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Phase transfer catalysed oxidation of benzaldehyde and substituted benzaldehydes by dichromate in organic medium

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Abstract
Benzaldehyde and substituted benzaldehydes were oxidised to benzoic acid and substituted benzoic acids by dichromate under acidic medium in non-polar solvents like toluene and ethyl acetate in presence of a phase transfer catalyst. Various quaternary onium salts were used as phase transfer catalyst. The products obtained were characterised by melting point determination and infra-red spectral technique. The reaction is found to be very smooth and yield of products were more than 90%. The effect of organic solvents and phase transfer catalysts on yield of product formed was studied.

Keywords: Benzaldehyde, substituted benzaldehydes, phase transfer catalysis, phase transfer catalyst, permanganate

1. Introduction
Synthesis of various organic compounds were commonly carried out by oxidation reactions using suitable oxidants [1-2]. Phase transfer catalysis (PTC) is relatively new technique that can be used to do a variety of chemical reactions under mild conditions with improved results. The introduction of PTC technique has revolutionised organic synthesis in respect of anion dissolution in non-polar solvents with their ability to catalyse the reaction. Cost reduction and pollution prevention are the aims of a chemical industry in the era of green chemistry which can be accomplished by adopting PTC method [3-5]. There are reports on using permanganate, chromate, hypochlorite etc. as oxidizing agent in organic synthesis under PTC [6-12]. Kinetic studies of such oxidations of various organic substrates in organic medium were also reported [13-16].

The present paper reports the oxidation of benzaldehyde and substituted benzaldehydes using various quaternary ammonium and phosphonium salts as phase transfer catalysts (PT catalyst) in various organic solvents like ethyl acetate and toluene by acidic chromate. The substituted benzyl alcohols used were 4-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, 4-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, 4-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-methylbenzaldehyde. The PT catalysts used were tetrabutylammonium bromide (TBAB), tetrabutylphosphonium bromide (TBPB), tetrabutylammonium hydrogen sulphate (TBAHS) and cetyltrimethylammonium bromide (CTMAB)

2. Materials and Methods
2.1. Materials
Analar grade potassium dichromate (Merck, India) was used as such in the entire work. Benzaldehyde and the substituted benzaldehydes such as 4-hydroxybenzaldehyde, 3-hydroxybenzaldehyde, 4-chlorobenzaldehyde, 3-chlorobenzaldehyde, 4-methoxybenzaldehyde, 3-methoxybenzaldehyde, 4-nitrobenzaldehyde, 3-nitrobenzaldehyde and 4-methylbenzaldehyde (spectrochem, India Ltd. Mumbai and Merck KGaA, Germany) were used as such. Tetrabutylammonium bromide (TBAB), tetrabutylammonium hydrogen sulphate (TBAHS) and cetyltrimethylammonium bromide (CTMAB) (Spectrochem India Ltd. Mumbai) and tetrabutylphosphonium bromide (Merck KGaA, Germany) were used as PT catalyst. The organic solvents toluene and ethyl acetate were purified according to the standard procedure [17-18]. The purified solvents were refluxed for 1-2 hours with a mixture of PT catalyst and potassium dichromate and then distilled.

2.2. Methods

Synthetic analyses were carried out in heterogeneous fashion. Benzaldehyde and substituted benzaldehydes (0.1 mol) dissolved in 50 mL of toluene or ethyl acetate which contains 0.01 mol PT catalyst was mixed with 50 mL potassium dichromate (0.5 mol) containing 0.02 mol dm^{-3} H_2SO_4. The mixture was kept at room temperature with gentle stirring using a magnetic stirrer for about thirty minute. The organic layer was extracted with ether three times and the obtained organic layer was again extracted with 10% sodium bicarbonate. Both the organic and aqueous layers were separated and the aqueous layer was acidified with concentrated HCl. The white crystalline precipitate formed was filtered, dried and weighed. The recrystallised product is analysed by melting point and infra-red spectral technique.

3. Results and discussion

The stoichiometry of the reaction was established by equilibrating known excess concentration of the phase transferred monochromate with known amount of benzaldehyde. Two moles of monochromate was found to be equivalent to three moles of benzaldehyde.

$$3PhCHO + 2QHCrO_4 \longrightarrow 3PhCOOH + 2QOH + 2CrO_3 + 2H_2O$$

Benzaldehyde and substituted benzaldehydes on oxidation under heterogeneous PTC condition gave corresponding acids as the product with very high yield (above 90%). The reactions were carried out at room temperature and were found to be very smooth. The recrystallised samples of products were characterised by its melting point and are given in Table 1.

Table 1: Melting point of products on oxidation of benzaldehyde and substituted benzaldehydes

Sl. No.	Substrate	Melting point of product (^{0}C)
1	Benzaldehyde	118 ± 2
2	4-chlorobenzaldehyde	240 ± 2
3	3-chlorobenzaldehyde	155 ± 2
4	4-nitrobenzaldehyde	237 ± 2
5	3-nitrobenzaldehyde	140 ± 2
6	4-hydroxybenzaldehyde	215 ± 2
7	3-hydroxybenzaldehyde	202 ± 2
8	4-methylbenzaldehyde	178 ± 2
9	4-methoxybenzaldehydeol	181 ± 2
10	3-methoxybenzaldehyde	171 ± 2

The obtained results of melting point were compared with that of authentic samples and found to be similar. This showed that the products formed may be corresponding acids. This was further confirmed by infra-red spectral analysis by taking benzaldehyde as the typical substrate.

The infra-red absorption spectrum was recorded from KBr pellets using Jasco FT-IR 4100 spectrophotometer (Japan) and is shown in Figure 2.

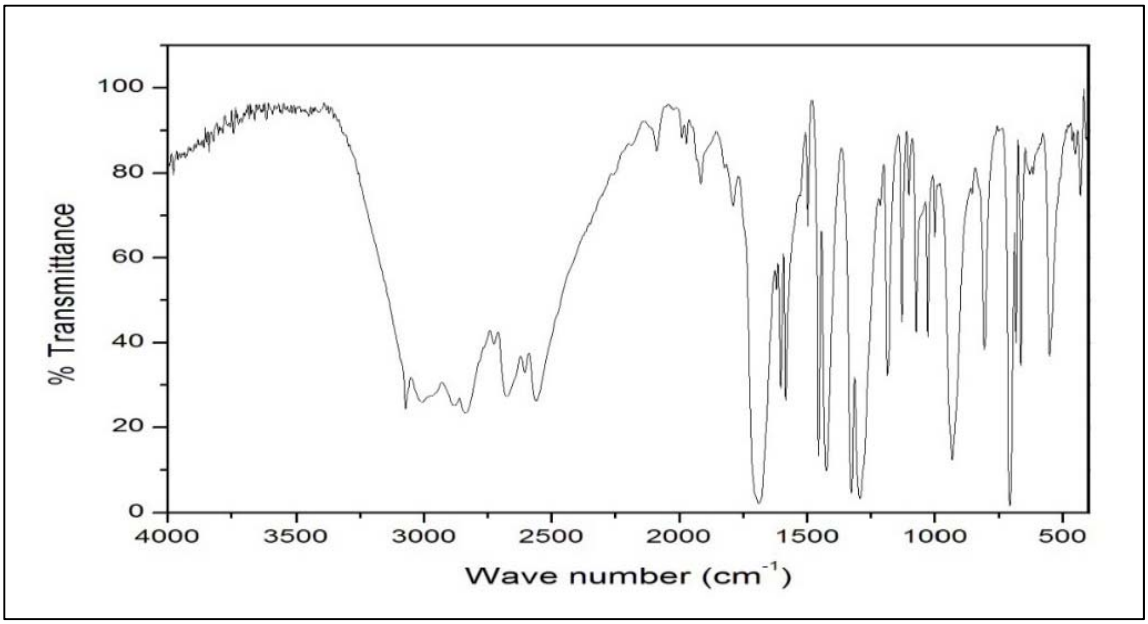


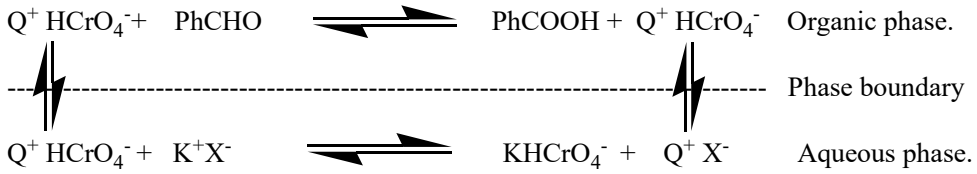
Fig 2: IR spectrum of obtained product

The infra-red spectrum gave sharp peaks at 3100 cm^{-1} (O–H stretching), 1720 cm^{-1} (C=O stretching) and 1620 cm^{-1} (C=C stretching). Presence of these peaks leads to the conclusion that the product formed may be benzoic acid. Moreover, this spectrum on comparison with the infra-red spectrum of pure benzoic acid showed excellent similarities.

All the above analyses, viz., melting point determination and infra-red spectral studies confirmed that the product formed on the oxidation of benzaldehyde and substituted benzaldehydes by acidified chromate under PTC were benzoic acid and corresponding substituted benzoic acids.

The reaction is found to be very smooth in both the solvents ethyl acetate and toluene employed in the oxidation. The yield of benzoic acids is found to be more in ethyl acetate than that in toluene. This may be due to the more polar nature of ethyl acetate than toluene. Solubility and partitioning of quaternary salts which are employed as PT catalysts are increased by increase in the polarity of the organic phase.

All the four catalysts perform well in the oxidation reactions of benzaldehydes by acidified chromate under PTC condition. But the yield and ease of reaction was found to be in the order TBPB > TBAB > TBAHS > CTMAB. This may be 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 mechanism of the reaction can be given in Scheme 1.



Scheme 1: PTC oxidation of benzaldehydes to corresponding benzoic acids

4. Conclusion

A simple and efficient method for the conversion of benzaldehydes to corresponding benzoic acids by acidified chromate in organic medium under PTC condition was reported. The yield of the products was excellent and were characterised by various analytical methods. Greener solvents like ethyl acetate and toluene were used for this conversion and there was no formation of by-products. So this method under PTC can be adapted to other reaction systems also.

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