

Kinetic Study of Permanganatic Oxidation of Dopamine Hydrochloride in Acidic Media

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ABSTRACT: Oxidation of Dopamine hydrochloride has been studied at different temperatures using spectrophotometer under acidic conditions. The effect of variation of substrate Dopamine hydrochloride (DPH), oxidant (KMnO₄) and acid H₂SO₄ was studied under pseudo first order reaction conditions. The effect of different salts and solvents on oxidation of DPH was also studied. The reaction was found to be first order with respect to oxidant, substrate and acid H₂SO₄.

Keywords: Dopamine hydrochloride (DPH); KMnO₄; Permanganatic oxidation; acidic media.

INTRODUCTION: Dopamine is a neurotransmitter, in the mammalian central nervous system [1,2] Dopamine when embedded with melanin forms nanospheres, which as unusual optical and chemical properties and hence it is a promising material for photoprotection, structural coloration and thermoregulation [3]. The abnormal level of dopamine in brain is responsible for neurological disorder and disease like Parkinson's disease [4]. The deficiency in dopamine results in symptoms such as rigidity and tremors, which are the clinical hallmarks of Parkinson's disease [5]. The abnormality also causes Schizophrenia, autism and attention deficit hyperactivity disorder [6] Dopamine can control our emotions, as it is closely related to drug addiction, such as nicotine and ethanol [7]. There are various papers appeared in last few years, in which potassium permanganate is used as oxidant [8-15].

MATERIALS AND METHODS: For the present study distilled water was prepared in the laboratory using all quick fit glass assembly distillation units. A pinch of KOH and KMnO₄ was added during its preparation. The pH of the distilled water was monitored. All solutions were prepared in double distilled water, a stock solution 0.01M KMnO₄ was prepared and standardized using oxalate. A thermostat of locally assembled Dinesh make was used to maintain temperature constant. DPH was purchased from local Chem-

ical traders of chemicals. All kinetic runs were carried out in thermostat by changing the conditions such as variation in oxidant, variation in substrate, variation in H₂SO₄ effect of temperature, effect of salt and effect of solvent. All kinetic runs were carried out using spectrophotometer (ELICO SL 210) at 525 nm.

RESULTS AND DISCUSSION:

Effect of variation of Substrate (DPH): To study and analyze the effect of variation concentration of substrate (DPH). The concentration of DPH was varied from 1×10^{-3} to 9×10^{-3} M, keeping constant concentration of [KMnO₄] = 1×10^{-3} M, [H₂SO₄] = 1 M. As the reaction has been studied under pseudo first order condition and pseudo first order rate constants were calculated. It is observed that pseudo first order rate constants were found to decrease with increase in concentration of DPH (Table No.1). When pseudo first order rate is plotted against concentration of DPH, the trend line is linear with negative slope (Fig. 1) Hence the reaction under pseudo first order rate depends on the concentration of substrate.

As the reaction has been studied under pseudo first order condition using equation:

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \text{ which is modified as;}$$

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

Table 1: Psuedo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in substrate (DPH).

[DPH]	[KMnO ₄]	[H ₂ SO ₄]	k
1 x 10 ⁻³	1 x 10 ⁻³	1M	7.79 x 10 ⁻²
2 x 10 ⁻³	1 x 10 ⁻³	1M	3.03 x 10 ⁻²
3 x 10 ⁻³	1 x 10 ⁻³	1M	2.97 x 10 ⁻²
4 x 10 ⁻³	1 x 10 ⁻³	1M	2.61 x 10 ⁻²
5 x 10 ⁻³	1 x 10 ⁻³	1M	2.76 x 10 ⁻²
6 x 10 ⁻³	1 x 10 ⁻³	1M	2.28 x 10 ⁻²
7 x 10 ⁻³	1 x 10 ⁻³	1M	2.25 x 10 ⁻²
8 x 10 ⁻³	1 x 10 ⁻³	1M	2.11 x 10 ⁻²
9 x 10 ⁻³	1 x 10 ⁻³	1M	2.09 x 10 ⁻²

Effect of variation of oxidant (KMnO₄): To evaluate and study the effect of variation of oxidant KMnO₄ was varied in the range of 1x10⁻³M to 9x10⁻³M. The concentration of substrate [DPH] was selected at 5x10⁻³M KMnO₄ and concentration of acid H₂SO₄ 1M and temperature was kept constant 25⁰C ± 0.5⁰C in thermostat. The pseudo first order rate constant decreases with increase in concentration of KMnO₄. It is also observed that higher concentration of KMnO₄, the rate suddenly increases (Table 2).

Table 2: Psuedo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in oxidation KMnO₄.

[DPH]	[KMnO ₄]	[H ₂ SO ₄]	k
5 x 10 ⁻³	1 x 10 ⁻³	1M	2.85 x 10 ⁻²
5 x 10 ⁻³	2 x 10 ⁻³	1M	2.79 x 10 ⁻²
5 x 10 ⁻³	3 x 10 ⁻³	1M	2.48 x 10 ⁻²
5 x 10 ⁻³	4 x 10 ⁻³	1M	2.27 x 10 ⁻²
5 x 10 ⁻³	5 x 10 ⁻³	1M	2.71 x 10 ⁻²
5 x 10 ⁻³	6 x 10 ⁻³	1M	2.38 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	1M	2.2 x 10 ⁻²
5 x 10 ⁻³	8 x 10 ⁻³	1M	4.21 x 10 ⁻²
5 x 10 ⁻³	9 x 10 ⁻³	1M	4.33 x 10 ⁻²

Effect of variation of H₂SO₄ concentration: To study the effect of variation of concentration of sulphuric acid H₂SO₄, in the experimental sets the concentration of H₂SO₄ was varied in the range of 1 x 10⁻¹ to 9 x 10⁻¹ M, keeping constant concentration i.e. [DPH]= 5 x 10⁻³ and [KMnO₄] = 7 x 10⁻³ M, at the 25⁰C ± 0.5⁰C constant temperature.(Table3)As the reaction has been studied under pseudo first order condition for varying [H₂SO₄] was made and pseudo first order rate constants were calculated. It is clear from that pseudo first order rate constants values was found to vary irregularly, hence

the rate constant doesn't show any particular trend and therefore, it can be concluded that, it is independent of concentration of H₂SO₄.

Table 3: Psuedo first order rate constant at = 25⁰C ± 0.5⁰C keeping variation in H₂SO₄

[DPH]	[KMnO ₄]	[H ₂ SO ₄]	k
5 x 10 ⁻³	7 x 10 ⁻³	1 x 10 ⁻¹	1.75 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	2 x 10 ⁻¹	1.02 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	3 x 10 ⁻¹	1.69 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	4 x 10 ⁻¹	3.44 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	5 x 10 ⁻¹	3.55 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	6 x 10 ⁻¹	5.35 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	7 x 10 ⁻¹	6.17 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	8 x 10 ⁻¹	4.65 x 10 ⁻²
5 x 10 ⁻³	7 x 10 ⁻³	9 x 10 ⁻¹	4.43 x 10 ⁻²

Effect of variation of temperature: The effect of temperature was studied keeping constant concentration of all reactants such as [KMnO₄] = 7 x 10⁻³ M, [DPH] = 5 x 10⁻³ M and [H₂SO₄] = 1M. The temperature variation was done in the range of 25⁰C to 50⁰C. (Table. 4) The energy of activation was calculated by plotting graph between log k versus 1/T, a straight line was obtained. The temperature dependence on a rate constant of reactions can be depicted by an equation. The modest enthalpy of activation and higher rate constant of slow step indicate 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: Psuedo first order rate constant at different Temperatures.

Temp.	[DPH]	[KMnO ₄]	[H ₂ SO ₄]	k
25 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	4.21 x 10 ⁻²
30 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	3.56 x 10 ⁻²
35 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	2.52 x 10 ⁻²
40 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	4.48 x 10 ⁻²
45 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	3.36 x 10 ⁻²
50 ⁰ C	5 x 10 ⁻³	7 x 10 ⁻³	1M	4.23 x 10 ⁻²

The energy of activation was calculated to be - 1725.15 J/mole. This activation energy was used to calculate the enthalpy of activation (ΔH) using equation:

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

The value of (ΔH) increases with increase with increase temperature. The average (ΔH) was found -

4306.65 J/mole with a range -4202.72 to -4410.57 J/mole. Then from this, we calculated entropy of activation.

Table 5: Thermodynamic parameter of the kinetic oxidation process.

T	k	$\Delta H^\#(\text{J mole}^{-1})$	$\Delta S^\#(\text{J mole}^{-1})$	$\Delta G^\#(\text{J mole}^{-1})$
298	0.0507	-4202.72	-123.92	32726.48
303	0.0523	-4244.29	-124.54	33493.63
308	0.0412	-4285.86	-125.81	34464.87
313	0.0717	-4327.43	-123.75	34408.16
318	0.068	-4369.00	-124.81	35321.92
323	0.0647	-4410.57	-124.00	35642.29

There was no regular trend of entropy change, it varies from the range of -123.92 to -124.00 J/mole. The average entropy of activation was found to be -124.47 J/mole which is negative and indicates that the transition state is highly organized due to loss of number of degrees of freedom. 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 34342.89 J/mol and it changes in the range of 32726.48 J/mole to 35642.29 J/mole (Fig. 4) A plot of (ΔH) verses (ΔS) is linear which is followed by this equation.

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

Where β is called isokinetic temperature, for CCL it was = 34.59k.

Effect of variation of solvent concentration: The reaction was monitored in four different solvents, namely 1,4-dioxane, acetic acid, DMF and acetone. The rate constants for acetone was found to be less compared to other solvent. In acetone rate constant decreases with increase in percentage of solvent. In DMF rate constant increases with increases in percentage of solvent. For acetic acid also rate constant decreases, but no regular trend was observed for 1,4-dioxane. (Table.6) The variation with solvent is also represented by figures 3(a) to 3(d).

Effect of variation of salts: To study the effect of variation of salts, the concentration of salts was varied from 1×10^{-2} to 9×10^{-2} M, keeping constant concentration of reactants such as $[\text{KMnO}_4] = 7 \times 10^{-3}$ M; $[\text{DPH}] = 5 \times 10^{-3}$ M; $[\text{H}_2\text{SO}_4] = 1\text{M}$. (Table. 7) From the obtained results, it is clear that pseudo first order rate constant k_{obs} decreases with the increase in con-

centration of salts. A plot of $\log k_{\text{obs}}$ vs $\sqrt{\mu}$, according to extended Bronsted-Debye-Huckel equation was found to be linear with positive slopes (NaCl , CaCl_2 , AlCl_3 , Na_2SO_4 , Na_3PO_4 and MnSO_4) indicating positive salt effect. (Fig.4 (a) to (e)).

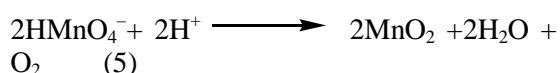
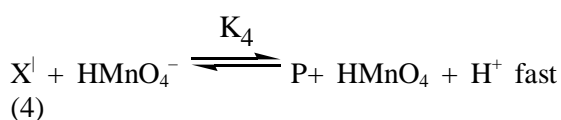
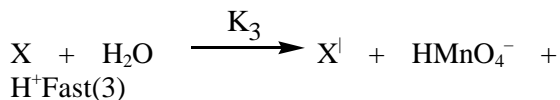
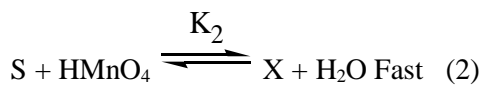
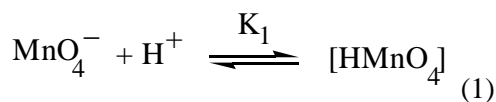
Table 6: Pseudo first order rate constant at = 25⁰C \pm 0.5⁰C keeping variation in solvent concentration. $[\text{DPH}] = 5 \times 10^{-3}$; $[\text{KMnO}_4] = 7 \times 10^{-3}$; $[\text{H}_2\text{SO}_4] = 1\text{M}$; $[\text{Temp.}] = 25^0\text{C} \pm 0.5^0\text{C}$

Percentage of Solvent	Rate Constant(sec ⁻¹)			
	1,4 dioxane	Acetic Acid	DMF	Acetone
10 %	4.97×10^{-1}	3.90×10^{-2}	6.05×10^{-2}	4.41×10^{-2}
20 %	4.55×10^{-1}	3.99×10^{-2}	4.87×10^{-2}	1.75×10^{-2}
30 %	4.32×10^{-2}	4.60×10^{-2}	6.03×10^{-2}	1.34×10^{-2}
40 %	3.5×10^{-2}	4.76×10^{-2}	5.45×10^{-2}	1.56×10^{-2}
50 %	3.62×10^{-2}	4.42×10^{-2}	6.17×10^{-2}	1.82×10^{-2}
60 %	5.04×10^{-2}	4.31×10^{-2}	5.27×10^{-2}	1.70×10^{-2}

Table 7: Pseudo first order rate constant at = 25⁰C \pm 0.5⁰C keeping variation in salts. $[\text{DPH}] = 5 \times 10^{-3}$; $[\text{KMnO}_4] = 7 \times 10^{-3}$; $[\text{H}_2\text{SO}_4] = 1\text{M}$; $[\text{Temp.}] = 25^0\text{C} \pm 0.5^0\text{C}$

Conc. of Salt	Rate Constant(sec ⁻¹)				
	NaCl	CaCl ₂	AlCl ₃	Na ₂ SO ₄	Na ₃ PO ₄
1×10^{-2}	7.18×10^{-2}	4.45×10^{-2}	3.7×10^{-2}	4.93×10^{-2}	3.14×10^{-2}
2×10^{-2}	4.65×10^{-2}	3.33×10^{-2}	2.12×10^{-2}	5.14×10^{-2}	5.03×10^{-2}
3×10^{-2}	3.86×10^{-2}	4.39×10^{-2}	3.37×10^{-2}	3.8×10^{-2}	4.93×10^{-2}
4×10^{-2}	5.02×10^{-2}	4.69×10^{-2}	2.22×10^{-2}	5.28×10^{-2}	4.89×10^{-2}
5×10^{-2}	4.60×10^{-2}	3.77×10^{-2}	2.55×10^{-2}	4.14×10^{-2}	4.80×10^{-2}
6×10^{-2}	3.96×10^{-2}	4.56×10^{-2}	2.86×10^{-2}	4.42×10^{-2}	4.42×10^{-2}
7×10^{-2}	4.10×10^{-2}	3.85×10^{-2}	2.43×10^{-2}	5.26×10^{-2}	4.6×10^{-2}
8×10^{-2}	5.86×10^{-2}	4.79×10^{-2}	2.21×10^{-2}	5.68×10^{-2}	5.17×10^{-2}
9×10^{-2}	4.63×10^{-2}	3.68×10^{-2}	2.54×10^{-2}	4.5×10^{-2}	5.49×10^{-2}

Depending on the experimental results, following mechanism is suggested. It is assumed that MnO_4^- species reacts with H^+ in solution to form HMnO_4 , which then reacts with substrate to form a complex, which further forms an intermediate and ultimately gets converted to product.



The rate of disappearance of $[\text{MnO}_4^-]$ may be given as:

$$-\frac{d[\text{MnO}_4^-]}{dt} = 2K_3 [\text{X}] [\text{H}_2\text{O}] \quad (6)$$

From equation (1);

$$K_1 = \frac{[\text{HMnO}_4]}{[\text{MnO}_4^-][\text{H}^+]}$$

$$\therefore [\text{HMnO}_4] = K_1 [\text{MnO}_4^-] [\text{H}^+] \quad (7)$$

Similarly from equation (2);

$$K_2 = \frac{[\text{X}]}{[\text{S}][\text{HMnO}_4]}$$

$$\begin{aligned} \therefore [\text{X}] &= K_2 [\text{S}] [\text{HMnO}_4] \\ &= K_1 K_2 [\text{MnO}_4^-] [\text{H}^+] [\text{S}] \end{aligned} \quad (8)$$

The concentrate of MnO_4^- i.e. $[\text{MnO}_4^-]_T$ at any time is given as:

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-] + [\text{HMnO}_4] + [\text{X}] \quad (9)$$

Substituting equation (7) and (8) in (9):

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-] + K_1 [\text{MnO}_4^-] [\text{H}^+] + K_1 K_2 [\text{MnO}_4^-] [\text{H}^+] [\text{S}]$$

$$[\text{MnO}_4^-]_T = [\text{MnO}_4^-] \{1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{S}]\}$$

$$[\text{MnO}_4^-] = \frac{[\text{MnO}_4^-]_T}{1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{S}]} \quad (10)$$

$$\therefore [\text{X}] = \frac{K_1 K_2 [\text{H}^+] [\text{S}] [\text{MnO}_4^-]_T}{(1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{S}])}$$

This can be rearrange as:

$$[\text{X}] = \frac{K_1 K_2 [\text{MnO}_4^-]_T [\text{H}^+] [\text{S}]}{(1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{S}])} \quad (11)$$

Hence the rate law can become;

$$-\frac{d[\text{MnO}_4^-]}{dt} = \frac{2K_3 K_1 K_2 [\text{MnO}_4^-]_T [\text{H}^+] [\text{S}]}{(1 + K_1[\text{H}^+] + K_1 K_2 [\text{H}^+] [\text{S}])}$$

This explains the experimental result i.e. first order dependence on the oxidant and decrease in order with increasing concentration of substrate.

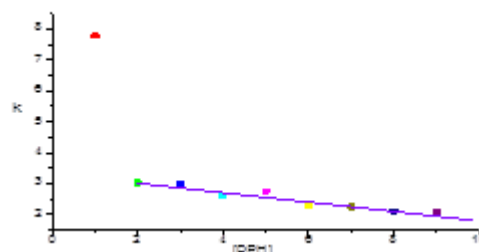


Figure 1: Effect of variation of Substrate DPH.

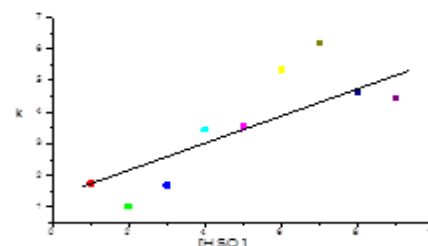


Figure 2: Effect of variation of acid $[\text{H}_2\text{SO}_4]$.

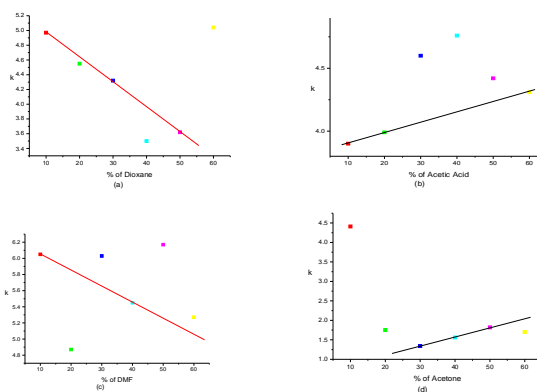


Figure 3: Effect of variation of solvent (a) 1,4dioxane (b) Acetic acid (c) DMF (d) Acetone.

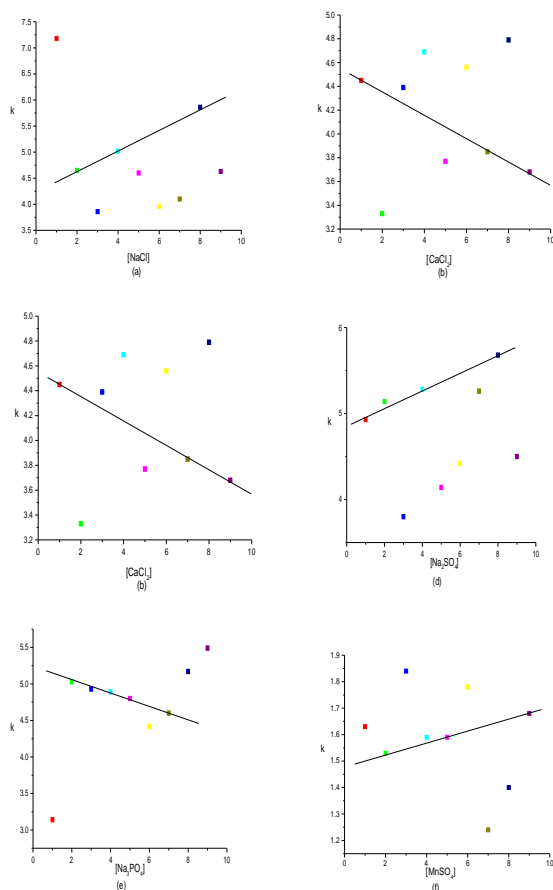


Figure 4: Effect of variation of salt (a) NaCl (b) CaCl₂ (c) AlCl₃ (d) Na₂SO₄ (e) Na₃PO₄ (f) MnSO₄.

CONCLUSION: This explains the experimental result i.e. first order dependence on the oxidant and decrease in order with increasing concentration of substrate

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