

Catalytic oxidation of 1,3-diisopropylbenzene using imidazolium ionic liquid as catalyst

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Abstract—Peroxidation of alkylaromatics is the key step in the synthesis of phenols. Different imidazolium ionic liquids were investigated for the oxidation of cumene. The selectivity of cumene hydroperoxide (CHP) increased with different ionic liquids in the order $[C_4mim]Cl < [C_4mim]Br < [C_4mim]BF_4 < [C_4mim]OH$. This finding could be interpreted as being due to the partial decomposition of CHP by the acidic proton of the imidazolium cation. Thus $[C_4mim]OH$ was chosen as the catalyst for the oxidation of 1,3-diisopropylbenzene to corresponding hydroperoxides and its derivatives. The catalytic performance of $[C_4mim]OH$ was also better than that of the traditional catalyst NaOH. Furthermore, the effects of the operating variables were investigated and the mechanism was discussed.

Key words: Catalysis, Ionic Liquid, 1,3-Diisopropylbenzene, Hydroperoxide, Oxidation

INTRODUCTION

Phenols are an important class of compounds needed for the synthesis of dyes, pharmaceuticals and polymers. The phenol synthesis through cumene hydroperoxide obtained by the aerobic oxidation of isopropylbenzene is well known as the Hock process, which is one of the main industrial chemical processes and has replaced traditional processes, such as the alkaline fusion of benzenesulfonic acid. So, hydroperoxides are important precursors for the synthesis of phenols.

Analogous methodology has been applied to the production of diphenols, such as resorcinol from 1,3-diisopropylbenzene (DIPB) and 2,6-naphthalenediol from 2,6-diisopropyl-naphthalene. In the oxidation of cumene a higher selectivity is achieved by keeping the conversion low, since cumene hydroperoxide can be easily separated from cumene through flash column [1]. However, a partial conversion of DIPB yields a mixture of mono- and dihydroperoxides, whose separation is more difficult. The dihydroperoxides were recovered by extraction of the oxidation products with an aqueous sodium hydroxide solution [2,3]. And only a complete oxidation of both isopropyl groups allows the industrial application of this process. Thus, the benzene sulfonation process is still competitive with the peroxidation process. However, the benzene sulfonation process forms 2.47 kg of sodium sulfite per kg of resorcinol [4]. Compared with the traditional processes, peroxidation is featured by low pollution and 100% utilization of reactant atoms. In other words, the peroxidation process is an ideal green synthesis route.

Peroxidation of alkylaromatics is the key step to synthesis of phenols. Alkali solutions, such as NaOH, are traditionally used for the oxidation of alkylbenzene to the corresponding hydroperoxides [5]. Recently, some attempts have been tried to improve the industrial peroxidation of both isopropyl groups by the catalysis of N-hydroxyphthalimide (NHPI) [6-11].

It is obvious that the low solubility of NHPI in alkylaromatics

would not allow high conversion. Therefore, the solvents with high polarity, such as CH_3CN , should be used to improve the catalytic performance.

Recently, ionic liquids have attracted increasing interest in the context of green synthesis. Although ionic liquids were initially introduced as alternative green reaction media because of their unique chemical and physical properties of nonvolatility, nonflammability, thermal stability and controlled miscibility, nowadays they have marched far beyond this border showing their significant role in controlling the reaction as catalysts [12-19]. Room temperature ionic liquids include acidic, neutral and basic ionic liquids. The acidic and neutral ionic liquids have been well recognized and successfully applied in many organic reactions [20-26]. The related report about the basic ionic liquids focused on Michael addition [27-29]. The application for others was rare.

In this paper, we first report the good performance of basic ionic liquid as the catalyst in oxidizing DIPB.

EXPERIMENTAL SECTION

1. Preparation of Ionic Liquids

The ionic liquids including 1-*n*-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$), 1-*n*-butyl-3-methylimidazolium bromide ($[C_4mim]Br$), 1-*n*-butyl-3-methylimidazolium tetrafluoroborate ($[C_4mim]BF_4$), 1-*n*-butyl-3-methylimidazolium hexafluorophosphate ($[C_4mim]PF_6$),

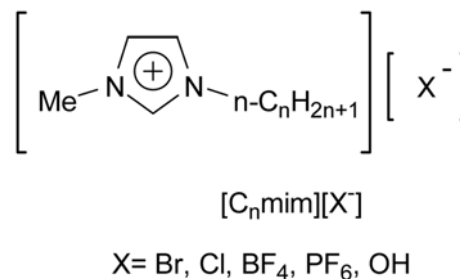


Fig. 1. Structure of imidazolium ionic liquids.

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1-*n*-butyl-3-methylimidazolium hydroxide ([C₄mim]OH), 1-ethyl-3-methylimidazolium hydroxide ([C₂mim]OH), 1-*n*-hexyl-3-methylimidazolium hydroxide ([C₆mim]OH), 1-*n*-octyl-3-methylimidazolium hydroxide ([C₈mim]OH) were synthesized according to the procedures described in the literature [27,30,31]. The structure of imidazolium ionic liquids is shown in Fig. 1.

2. General Procedure for the Oxidation Reaction

Cumene was oxidized in a 100 ml three-necked flask supplied with a mechanical stirrer with a rotation counter, the bubbler, reflux condenser and the oil bath. Cumene was placed in the reactor, heated to 90 °C. After that the catalyst was added and the air was passed through. The stir speed was above 1,000 r/min.

The oxidation method of DIPB was similar to that of cumene except that the reaction temperature was different. The oxidation of DIPB was carried out at 95 °C.

3. Analysis of Products

The oxidation products were analyzed on VARIAN PROSTAR 330 HPLC. HPLC analyses were conducted utilizing a photo diode

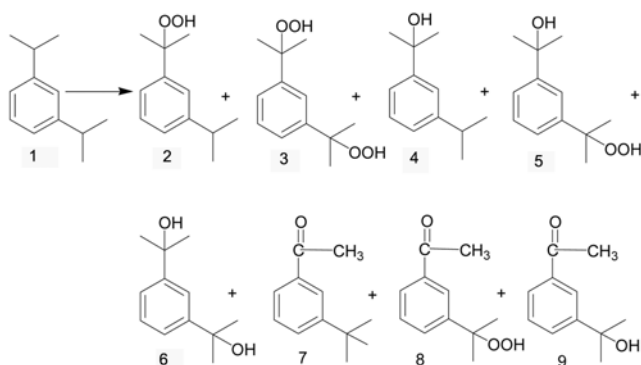


Fig. 2. The main products of the oxidation of 1,3-diisopropylbenzene.

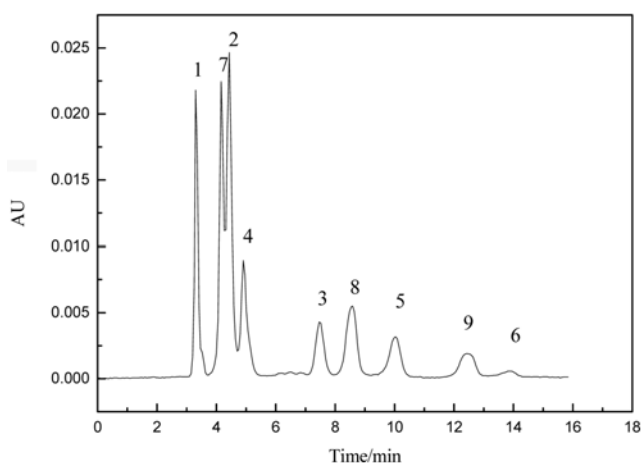


Fig. 3. Typical HPLC chromatogram of the oxidation products of 1,3-diisopropylbenzene.

Peaks: 1=1,3-diisopropylbenzene; 2=1,3-diisopropylbenzene monohydroperoxide; 3=1,3-diisopropylbenzene dihydroperoxides; 4=1-isopropyl-3-(2-hydroxy-2-propyl)-benzene; 5=1-(2-Hydroperoxy-2-propyl)-3-(2-hydroxy-2-propyl)-benzene; 6=1,3-Bis(2-propanol)benzene; 7=1-acetyl-3-isopropyl-benzene; 8=1-acetyl-3-(2-hydroperoxy-2-propyl)-benzene; 9=1-acetyl-3-(2-hydroxy-2-propyl)-benzene.

Table 1. External standard calibration: Linear regression ($Y=f_0+f_1X$) by least-squares method for a plot of peak area versus mass injected^a

Compound	f_0	f_1	Correlation coefficient	Recovery rate
Cumene	34990	4.007×10^8	0.99946	99.26%
Acetophenone	-141464	2.719×10^9	0.99935	98.91%
Cumene hydroperoxide	43993	3.277×10^8	0.99968	99.04%
2-Phenyl-2-propanol	-17792	3.273×10^8	0.99966	99.09%

^aNumber of calibration points for each compounds, $n=5$; Number of replicates of each injection, $m=5$

Table 2. External standard calibration: Linear regression ($Y=f_0+f_1X$) by least-squares method for a plot of peak area versus mass injected^a

Compound	f_0	f_1	Correlation coefficients	Recovery rate
DIPB	-65347.40722	376826000	0.99952	99.76%
DCL	-95228.37604	262136000	0.99946	99.53%

^aNumber of calibration points for each compounds, $n=5$; Number of replicates of each injection, $m=5$

array (PDA) detector and 25 cm×4.6 mm stainless-steel column filled with InterSil (5 μm). Compounds were detected at 257 nm. The mobile phases were *n*-hexane-isopropanol mixture (95 : 5, v/v) at a flow-rate 1 ml/min for DIPB. The ratio of *n*-hexane/isopropanol was changed to 97 : 3 (v/v) for cumene.

The main oxidation products of DIPB are shown in Fig. 2. The samples of the oxidation products were collected from the outlet of the detector of HPLC for several times, respectively. Then the samples were concentrated and identified by LC-MS. The typical HPLC chromatogram of the oxidation products of DIPB is presented in Fig. 3.

The yields of the products were estimated from the peak areas based on the external standard technique. The results of the external standard calibration for cumene are summarized in Table 1. The structure of 1,3-diisopropylbenzene dihydroperoxides (DHP) is similar to that of 1-(2-Hydroperoxy-2-propyl)-3-(2-hydroxy-2-propyl)-benzene (HHP) and 1,3-Bis(2-propanol)benzene (DCL). And their spectrum properties are similar. Therefore, DCL was chosen as the standard sample for the external standard calibration of DHP and HHP. The results can be seen in Table 2.

RESULTS AND DISCUSSIONS

1. Effect of the Anion

Cumene was chosen as a model to investigate the effect of different ionic liquids on the oxidation. Alkylbenzene hydrocarbons with an isopropyl group are oxidized with O₂ in the liquid-phase according to the widely known free-radical mechanism as presented in Scheme 1. The products of the cumene oxidation were acetophenone, 2-phenyl-2-propanol and cumene hydroperoxide (CHP). The results are shown in Table 3.

It is obvious that the conversion and selectivities using [C₄mim]

Table 3. Effect of different ionic liquids on the oxidation of cumene^a

Ionic liquids	Conversion (%)	Selectivity (%)		
		Acetophenone	CHP	2-Phenyl-2-propanol
--	7.7	3.4	91.5	5.1
[C ₄ mim]Cl	59.1	11.5	28.2	60.3
[C ₄ mim]Br	64	9.6	37.1	53.3
[C ₄ mim]BF ₄	44.5	6.4	56.4	37.2
[C ₄ mim]PF ₆	7.8	3.5	90.6	5.9
[C ₄ mim]OH	50.3	2.7	68	29.3

^aReaction conditions: n (cumene)=0.35 mol, n (ionic liquids)=0.0015 mol, air flow=160 ml/min, CHP (as initiator)=0.8 g, T=90 °C, time=10 h

PF₆ as catalyst were almost as the same as that of the blank experiment. At this reaction condition, [C₄mim]PF₆ had little influence on the oxidation. The selectivity of CHP increased with different ionic liquids in the order [C₄mim]Cl<[C₄mim]Br<[C₄mim]BF₄<[C₄mim]OH. The conversion and the selectivity of CHP were 50.3% and 68%, respectively. It is well known that the hydrogen at the C(2) position of the imidazolium ring is acidic [32]. This finding could be interpreted as being due to the partial decomposition of CHP by the acidic proton. So the basic ionic liquid [C₄mim]OH could improve the selectivity of CHP.

2. Effect of the Alkyl of the Imidazolium Ring

In section 3.1, it was found that the basic ionic liquid [C₄mim]OH exhibited a good performance for the oxidation of cumene. To improve the selectivity of CHP further, the effect of the alkyl of the imidazolium ring on the oxidation was investigated. The results are listed in Table 4. The alkyl chain was changed from C2 to C8; however, the selectivity of CHP was not improved accordingly. Thus, the alkyl chain had no influence on the oxidation.

3. Comparison of [C₄mim]OH with the Traditional Catalyst NaOH

Based on the results above, [C₄mim]OH was chosen as the catalyst for the oxidation of DIPB. To investigate the catalytic performance, [C₄mim]OH was compared with the traditional catalyst NaOH. As we all know, only a complete oxidation of both isopropyl groups of DIPB allows the industrial application of this process to produce resorcinol. The HHP and DCL can be oxidized to DHP by H₂O₂

Table 4. Effect of alkyl of the imidazolium ring on the oxidation of cumene^a

Ionic liquids	Conversion (%)	Selectivity (%)		
		Acetophenone	CHP	2-Phenyl-2-propanol
[C ₂ mim]OH	49.2	3.0	67.1	29.9
[C ₄ mim]OH	50.3	2.7	68	29.3
[C ₆ mim]OH	51.4	2.7	67.8	29.5
[C ₈ mim]OH	49.6	2.3	68.2	29.5

^aReaction conditions: n (cumene)=0.35 mol, n (ionic liquids)=0.0015 mol, air flow=160 ml/min, CHP (as initiator)=0.8 g, T=90 °C, time=10 h

Table 5. The oxidation of DIPB by [C₄mim]OH compared with NaOH^a

Catalyst	Conversion (mol%)	Yield (mol%)	
		DHP	DHP+HHP+DCL
NaOH ^b	56	8	10
NaOH ^c	85	27	34
[C ₄ mim]OH ^d	98	28	75

^a1,3-diisopropylbenzene (123 mmol) was oxidized by air (1 atm) at 95 °C. Cumene hydroperoxide (2.6 mmol) was added as the initiator at the beginning. Air flow was 160 ml/min

^bFor 28 h. NaOH (1.5 mmol). NaOH_{aq} (2 wt%) was used

^cFor 45 h. The amount of NaOH was as the same as [b]

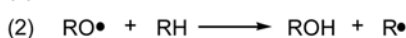
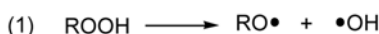
^dFor 28 h. [C₄mim]OH (1.5 mmol)

with H₂SO₄ as the catalyst [33]. So, the total yield of DHP, HHP and DCL was very important. The results are summarized in Table 5.

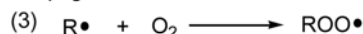
After reaction for 28 h in the presence of NaOH, the conversion was 56%, and the total yield of DHP, HHP, DCL was 10%. Compared with [C₄mim]OH, the conversion and yield were much lower in this case. A large amount of mono-hydroperoxide remained in the oxidation system. When the oxidation was performed for 45 h, the conversion and yield were increased, but they were still lower than those of [C₄mim]OH.

The oxidation rate was much faster with [C₄mim]OH as catalyst than that of using NaOH. Two mechanisms are generally involved in catalyzed aerobic oxidations: (1) the oxygenation of the compounds by O₂ through chain processes, in which the catalyst takes part in both the initiation and propagation steps; (2) the direct oxidation of the organic compounds by the catalysts, which are then regenerated by O₂ [10]. The observation may be attributed to the participation of the catalyst [C₄mim]OH in both the initiation and propagation steps (Scheme 1). The tertiary C-H of cumene could be activated via the interaction between cumene with the cation of the ionic liquids. On the other hand, the CHP may be decomposed by the ionic liquids to form cumylhydroxy radical. Thus, the oxi-

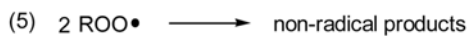
Initiation



Propagation



Termination



Degenerate chain branching



β-scission

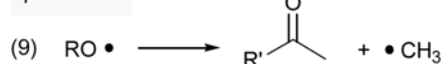
**Scheme 1. Oxidation mechanism of alkylbenzene hydrocarbons.**

Table 6. Oxidation of DIPB with air by [C₄mim]OH under various conditions^a

Run	[C ₄ mim]OH (mol%) ^b	Air flow (ml/min)	Conversion (mol%)	Yield (mol%)	
				DHP	DHP+HHP+DCL
1	0.26	160	73	22	37
2	0.52	160	98	34	69
3	1.25	160	98	28	75
4	2.5	160	98	26	81
5	1.25	40	90	23	47
6	1.25	100	98	27	76
7	1.25	300	98	27	76
8 ^c	1.25	160	97	29	64
9 ^d	1.25	160	99	0	4.75
10 ^e	1.25	160	90	18	53
11 ^f	1.25	160	99	30	83

^a1,3-diisopropylbenzene (123 mmol) was oxidized by air (1 atm) with [C₄mim]OH as catalyst at 95 °C for 28 h. Cumene hydroperoxide (2.6 mmol) was added as the initiator at the beginning. Air flow was 160 ml/min

^bBased on 1,3-diisopropylbenzene used

^cAt 80 °C

^dAt 105 °C. Hydroperoxides were converted to ketones

^eAt 105 °C for 10 h

^fFor 45 h

dation rate was increased by the ionic liquids.

4. Effect of the Oxidation Conditions

The results of the effect of the oxidation conditions on the oxidation are shown in Table 6. The yield of DHP was up to 34% in the case of [C₄mim]OH (0.52 mol%) as the catalyst. However the total yield of DHP, HHP and DCL increased with the amount of [C₄mim]OH (run 1–4). The total yield was 81% under the catalysis of [C₄mim]OH (2.5 mol%). It can be seen that the best air flow was 160 ml/min (run 3, 5–7). When the air flow reached 100 ml/min, little influence of the further increase of air flow on the yield was observed. We next examined the effect of temperature (run 3, 8, 9). Hardly any DHP was found at 105 °C for 28 h, and the total yield of DHP, HHP and DCL was also very low. When DIPB was oxidized at 105 °C for 10 h, the conversion was already 90%. The reaction rate of DIPB increased with temperature. At the same time hydroperoxides were decomposed to cumylhydroxy radical. Cumylhydroxy radical can form cumyl alcohol by abstracting hydrogen atom from 1,3-diisopropylbenzene (Eq. (2) in Scheme 1). And cumylhydroxy radical can also form acetophenone through β -scission (Eq. (9) in Scheme 1). Temperature affects unimolecular (Eq. (9)) more than bimolecular (Eq. (2)) reactions; an increase in temperature favors β -scission [4]. Therefore, the yields of hydroperoxides were very low at 105 °C. The oxidation at 95 °C gave better total yield of DHP, HHP and DCL. The yield of the three products, namely DHP, HHP, and DCL, reached 83% when the oxidation reaction time was 45 h (run 11).

CONCLUSION

Basic ionic liquid [C₄mim]OH was first used as a catalyst for the

oxidation of cumene and DIPB. The catalytic performance increased in the order [C₄mim]PF₆ < [C₄mim]Cl < [C₄mim]Br < [C₄mim]BF₄ < [C₄mim]OH. The [C₄mim]OH exhibited better catalytic performance than the conventional catalyst NaOH. The conversion and the yield of DHP, and DHP+HHP+DCL were 56%, 8% and 10%, respectively, in the presence of NaOH. For [C₄mim]OH, they were 98%, 28% and 75%, respectively, at the same conditions. The yield of DHP and its derivatives reached 81% when the DIPB was oxidized with 2.5 mol% [C₄mim]OH at 95 °C for 28 h. The increase of the oxidation rate can be explained by the participation of [C₄mim]OH in both the initiation and propagation steps of the reaction mechanism.

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