

Alcohol Oxidation in Ionic Liquid with UHP and Recyclable Amberlite IR-120 Acidic Resin: A Green Approach

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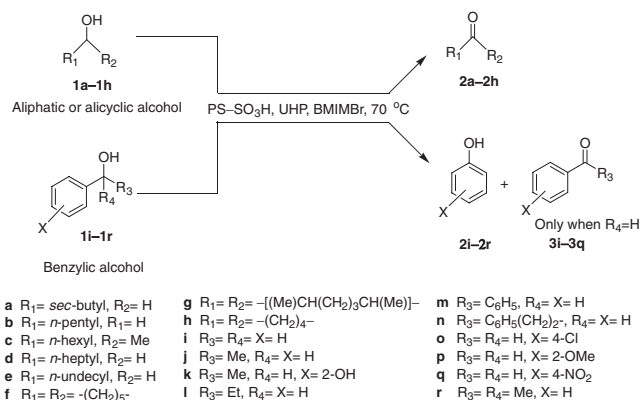
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Amberlite IR-120 acidic resin, an age old polymer matrix, plays a significant role as catalyst in the oxidation of aromatic alcohols with urea-hydrogen peroxide in ionic liquid at 70 °C to disproportionate into phenols and carbonyl compounds in 30–60 min following two pathways. Under similar condition tertiary aromatic alcohol gave exclusively monohydroxyphenol accompanied by acetone. However, aliphatic and alicyclic alcohols yielded carbonyl compounds in moderate to good yields in 1–5 h.

The development of new catalytic methods without use of any metal catalyst and toxic organic solvents with efficient recycling of catalyst avoiding stringent reaction conditions is a *conditio sine quo non* in chemical research for economically and environmentally attractive processes world wide. Oxidative transformation of alcohols to carbonyl and other industrially important molecules such as phenols is one such attractive area due to the wide ranging utility of these products as precursors and intermediates for many drugs, resins, vitamins, fragrances, plasticizers, pharmaceuticals, disinfectant, bis-phenol A, and other uses. Apart from the conventional methods,^{1–5} there have been several reports for preparation of such oxidative products using oxygen or hydrogen peroxide as the oxidants under the influence of different metal catalysts.^{6–10} On the other hand, phenol is generally prepared by indirect three steps cumene process in which benzene and propylene are first reacted to form cumene which is oxidized with oxygen to hydroperoxide under high temperature and pressure. Hydroperoxide thus formed was then treated with sulfuric acid to form phenol and acetone. Boger and Coleman¹¹ have however reported preparation of phenol through rearrangement of benzyl hydroperoxide as an alternative to the Baeyer–Villiger rearrangement. Incessant efforts have been reported,^{12,13} for direct hydroxylation of benzene either through liquid phase using hydrogen peroxide,^{14,15} or through gas phase using oxygen,¹⁶ in presence of different catalyst. However, success rate with considerable yield is very poor.

One of the strategic developments in organic synthesis is the use of reagents and catalysts which are bound to polymeric matrix insoluble in the reaction media so that it can be recycled.¹⁷ Organic reactions in green solvents such as water or ionic liquid using insoluble, recoverable, and reusable catalyst system are of high current interest.^{18,19} For polymer-supported catalysts that work efficiently in water or in ionic liquids, hydrophobic interactions between the polymer and the organic substrate play an important role in the catalytic activity.²⁰ Having encouraged by such ideas it was deemed desirable to use a hydrophobic polymer-supported catalyst in water or in an ionic liquid to carry out the transformation of alcohol to carbonyl compounds.

In the course of our study on the oxidation of 1-phenyletha-



Scheme 1. Alcohol oxidation with UHP in the presence of Amberlite sulphonic acid resin in ionic liquid (BMIMBr).

anol to carbonyl compounds with 50% hydrogen peroxide as an oxidizing agent in water in presence of polystyrene-supported sulphonic acid resin (Amberlite IRA-120), we found that phenol was formed in 66% isolated yield accompanied by minor amounts of acetophenone (10%) at 90 °C in 45 min (Scheme 1). However, the resin simultaneously underwent complete decomposition to form a clear aqueous solution inhibiting catalyst recycling. The degradation of the resin in 50% H₂O₂ solution also occurred in the absence of the alcohol when a blank reaction was carried out. We could not determine the fate of the decomposed resin in aqueous solution.

The reaction was then shifted to carry out with urea-hydrogen peroxide adduct instead of aqueous hydrogen peroxide. The reaction was studied in four different solvents viz. 1-butyl-3-methylimidazolium bromide, 1-butyl-3-methylimidazolium tetrafluoroborate, toluene, and 1,2-dichloroethane taking 1-phenylethanol as a substrate. The maximum yield was obtained when the reaction was carried out in the ionic liquid [BMIMBr] in which the resin remained intact. After completion of the reaction the insoluble resin catalyst and the ionic liquid were recovered by filtration and the resin was washed with dichloromethane (3 times). The recovered resin and the ionic liquid were reused for 5 times (Table 1) without any appreciable loss of activity to get similar yields. The reaction was then repeated with various aromatic, aliphatic, and alicyclic alcohols (Table 2). It was observed that both phenols and carbonyl compounds were formed from all the 1-phenyl-substituted alcohols **1i–1q** as the major and minor products respectively accompanied by 2–6% formaldehyde leaving behind the resin intact except for **1r** in which exclusively phenol and minor amount of acetone were formed. In case of alicyclic alcohols **1f–1h**, it was found the oxidized products to be exclusively corresponding ketones with good yields (75–81%). However, both primary and secondary

Table 1. Oxidation of 1-phenylethanol with UHP in the presence of recycled Amberlite IRA-120 resin at 70 °C for 30 min in BMIMBr^a

Run	1	2	3	4	5
Yield ^b /%	65	65	64	64	63

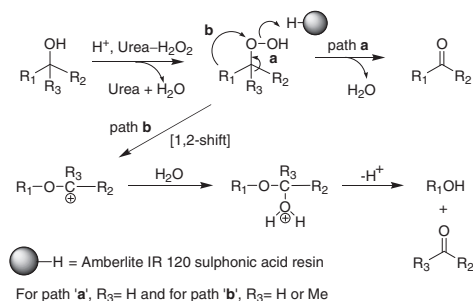
^aReaction conditions: as given in ref. 21. ^bYield of isolated phenol.**Table 2.** PS-SO₃H catalyzed oxidation of alcohols to phenols and carbonyl compounds in ionic liquid (BMIMBr) at 70 °C

Entry	Substrate	Phenol ^a (A)	Carbonyl ^a (B)	Time /min	Yield ^b /%	
					A	B
1	1a	—	2a	300	—	20
2	1b	—	2b	120	—	37
3	1c	—	2c	240	—	25
4	1d	—	2d	120	—	35
5	1e	—	2e	120	—	28
6	1f	—	2f	60	—	81
7	1g	—	2g	60	—	79
8	1h	—	2h	240	—	75
9	1i	2i	3i	30	59	27
10	1j	2j	3j	30	65	32
11	1k	2k	3k	55	45	20
12	1l	2l	3l	45	57	30
13	1m	2m	3m	40	58	30
14	1n	2n	3n	50	60	31
15	1o	2o	3o	40	52	17
16	1p	2p	3p	60	53	28
17	1q	2q	3q	35	51	18
18	1r	2r	—	40	70	—

^aProducts²¹ have been identified from their respective spectral (IR, ¹H NMR, ¹³C NMR, MS, GC), physical data and comparison with the reported values.^{22,23} ^bYields mentioned are the isolated yields.

open chain aliphatic alcohols **1a–1e**, although the oxidized products were found to be the corresponding carbonyl compounds, the yields were found to be poor (20–37%).

The mechanism of the reaction is uncertain. A plausible mechanism is that the reaction proceeds through two pathways “a and b” in case of the aromatic alcohols (Scheme 2). Initially the substrate aromatic alcohol in presence of UHP and the acidic resin forms a hydroperoxide. This hydroperoxide in the presence of the acidic resin partly follows the path “a” to form the ketonic products and partly follows the path “b” that involves a 1,2-shift of the good migrating phenyl group through subsequent hydrolysis to form phenol. The driving force of the

**Scheme 2.** A plausible mechanism of the alcohol oxidation.

reaction triggered by the acidic resin catalyst to release the proton at the hydroperoxide group bearing carbon to form the carbonyl compound through elimination of a water molecule via path “a” parallelly facilitates the migration of the phenyl group to the electron-deficient oxygen via path “b.” As a result, a mixture of phenols and carbonyls were isolated. However, lack of tertiary hydrogen atom in case of 2-phenyl-2-propanol (**1r**) pushed the reaction to follow the path “b” only to give monohydroxyphenol and acetone. Similarly, lack of good migrating groups in case of the open chain aliphatic and alicyclic alcohols **1a–1h** leads the reaction to follow the path “a” only.

In conclusion, a mild, efficient, green, and less energy intrinsic method has been developed for industrial synthesis of phenol and other important ketonic compounds exploiting a significant role of the acidic Amberlite resin using UHP as the oxidizing agent in ionic liquids. The resin and the ionic liquids used can be recycled several times without any appreciable loss of activity.²⁴

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- To a stirred solution of alcohol (10 mmol) and Amberlite IRA-120 resin (50 mg) in BMIMBr (3 g, 13.7 mmol), UHP (3 g, 32 mmol) was added and heated at 70 °C for 30–60 min for benzylic alcohols and 1–5 h for alicyclic and aliphatic alcohols. The products were extracted in dichloromethane and concentrated in rotavapor with simultaneous recovery of the resin and ionic liquid.
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