

Kinetics of the Oxidation of Benzhydrols with Permanganate under Phase Transfer Catalysis in Organic Solvents

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ABSTRACT

Kinetic studies of the oxidation of benzhydrol and some of its para-substituted derivatives using phase transferred permanganate in organic solvents that are immiscible with water have been carried out. The products of oxidation were the corresponding benzophenones. Kinetically first order dependence on the concentrations of substrate as well as the oxidant has been observed. The reaction rate was found to decrease with an increase in the dielectric constant of the organic solvent employed. The electronic effects of the substituents were found to be interesting. Both electron withdrawing and electron releasing groups at the para position of benzhydrol increased rate of the oxidation. The effects of different phase transfer catalysts (PTC) were also compared. The activation parameters have been evaluated and a mechanism consistent with the kinetic results has been proposed.

Keywords: Phase Transfer Catalysis; Kinetics; Oxidation; Benzhydrols; Permanganate

1. Introduction

Permanganate is an inexpensive oxidant being widely used in organic synthesis. It is not soluble in organic solvents and hence, oxidations have traditionally been conducted in the aqueous medium. The discovery that materials known as phase transfer catalysts such as crown ethers or quaternary ammonium salts can transport permanganate ions into organic solvents across the aqueous-organic solvent boundary helped to extend its use in organic syntheses to a great extent when the organic substrates are soluble in organic solvents only [1,2]. Kinetics of the permanganate oxidation of some other organic compounds, have been investigated under phase transfer catalysis and the results reported elsewhere [3-5]. We have reported the kinetics of the monochromate oxidation of benzhydrols in non-polar media [6]. In the present kinetic study, we report the results of the kinetic study of the PTC catalysed oxidation of benzhydrols with permanganate along with its p-chloro, p-methyl and p-methoxy derivatives in benzene, chlorobenzene, chloroform and methylene chloride as the organic solvents used.

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2. Experimental

Benzhydrol (BH), para-chlorobenzhydrol p-(ClBH), parathylbenzhydrol (p-MeBH) and para-methoxy-benzhydrol (p-MeOBH) used were Lancaster make. The organic solvents were purified by methods known and refluxed with PTC and KMnO_4 for three hours and then distilled before use. Analar grade potassium permanganate (Fluka) was used and its solution was prepared in doubly distilled water. Tetrabutylammonium bromide (TBAB) and tetrabutylammoniumhydrogen sulphate (TBAHS) were SRL make and tetrabutylphosphonium bromide (TBPB) was Merck quality and were used as such without further purification.

Solutions of permanganate ions in organic solvents were prepared by shaking an aqueous solution of KMnO_4 (0.005 M) with an equal volume of PTC solution (0.01 M) in the organic solvent. Transports of the permanganate ions were almost quantitative. The organic layer was separated and dried over anhydrous Na_2SO_4 and the concentration of the ions ascertained.

The stoichiometry of the reaction was determined by treating a known amount of benzhydrol with a known

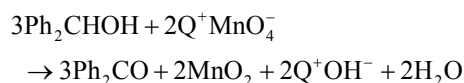
excess of phase transferred permanganate and by estimating the permanganate remaining after completion of the reaction. Formation of benzophenone as the only product was qualitatively and quantitatively ascertained by its conversion into the 2, 4-DNP derivative.

Kinetic measurements were carried out under pseudo-first order conditions where, [substrate] \gg [oxidant] at all the four different temperatures employed. Progress of the reaction was monitored through spectral measurements at definite intervals of time by measuring the absorbance (OD) at 528 nm using the Systronics double beam uv-vis spectrophotometer (model 2201). The pseudo-first order rate constants, k_{obs} , were calculated from the slope of the linear plots of log Absorbance versus time. The second order rate constant, k_2 was obtained from the relation.

$k_2 = k_{obs}/[\text{substrate}]$. Successive scan of the absorption spectra taken at definite time intervals yielded isosbestic points at 498 nm and 582 nm. Experiments were carried out at various concentrations of oxidant and substrate, at different temperatures and in various organic solvents. Different PTCs were also used.

3. Results and Discussion

The stoichiometry of the oxidation was found to be in the molar ratio benzhydrol: permanganate as 3:2. The reaction may be represented by the equation:



The successive scans of the absorption spectra which showed isosbestic points at 498 nm and 582 nm, suggests formation of a single product. This oxidation reaction failed to induce any polymerization of added acrylonitrile, which rules out involvement of any radical intermediate during the course of the reaction (Q^+ represents the quaternary ammonium cation).

The values of rate constants determined at different substrate concentrations and oxidant concentrations are given in **Table 1**. The plots of log absorbance due to the [oxidant] versus time were linear, indicating first order dependence on the [oxidant]. This is further supported by the fact that k_{obs} values are constant for different initial concentrations of Q^+MnO_4^- when the substrate concentration was fixed. The second order rate constant, k_2 values are reasonably constant indicating first order dependence on the [substrate] also. This is further supported by the linearity of the log k_{obs} versus log [substrate] plots with a slope of almost unity (slope = 0.9113) and good correlation coefficient ($r = 0.9960$).

The rates of oxidation of benzhydrol in different organic solvents were found to decrease with increase in the dielectric constant (D) of the medium (**Table 2**). The

plot of log k_2 vs $1/D$ is linear. The decrease in rate of oxidation in solvents with high dielectric constant can be attributed to larger stabilization by solvation extended to the organic part of the quaternary catalyst-oxidant moiety. Moreover, solvents with low dielectric constant exert larger relative desolvation effect on the inorganic MnO_4^- ion part and make it more reactive so that the reaction proceeds faster in solvents with lower D-values.

The experimental activation energy for the oxidation of benzhydrol in chlorobenzene using TBAB as PTC has been found to be $44.04 \text{ kJ}\cdot\text{mol}^{-1}$, that with TBPB is $38.26 \text{ kJ}\cdot\text{mol}^{-1}$ and that with TBAHS is $32.5 \text{ kJ}\cdot\text{mol}^{-1}$. The other thermo dynamical parameters such as enthalpy, entropy and free energy of activation values for these different catalysts are given (**Table 3**). The entropies of activation values being largely negative suggests formation of an ordered transition state, possibly with involvement of internal bonding, both inter nuclear and intra-nuclear. The free energies of activation values remain practically constant at $86 \text{ kJ}\cdot\text{mol}^{-1}$ which is indicative of the operation of similar mechanistic modes for the oxidations.

The same trend is kept up with the oxidation of the para substituted derivatives also (**Table 4**).

Table 1. Effect of change in [oxidant] and [substrate] on the rate of oxidation of benzhydrol.

$[\text{BH}] \times 10^2$ ($\text{mol}\cdot\text{dm}^{-3}$)	$[\text{Q} + \text{MnO}_4^-]$ $\times 10^4$ ($\text{mol}\cdot\text{dm}^{-3}$)	$k_{obs} \times 10^4 \text{ s}^{-1}$	$k_2 \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
5.00	3.75	2.207	4.414
5.00	5.00	2.240	4.480
5.00	6.25	2.147	4.294
5.00	7.50	2.222	4.444
3.75	7.50	1.735	4.627
5.00	7.50	2.222	4.444
6.25	7.50	2.633	4.213
7.50	7.50	3.263	4.351

Solvent: Chlorobenzene; PTC: TBAB; Temperature: 298 K.

Table 2. Effect of dielectric constant (D) of the medium on the rate of oxidation of BH by $\text{Q} + \text{MnO}_4^-$.

Solvent	D	$k_2 \times 10^3 \text{ dm}^3\cdot\text{mol}^{-1}\cdot\text{s}^{-1}$
Benzene	2.3	6.056
Chloroform	4.8	4.738
Chlorobenzene	5.6	4.444
Methylene chloride	8.9	4.202

$[\text{Q} + \text{MnO}_4^-] \times 10^4 = 7.5 \text{ mol}\cdot\text{dm}^{-3}$ $[\text{BH}] \times 10^2 = 5.0 \text{ mol}\cdot\text{dm}^{-3}$; PTC: TBAB; Temperature: 298 K.

Table 3. Activation parameters for the oxidation of BH by $Q + MnO_4^-$ assisted by different PTCs in chlorobenzene.

PTC	$k_2 \times 10^3 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$				Activation parameters at 298 K		
	293 K	298 K	303 K	308 K	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger
TBAB	3.360	4.444	5.924	8.116	41.53	-150.64	86.42
TBPB	4.352	5.464	7.204	9.278	35.77	-168.25	85.91
TBAHS	5.042	6.188	7.759	9.618	29.99	-186.6	85.60

$$[Q + MnO_4^-] \times 10^4 = 7.5 \text{ mol} \cdot \text{dm}^{-3}; [BH] \times 10^2 = 5.00 \text{ mol} \cdot \text{dm}^{-3}.$$

Table 4. Reaction rates at different temperatures and activation parameters for the oxidation of parasubstituted benzhydrols by $Q + MnO_4^-$ in chlorobenzene.

Substrate	$10^3 k_2 \text{ dm}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$				Activation parameters at 298 K		
	293 K	298 K	303 K	308 K	ΔH^\ddagger	ΔS^\ddagger	ΔG^\ddagger
BH	3.360	4.444	5.924	8.116	41.53	-150.64	86.42
4-CIBH	4.798	6.276	8.064	10.27	35.61	-16.61	85.55
4-MeBH	4.302	5.456	6.958	9.702	37.76	-161.58	85.91
4-MeOBH	5.164	6.840	8.650	10.80	34.32	-171.26	85.35

$$[Q + MnO_4^-] \times 10^4 = 7.5 \text{ mol} \cdot \text{dm}^{-3}; [\text{Substituent}] \times 10^2 = 5.0 \text{ mol} \cdot \text{dm}^{-3};$$

PTC: TBAB.

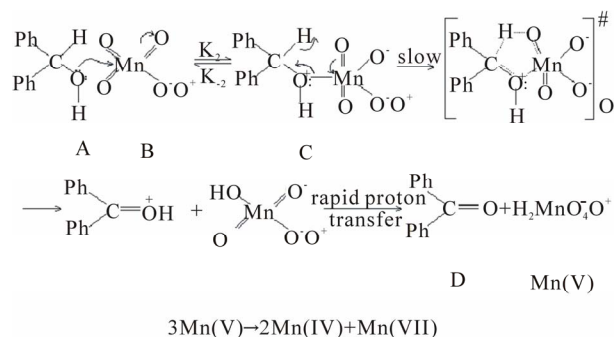
The rates of oxidation of BH at different temperatures were determined using $Q^+MnO_4^-$, phase transferred using different PTCs, and the activation parameters were computed (Table 3). The efficiency of different PTCs were found to be in the order TBAHS > TBPB > TBAB.

The higher rate with TBPB in comparison with TBAB may be due to the stronger cation-anion interaction of the ion-pair with TBAB which makes the anion less available for oxidation. The higher rate with TBAHS compared to TBPB may be attributed to the easy ion-pair formation between catalyst cation and reagent nucleophile in non-polar solvent. Moreover, the HSO_4^- anion of TBAHS is highly hydrophilic compared to bromide and readily get partitioned into the aqueous phase, making the transfer of MnO_4^- ions into the organic phase with better ease. Further, the values of ΔG^\ddagger are very close to each other ($\sim 85 \text{ kJ} \cdot \text{mol}^{-1}$) indicating that same mechanism operates with different PTCs.

Study of the effect of substituents at the para position of one of the benzene rings showed that, both electron donating and electron withdrawing groups enhance the rate (Table 4).

The log k_2 vs σ plot is non-linear which was concave upwards. The activation enthalpies and entropies are linearly related. The linear isokinetic correlation implies that all the substituted benzhydrols under investigation are oxidised by the same mechanism. This is further confirmed by the in ΔG^\ddagger values.

According to the Frontier Molecular orbital approach the reaction would be initiated by an interaction of the HOMO of the substrate (an oxygen 2P-orbital containing a lone pair of electrons) with the LUMO of the oxidant (an antibonding orbital located primarily on Mn) resulting in the formation of a permanganate ester [7]. This is followed by the rate limiting slow decomposition of the ester via a five membered cyclic transition state. The large negative entropy of activation is consistent with the formation of a transition state having greater degree of order in its structure.



A rate expression consistent with the above mechanism can be given from the equilibrium, $[C] = K_{eq} [A] [B]$

$$\begin{aligned} \text{rate} &= k_2(C) = k_2 K_{eq} [A] [B] \\ &= k_{obs} [B] \text{ When } [A] \gg [B]. \end{aligned}$$

In the rate determining slow decomposition of the permanganate ester, breaking away of the $\alpha C-H$ bond and formation of the carbon-oxygen double occurs. It is probable that electron donating groups enhance the rate by facilitating the cleavage of $\alpha C-H$ bond, while electron withdrawing groups enhance the rate by facilitating the formation of carbon-oxygen double bond.

4. Conclusion

The kinetics of the permanganate oxidation of benzhydrols under PTC in water immiscible organic solvents have been made. The oxidation proceeds faster in solvents with low dielectric constants. Of the three catalysts used TBAHS gave maximum rate. It was interesting to see that both electron donating and electron withdrawing substituents increased the rate. The mechanism explained with necessary kinetic parameters.

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