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Efficiency of phase transfer catalysts in permanganate mediated oxidation of benzaldehyde in aqueos medium: an eco-benign approach

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ABSTRACT

Oxidation of benzaldehyde by permanganate in water medium using various PTC has been performed. Reactions conducted in unstirred condition offered good yields compared to stirred condition reactions. Catalyst TBAB, CTAB and BTEAC gave high yields respectively 77 %, 69 % and 65 %.

Keywords: Oxidation, water reaction, phase transfer catalysts, eco-protection.

Introduction

Organic transformations leading to the desired final products also generates undesired impurities due to side reactions [1, 2]. Phase transfer catalysis is an efficient and eco-benign synthetic tool generates pure and high yield products by enhancing the reactivity and selectivity [3,4]. It gains importance in various fields of organic chemistry including pharmaceutical and agrochemicals [5-7]. Phase transfer catalysts (PTCs) facilitates the migration of a reactant from one phase to another phase [8, 9]. Benzoic acid, an oxidation product of benzaldehyde gains importance in the synthesis of organic intermediates [10].

The utility of PTCs in the permanganate mediated oxidation of benzaldehyde and their efficiency (based on their electrical potential oscillations) are reported in literature [11, 12] . In environmental aspects use of organic solvents in chemical reactions has to be limited [13]. PTCs eliminate the need for organic solvents in synthetic procedures [13]. PTCs differ in their potential of specificity and selectivity towards individual chemical reaction.

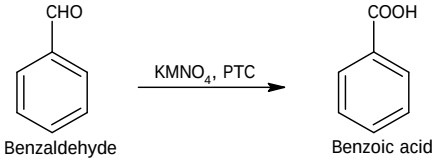
These facts prompted us to study the oxidation of benzaldehyde in environmentally benign-aqueous medium using different PTCs. Acidic potassium permanganate along with PTC acts as aqueous phase and benzaldehyde acts as organic phase (bi-phasic system). The reaction is conducted in both unstirred and stirred condition to examine the effect of stirring on the yield. Quantum chemical properties of PTCs can influence the organic transformation, which are determined and correlated with the percentage yield of benzoic acid.

Experimental

Melting points were determined in DBK program melting point apparatus and are uncorrected. Reactions were examined by thin layer chromatography using aluminium backed plates coated with silica 60 F254. The chromatograms were visualized under UV light (254 and 366 nm). The IR spectra were recorded on Schimadzu IR affinity-1 spectrophotometer expressed in cm^{-1}. pH measurements are done using pH meter with Ag/Agcl electrode (Vanira, Hyderabad). Quantum chemical calculations were determined using ArgusLab 4.0.1 [14].

Permanganate mediated oxidation of benzaldehyde

Aqueous potassium permanganate (10 mmol, 10 ml), benzaldehyde (5 mmol) and PTC (70 mmol, 5 ml) were taken in beaker. In one set of beaker, reaction is conducted with stirring and in another set without stirring. The oxidation is continued for the period of 4 hrs, the mixture is allowed to precipitate and purified by simple washing with water. The formed benzoic acid is characterized by m. p, TLC and IR spectral studies. m.p: 122-124 °C, IR (KBr, cm^{-1}): 3016, 1712, 1292.



Scheme-1: PTC assisted permanganate oxidation of benzaldehyde

Quantum mechanical calculations

2D structures of PTCs were sketched using ArgusLab 4.0.1 draw applet. The structures were geometry optimized using Hamiltonian PM3 method; allowing maximum of 300 iterations and gradient conversion of 10^{-1} kcal/mol/Å. Single point energy calculation was performed using ZINDO quantum mechanical method in RHF closed shell mode. Highest Occupied Molecular Orbital (HOMO), Lowest Unoccupied Molecular Orbital (LUMO), Mulliken charges and dipole were calculated and are recorded in Table 1.

Results and discussion

The stoichiometry of potassium permanganate and benzaldehyde in 1: 0.5 ratio offered good yields. The change of permanganate colour to brownish manganese dioxide confirmed the progress of oxidation reaction. In absence of PTC, mixture remains as two phases and there is no colour in pH medium also examined using silver/silver chloride electrode, and drop in pH is observed towards 4 hrs. TBAC offered good yields in both unstirred (41 %) and stirred (42 %) conditions change is observed.

PTCs forms liphophilic ion pair (organic soluble) with permanganate and facilitate its migration in to organic phase (fig-1). Benzoic acid is purified by non-chromatographic methods and characterized by m.p., TLC and IR. The overlay spectrum of formed product and reference benzoic acid further supports the purity of the benzoic acid (Fig. 2).

Table 1: Quantum mechanical data of phase transfer catalysts

Catalyst	HOMO	LUMO	Dipole	Mulliken charges		Yield
				X	N	
TBAB	-9.889	-3.506	5.37	-0.32	-0.146	77
TPAB	-9.263	-2.610	0.52	-0.34	-0.00	27
TBAC	-10.269	-4.081	1.38	-0.35	-0.149	41
TEAB	-8.5963	-2.863	5.49	0.17	1.25	69
TBAI	-10.008	-4.080	2.18	5.19	0.26	13
CTAB	-7.77	-0.39	1.63	0.063	-0.35	65
BTEAC	-5.099	-1.925	5.24	-0.81	0.64	54
BTMAC	-5.127	-0.229	1.28	-0.63	1.32	46

HOMO: Highest Occupied Molecular Orbital; LUMO: Lowest Unoccupied Molecular Orbital; X: Mulliken charge of PTC halogen (-Cl, -Br, -I), X: Mulliken charge of PTC nitrogen

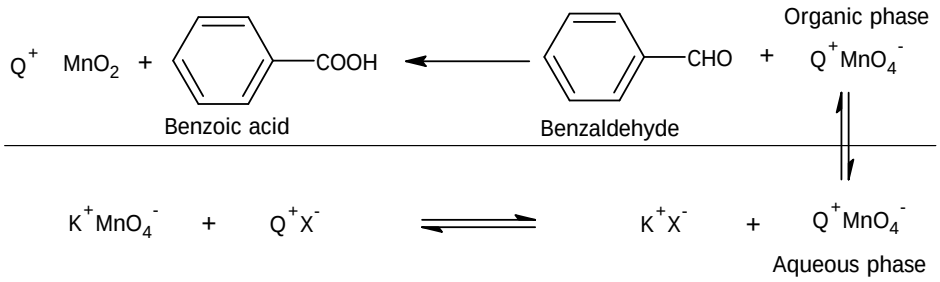


Fig. 1 : Proposed mechanism of catalysis

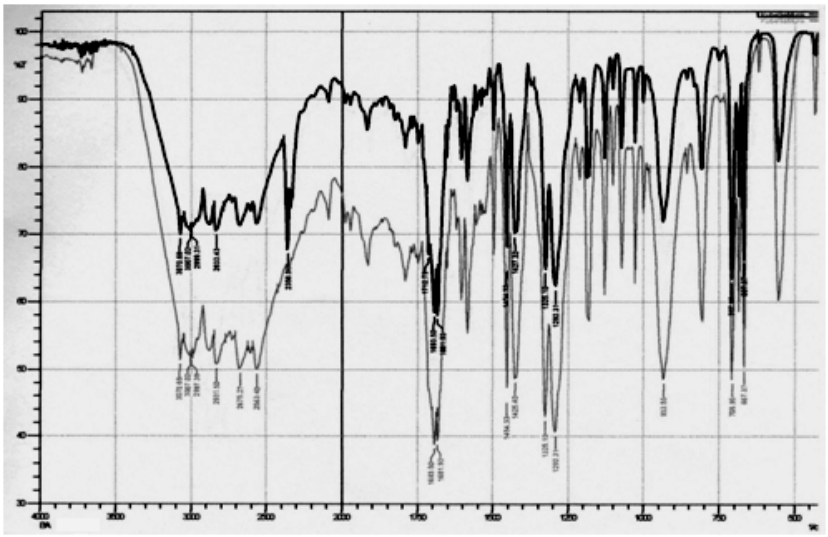


Fig. 2 : Overylay spectrum of prepared and reference benzoic acid.

The reaction is carried out in stirred and unstirred condition, in order to investigate the effect of mechanical agitation. In case of unstirred reactions, the yield obtained was very high compared to stirred conditions (Fig. 3). This suggests the lower rate of reactant migration in stirred condition. In unstirred condition the percent yield of benzoic acid ranges from 13 to 69, where as in stirred condition 11 to 42 (Table 2).

The ability of PTC to form cation by releasing halides determines the effectiveness as catalyst. Quantum chemical properties calculated were correlated with the % yield and found good.

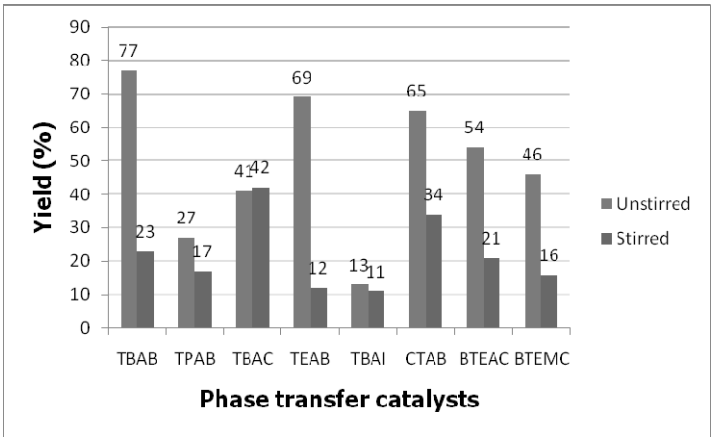


Fig. 2 : Histogram showing the benzoic acid yields in unstirred and stirred condition.

All the reactions are carried out in triplicate and average is considered. The change. In case of TBAB and CTAB abrupt change in the yield is observed between stirred and unstirred condition (Table 2).

Table 2: Yield of benzoic acid in both stirred and unstirred condition

Catalyst	Yield (%)	
	Unstirred	***Stirred***
TBAB	77	23
TPAB	27	17
TBAC	41	42
TEAB	69	12
TBAI	13	11
CTAB	65	34
BTEAC	54	21
BTMAC	46	16

Conclusion

In search of eco-benign procedure for the oxidation of benzadehyde, most efficient methodology for the conversion of benzaldehyde to benzoic acid using phase transfer catalyst is developed. An attempt is made to grade the catalyst effectiveness using their quantum chemical properties. Through quantum chemical calculations the effect of mullikan charge and dipole of PTC in the yield is established.

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