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Oxidation of alcohols with hydrogen peroxide catalyzed by a new imidazolium ion based phosphotungstate complex in ionic liquid

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Abstract

A new catalyst based on imidazolium and tungstate ion (tris(imidazolium)-tetrakis(diperoxotungsto)phosphate (3-)) has been synthesized and characterized by FT-IR spectroscopy. An efficient and environmentally friendly procedure is described for the catalyst recycling and easy product isolation for the oxidation of alcohols with hydrogen peroxide catalyzed by imidazolium ion-based phosphotungstate complex in ambient-temperature ionic liquid.

Keywords: Oxidation; H_2O_2; Ionic liquid; Alcohol; Green chemistry

1. Introduction

Carbonyl compounds constitute an important group of molecules in organic chemistry, as carbonyl groups are present as an essential constituent of pharmaceuticals, dyes, fragrances, industrially important chemicals, and natural products [1,2]. The oxidation of alcohols to the corresponding carbonyl groups is a fundamental transformation in organic chemistry and industrially important [3]. Because of the advantageous properties of hydrogen peroxide, a number of useful procedures have been developed for H_2O_2-mediated oxidation of alcohols catalyzed by tungsten systems such as tungstic acid [4], quaternary ammonium tetrakis(diperoxotungsto)phosphates [5], sodium tungstate + $[(n\text{-}C_4H_9)_4N]Cl$ [6], and sodium tungstate + quaternaryammoniumhydrogen sulfate [7]. These reported procedures have used chlorohydrocarbon as a solvent, and in most of the cases the catalyst was not recovered. The recent increased awareness of the detrimental effects of these organic solvents in the environment has led to rapid growth in the research on alternative reaction media. More attention is being given to the reusability of solvents and catalysts of the reaction systems for the development of cost-effective protocols.

There is considerable interest in the use of room temperature ionic liquids as promising substitutes for volatile organic solvents [8]. These ambient-temperature ionic liquids, especially those based on 1,3-dialkylimidazolium cations, have been emerging as promising green solvents in recent decades [9–11]. Their nonvolatile nature, without any detectable vapor pressure, gives them a significant advantage in minimizing solvent consumption. They have been employed as reaction media for several organic reactions, namely alkylation [12], hydrogenation [13], oxidation [14–16], and heterocyclization [17]. Because of their tunable polarity and hydrophobicity, they can solvate various organic, inorganic, and polymeric compounds, and have been used as green solvents for liquid–liquid separations, extractions, and recycling in homogeneous catalysis [18]. Here we report the synthesis of imidazolium-based phosphotungstate catalyst (**1**) and its catalytic function in the oxidation of alcohols with H_2O_2 in ionic liquid [bmim][BF_4] [19].

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$$Q^{+}{}_3[PO_4(W(O)(O_2)_2)_4]^{3-}$$

1: Q^{+}=

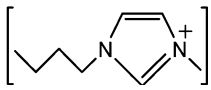


Fig. 1. Phosphotungstate catalyst **1**.

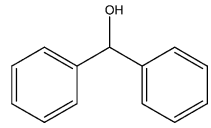
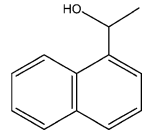
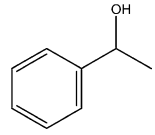
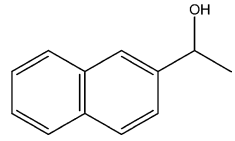
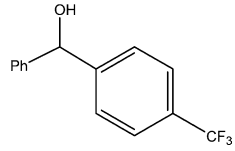
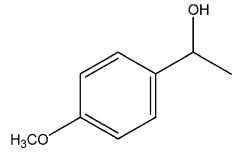
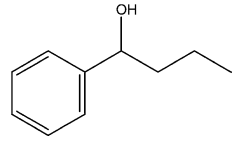
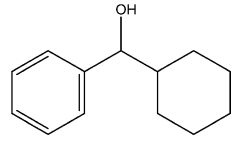
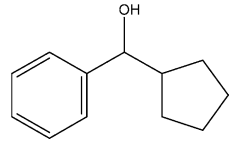
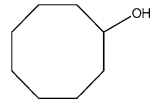
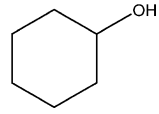
2. Experimental

All chemicals and reagents used in the present study were of analytical grade and procured from Sigma Aldrich and Spectrochem Pvt Ltd, India. Organic solvents were freshly distilled and purified before use. IR spectra were recorded on a FT-IR Perkin–Elmer Spectrum BX spectrophotometer with either NaCl plates or KBr pallets. NMR spectral characterization was carried out with a Bruker 300 MHz instrument operating near 300 (1H) and 100 (13C) MHz, with tetramethylsilane as an internal standard for the chemical shifts measurement. The FAB mass spectra were recorded from Central Drug Research Institute (Lucknow, India) on a Jeol SX 102/DA-6000 mass spectrometer with an *m*-nitrobenzyl alcohol matrix. Gas chromatographs were recorded with a Shimadzu GC-14B instrument, a flame ionization detector, and a Varian CP-Sil 5 CB capillary column and packed column, with nitrogen as the carrier gas. The required ionic liquid [bmim][BF_4] was prepared according to the reported procedure by the alkylation of 1-methylimidazole with 1-bromobutane followed by substitution of bromide anion with tetrafluoroborate in acetone [20]. [^{1}H NMR ($CDCl_3$, 300 MHz, δ ppm): 8.98 (s, 1H, C–2H), 7.49 (s, 2H, C–4H and C–5H), 4.21 (t, $J = 7.11$ Hz, 2H, $NCH_2CH_2CH_2CH_3$), 4.01 (s, 3H, NCH_3), 1.85 (p, $J = 7.20$ Hz, 2H, $–NCH_2CH_2CH_2CH_3$), 1.35 (sexet, $J = 7.20$ Hz, 2H, $NCH_2CH_2CH_2CH_3$), 0.91 (t, $J = 7.12$ Hz, 3H, $NCH_2CH_2CH_2CH_3$). ^{13}C NMR ($CDCl_3$, 75 MHz, δ ppm): 13.27, 19.23, 31.87, 36.13, 49.57, 122.49, 123.79 and 136.12.]

2.1. Synthesis of phosphotungstate complex *1*

Tungstic acid (5 g, 20 mmol) was added portion wise to a 30% solution of H_2O_2 (14 mL) with stirring and heated to 65 °C, and mixture was stirred for 2 h. The reaction mixture was filtered through a sintered funnel (G3). H_3PO_4 (0.6 mL of 80% sol., calc. 2.5 mmol) was added to the filtrate at room temperature. [bmim]Br (2.2 g, 2 mmol) in CH_2Cl_2 (20 mL) was added dropwise to the above solution. A brownish yellow solid separated out with shaking. The supernatant solvent was decanted away, and solid settled at the bottom was washed with water to obtain the light brownish yellow viscous solid product (4 g). [IR (KBr, cm^{-1}): 3435, 3152, 3096, 2921, 2858, 1626, 1560, 1458, 1348, 1167, 1094, 1082, 1023, 961, 872, 816, 737, 618, 523, 471.]

Table 1
Oxidation of secondary alcohols with H_2O_2 catalysed by **1** in ionic liquid

Entry	Substrate	Time (h)	Yield[a] (%)
1		2	98 (96)[b]
2		3	97
3		3	93
4		3	96
5		3	78
6		4	84
7		2	86
8		3	92
9		4	90
10		3	96
11		4	98

[a] Yield from GC.
[b] Yield in recovered ionic liquid and catalyst **1**.

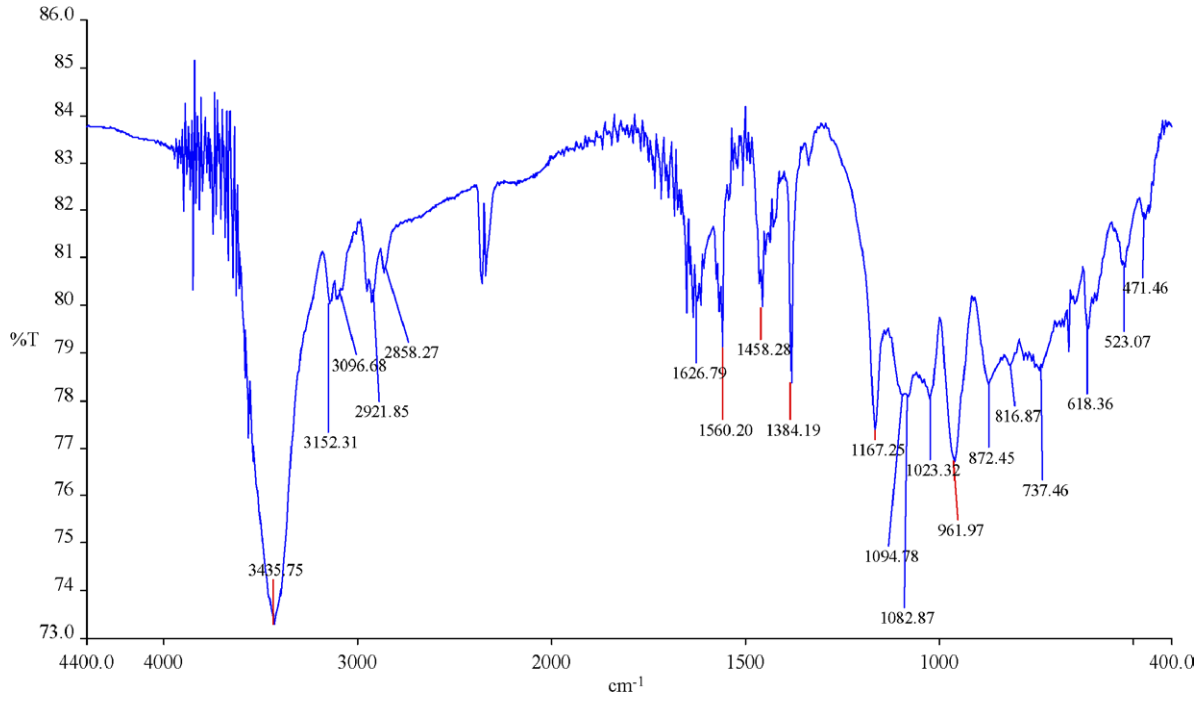
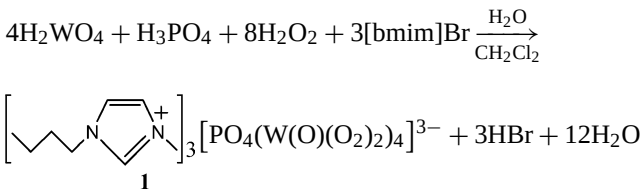
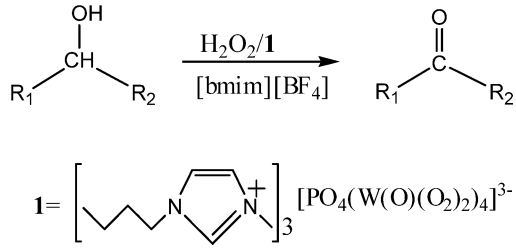


Fig. 2. FT-IR spectrum of catalyst **1**.



Scheme 1. Synthesis of catalyst **1**.



Scheme 2. Oxidation of alcohols with catalyst **1**.

2.2. General procedure for the oxidation of alcohols

Presaturated phosphotungstate catalyst **1** (0.05 mmol) was dissolved in the ionic liquid [bmim][BF_4] (3 mL) at 90 °C with stirring. Alcohol (1 mmol) was added, followed by the dropwise addition of H_2O_2 (1.5 mmol) with continuous stirring. After completion of the reaction, the reaction mixture was extracted with diethyl ether (4 × 1 mL), dried over Na_2SO_4, and concentrated to obtain the respective ketones in 82–98% yield (Table 1).

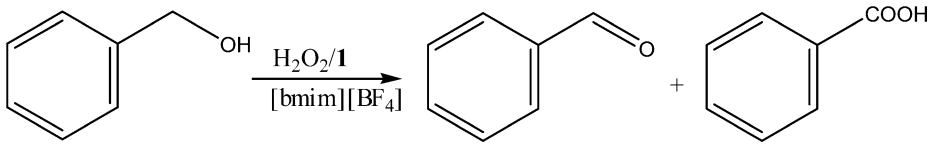
3. Results and discussion

The catalyst tris(imidazolium)-tetrakis(diperoxotungsto)-phosphate (3-) (**1**) was synthesized from tungstic acid, hydrogenperoxide, phosphoric acid, and 1-butyl-3-methylimidazolium bromide by slight modification of the reported procedure [21–23] (Scheme 1).

The catalyst was purified, and its structure was confirmed by FT-IR spectroscopic data (Fig. 2) (see Section 2). The absorption in the region 1050 (peaks at 1094, 1082, and 1023) were assigned to P–O stretching vibrations [24].[1] A strong peak at 961 indicated the presence of W=O, and peaks at 872, 816 (O–O) and 618 (W–O–O asym), 523 (W–O–O sym) confirmed the tungstate structure [22]. Absorption at 2921, 2858, 1560, and 1458 is due to an organic imidazolium moiety. Interestingly this phosphotungstate catalyst was found to be soluble in dimethylsulfoxide and ionic liquid [bmim][BF_4] and remained insoluble in most of the other laboratory solvents.

Catalyst **1** was dissolved in [bmim][BF_4] by simply mixing at ambient temperature, and oxidation of different alcohols was carried out in homogeneous medium. A mixture of diphenyl carbinol and **1** in [bmim][BF_4] was stirred for 120 min after the addition of hydrogen peroxide to give benzophenone in 98% yield. Similarly, oxidation of other secondary alcohols with H_2O_2 catalyzed by **1** in [bmim][BF_4] was carried out; the results are shown in Table 1. The ke-

[1] Peaks in the region of 1050 cm^{-1} has been observed with tungstophosphates.



Scheme 3. Oxidation of benzyl alcohol.

tones were extracted with diethyl ether from the ionic liquid after completion of the reaction, leaving behind the catalyst solubilized in ionic liquid.

Evaporation of diethyl ether gave respective ketones. Formation of product was confirmed by comparison of physical, spectroscopic data and GC retention time with those of authentic samples. All of the alcohols were converted to respective ketones in good to excellent yield. The yellowish brown ionic liquid and catalyst system left over after the extraction of ketones can be reused for further catalytic oxidation. Water formed as the only side product from hydrogen peroxide was removed under vacuum. The recovered system was found to have comparable activity up to three recycling experiments, with a slight decrease in yield of product in each cycle (Table 1, entry 1).

In the case of primary alcohols, oxidation in the presence of catalyst **1** under the same conditions as employed for the ketonization of secondary alcohols takes place to yield corresponding aldehyde and carboxylic acid, but with slow reaction rates. Benzyl alcohol (1 mmol) on oxidation with hydrogen peroxide (2 mmol of 30% aqueous solution) yielded benzaldehyde in good yield (78% yield by GC) in 8 h together with a modest amount of benzoic acid (Scheme 3).

With the increase in hydrogen peroxide to 4 equivalents, benzoic acid is obtained in good yield (96% conversion).

4. Conclusion

In summary, we present here a simple and efficient protocol for the oxidation of a variety of alcohols with ionic liquid [bmim][BF_4] as a solvent. The oxidation of alcohols with phosphotungstate complex (catalyst **1**) in ambient-temperature ionic liquid [bmim][BF_4] shares the advantage of a homogeneous reaction mixture, easy recovery of the catalytic system, excellent yield of the products, a small degree of consumption of the solvent, ready separation of the products, and recycling of the catalytic system without much decrease in the yield of the product.

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