

# Kinetics of Permagnetic oxidation of 4-hydroxy Benzaldehyde in acidic media

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**Abstract:** Paramagnetic oxidation of 4-hydroxy benzaldehyde has been investigated at 25°C using UV –Visible double beam spectrophotometer under acidic condition. The effect of variation of substrate, oxidant and H<sub>2</sub>SO<sub>4</sub> was studied under pseudo first order reaction conditions. The order of reaction was found to be first order on oxidant, zero for substrate, and fractional order on [H<sub>2</sub>SO<sub>4</sub>]. The effect of salts such as KCl, KBr, KI, AlCl<sub>3</sub>, Al(NO<sub>3</sub>)<sub>3</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> and MgCl<sub>2</sub>, etc. on oxidation of 4-hydroxy benzaldehyde was studied.

**Keywords:** Spectrophotometer, KMnO<sub>4</sub>, Oxidation, 4-hydroxybenzaldehyde.

## Introduction

In the recent years, kinetic studies of oxidation of various organic compounds by oxidants such as Quinolinium fluorochromate<sup>1</sup>, alkaline permanganate<sup>2-3</sup>, lead tetra acetate<sup>4</sup>, N-chloro-p-toluenesulfonamides<sup>5</sup>, N-bromobenzamide<sup>6</sup>, N-bromosucinimide<sup>7</sup>, Pyridinium bromochromate<sup>8</sup>, benzyltriethyl ammonium chlorochromate<sup>9</sup>, peroxydisulphate<sup>10</sup> etc. have been reported. Literature survey reveals that very little work is reported on oxidation of benzaldehyde using KMnO<sub>4</sub><sup>2</sup>. The utility of KMnO<sub>4</sub> as an oxidant in the kinetic study may be attributed to the vital role of it in various paramagnetic synthesis also in various media<sup>2</sup> such as acidic, basic, neutral or even in organic solvents. The present investigation reports the oxidation of 4-hydroxybenzaldehyde by potassium permanganate under pseudo first order reaction conditions in acidic medium.

## Experimental

### Materials and methods

All chemicals used for kinetic study were A.R. grade. Purity of chemicals checked by reported method.

Kinetic investigations were performed under pseudo first order conditions with excess of the 4-hydroxy benzaldehyde over the oxidant at 25° C. Requisite amount of solution of substrate, H<sub>2</sub>SO<sub>4</sub> and water were equilibrated. A measured amount of KMnO<sub>4</sub> was rapidly added to the reaction mixture with stirring. The progress of the reaction was monitored by double beam UV-Visible spectrophotometer (Elico-198) at its maximum absorption at 526nm. The course of the reaction was studied for 2 hours and pseudo first order rate constant k' calculated by least square method.

### Stoichiometry

4-hydroxy benzaldehyde (0.1M), KMnO<sub>4</sub> (0.2M), H<sub>2</sub>SO<sub>4</sub> (1M) and water (total volume to 100ml) kept aside for 24 hours. The unconsumed KMnO<sub>4</sub> was determined spectrophotometrically and the product 4-hydroxy benzoic acid was isolated which was confirmed by TLC, M.P. and qualitatively. 1:1 stoichiometry shown by the reaction with yield above 90%.

## Results and Discussion

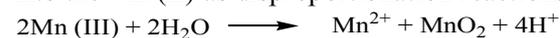
In the kinetic run we observed that when the substrate in excess at constant 4-hydroxy benzaldehyde and H<sub>2</sub>SO<sub>4</sub>, the Plots of log O.D. v/s Time were linear indicating first order dependent on KMnO<sub>4</sub>. The plot of log [KMnO<sub>4</sub>] Vs Time was linear also supports first order independence of rate on KMnO<sub>4</sub>. The pseudo first order rate constant was independent of concentration of KMnO<sub>4</sub> further confirming the first order dependence of KMnO<sub>4</sub> values of k' did not change with increase in [4-HB] indicating zero order dependence of the rate on 4-hydroxybenzaldehyde. The rate increased with increase in concentration of H<sub>2</sub>SO<sub>4</sub> and the plot of log k' Vs log [H<sub>2</sub>SO<sub>4</sub>] indicated a fractional order dependence of the reaction rate on [H<sub>2</sub>SO<sub>4</sub>]. The results are reported in Table 1.

The compound 4-hydroxy benzaldehyde is easy to oxidize due to excess of valence electrons for bonding. The exact nature of the oxidizing species in solution of the various strong inorganic oxidants has been the subject of much investigation and speculation. Since the point of attack on the reductant is assumed to be an electronegative site. Such attack is obviously favoured by the presence of positive charges. Since the positively charged species are

generated in an acid medium. The permagnative oxidation easily takes place in acidic medium. There are various oxidation states of Mn like (+II, +III, +IV, +V, +VI and +VII). Hence it become very complicated to find out the exact species involved in it. It is assumed that during the oxidation of aldehyde, positively charged species attack a lone pair of electron of the reductant at a centre of high electron density.



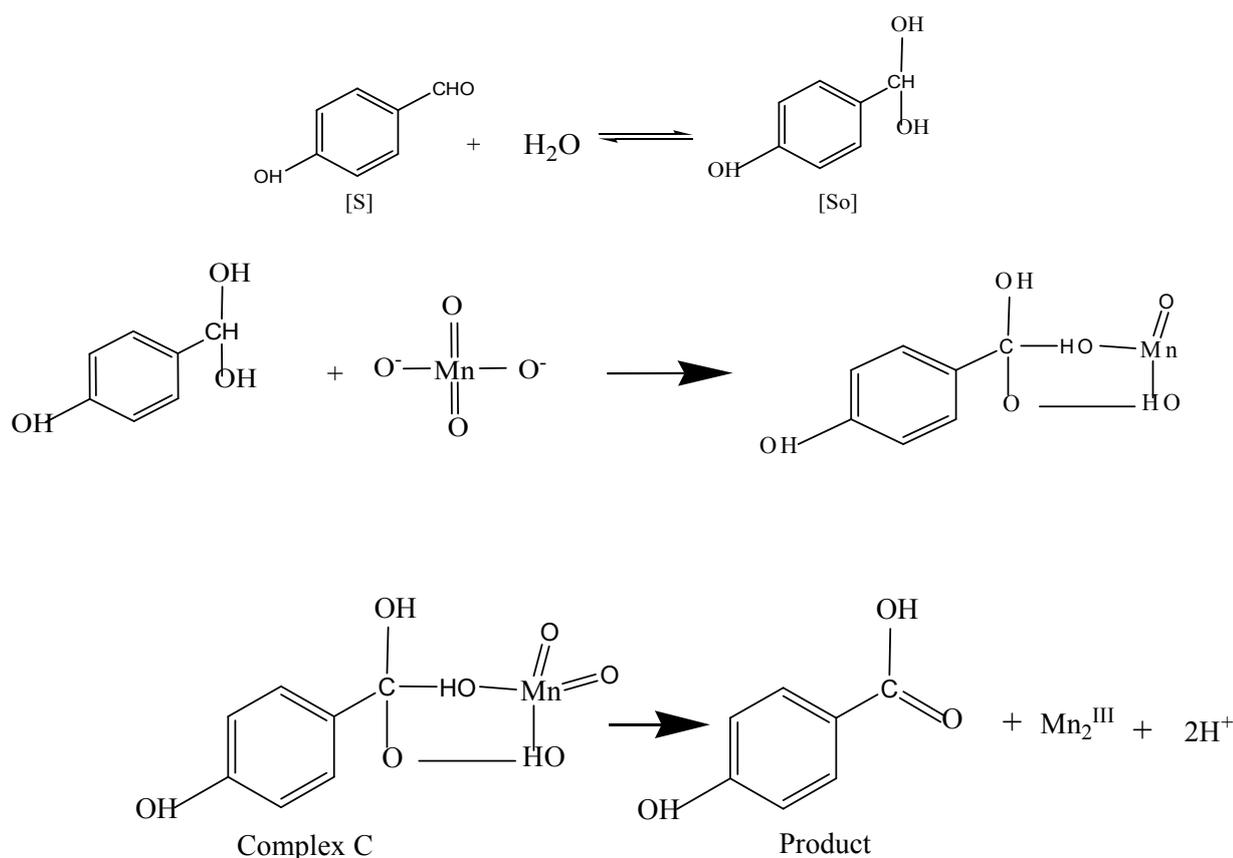
The oxidation state of Mn in MnO<sub>4</sub><sup>-</sup> is +VII. Therefore, it can be represented as Mn (VII) which is a powerful oxidizing agent and usually reduced to Mn (II). The possibility of involvement of Mn (VI) is ruled out since it is stable in basic medium only even Mn (V) is also stable in strong alkali only. The normal form of Mn (IV) is MnO<sub>2</sub>. It is grey to grey-black solid. Since we do not observed in precipitation in the reaction there is no formation of MnO<sub>2</sub> or it may be consumed as soon as formed. The formation of Mn (III) is not possible it is unstable and gets converted into the Mn (II) as disproportionation reactions.



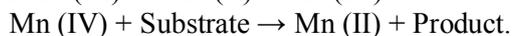
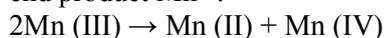
**Table 1. Effect of varying concentration of reactants at 25°C.**

[4-HB] 10 <sup>-4</sup> M	10 <sup>-3</sup> M [Oxidant]	[H <sub>2</sub> SO <sub>4</sub> ] M	k'(sec <sup>-1</sup> )
2.0	1.0	1.0	1.1504
4.0	1.0	1.0	1.0355
5.0	1.0	1.0	1.2349
7.0	1.0	1.0	1.3764
9.0	1.0	1.0	1.3764
10	1.0	1.0	1.4281
10	2.0	1.0	1.1918
10	3.0	1.0	1.2799
10	5.0	1.0	1.3270
10	6.0	1.0	1.4281
10	1.0	0.3	1.0355
10	1.0	0.5	1.2349
10	1.0	0.8	1.4826

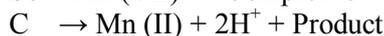
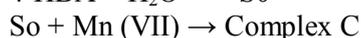
The probable mechanism can be depicted as,



The formation of oxo-bridge in intermediate compound indicates the passage of one electron from the substrate to the oxygen bonded Mn<sup>7+</sup>. This bridge due to protonation, rupture and gives Mn<sup>3+</sup> species. Since the solution does not indicate any presence of Mn (III) or precipitated MnO<sub>2</sub> it is quite logical to state that Mn (III) reacts or its disproportionated product Mn (IV) instantaneously reacts with substrate giving final end product Mn<sup>2+</sup>.



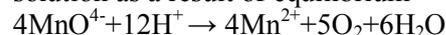
Considering the following steps the kinetic expression can be given,



(Where S= substrate, So = hydrated benzaldehyde and C = Complex)

It is assumed that the oxidation takes place by three different ways that is hydrogen atom abstraction, electron abstraction and oxygen atom transfer. In hydrogen abstraction mechanism hydrogen atom may

be removed directly by an oxo ion or by radical (OH<sup>-</sup>, OH<sup>2-</sup>) forming free radicals. The electron abstraction takes place with simple ionic oxidizing agents examples Fe<sup>3+</sup>, Ce<sup>4+</sup>, etc. Generally in acid media, oxidation takes place by Mn (III) and Mn (IV) these ions are formed by reaction between Mn (II) and Mn (VII). The divalent manganese ion Mn (II) is present in solution as a result of equilibrium



Ions with intermediate states are also produced. Hence there is possibility of several simultaneous oxidation reactions.

#### Effect of salt

The effect of salt on rate constant shows appreciable decrease, this may be due to the negative catalytic effect of salt. It is observed that rate constant in presence of K<sub>2</sub>SO<sub>4</sub>, MgCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub> does not depend on the salt concentration. In KBr rate constant increases first and then decreases. Whereas in case of KI and KCl no sequence or trend of rate constant is observed. This may be due to the involvement of I<sup>-</sup> and Cl<sup>-</sup> oxidation processes.

**Table 2. Effect of salts on reaction rate.**[4-HB] =  $1 \times 10^{-3}$  M, [H<sub>2</sub>SO<sub>4</sub>] = 1M, [KMnO<sub>4</sub>] =  $1 \times 10^{-3}$  M, Temp. = 25 °C

M [salt]	K <sub>2</sub> SO <sub>4</sub>	KBr	AlCl <sub>3</sub>	KI	MgCl <sub>2</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>	KCl	Al(NO <sub>3</sub> ) <sub>3</sub>
0.01	0.0336	0.0505	0.0439	0.0750	0.0281	0.0348	0.0300	0.0409
0.02	0.0275	0.0440	0.0434	0.0437	0.0273	0.0313	0.0379	0.0338
0.03	0.0343	0.0542	0.0341	0.0744	0.0282	0.0345	0.0319	0.0421
0.04	0.0304	0.0642	0.0414	0.0016	0.0319	0.0321	0.0378	0.0576
0.05	0.0359	0.0741	0.0439	0.1441	0.0286	0.0292	0.0395	0.0405
0.06	0.0342	0.0739	0.0397	0.0267	0.0288	0.0314	0.0505	0.0484
0.07	0.0362	0.0714	0.0384	0.0052	0.0273	0.0345	0.0453	0.0383
0.08	0.0316	0.0576	0.0367	0.0365	0.0286	0.0341	0.0364	0.0392
0.09	0.0340	0.0471	0.0353	0.0213	0.0297	0.0293	0.0434	0.0430

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