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## **Oxidation of p-nitro benzyl alcohol by Dess Martin Periodinane: A Kinetic and Mechanistic Study**

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### **Abstract**

The Kinetics of oxidation of p-nitro benzyl alcohol by Dess Martin Periodinane (DMP) has been studied Spectrophotometrically at 245nm in presence of Sulphuric acid in aqueous acetic acid medium. The reaction is first order with respect to both p-nitro benzyl alcohol and Dess Martin Periodinane (DMP). The reaction was studied in the temperature range 292-318K. The activation parameters for the slow steps were calculated. Effect of dielectric constant and ionic strength of medium has been studied. A suitable mechanism has been proposed.

**Key words:** p-nitro benzyl alcohol, Dess Martin Periodinane (DMP), Oxidation, Kinetics.

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### **INTRODUCTION**

Selective oxidation of alcohols to their corresponding aldehydes and ketones is an important transformation in organic chemistry which has received the most attention over years, especially in the search of versatile and selective reagent for this purpose. The kinetics and mechanisms of oxidation of p-nitro benzyl alcohol can provide some valuable information for organic synthesis and chemical industry. Dess Martin Periodinane being one of the most versatile and selective available oxidizing reagent. The synthesis of newer oxidizing agent for the oxidation of organic substrates continues to be interest. In recent years significant improvements were achieved by the use of new oxidizing agents for the study of kinetics and mechanism of various organic compounds. Literature survey reveals that there is no

report available on kinetics and mechanism of oxidation of p-nitro benzyl alcohol by Dess Martin Periodinone (DMP); hence we have considered it to study the kinetics and mechanism of oxidation of p-nitro benzyl alcohol by DMP.

### **DETERMINATION OF STOICHIOMETRY AND PRODUCT ANALYSIS**

The stoichiometry of the reaction was determined by carrying out several sets of experiment with varying amount of (DMP) largely in excess over p-nitro benzyl alcohol in 20% acetic acid by using 0.1N H<sub>2</sub>SO<sub>4</sub>. The remaining (DMP) was then analyzed spectrophotometrically. The result indicated that 1 mole of alcohols react with 2 mole (DMP).

The product analysis was carried out under kinetic conditions. In a typical experiment, p-nitro benzyl alcohol (0.05 mol) and DMP (0.01) were made up to 50

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ml in 20% acetic acid and kept in dark for about 24 hours to ensure the completion of the reaction. The solution was then treated with an excess (200 ml) of a saturated solution of 2, 4-dinitrophenylhydrazine in 2 mol dm<sup>-3</sup>HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitrophenylhydrazone (DNP) was filtered off, dried, weighed, recrystallized from ethanol and weighed again. The yield of DNP before and after recrystallization was 1.8 g (90%) and 1.5 g (75%) respectively. The DNP was found identical with the DNP of benzaldehyde by melting point. The products were also characterized by TLC, IR, and NMR spectra

#### KINETIC MEASUREMENTS

The reactions were followed under pseudo-first-order conditions by keeping large excess (x 15 or greater) of the p-nitro benzyl alcohol over DMP. The temperature was kept constant to +/- 0.1 K. The solvent was acetic acid. The reactions were followed by monitoring the decrease in the concentration of DMP spectrophotometrically at 245 nm for 80% completion of the reaction. The pseudo-first-order rate constants  $K_{obs}$ , were evaluated from the linear ( $r=0.990-0.999$ ) plots of  $\log [DMP]$  against time.

**[DMP]= 0.001 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.1 N, Temperature =303 K, AA = 20% (v/v)**

[p-n.BA]	0.01 M	0.02M	0.03M	0.04M	0.05M	0.06M	0.07M	0.08M
$k \times 10^3 \text{sec}^{-1}$	2.08	2.32	2.64	2.86	3.28	3.66	3.97	4.38

**Figure: 1: Plot of 2+ Log [p-nitro benzyl alcohol] Vs 3+Logk`**

Duplicate kinetic runs showed that the rate constants were reproducible to within +/- 3%.

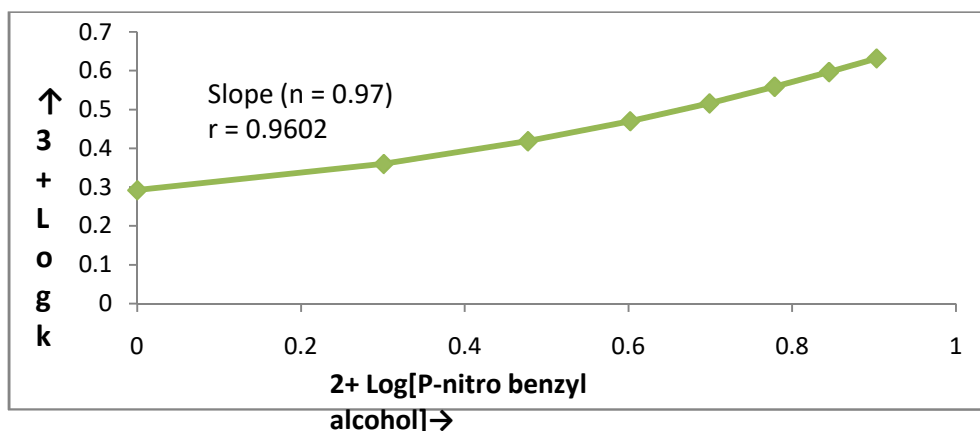
#### RESULT AND DISCUSSION

The results of oxidation of p-nitro benzyl alcohol by DMP are represented in table 1-7.

#### Effect of variation of concentration p-nitro benzyl alcohol:-

The oxidation of p-nitro benzyl alcohol with DMP in 20% of acetic acid in presence of sulphuric acid yields p-nitrobenzaldehyde. By keeping constant [DMP] and [H<sub>2</sub>SO<sub>4</sub>], the increase in [P-nitro benzyl alcohol] increases the rate of reaction (Table-1). The plot of  $\log$  of  $k_{obs}$  versus  $\log$  [P-nitro benzyl alcohol] for different initial concentration of p-nitro benzyl alcohol, is linear with unit slope demonstrate the first order dependence of rate on p-nitro benzyl alcohol (Figure: 1).

#### Table 1: Effect of variation of [p-nitro benzyl alcohol] on reaction rate



**Effect of variation of concentration of DMP:-**

At constant [P-nitro benzyl alcohol] and [H<sub>2</sub>SO<sub>4</sub>], the increase in [DMP] increases the rate of reaction (Table-2). The plot of log k<sub>obs</sub> versus log [DMP] for different initial concentration of DMP is linear, with unit slope; present the first-order dependence of rate on DMP.

**Table 2: Effect of variation of [DMP] on reaction rate**

[P-nitro benzyl alcohol]= 0.01 M, [H<sub>2</sub>SO<sub>4</sub>] = 0.1 N, Temp =303 K, AA = 20% (v/v)

[DMP] Mole	0.001	0.002	0.003	0.004	0.005	0.006	0.007	0.008
<b>k x 10<sup>3</sup>sec<sup>-1</sup></b>	2.08	2.27	2.58	2.87	3.18	3.51	3.84	4.17

**Effect of variation of concentration of H<sup>+</sup>:-**

In order to study the effect the H<sup>+</sup> ion concentration on the rate of oxidation reaction of p-nitro benzyl alcohol, the dependence of reaction rate has been investigated at different initial concentration of H<sub>2</sub>SO<sub>4</sub>. The rate of reaction increases with increase in [H<sub>2</sub>SO<sub>4</sub>] (Table-3). The plot of log K<sub>obs</sub> versus log [H<sup>+</sup>] are also straight line with slope less than unity, indicating a fractional order dependence on [H<sup>+</sup>].

**Table 3: Effect of variation of [H<sub>2</sub>SO<sub>4</sub>] on reaction rate**

[DMP]= 0.001 M, [P-nitro benzyl alcohol] = 0.01 M, Temp. =303 K, AA = 20% (v/v)

[H <sub>2</sub> SO <sub>4</sub> ]	0.1M	0.2M	0.3M	0.4M	0.5M	0.6M	0.7M	0.8M
<b>k x 10<sup>3</sup>sec<sup>-1</sup></b>	2.08	2.25	2.46	2.66	2.87	3.09	3.28	3.49

**Effect of ionic strength:-**

In the present investigation effect of salt on the rate of reaction is carried out. The salts selected are KCl, KBr, and KI. These will give effect of anion particularly halides on the rate of reaction. The divalent and trivalent cationic salt were also used such as CaCl<sub>2</sub>, Ca(NO<sub>3</sub>)<sub>2</sub>,

$\text{Al}(\text{NO}_3)_3$  and  $\text{K}_2\text{SO}_4$ . The experiments were carried out under pseudo- first- order condition. These results were used to determine first order rate constant. The rate constants for the oxidation of p-nitro benzyl alcohol in presence of different salt are shown in (Table 4). From table it is clear that, the rate increases with increase in cationic charge and decreases with increase in anionic charge.

**Table 4: Effect of variation of [salts] on reaction rate**

[DMP]= 0.001 M, [p-n.BA] = 0.01 M,  $[\text{H}_2\text{SO}_4]$  = 0.1 N, Temp. =303 K, AA = 20% (v/v)

Salts 0.1M	KCl	KBr	KI	$\text{CaCl}_2$	$\text{Ca}(\text{NO}_3)_3$	$\text{Al}(\text{NO}_3)_3$	$\text{K}_2\text{SO}_4$
$k \times 10^3 \text{sec}^{-1}$	2.08	2.36	2.37	2.56	2.79	3.99	2.38

**Effect of solvent composition:-**

At fixed p-nitro benzyl alcohol, [DMP] and  $[\text{H}^+]$ , the rate of oxidation of p-nitro benzyl alcohol with DMP increases with decrease in polarity of solvent (Table 5). This is due to polar character of transition state as compared to the reactant. The plot of  $\log k_{\text{obs}}$  versus  $1/D$  is linear with positive slope indicating ion- dipole type of reaction.

**Table5: Effect of variation of Acetic Acid % on reaction rate**

[DMP]= 0.001 M,  $[\text{H}_2\text{SO}_4]$  = 0.1 N, [P-nitro benzyl alcohol]=0.01M, Temp=303 K

Acetic acid	10 %	20 %	30 %	40 %	50 %	60 %	70 %	80 %
$k \times 10^3 \text{sec}^{-1}$	1.72	2.08	2.27	2.48	2.73	2.89	3.07	3.25

**Effect of temperature:-**

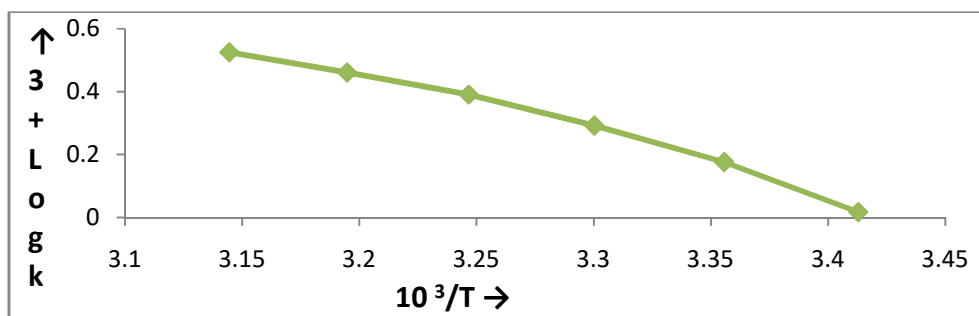
The study of effect of temperature on rate of oxidation of p-nitro benzyl alcohol by DMP has been subjected to different temperature range 293K to 313K by keeping the concentration of p-nitro benzyl alcohol and reagent constant. Rate constants are given in Table 6. The plots of  $\log k_{\text{obs}}$  versus  $1/T$  are linear (Figure: 2)

**Table 6: Effect of variation of Temperatures on reaction rate**

[DMP]= 0.001 M, [P-nitro benzyl alcohol] = 0.01 M,  $[\text{H}_2\text{SO}_4]$  = 0.1 N, AA = 20% (v/v)

Temperatures (K)	293	298	303	308	313	318
$k \times 10^3 \text{sec}^{-1}$	1.04	1.50	1.96	2.46	2.89	3.35

**Figure: 2: Arrhenius plot of oxidation of p-nitro benzyl alcohol**



Activation parameters are presented in (Table 7). The negative values of entropy of activation reflect that the transition state is more ordered than initial state. The nearly constant  $\Delta G^\ddagger$  value indicates that similar mechanism is operative for the oxidation of p-nitro benzyl alcohol.

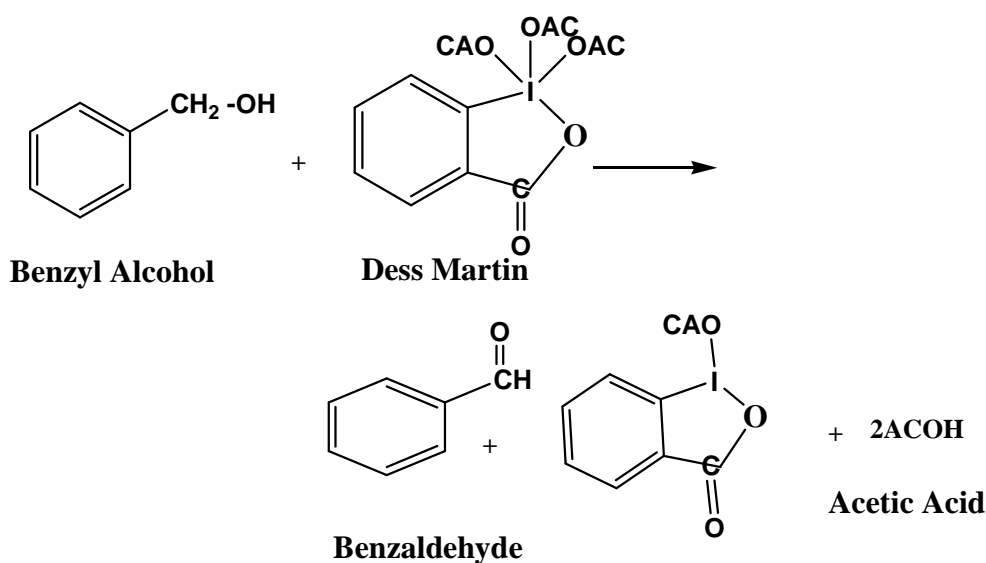
**Table 7: Activation Parameters**

[DMP]= 0.001 M, [p-n.BA] = 0.01 M. [H<sub>2</sub>SO<sub>4</sub>] = 0.1 N, Temp. =303 K, AA = 20 % (v/v)

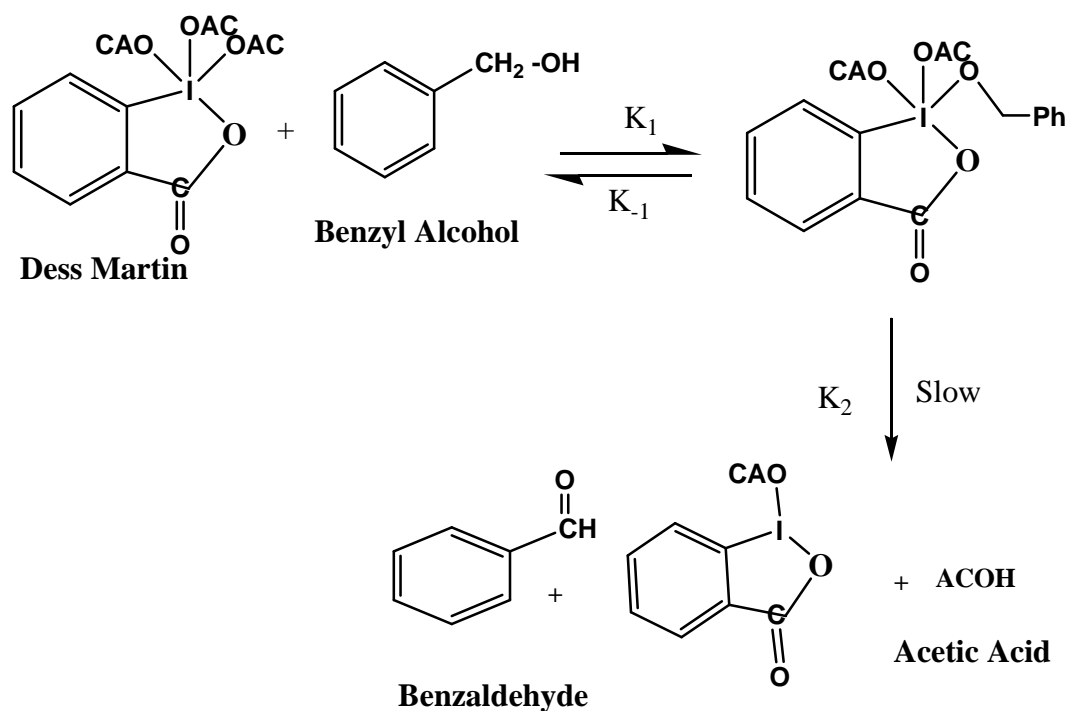
Activation parameters	$\Delta E_a$ KJ mole <sup>-1</sup>	$\Delta H^\ddagger$ KJmol <sup>-1</sup>	$\Delta S^\ddagger$ JK <sup>-1</sup> mole <sup>-1</sup>	$\Delta G^\ddagger$ KJ mole <sup>-1</sup>
	30.9	29.12	-206.15	88.95

The values of entropy of activation also suggested that the reaction is entropy as well as enthalpy controlled. The values of free energies of activation of reaction were found to be more or less similar. These trends also support the identical reaction mechanism being followed in these reactions.

**Reaction:**



**Mechanism of oxidation of benzyl alcohol by DMP:-**



**CONCLUSION**

The active species of DMP is understood for the said reaction. The rate constants of the slow step involved in the mechanism were evaluated and activation parameters were also computed. The negative value of  $\Delta S^\ddagger$  provides support to the formation of rigid transition state. The

overall mechanism described here is consistent with product and kinetic studies.

**Acknowledgement:-**

Author is very much thankful to Dr. Shamamaparveen, President of RECWS Aurangabad and Dr. Shaikh Kabeer Ahmed, Principal Sir Sayyed College, Aurangabad, for providing laboratory facilities.

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