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Selective Oxidation of Benzyl Alcohols by Hydrogen Peroxide under Phase Transfer Catalysis

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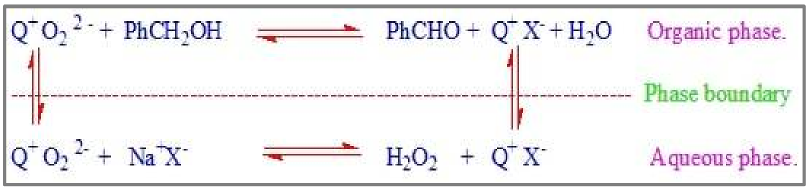
ABSTRACT

It reports the selective oxidation of benzyl alcohol and substituted benzyl alcohols in non-polar solvents like toluene and ethyl acetate using hydrogen peroxide as oxidant under phase transfer catalysis in presence of catalytic amount of sodium tungstate dihydrate. Tetrabutylammonium bromide, tetrabutylammonium hydrogen sulphate, tricaprylylmethylammonium chloride and Cetyltrimethyl ammonium bromide were used as phase transfer catalysts. The products of oxidation were characterized by melting point and infra-red and UV-Visible spectral techniques. Benzaldehyde and substituted benzaldehydes were formed in a selective manner with good yield (>85%) at room temperature and there were no traces of benzoic acid. All the catalysts were capable of bringing out the reaction but based on yield and ease of reaction, the order of reactivity is tricaprylmethyl ammonium chloride >Tetrabutylammonium bromide> tetrabutylammonium hydrogen sulphate > Cetyltrimethylammonium bromide. The selective oxidation of benzyl alcohols practically did not occur in non-polar organic solvents without the involvement of a phase transfer catalyst. The reaction is found to be very smooth in both the solvents namely ethyl acetate and toluene. But the yield of benzaldehydes is found to be more in ethyl acetate than that in toluene due to the difference in polarity.

Graphical Abstract



PT catalyzed oxidation of benzyl alcohol by peroxide ion in non-polar solvents.

Keywords: Selective oxidation, Benzyl alcohol, Benzaldehyde, Phase transfer catalysis

INTRODUCTION

Phase transfer catalysis (PTC) can be used to carry out a variety of chemical reactions under mild conditions with improved results. PTC technique is now utilized in many applications, from research in chemistry to full-scale synthetic production of chemicals like pharmaceuticals, fine chemicals, polymers, dyes etc. [1-4]. It is also of great significance to develop technological methods to minimize problems related to environmental pollution. PTC techniques are used in pollution prevention, pollution treatment and removal or destruction of impurities in waste and product streams. Cost reduction and pollution prevention are the two most powerful driving forces in the chemical industry today, and these can be achieved to a great extent by the PTC technique, if properly adopted.

Oxidation of organic compounds is very significant and found useful in chemical industries for the production of various commercial products. Most of the industrially important organic compounds like aldehydes, ketones, carboxylic acids etc. can be produced by the oxidation of related substrates by various oxidizing agents [5-7]. Permanganate, chromate, hypochlorite etc. are extensively used for the primary and secondary alcohol oxidation reactions in a selective manner to get corresponding aldehydes [8-13].

Excluding oxygen, H_2O_2 is the most valuable oxidant with an atom efficiency of 60 to 70 %, generating water as the only by-product. Lipophilic quaternary ammonium salts such as aliquat 336 or tetrabutylphosphonium bromide (TBPB) are capable to efficiently extract H_2O_2 from the aqueous to the organic phase, allowing fast oxidation reactions under PTC conditions. In some cases, the H_2O_2 oxidation processes are accelerated by the addition of molybdates or tungstates as co-catalysts. Even though sufficient reports are available on the selective oxidation of benzyl alcohol by chromate, hypochlorite, permanganate etc. in non-polar medium under PTC, such reports with hydrogen peroxide are scanty which prompted us to carry out this work [14-16].

The present paper reports the selective oxidation of benzyl alcohol and substituted benzyl alcohols to corresponding benzaldehydes by using various quaternary ammonium salts as phase transfer (PT) catalysts in various organic solvents like ethyl acetate and toluene by hydrogen peroxide in presence of catalytic amount of sodium tungstate. PT catalyst transfers the peroxide ion as an ion pair from the aqueous phase to organic phase and the oxidation occurs there with ease.

MATERIALS AND METHODS

Analar grade hydrogen peroxide (SRL, Mumbai) is used as such throughout the experiment. Benzyl alcohol (AR, SRL, Mumbai) was further purified by distillation under reduced pressure. All the substituted benzyl alcohols viz 4-chlorobenzyl alcohol, 3-chlorobenzyl alcohol,4-nitrobenzyl alcohol, 3-nitrobenzyl alcohol, 4-hydroxybenzyl alcohol, 3-hydroxybenzyl alcohol, 4-methylbenzyl alcohol, 4-methoxybenzyl alcohol and 3-methoxybenzyl alcohol (SRL, Mumbai, Merck, India) were used as such. The PT catalysts, tetrabutylammonium bromide (TBAB) (Spectrochem, Mumbai), Cetyl trimethylammonium bromide (CTMAB) (Spectrochem, Mumbai), tetrabutylammonium hydrogen sulphate (TBAHS) and tricaprylylmethylammonium chloride (TCMAC), (SRL, Mumbai) were used as such. Sodium tungstate dihydrate (Extra pure, AR 99%, SRL, Mumbai) is used as such. The organic solvents toluene and ethyl acetate were purified according to the standard procedure [17-18]. All the purified solvents were refluxed for 1-2 h with a mixture of PT catalyst and hydrogen peroxide and then distilled.

Synthetic analysis was carried out in a heterogeneous fashion. Benzyl alcohol (0.1 mol) and substituted benzyl alcohols were dissolved in 50 mL ethyl acetate or toluene which contains 0.01 mol PT catalyst was mixed with 50 mL H_2O_2 (0.5 mol) in presence of a pinch of sodium tungstate dihydrate. The mixture was stirred vigorously using a magnetic stirrer for about one hour at room temperature. The organic layer of the reaction mixture was extracted with ether three times. This organic layer was again extracted with 10% sodium bicarbonate and both organic and aqueous layers were separated. A saturated solution of 2, 4-dinitrophenylhydrazine in HCl was added to the organic layer and kept overnight in refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, recrystallized from ethanol, dried and weighed. The product was analysed with its melting point in triplicate and other qualitative analytical methods like infra-red and UV-Visible spectroscopy. The aqueous layer after extraction with sodium bicarbonate was acidified with concentrated HCl.

RESULTS AND DISCUSSION

The products in the form of 2, 4-dinitrophenyl hydrazone obtained on oxidation of benzyl alcohol and substituted benzyl alcohols have been recrystallised and the pure products were characterized by determining its melting point and is given in table 1.

Table 1. Melting point of products on oxidation of benzyl alcohol and substituted benzyl alcohols

S.No.	Substrate	Melting point of 2, 4-dinitrophenylhydrazone of product (^{0}C)
1	Benzyl alcohol	236 ± 2
2	4-chlorobenzyl alcohol	254 ± 2
3	3-chlorobenzyl alcohol	256 ± 2
4	4-nitrobenzyl alcohol	321 ± 2
5	3-nitrobenzyl alcohol	289 ± 2
6	4-hydroxybenzyl alcohol	273 ± 2
7	3-hydroxybenzyl alcohol	254 ± 2
8	4-methylbenzyl alcohol	232 ± 2
9	4-methoxybenzyl alcohol	253 ± 2
10	3-methoxybenzyl alcohol	251 ± 2

The infra-red absorption spectrum of the product on oxidation of benzyl alcohol was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in figure 1.

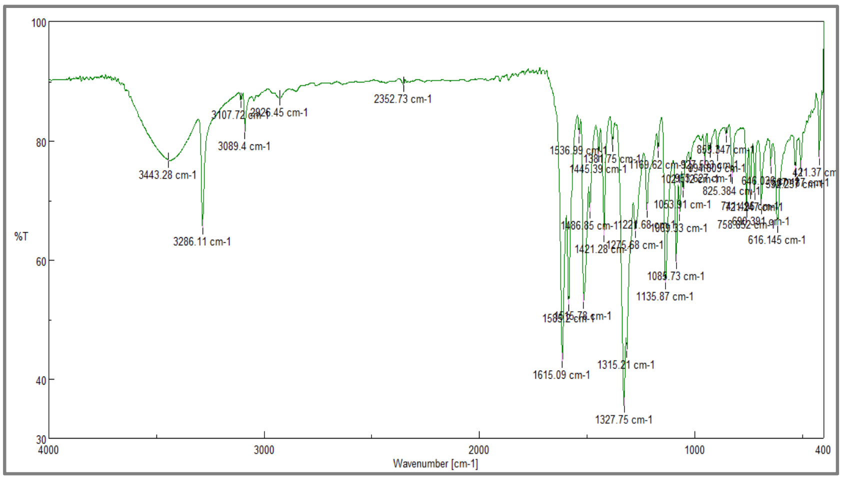


Figure 1. Infra-red spectrum of 2, 4- dinitrophenylhydrazone of product.

The IR spectrum of the product gave sharp peaks at 3287 cm^{-1} (N–H stretching), 3090 cm^{-1} (Aromatic C–H stretching), 1744 cm^{-1} (C=N stretching), 1620 cm^{-1} (C=C) stretching), 1516 cm^{-1} (Ar–NO$_2$ asymmetric stretching), 1329 cm^{-1} (Ar–NO$_2$ symmetric stretching), and 1136 cm^{-1} (C–NH stretching). These peaks shown by the product support the formation of be2,4-dinitrophenylhydrazone of benzaldehyde. More over this spectrum was compared with that of 2, 4-dinitrophenylhydrazone of pure benzaldehyde and found to have excellent similarities.

The UV-Visible absorption spectrum of the product obtained on the oxidation of benzyl alcohol was recorded by Hitachi U-3000 UV-Visible spectrophotometer using 1 cm quartz cell and spectrograde ethanol (Merck, India) as solvent and is given in figure 2.

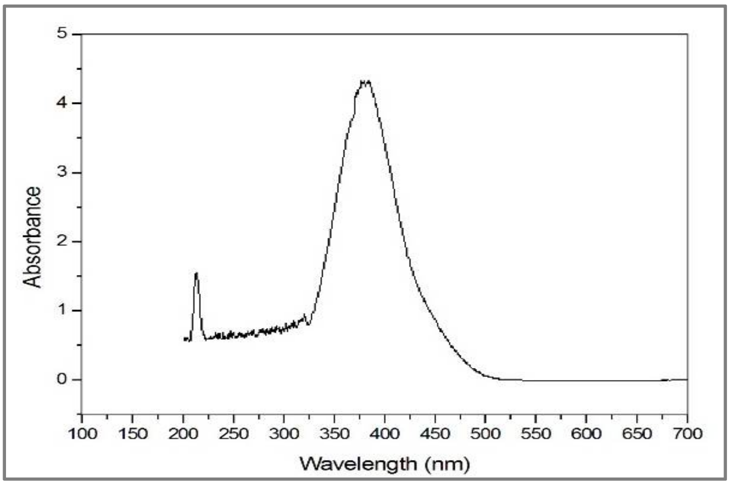


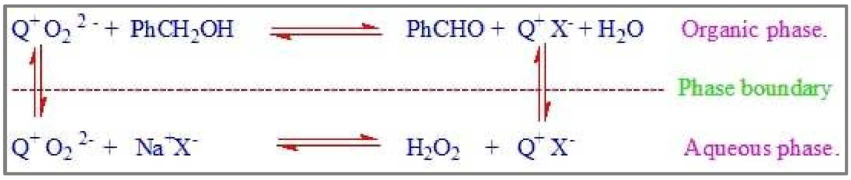
Figure 2. UV-Visible spectrum of 2, 4-dinitrophenylhydrazone of the product.

The UV-Visible spectrum of 2, 4-dinitrophenylhydrazone of the product on the oxidation of benzyl alcohol showed intense peaks at 235 nm and 355 nm was assigned to π-π*and n-π* transitions of the aromatic compound which are characteristic peaks of benzaldehyde.

All the above analyses, viz., melting point determination, infra-red and UV-Visible spectral studies showed that the products formed on the oxidation of benzyl alcohols by peroxide ion under phase transfer catalysis in non-polar solvents were found to be corresponding benzaldehydes. This method is found to be highly selective since no traces of acid is formed and the product, benzaldehyde and substituted benzaldehydes were obtained with high yield and purity.

All the PT catalysts function well in the oxidation reactions but the yield and ease of reaction is in the order TCMAC >TBAB > TBAHS >CTMAB. This is attributed due to the changes in combination of alkyl groups or may be due to the difference in the activity of anions for phase transfer.

The reaction proceeds smoothly in both the solvents viz, ethyl acetate and toluene. The yield of product is found to be more in ethyl acetate than that in toluene. This may be due to the fact that ethyl acetate is more polar than toluene. Solubility and partitioning of quaternary salts are increased by increase in the polarity of the organic phase. Based on the above experimental results obtained, a possible mechanism suggested is given in scheme 1.



Scheme 1. PT catalysed oxidation of benzyl alcohol by peroxide ion in non-polar solvents.

APPLICATION

Various commercial compounds like dyes, odorants, flavours, perfumes etc. are manufactured by using benzaldehyde. Currently benzaldehyde is commercially produced by the direct oxidation of toluene or by side chain chlorination of toluene followed by hydrolysis of benzal chloride. Both these industrial methods have disadvantages like requirement of high temperature, low yield, formation of by-products etc. The use of PTC can overcome all these difficulties and give good yield of the product. The reaction will not occur or will be very slow without the use of PT catalysts in polar and non- polar medium. The use of hydrogen peroxide as an oxidant for the selective oxidation of benzyl alcohols giving benzaldehydes in greener solvents like ethyl acetate and toluene is having great industrial significance in the era of green chemistry.

CONCLUSION

Oxidation of benzyl alcohols has been carried out in toluene and ethyl acetate using phase transferred peroxide ion as oxidant in presence of sodium tungstate dihydrate under PTC. The product of the oxidation was found to be benzaldehyde in a selective manner with excellent yield. The solvents employed were ethyl acetate and toluene which are considered as greener solvents. Product was characterised by melting point and by various spectral techniques. The selective oxidation of benzyl alcohol practically did not occur in non-polar organic solvents without the involvement of a PT catalyst. The PTC method offers a convenient route for the selective oxidation of these organic compounds in non-polar organic solvents which is having great significance in industry by cost reduction and pollution prevention. The method adopted is highly significant due to the facts that the solvents used are greener, ambient temperature, no by-products, high yield, selective and mild reaction, cheap oxidant etc. Nowadays extensive research is going on in this field with solvent free PTC technique which is having great significance in chemical industry.

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