less. The maximum selectivity of p-TBP is observed at 1:5 molar ratio of phenol to TBA, while minimum selectivity observed at 1:3 molar ratio of phenol to TBA.

- Selectivity of 2, 4-DTBP

The Effect of reactant concentration on the selectivity of 2,4-DTBP. The reaction was carried out at speed of agitation of 200 rpm and 1:1 catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid). The reactant molar ratio of phenol to tertiary butyl alcohol was varied from 1:2 to 1:5. Selectivity of 2,4-DTBP increases with time. The maximum selectivity of 2,4- DTBP obtained at 1:3 molar ratio of phenol to TBA. While the minimum selectivity obtained at 1:2 molar ratio of phenol to TBA. Above 1:3 molar ratio, the selectivity does not increase due to dilution of catalyst by TBA.

Conclusion:

From the experiment conducted, 1:3 molar ratio of phenol to TBA considered as optimum molar ratio because of following reasons

1. Highest conversion of phenol
2. Maximum formation of 2,4 DTBP
3. Highest di-alkylation.
4. Minimumselectivityofo-TBPandp-TBP

3.4 Effect of catalyst loading

3.4.1 Effect of catalyst loading on phenol conversion.

The effect of catalyst loading on the conversion of phenol. The reaction was carried out at speed of agitation of 200 rpm, 1:3 molar ratio of phenol to Tertiary butyl alcohol and the temperature of 80°C. Catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid) varied from 1:0.2 to 1:1. Maximum conversion obtained at 1:0.5 catalyst loading phenol to ionic liquid while minimum conversion obtained at 1:0.2 catalyst loading.

3.4.2 Selectivity of products

- Selectivity of o-TBP

The effect of Catalyst loading on the selectivity of o-TBP. The reaction was carried out at speed of agitation of 200 rpm, 1:3 molar ratio of phenol to Tertiary butyl alcohol and the temperature of 80°C. Catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid) varied from 1:0.2 to 1:1. At all the catalyst loading selectivity of o-TBP decreases with time. The maximum selectivity of o-TBP obtained at 1:0.2 molar ratio of phenol to ionic liquid, causes dilution of catalyst. Weak acid favours the formation of o-TBP. Thus selectivity is maximum at 1:0.2 molar ratio compare to other ratios. The minimum selectivity of o-TBP obtained at 1:0.5 molar ratio of phenol to ionic liquid because of good poly-alkylation of o-TBP.

- Selectivity of p-TBP

The effect of catalyst loading on the selectivity of p-TBP. The reaction was carried out at speed of agitation of 200 rpm, 1:3 molar ratio of phenol to Tertiary butyl alcohol and the temperature of 80°C. Catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid) varied from 1:0.2 to 1:1. The selectivity of p-TBP continuously decreases with time at all catalyst loading, due to Di-alkylation of p-TBP. The selectivity of p-TBP is maximum at 1:0.2 molar ratio of phenol to TBA, while minimum at 1:0.5.

- Selectivity of 2,4-DTBP

The effect of catalyst loading on the selectivity of 2, 4-DTBP. The reaction was carried out at speed of agitation of 200 rpm, 1:3 molar ratio of phenol to Tertiary butyl alcohol and the temperature of 80°C. Catalyst loading of phenol to Ionic liquid (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid) varied from 1:0.2 to 1:1. With time the selectivity of 2, 4-DTBP increases. The maximum selectivity of 2,4 -DTBP obtained at 1:0.5 molar ratio of phenol to ionic liquid, while the minimum selectivity obtained at 1:0.2 molar ratio of phenol to ionic liquid.

Conclusion:

From the experiment conducted, catalyst loading of 1:0.5 considered as optimum because of following reasons

1. Higher conversion of phenol
2. Highest selectivity of 2,4 DTBP
3. Less formation of monoproducts

IV. CATALYST REUSABILITY.

In order to examine the recoverability and recyclability of the ionic liquid, after the reaction, the ionic liquid was extracted with toluene and water then dried under vacuum for 5 h. After vacuum drying, IL-1 was repeatedly used 4 times without significant decrease in phenol conversion as well as desired product selectivity is also not been affected much, as shown in Table 3.2.

Experimental run	**Conversion of phenol (%)**	**Selectivity (%)**		
		2-TBP	**4-TBP**	**2,4-TBP**
Fresh catalyst	78.1	13.79	10.9	75.29
Recycle 1	77.39	13.99	11.16	74.84
Recycle 2	77.29	13.69	11.11	75.13
Recycle 3	77.12	13.91	11.41	74.66
Recycle 4	76.67	13.57	10.91	75.5

Table 3.2 Catalyst reusability

V.CONCLUSIONS

1. Better selectivity of 2,4-DTBP is observed using laboratory synthesized IL (1-(4-sulfonic acid) butyl triethylammonium p-toulene sulfonic acid.

2. Reaction occurs at mild acidic condition and lower temperature at 80°C
3. Di-alkylated product i.e. 2,4-ditertbutylphenol is selectively formed in higher concentration as compared to mono-products. And very negligible formation of 2,6-ditertbutylphenl is observed.
4. Optimum condition is at 80°C, 1:3:0.5 molar ration of Phenol: TBA: IL, 8 hr.
5. Reaction is pseudo 2nd order with respect to phenol and TBA.

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