

Research Article

Selective Oxidation of Benzyl alcohols to Benzaldehydes under Phase Transfer Catalysis

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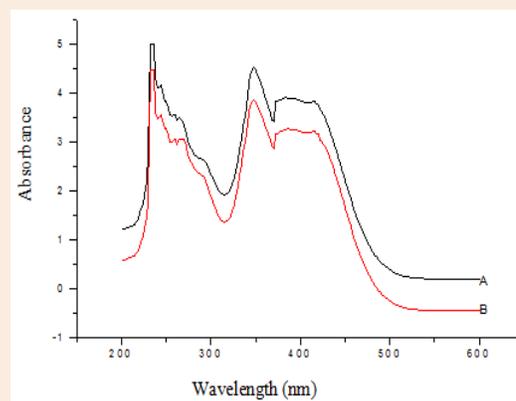
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Abstract

A rapid, efficient and selective method for the oxidation of benzyl alcohols to benzaldehydes under phase transfer catalysis (PTC) has been reported. The selective oxidation of benzyl alcohol, 4-chlorobenzyl alcohol, 4-methoxybenzyl alcohol and 4-methylbenzyl alcohol was carried out in organic solvents like toluene and chloroform. The phase transfer catalysts (PT catalyst) used were tetrabutylphosphonium bromide (TPBP), tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulphate (TBAHS). The substrate in an organic solvent is stirred with aqueous acidic dichromate in presence of a PT catalyst at room temperature. The product, corresponding benzaldehydes were precipitated as 2, 4 - dinitrophenylhydrazone. The recrystallised products were analyzed by melting point and other spectrophotometric techniques.

Keywords: Selective oxidation, Phase transfer catalysis, Phase transferred monochromate.

This reaction is found to be highly selective since no traces of benzoic acid have been detected.

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Introduction

Oxidation of organic compounds using different oxidizing agents is of great significance synthetically [1-2]. The introduction of phase transfer catalysis has revolutionized organic synthesis in respect of anion dissolution in non polar organic solvents with their ability to catalyze the reaction. Phase transfer catalysis is one of the most efficient new techniques which can be used to carry out a variety of chemical reactions under mild conditions with improved results [3-8]. There are many reports on the kinetic studies on the oxidation of various organic substrates by permanganate and dichromate under phase transfer catalysis [9-13]. But reports on the use of PTC in synthetic preparation of organic compounds are less and this prompted us to carry out this work [14-17]. The present paper reports the selective oxidation of benzyl alcohols using various quaternary ammonium salts as PT catalyst in various organic solvents by acidic potassium dichromate. It has been shown that both HCrO_4^- and HCr_2O_7^- are easily phase transferred provided the aqueous phase is acidic [3]. According to the present study the dichromate anion $\text{Cr}_2\text{O}_7^{2-}$ is difficult to be transferred into the organic medium due to the difficulty in transferring a bivalent ion.

Experimental**Materials and Reagents**

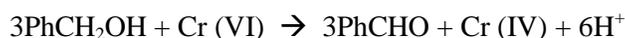
Analar grade potassium dichromate (Merck, India) was used and its solution was prepared in doubly distilled water. Benzyl alcohol (AR) (Spectrochem, India) was purified by distillation under reduced pressure. 4-Chlorobenzyl alcohol, 4-methoxybenzyl alcohol and 4-methylbenzyl alcohol (Lancaster, England) were used as such. The PT catalysts, tetrabutylphosphonium bromide (TPBP) (Merck KGaA, Germany), tetrabutylammonium bromide (TBAB) and tetrabutylammonium hydrogen sulphate (TBAHS) (Spectrochem, India) were used as such. The organic solvents

such as toluene and chloroform were purified according to the standard procedure [18]. All the purified solvents were refluxed for 1-2 hours with a mixture of PT catalyst and potassium dichromate and then distilled.

Synthetic procedure was carried out in a heterogeneous medium. Benzyl alcohol (0.1 mol) dissolved in 50 mL toluene which contains 0.01 mol PT catalyst was mixed with 50 mL $K_2Cr_2O_7$ (0.5 mol) containing 2 mol dm^{-3} H_2SO_4 . The mixture was stirred vigorously using a magnetic stirrer for about two hours at room temperature. The mixture was allowed to settle and the organic layer was extracted with ether three times. The 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, recrystallised from ethanol, dried and weighed. The product was analysed with its melting point and other qualitative analytical methods like UV-Visible and infra red spectral analyses. The aqueous layer after extraction with sodium bicarbonate was acidified with concentrated HCl. This procedure was repeated with other PT catalysts and using chloroform as the solvent. The entire procedure was also repeated with other substituted benzyl alcohols.

Results and discussion

The stoichiometry of the reaction was established by equilibrating known excess concentration of the phase transferred monochromate with known amount of the alcohol. One mole of monochromate was found to be equivalent to three moles of alcohol, viz., benzyl alcohols.



Benzyl alcohol and substituted benzyl alcohols on oxidation under heterogeneous condition gave corresponding aldehyde as the product with very high yield (above 90%). The yield of the products is found to be more or less same with all PT catalysts. But the yield of the product is slightly more in chloroform than in toluene. This may be due to the fact that chloroform is more polar than toluene. Solubility and partitioning of quaternary salts are increased by increase in the polarity of the organic phase. The recrystallised sample of products were characterised by its melting point and is given in **Table 1**.

Table 1 Melting points of 2,4-dinitrophenylhydrazone of products on the oxidation of benzyl alcohols

Sl. No.	Substrate	Melting point of 2,4-dinitrophenylhydrazone of product
1	Benzyl alcohol	239 ± 2
2	4-chlorobenzyl alcohol	267 ± 2
3	4-methylbenzyl alcohol	233 ± 2
4	4-methoxybenzyl alcohol	252 ± 2

The above result is compared with the reported data and found to be close with that of reported values. The products obtained on the oxidation of benzyl alcohol was further analysed by infra red and UV-Visible spectrophotometric techniques.

IR spectral studies

The infra-red absorption spectrum was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in **Figure 1**. The IR spectrum showed sharp peaks at 3287 cm^{-1} (N-H stretching), 3090 cm^{-1} (Aromatic C-H stretching), 1744 cm^{-1} (C=O stretching), 1620 cm^{-1} (C=C) stretching), 1516 cm^{-1} (Ar-NO₂ asymmetric stretching), 1329 cm^{-1} (Ar-NO₂ symmetric stretching), and 1136 cm^{-1} (C-NH stretching). Presence of all these peaks leads to the conclusion that the product formed may be 2, 4 - dinitrophenylhydrazone of benzaldehyde. Further this spectrum was compared with that of 2,4-dinitrophenylhydrazone of pure benzaldehyde and found to have excellent similarities.

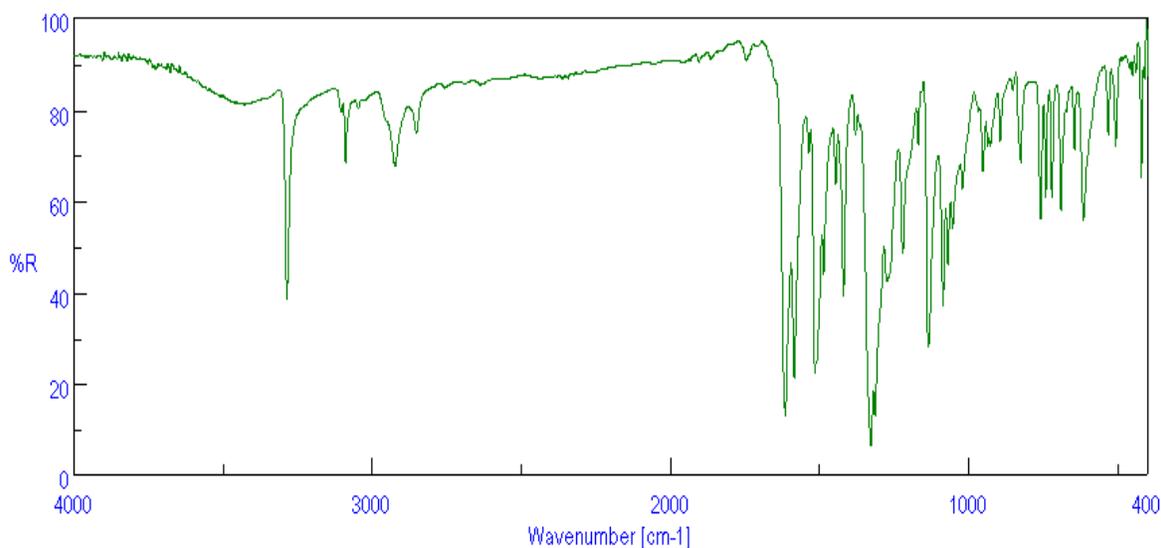


Figure 1 IR spectrum of 2,4-dinitrophenylhydrazone of product on the oxidation of benzyl alcohol

UV-Visible spectral studies

UV-Visible absorption 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. In the UV-Visible spectrum of 2, 4 - dinitrophenylhydrazone of the product on the oxidation of benzyl alcohol showed intense peaks at 235 nm and 353 nm was assigned to π - π^* and n- π^* transition of the aromatic compound. The UV-Visible spectrum of the obtained product was compared with that of 2, 4 - dinitrophenylhydrazone of pure benzaldehyde and gave excellent similarities.

All the above analyses, viz., melting point determination, IR and UV-Visible spectral studies showed that the product formed on the oxidation of benzyl alcohols by acidic monochromate under phase transfer catalysis was the corresponding aldehydes. This method is found to be highly selective since no traces of acid is formed and the product, corresponding benzaldehyde is obtained with high yield.

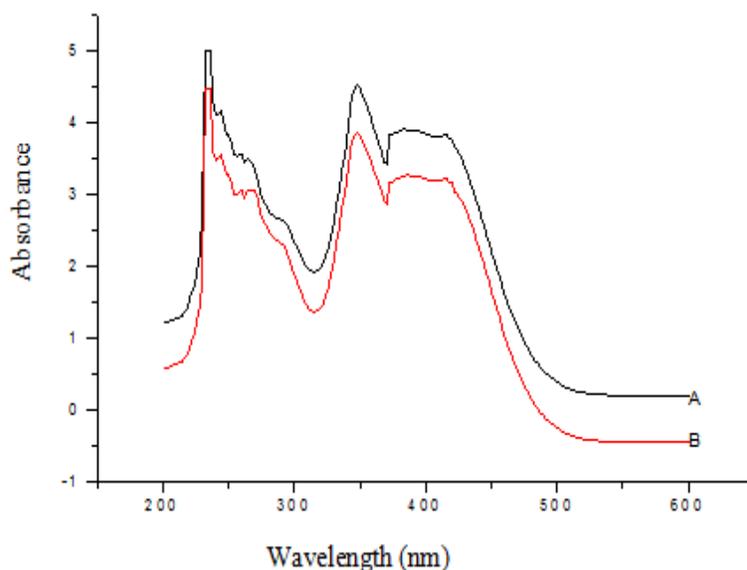


Figure 2 UV-Visible spectrum of **A**: 2, 4 - dinitrophenylhydrazone of pure benzaldehyde;
B: 2, 4 - dinitrophenylhydrazone of product on the oxidation of benzyl alcohol

Conclusions

The oxidation of benzyl alcohols by using phase transferred acidic monochromate with the help of PT catalysts in water immiscible organic solvents at room temperature has been reported. The product obtained is the corresponding benzaldehyde with excellent yield. This procedure under phase transfer catalysis was found to be highly selective, simple with high yield and minimum industrial waste.

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