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Research Article

KINETICS AND MECHANISTIC OXIDATION OF 2,4-DICHLOROBENZALDEHYDE USING POTASSIUM PERMANGANATE

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ABSTRACT

Permagnetic oxidation of 2,4-diChlorobenzaldehyde has been studied at different temperatures using spectrophotometer under acidic conditions. The effect of variation of substrate (2,4-diCB), oxidant ($KMnO_4$) and H_2SO_4 was studied under pseudo first order reaction conditions. The effect of different salts on oxidation of 2,4-diCB was also studied. The reaction was found to be first order with respect to oxidant, substrate and H_2SO_4. A suitable mechanism is also suggested for the oxidation reaction.

Keywords: 2,4-diChlorobenzaldehyde (2,4-diCB)

1. INTRODUCTION

A survey of most recent literature on kinetic study reveals that there is a lots of scope for the study of oxidation process involving various oxidants [1-4]. There are different system reported in the literature such as oxidation of 2,4-diCB by Mn(III): oxidation of aldehyde by Cr(VI), acid permanganate, N-Bromoacetamide, Os(VII) pyridinium hydrobromide and bis 2,2 (bipyridyl), Cu(II) permanganate [5-8].

The present investigation reports that the oxidation of 2,4-diChlorobenzaldehyde by $KMnO_4$ under pseudo first order condition in acidic medium. The oxidation state of Mn in MnO_4^- is (VII). Therefore it can be represented as Mn(VII) which is a powerful oxidizing agent and usually reduced to Mn(II).

2. MATERIALS AND METHODS

All the chemicals used for this kinetic study were of A.R. Grade. Kinetic investigations were performed under pseudo first order conditions with excess of 2, 4-diCB over the oxidant at 25°C to 45°C. Required amount of solution of substrate, H_2SO_4 were equilibrated. A measured amount of $KMnO_4$ was added to the reaction mixture with constant stirring. The time of initiation of the reaction was recorded when half of the content of pipette were released. The solution was taken in a cuvette and absorbance was measured at 526nm using double beam spectrophotometer SL 210.

2, 4-diCB (0.001M), $KMnO_4$ (0.0002M) and H_2SO_4 (1M) and water volume 100ml kept a side for 24hrs. The unconsumed $KMnO_4$ was determined spectrophotometrically and the product 2,4-diChlorobenzoic acid was verified by TLC. The stochiometry is determined to be 1:1.

Product Analysis

Product study was made under acidic condition in benzaldehyde. Keeping concentration of $KMnO_4$ in excess over benzaldehyde. The two solutions were mixed and sulphuric acid was also added. The reaction mixture was set aside for about 24hr. to ensure completion of the reaction. The reaction mixture was then evaporated and extracted with ether. The ether layer was washed with water many times. The ether layer was than kept as a water bath for the evaporation of ether and cooled in ice-bath to obtain the product. The product was dissolved in benzene and a TLC analysis was done with substituted benzoic acid and respective benzaldehyde as references. Only one spot corresponding to respective benzoic acid was obtained. Formation of benzoic acid was further confirmed by mixing the product with pure benzoic acid and noting that there was no change in the melting point.

3. RESULTS AND DISCUSSION

3.1. Effect of variation of potassium permanganate ($KMnO_4$) concentration:- To study the effect of variation of $KMnO_4$ concentration, the experimental sets were prepared in which concentration of $KMnO_4$ was varied from 1 x10 $^{-3}$ to 9 x 10 $^{-3}$ M keeping constant concentration of 2,4-diChlorobenzaldehyde (2,4-diCB) and H_2SO_4 (Sulphuric acid). As the reaction has been studied under pseudo first order condition (Table 1 and 2) using equation

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

Which was modified as

$$k = \frac{2.303}{t}\log\frac{(OD)_{\infty}-(OD)_{0}}{(OD)_{\infty}-(OD)_{t}}$$

pseudo first order rate constants were calculated.

When initial rate is plotted against concentration of $KMnO_4$ the trend line has been found to be almost straight with negative slope indicating first order reaction at low concentration of KMnO4 but at high concentration of KMnO4 the initial rate is found to be constant (Fig. 1). This has been further confirmed when log [$KMnO_4$] versus log [FOR] is plotted (Fig. 2). Hence the reaction under pseudo first order rate depends on the concentration of oxidant. Secondly, from the obtained results, it is clear that pseudo first order rate constant decrease with increase in concentration of potassium permanganate.

Table 1. Effect of Variation of concentration of $KMnO_4$ on initial rate and rate constant of 2,4-diChlorobenzaldehyde

[$KMnO_4$] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec^{-1})
$1 x10^{3}$	3.9312	2.1325	0.0722
$2 x10^{-3}$	3.6212	2.1823	0.0710
$3 x10^{-3}$	4.1727	2.1992	0.0693
$4 x10^{-3}$	4.2815	2.6318	0.0699
$5 x10^{-3}$	4.9327	2.9913	0.0775
$6 x10^{-3}$	5.1318	2.1182	0.0783
$7 x10^{-3}$	5.2719	2.1518	0.0802
$8 x10^{-3}$	4.9939	2.2783	0.0791
$9 x10^{-3}$	4.0125	2.1912	0.0735

Table 2. Average rate determination of oxidation of 2, 4-diChlorobenzaldehyde

Time (s)	O.D.	10^5 Conc. (mole/lit)	10^5<c>	$10^5 \Delta$ c	Δ t	10^8<rate> mol/lit/sec	log <c>	Log <rate>
0	0.111	5.4599						
3	0.109	5.3615	5.4107	0.0984	3	32.7923	0.7333	1.5158
6	0.107	5.2632	5.3123	0.0984	3	32.7923	0.7253	1.5158
9	0.105	5.1648	5.2140	0.0984	3	32.7923	0.7172	1.5158
12	0.104	5.1156	5.1402	0.0492	3	16.3961	0.7110	1.2147
15	0.102	5.0172	5.0664	0.0984	3	32.7923	0.7047	1.5158
18	0.1	4.9188	4.9680	0.0984	3	32.7923	0.6962	1.5158
21	0.099	4.8697	4.8942	0.0492	3	16.3961	0.6897	1.2147
24	0.097	4.7713	4.8205	0.0984	3	32.7923	0.6831	1.5158
27	0.097	4.7713	4.7713	0.0000	3	0.0000	0.6786	1.5158
30	0.095	4.6729	4.7221	0.0984	3	32.7923	0.6741	1.5158
33	0.096	4.7221	4.6975	-0.0492	3	-16.3961	0.6719	1.5158
36	0.094	4.6237	4.6729	0.0984	3	32.7923	0.6696	1.5158
39	0.092	4.5253	4.5745	0.0984	3	32.7923	0.6603	1.5158
42	0.091	4.4761	4.5007	0.0492	3	16.3961	0.6533	1.2147
45	0.09	4.4270	4.4515	0.0492	3	16.3961	0.6485	1.2147
48	0.089	4.3778	4.4024	0.0492	3	16.3961	0.6437	1.2147
51	0.087	4.2794	4.3286	0.0984	3	32.7923	0.6363	1.5158
54	0.085	4.1810	4.2302	0.0984	3	32.7923	0.6264	1.5158
57	0.084	4.1318	4.1564	0.0492	3	16.3961	0.6187	1.2147

3.2. **Effect of variation of 3-Nitrobenzaldehyde concentration:**- To study the effect of variation of concentration of substrate, the sets were prepared in which the concentration of 2,4- diCB was varied from 1 x 10^{-3} to 9 x 10^{-3} M, keeping constant concentration of [$KMnO_4$]=7 x10^{-4} M, [H_2SO_4] = 2 x10^{-1} M (Table 3). As the reaction has been studied under pseudo first order condition pseudo first order rate constants were calculated. It is clear that pseudo first order rate constants were found to decrease with increase with concentration of 2,4-diCB in irregular way. When initial rate is plotted against concentration of 2,4-diCB, the trend line is linear with negative slope (Fig. 3) when log [FOR] versus log [2,4-diCB] is plotted it confirm the fractional order of reaction (Fig. 4). Hence the reaction under pseudo first order rate depends on the concentration of substrate.

Table 3. Effect of Variation in concentration of 2, 4-diChlorobenzaldehyde on initial rate and rate constant

[2,4-diCB] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec $^{-1}$)
1 x 10^{-3}	5.1712	2.0012	0.0802
2 x 10^{-3}	4.9132	1.9998	0.0778
3 x 10^{-3}	4.2375	1.6912	0.0712
4 x 10^{-3}	4.2218	1.8132	0.0699
5 x 10^{-3}	4.6812	1.7517	0.0758
6 x 10^{-3}	4.5310	1.2318	0.0783
7 x 10^{-3}	4.2371	1.9217	0.0812
8 x 10^{-3}	5.1719	2.0318	0.0793
9 x 10^{-3}	5.0001	2.8812	0.0772

3.3. Effect of variation of H_2SO_4 concentration:- 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 2 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration i.e.[2,4-diCB]= 1 x 10^{-4} and [$KMnO_4$] = 1 x 10^{-4}M (Table 4 and 5). As the reaction has been studied under pseudo first order condition for varying [H_2SO_4] was made (Fig. 1.5) and pseudo first order rate constants were calculated. It is clear from that pseudo first order rate constants decreases with change in concentration of H_2SO_4 confirming the first order dependence with respect to acid. Hence the reaction under pseudo order rate depends on the concentration of acid. The average rate determination data confirm that the order with respect to acid concentration is unity.

Table 4. Effect of Variation in concentration of H_2SO_4 on initial rate and rate constant of [2,4-diCB] oxidation

Sr. No.	[H_2SO_4] (M)	Initial Rate (10^{-4} x mol/lit/sec)	log (FOR)	Rate constant (k) (sec $^{-1}$)
1	0.02	3.7871	2.0138	0.0755
2	0.04	3.9312	1.9992	0.0722
3	0.6	4.1517	2.5182	0.0702
4	0.08	4.2390	2.1518	0.0698
5	0.10	5.1711	2.9312	0.0713
6	0.12	4.2312	2.1318	0.0799
7	0.14	4.0072	2.6872	0.0745
8	0.16	4.2212	2.2315	0.0685
9	0.18	5.0012	2.9892	0.0724

[$KMnO_4$]=1 x10^{-4}M; [2,4-diCB]= 1 x 10^{-4} M

3.4. Effect of variation of temperature: - The effect of temperature was studied keeping constant concentration of all reactants such as [$KMnO_4$] = 7 x 10^{-4} M, [2,4-diCB] = 5 x 10^{-3} M and [H_2SO_4] = 8 x 10^{-2} M (Table 4-6). The temperature variation was done in the range of 25 to 45°C (Fig. 6). The energy of activation was calculated by plotting graph between log k verses 1/T, a straight line was obtained (Fig. 7). The temperature dependence on a number of reactions can be depicted by an equation,

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

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 ($\Delta G^{\neq}$), enthalpy changes ($\Delta H^{\#}$) and entropy change ($\Delta S^{\#}$) was determined and given in the table 7.

The energy of activation was found to be -2781.11 J/mole. This activation energy was used to calculate the enthalpy of activation ($\Delta H^{\#}$) using equation

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

The value of (ΔH) decreases with increase in temperature; which is obvious. The average (ΔH) was found to be -5341.82 J/mole with a range -5258.68 to -5424.96 J/mole. From this, we calculated entropy of activation using formula

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

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

There was no regular trend of entropy change, it varies from -124.06 to -123.19 J/mole. The average entropy of activation was found to be -123.52 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 32701.52 J/mole, and changes from 31711.03 to 33750.35 J/mole.

A plot of (Δ*H*) verses (ΔS) is linear (Fig. 4.5.8) which is followed by this equation

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

Where β is called isokinetic temperature, for 2,4-diCB it was -169.08868 K.

Table 5. Average rate determination of oxidation of 2, 4-diChlorobenzaldehyde

Time (s)	O.D.	10^{-5}Conc (mole/lit)	10^{-5}< c >	10^{-5}Δ c	Δ t	10^{-8}<rate> mole/lit/sec	log <c >	log <rate>
0	0.112	5.5091						
3	0.11	5.4107	5.4599	0.0984	3	32.7923	0.7372	1.5158
6	0.108	5.3123	5.3615	0.0984	3	32.7923	0.7293	1.5158
9	0.106	5.2140	5.2632	0.0984	3	32.7923	0.7212	1.5158
12	0.103	5.0664	5.1402	0.1476	3	49.1884	0.7110	1.6919
15	0.099	4.8697	4.9680	0.1968	3	65.5845	0.6962	1.8168
18	0.096	4.7221	4.7959	0.1476	3	49.1884	0.6809	1.6919
21	0.094	4.6237	4.6729	0.0984	3	32.7923	0.6696	1.5158
24	0.091	4.4761	4.5499	0.1476	3	49.1884	0.6580	1.6919
27	0.088	4.3286	4.4024	0.1476	3	49.1884	0.6437	1.6919
30	0.087	4.2794	4.3040	0.0492	3	16.3961	0.6339	1.2147
33	0.086	4.2302	4.2548	0.0492	3	16.3961	0.6289	1.2147
36	0.084	4.1318	4.1810	0.0984	3	32.7923	0.6213	1.5158
39	0.081	3.9843	4.0580	0.1476	3	49.1884	0.6083	1.6919
42	0.08	3.9351	3.9597	0.0492	3	16.3961	0.5977	1.2147
45	0.079	3.8859	3.9105	0.0492	3	16.3961	0.5922	1.2147
48	0.076	3.7383	3.8121	0.1476	3	49.1884	0.5812	1.6919
51	0.075	3.6891	3.7137	0.0492	3	16.3961	0.5698	1.2147
54	0.072	3.5416	3.6153	0.1476	3	49.1884	0.5581	1.6919
57	0.07	3.4432	3.4924	0.0984	3	32.7923	0.5431	1.5158

[2,4-diCB] = 5×10^{-3}; [$KMnO_4$] = 7×10^{-4}M; [H_2SO_4] = 1M

Table 6. Effect of Temperature on Kinetics of permanganate Oxidation of 2, 4-diChlorobenzaldehyde in acidic media

Rate k	t^0C	T K	1 / T	3+logk
0.1172	25	298	0.003356	2.068928
0.0814	30	303	0.003300	1.910624
0.0799	35	308	0.003247	1.902547
0.0713	40	313	0.003195	1.85309
0.0692	45	318	0.003145	1.840106

Table 7. Effect of Temperature on Kinetics of permanganate Oxidation of 2, 4-diChlorobenzaldehyde in acidic media

Sr. No.	temp K	ΔH(J/mole)	ΔS (J/mole)	ΔG (J/mole)
01	298	-5258.68	-124.06	31711.03
02	303	-5300.25	-123.30	32058.79
03	308	-5341.82	-123.75	32773.08
04	313	-5383.39	-123.32	33214.36
05	318	-5424.96	-123.19	33750.35
Average		**-5341.82**	**-123.52**	**32701.52**

[$KMnO_4$]=7x10^{-4} M; [2,4-diCB]= 5x10^{-3} M; [H_2SO_4]=8x10^{-2}M;Activation Energy = – 2781.11 J/mole

3.5. Effect of variation of salts:- To study the effect of variation of salts, the concentration of salts was varied from 1 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration of reactants such as [KMnO4] = 7 x 10^{-4} M, [3-NB] = 5 x 10^{-3} M, [H_2SO_4] = 8 x 10^{-2} M. From the 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 √μ, according to extended Bronsted Debye-Huckel equation was found to be linear with positive slopes (K_2SO_4, $Ca(NO_3)_2$, and $CaCl_2$) indicating positive salt effect. On the other hand pseudo first order rate constant decreased with increase in concentration of salts. A plot of log k_{obs} versus √μ was found to be linear with negative slopes (KBr, KI, KCl, $MgCl_2$, $AlCl_3$ and $MnSO_4$) indicating negative salt effect [Fig. 9 (a) to (d)].

Table 8. Effect of added Salt on first order rate constant

Conc. of salts (M)	Rate constant (k), S^{-1}								
	KCl	KBr	KI	K_2SO_4	$MgCl_2$	$Ca(NO_3)_2$	$CaCl_2$	$AlCl_3$	$MnSo_4$
0.01	0.0813	0.0798	0.0891	0.0629	0.0818	0.0755	0.0515	0.0789	0.0881
0.02	0.0800	0.0813	0.0768	0.0658	0.0800	0.0723	0.0623	0.0752	0.0852
0.03	0.0792	0.0733	0.0753	0.0693	0.0811	0.0700	0.0662	0.0741	0.0841
0.04	0.0782	0.0711	0.0729	0.0725	0.0792	0.0798	0.0712	0.0702	0.0800
0.05	0.0691	0.0705	0.0712	0.0699	0.0782	0.0813	0.0748	0.0698	0.0795
0.06	0.0699	0.0812	0.0698	0.0711	0.0755	0.0888	0.0658	0.0745	0.0773
0.07	0.0753	0.0702	0.0758	0.0725	0.0731	0.0799	0.0740	0.0779	0.0812
0.08	0.0748	0.0695	0.0733	0.0758	0.0739	0.0718	0.0722	0.0792	0.0765
0.09	0.0797	0.0783	0.0729	0.0733	0.0768	0.0723	0.0698	0.0712	0.0722

Kinetic expression:

On the basis of above discussion following kinetic schemes has been suggested

$$MnO_4^- + H^+ \underset{}{\overset{K}{\rightleftharpoons}} HMnO_4 \qquad \text{Fast}$$

$$HMnO_4 + S \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} X \qquad \text{Fast}$$

$$X \xrightarrow{k_3} X' \qquad \text{slow and RDS}$$

$$X' + H_2O \xrightarrow{k_4} \text{Product} \qquad \text{fast}$$

Where S is a substrate X, X' are intermediate species since third step is rate determining step

$$\text{Rate} = k_3 [X] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 1$$

Applying steady state approximation to X

$$K_2[HMnO_4][S] - k_{-2}[X] - k_3[X] = 0$$

$$K_{-2} [X] + k_3[X] = k_2[HMnO_4][S] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 2$$

Applying Law of mass action to first step

$$K = \frac{[HMnO_4]}{[MnO_4^-][H^+]}$$

$$\therefore [HMnO_4] = k[MnO_4^-][H^+] \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 3$$

Substituting equation 3 in 2

$$[X](k_{-2} + k_3) = Kk_2[MnO_4][H^+][S]$$

$$[X] = \frac{Kk_2[MnO_4^-][H^+][S]}{k_{-2} + K_3} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots 4$$

Substituting equation 4 in equation 1

$$\therefore Rate = \frac{Kk_3k_2[MnO_4^-]\,[S][H^+]}{k_{-2} + k_3}$$

If the concentration of acid and substrate is kept constant than

$$Rate = k_{obs}\left[MnO_4^{-}\right]$$

Where $k_{obs} = \dfrac{Kk_3k_2\left[H^+\right]\left[S\right]}{k_{-2}+k_3}$

Hence the graph of k $_{obs}$ against concentration of acid [H^+] is a straight line which confirms that the present model is for kinetics.

The reaction rates observed allows us to assume that protonated MnO_4 i.e. $HMnO_4$ as a active oxidising species involved [9].

$KMnO_4$ is selected as an oxidizing agent for this study because it is a economically low cost material. It has high oxidation potential (E^0 = 1.7V). It can oxidize wide variety of substances and it is effective over wide range of pH. There are various oxidation states of Mn like (=II, +III, +IV, +V, +VI and +VII). Hence it is complicated to find out the exact species [10] involved in it. In acidic media

$MnO_4^- + 4\ H^+ \rightarrow 3O_2 + 2H_2O + 4MnO_2$ even MnO_4^{-2} is converted to Mn^{+2}.

$$MnO_4^{-2} + 8H+ + 6e^- \longrightarrow Mn^{2+} + 4H_2O$$

The Mn^{2+} may react with MnO_4^- and the product is MnO_2.

$$2MnO_4^{-2} + 3Mn^{2+} + 2H_2O \longrightarrow 5MnO_2 + 4H^+$$

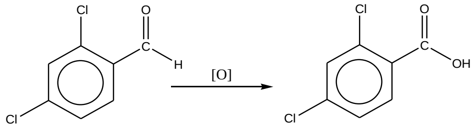
It is assumed that during oxidation of aldehyde positively change species attack a lone pair of electron of the reductant at centre of high electron density [11].

The formation of oxo-bridge in intermediate compound indicates the oxygen passage of one electron from the substrate binded to Mn^{+7}. This bridge due to protonation, rupture and give Mn^{+3} species. Since the solution dies not indicate any presence of Mn(III) is precipitated MnO_2 it is quite logical to state that Mn(III) react or its disproportionated product Mn(IV) instantaneously react with substrate giving final product Mn^{+2} [12-13].

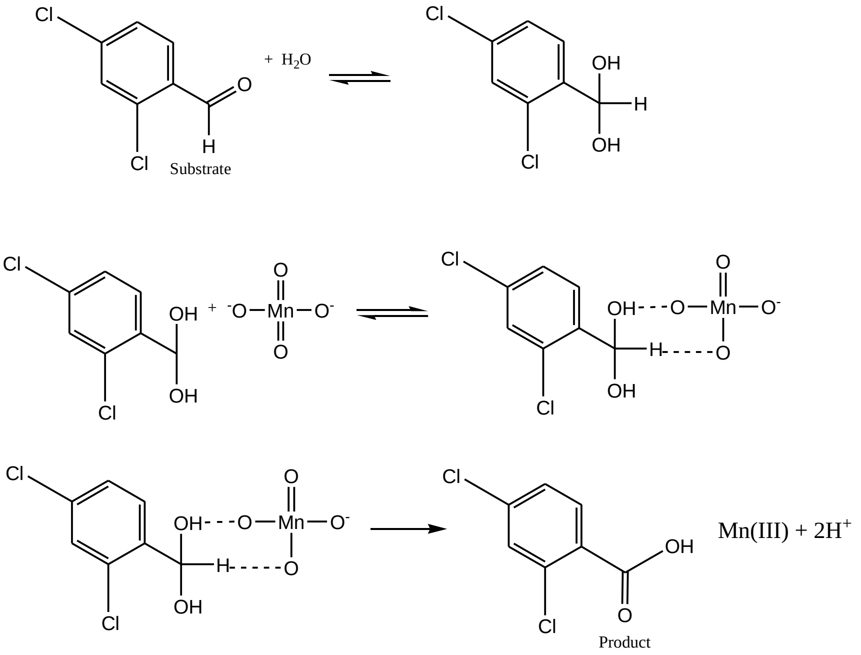
$$2Mn(III) \longrightarrow Mn(II) + Mn(IV)$$

$$Mn(IV) + substrate \longrightarrow Mn(II) + product$$

Considering the following step in the reaction is as



And the mechanism can be depicted as



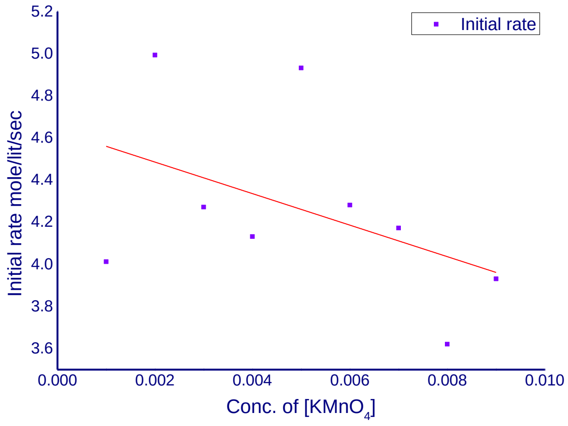


Fig. 1: Variation of Conc. of $KMnO_4$ Vs Initial rate at constant [2,4-diCB] = $1x10^{-3}$

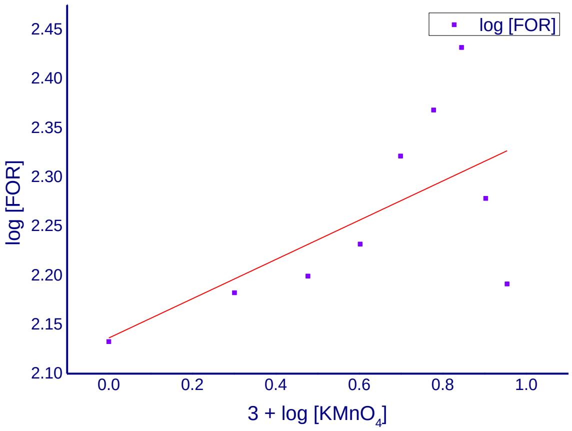


Fig. 2: Variation of conc. of $KMnO_4$ Vs log [FOR] at constant [2,4-diCB]

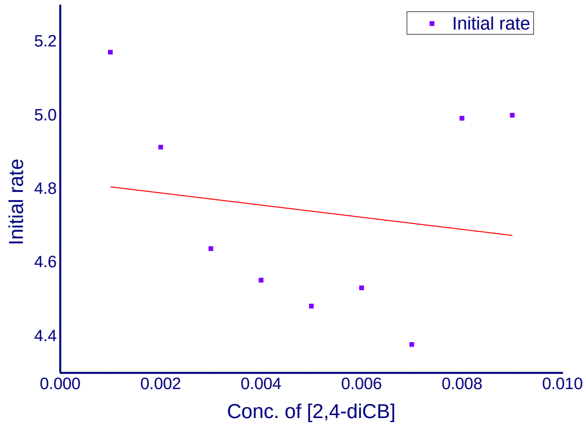


Fig. 3: Variation of Conc. of 2,4-diCB Vs initial rate

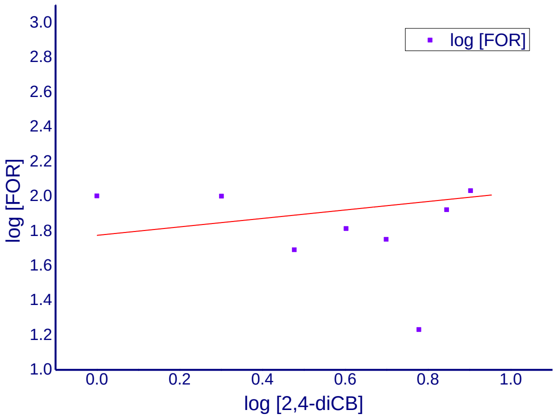


Fig. 4: Variation of Conc. of 2,4-diCB Vs log [FOR]

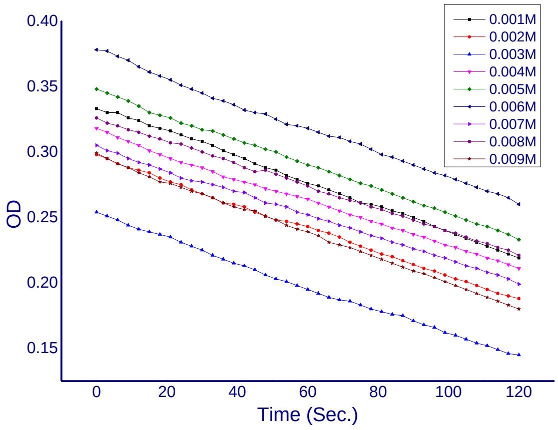


Fig. 5: Effect of variation of $[H_2SO_4]$

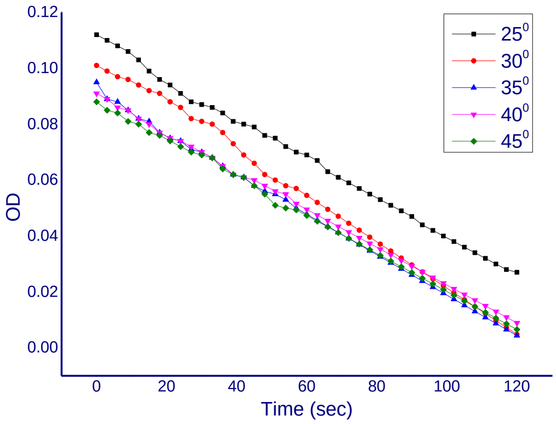


Fig. 6: Effect of temperature

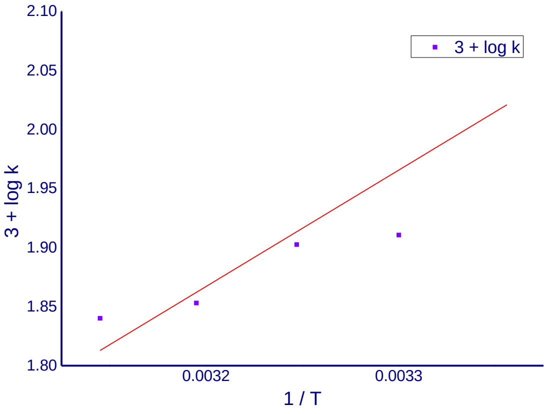


Fig. 7: 3+log K Vs 1 / T

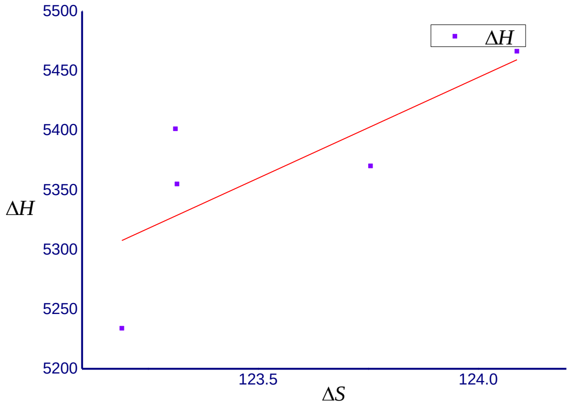


Fig. 8: ΔS Vs ΔH

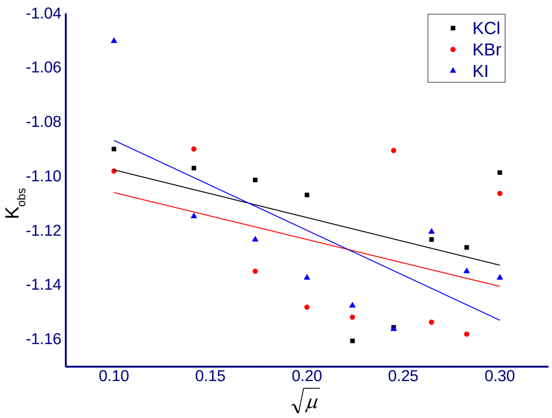


Fig. 9 (a): Effect of Salt

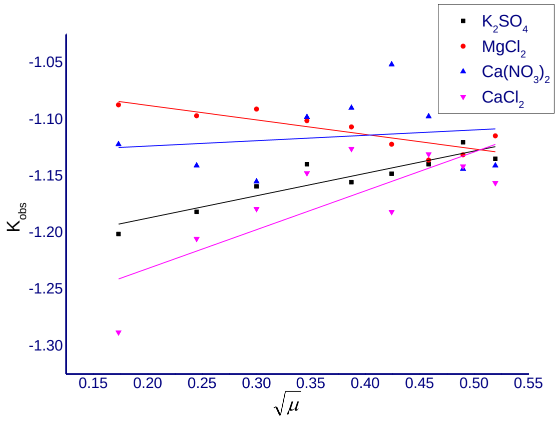


Fig. 9 (b): Effect of Salt

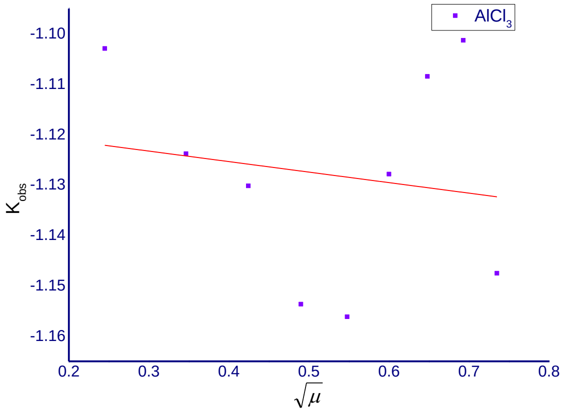


Fig. 9 (c): Effect of Salt

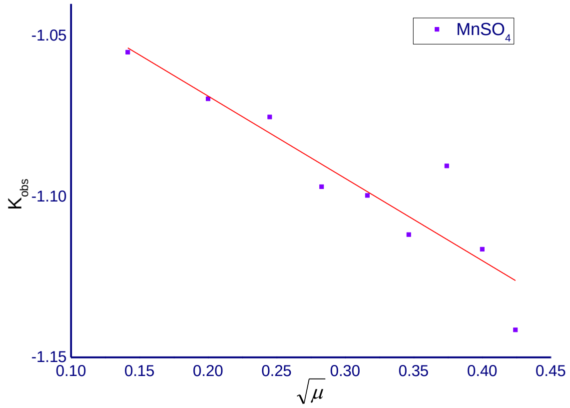


Fig. 9 (d): Effect of Salt

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