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Para Amino Benzoic: Kinetic Study of Oxidation by Acidic Potassium Permanganate in Acidic Media

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ABSTRACT

A study of oxidation of P-amino benzoic acid has been carried out at various temperatures using acidic Potassium Permanganate ($KMnO_4$) using spectrophotometer under acidic conditions. Effect of variation of substrate Para Amino Benzoic Acid (PABA), variation of oxidant ($KMnO_4$) and variation of acid H_2SO_4 was studied under pseudo first order reaction conditions. The study also included effect of variation of different salts and variation in solvent. The reaction was found to be first order with respect to oxidant, substrate and acid H_2SO_4. The reaction was monitored spectrophotometrically.

Keywords: PABA, $KMnO_4$, Permanganatic oxidation, Acidic media

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INTRODUCTION

P-amino Benzoic Acid (PABA) is a biologically active compound and it has UV absorption and photosensitive it is a member of vitamin B_X it acts as a bacterial co-factor involved in the synthesis of folic acid. PABA was wide application in perfumes, dyes, sunscreen agents and feedstock additives. In medicine it is used as protective drugs against UV irradiation [1]. PABA is an arylated in cancer cells over expressing glutathione S-transferase [2]. It also possesses antiviral effect, anticoagulant and antibiotic [3].

There are various oxidizing agents, but potassium permanganate is widely used, as it has some advantages over the other oxidizing agents [4-7]. Not only inorganic compounds but organic compounds can be oxidized by potassium permanganate. It can oxidize the substrate in all media including acidic, basic and neutral.

MATERIALS AND METHODS

Distilled water was prepared in the laboratory using all quick fit glass assembly. A pinch of Potassium Hydroxide (KOH) and permanganate was added the pH of distilled water. All solutions were prepared in double distilled water a stock solution 0.01 M $KMnO_4$. It was standardized using oxalate. The temperature was maintained constant using thermostat of Dinesh make assembled Dinesh make was used to maintain temperature constant. PABA was purchased from Lab Trading Co. of Hi-media Chemicals. All kinetic runs were carried out in thermostat by changing the conditions such as variation in oxidant, variation in substrate, variation in H_2SO_4 effect of temperature, effect of salt and effect of solvent. All kinetic runs were carried out using (ELICO SL 210) at 525 nm. Spectrophotometer was used to carry at all kinetic runs.

RESULTS AND DISCUSSION

Effect of variation of substrate (PABA)

To study the effect of variation of concentration of substrate, the sets are prepared in which the concentration of PABA was varied from 1×10^{-3} to 9×10^{-3} M, keeping constant concentration of $[KMnO_4]=1 \times 10^{-2}$ M, $[H_2SO_4]=1$ M. As the reaction has been studied under pseudo first order condition pseudo first order rate constants were calculated. Initially at low concentration of PABA, the rate constant was found 7.26×10^{-2} s^{-1} but with increasing the concentration of PABA the rate constant decreases with increasing concentration (Figure 1 and Table 1).

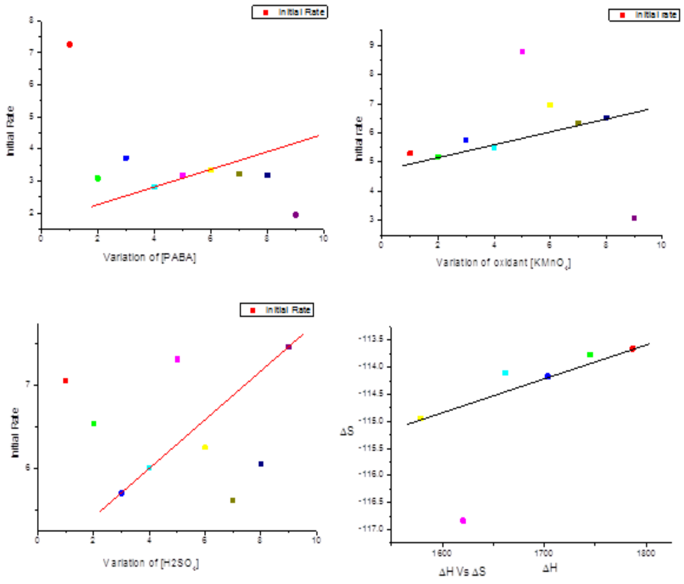

Figure 1: Pseudo first order rate constant at variation in oxidant, substrate, acid and temperature

Table 1: Pseudo first order rate constant at=25°C ± 0.5°C keeping variation in substrate (PABA)

PABA	$KMnO_4$	H_2SO_4	K
1×10^{-3}	1×10^{-2}	1 M	7.26×10^{-2}
2×10^{-3}	1×10^{-2}	1 M	3.08×10^{-2}
3×10^{-3}	1×10^{-2}	1 M	3.72×10^{-2}
4×10^{-3}	1×10^{-2}	1 M	2.82×10^{-2}
5×10^{-3}	1×10^{-2}	1 M	3.19×10^{-2}
6×10^{-3}	1×10^{-2}	1 M	3.33×10^{-2}
7×10^{-3}	1×10^{-2}	1 M	3.21×10^{-2}
8×10^{-3}	1×10^{-2}	1 M	3.17×10^{-2}
9×10^{-3}	1×10^{-2}	1 M	1.94×10^{-2}

The reaction has been studied under pseudo first order condition using Equation:

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

This is modified as,

$$k = \frac{2.303}{t} \log \frac{(OD)_\infty - (OD)_0}{(OD)_\infty - (OD)_t}$$

Effect of variation of oxidant ($KMnO_4$)

To study the effect of variation of oxidant, we have taken substrate concentration of [PABA]=1 × 10^{-3} mol/dm^3, [H_2SO_4]=1 M and temperature was kept constant 25°C ± 0.5°C in thermostat and varied the concentration of oxidant from 1 × 10^{-2} to 9 × 10^{-2} M. At low concentration of $KMnO_4$ below (5 × 10^{-2}) all irregular nature of rate constant observed but above 5 × 10^{-2} M $KMnO_4$, rate constant decrease with increase in concentration of oxidant (Table 2).

Table 2: Pseudo first order rate constant at=25°C ± 0.5°C keeping variation in oxidant ($KMnO_4$)

PABA	$KMnO_4$	H_2SO_4	k
1×10^{-3}	1×10^{-2}	1 M	5.3×10^{-2}
1×10^{-3}	2×10^{-2}	1 M	5.19×10^{-2}
1×10^{-3}	3×10^{-2}	1 M	5.74×10^{-2}
1×10^{-3}	4×10^{-2}	1 M	5.47×10^{-2}
1×10^{-3}	5×10^{-2}	1 M	8.8×10^{-2}
1×10^{-3}	6×10^{-2}	1 M	6.95×10^{-2}
1×10^{-3}	7×10^{-2}	1 M	6.32×10^{-2}
1×10^{-3}	8×10^{-2}	1 M	6.52×10^{-2}
1×10^{-3}	9×10^{-2}	1 M	3.07×10^{-2}

Effect of variation of (H_2SO_4)

To study the effect of variation of concentration of Sulphuric acid H_2SO_4, in the experimental sets the concentration of H_2SO_4 is varied from 1 × 10^{-1} to 9 × 10^{-1} M, keeping constant concentration i.e., [PABA]=1 × 10^{-3} and [$KMnO_4$]=7 × 10^{-2} M. As the reaction has been studied under pseudo first order condition for varying [H_2SO_4] was made and pseudo first order rate constants were calculated. Hence it is clear from the Table 3 that rate constant does not shows any specific trends.

Table 3: Pseudo first order rate constant at=25°C ± 0.5°C keeping variation in H_2SO_4 concentration

[PABA]	[$KMnO_4$]	[H_2SO_4]	k
1×10^{-3}	7×10^{-2}	1×10^{-1}	7.05×10^{-2}
1×10^{-3}	7×10^{-2}	2×10^{-1}	6.53×10^{-2}
1×10^{-3}	7×10^{-2}	3×10^{-1}	5.70×10^{-2}
1×10^{-3}	7×10^{-2}	4×10^{-1}	6.0×10^{-2}
1×10^{-3}	7×10^{-2}	5×10^{-1}	7.31×10^{-2}
1×10^{-3}	7×10^{-2}	6×10^{-1}	6.25×10^{-2}
1×10^{-3}	7×10^{-2}	7×10^{-1}	5.62×10^{-2}
1×10^{-3}	7×10^{-2}	8×10^{-1}	6.05×10^{-2}
1×10^{-3}	7×10^{-2}	9×10^{-1}	7.46×10^{-2}

Effect of variation in temperature

The effect of temperature was studied keeping constant concentration of all reactants such as [$KMnO_4$]=7 × 10^{-2} M, [PABA]=1 × 10^{-3} M and [H_2SO_4]=1 M. The temperature variation was done in the range of 298 to 323 k. The energy of activation was calculated by plotting graph between log k verses 1/T, a straight line with negative slope was obtained. The temperature dependence on a number of reactions can be given by an Equation:

$$k = \frac{k_b}{T} e^{\frac{\Delta Ea^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}}$$

The moderate enthalpy of activation and higher rate constant of slow step reveals that the oxidation presumably occurs by an inner sphere mechanism. The free energy change (ΔG), enthalpy changes (ΔH) and entropy change (ΔS) was determined (Table 4).

Table 4: Pseudo first order rate constant at different temperatures

Temperatures	PABA	$KMnO_4$	H_2SO_4	K
25°C	1×10^{-3}	7×10^{-2}	1 M	6.44×10^{-2}
30°C	1×10^{-3}	7×10^{-2}	1 M	6.55×10^{-2}
35°C	1×10^{-3}	7×10^{-2}	1 M	6.12×10^{-2}
40°C	1×10^{-3}	7×10^{-2}	1 M	6.10×10^{-2}
45°C	1×10^{-3}	7×10^{-2}	1 M	3.18×10^{-2}
50°C	1×10^{-3}	7×10^{-2}	1 M	5.59×10^{-2}

The activation energy was found to be 13196.21 J/mol. This activation energy was used to calculate the enthalpy of activation (ΔH) using Equation:

$$\Delta H = \Delta E - RT$$

The value of (ΔH) decreases with increase in temperature. The average (ΔH) was found to be 10614.71 J/mol from this; we calculated entropy of activation using formula (Table 5):

$$k = \frac{k_B}{T} e^{\frac{\Delta Ea^{\#}}{RT}} e^{\frac{\Delta S^{\#}}{R}}$$

Where, k= pseudo first order rate constant, k_B=Boltzmann constant, T=Temperature.

Table 5: Thermodynamic parameter of the kinetic oxidation process

T	k	$\Delta H^{\#}$ (J/mol^{-1})	$\Delta S^{\#}$ (J/mol^{-1})	$\Delta G^{\#}$ (J/mol^{-1})
298	0.0644	10718.63	-100.64	40710.60
303	0.0655	10677.06	-100.96	41268.08
308	0.0612	10635.49	-101.57	41919.59
313	0.0650	10593.92	-101.93	42500.81
318	0.0318	10552.35	-104.63	43826.63
323	0.0559	10510.78	-102.93	43758.65

There was regular trend of enthalpy change; it changes from 10718.63 to 10510.78 J/mole. The average entropy of activation was found to be -102.11 J/mol. The entropy change remains almost constant, indicating that in the range of 298 to 323 k, the degree of freedom remains same. The average free energy (ΔG) was then calculated using (ΔH) and (ΔS) as per the Equation:

$$\Delta G = \Delta H - T\Delta S$$

It was observed that (ΔG) increases with increase in temperature. The average (ΔG) was found to be 42330.73 J/mol. A plot of (ΔH) verses (ΔS) is linear which is according to following Equation:

$$(\Delta H)=\beta \Delta S$$

Where, β is called iso kinetic temperature, for PABA it is=-103.95 k

Effect of variation of solvent

The reaction was monitored in four different solvents, namely 1,4-dioxane, acetic acid, Dimethylformamide (DMF) and acetone. The rate constant decreases with increase in acetone percentage where as it increases with increases in percentage of acetic acid. This may be due to ionic and covalent nature of solvent. Acetic acid get ionized producing proton which may catalyze the reaction and hence rate increases. In DMF and 1,4-dioxane no specific trends is observed (Table 6 and Figure 2).

Table 6: Pseudo first order rate constant at=25°C ± 0.5°C keeping variation in solvent concentration

Percentage of solvent	Rate constant (s^{-1})			
	1,4-dioxane	Acetic Acid	DMF	Acetone
10%	1.44×10^{-2}	3.55×10^{-2}	5.49×10^{-2}	3.78×10^{-2}
20%	1.15×10^{-2}	3.95×10^{-2}	6.66×10^{-2}	3.79×10^{-2}
30%	6.91×10^{-2}	4.26×10^{-2}	5.48×10^{-2}	3.38×10^{-2}
40%	5.50×10^{-2}	4.13×10^{-2}	6.27×10^{-2}	3.46×10^{-2}
50%	2.64×10^{-2}	5.17×10^{-2}	6.07×10^{-2}	3.01×10^{-2}
60%	2.34×10^{-2}	5.45×10^{-2}	6.78×10^{-2}	3.01×10^{-2}

[PABA]=1×10^{-3}; [$KMnO_4$]=7×10^{-2}; [H_2SO_4]=1 M; Temparature=25°C ± 0.5°C

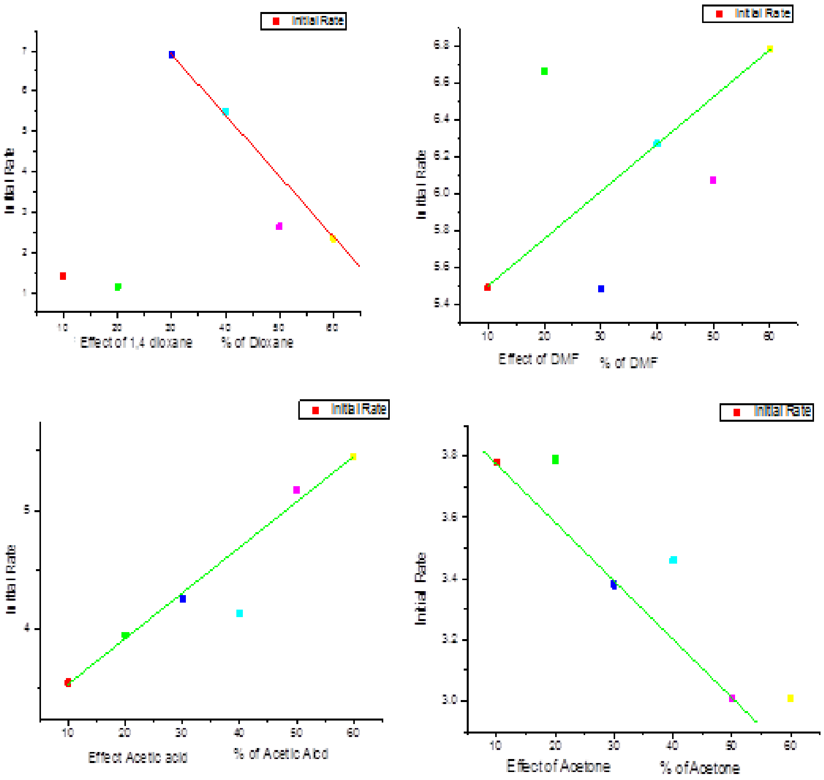

Figure 2: Pseudo first order rate constant at variation in solvent and its concentration

Effect of variation of salts

To study the effect of variation of salts, the concentration of salts was varied from 1×10^{-3} to 9×10^{-3} M, keeping constant concentration of reactants such as [$KMnO_4$]=7×10^{-2} M, [PABA]=1×10^{-3} M, [H_2SO_4]=1 M. These results are given in the Table 7 form obtained results, it is clear that pseudo first order rate constant k_{obs} increases with the increase in concentration of salts. A plot of log k_{obs} vs $\sqrt{\mu}$, according to extended Bronsted Debye-Huckel equation was found to be linear with negative slopes (NaCl, $CaCl_2$, $AlCl_3$, Na_2SO_4, Na_3PO_4 and $MnSO_4$) indicating negative salt effect (Figure 3).

Table 7: Pseudo first order rate constant at=25°C ± 0.5°C keeping variation in salts concentration

Concentration of salt	**Rate constant (s^{-1})**					
	NaCl	**$CaCl_2$**	**$AlCl_3$**	**Na_2SO_4**	**Na_3PO_4**	**$MnSO_4$**
1×10^{-3}	4.15×10^{-2}	3.78×10^{-2}	4.46×10^{-2}	3.64×10^{-2}	3.44×10^{-2}	4.9×10^{-2}
2×10^{-3}	4.21×10^{-2}	3.72×10^{-2}	4.36×10^{-2}	3.87×10^{-2}	3.55×10^{-2}	4.7×10^{-2}
3×10^{-3}	4.65×10^{-2}	3.79×10^{-2}	4.43×10^{-2}	3.86×10^{-2}	4.51×10^{-2}	5.08×10^{-2}
4×10^{-3}	4.26×10^{-2}	3.81×10^{-2}	4.55×10^{-2}	3.86×10^{-2}	3.69×10^{-2}	2.55×10^{-2}
5×10^{-3}	4.25×10^{-2}	3.83×10^{-2}	4.49×10^{-2}	3.78×10^{-2}	3.71×10^{-2}	2.11×10^{-2}
6×10^{-3}	3.88×10^{-2}	3.96×10^{-2}	4.22×10^{-2}	3.78×10^{-2}	3.7×10^{-2}	5.05×10^{-2}
7×10^{-3}	4.88×10^{-2}	3.85×10^{-2}	4.78×10^{-2}	3.72×10^{-2}	3.58×10^{-2}	5.47×10^{-2}
8×10^{-3}	3.92×10^{-2}	3.73×10^{-2}	4.18×10^{-2}	3.70×10^{-2}	3.54×10^{-2}	1.77×10^{-2}
9×10^{-3}	3.74×10^{-2}	3.73×10^{-2}	4.37×10^{-2}	3.79×10^{-2}	3.51×10^{-2}	4.31×10^{-2}

[PABA]=1×10^{-3}; [$KMnO_4$]=7×10^{-2}; [H_2SO_4]=1 M; Temperature=25°C ± 0.5°C

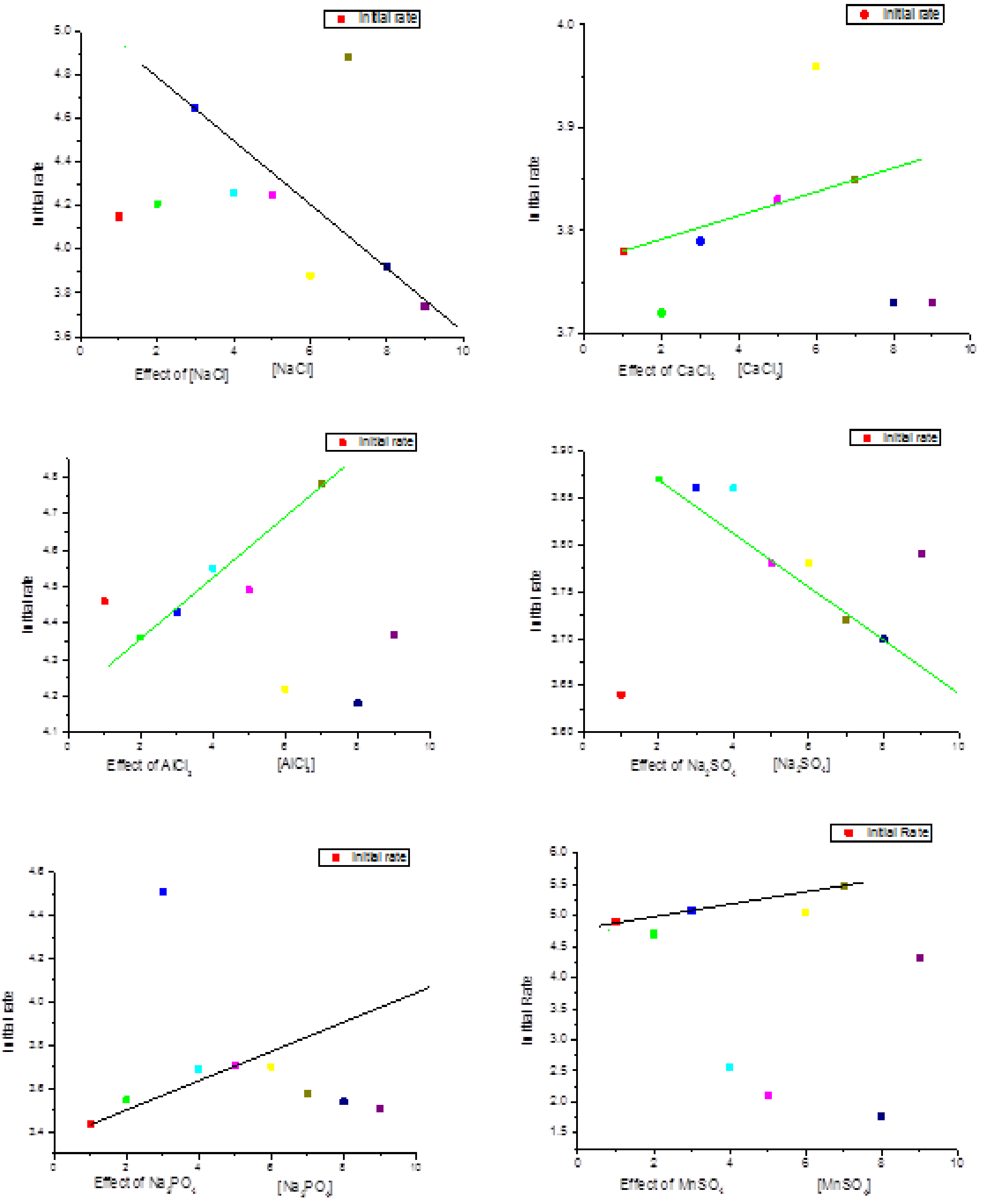

Figure 3: Pseudo first order rate constant at variation in salts and its concentration

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REFERENCES

[1] S.K. Chandran, R. Paulraj, P. Ramasamy, *Optical Materials.*, **2016**, 52, 49-55.
[2] Y. Kim, A.E. Maciag, Z. Cao, J.R. Deschamps, J.E. Saavedra, L.K. Keefer, R.J. Holland, *Bioorg. Med. Chem*., **2015**, 23, 4980-4988.
[3] S. Acharya, R. Soni, *Rasayan J. Chem*., **2013**, 1(6), 24-28.
[4] B. Dhobhal, R. Shimpi, M. Hebade, M. Farooqui, *JMCDD.*, **2016**, 2347-9027.
[5] S. Gour, R.P. Phase, B.R. Agarwal, M. Farooqui, *IJCS.*, **2016**, 1(3), 107-117.
[6] S.B. Pakhare, S. Fatema, J. Gawai, M. Farooqui, *JCBPS.*, **2015**, 5(3), 1000-1002.
[7] S.B. Pakhare, M. Ubale, J. Gawai, M. Farooqui, *JASR.*, **2016**.