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Kinetics And Mechanism of The Reaction With Respect To Osmium Tetroxide In The Oxidation Of Propane-1, 2-Diol In Aqueous Alkaline Medium

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ABSTRACT:

The present series of experiment were perform with Propane -1,2 Diol used as organic substrate. To find out the order of reaction with respect to Osmium tetroxide the concentration of all the reactants except to Osmium tetroxide qas kept constant. Manifold variation of Osmium tetroxide concentration are present in the table. The ionic strength of medium was kept constant with the help of standard solution of potassium chloride. Average of the calculated K_1 values along with graphical K_1 values are given at the bottom of each table. In this case it is also observe that the calculated K_1 values are constant in particular run.

From the literature it is also obvious that the Osmium tetroxide shows the typical nature during the catalytic behaviour in alkaline medium. Now in order to examine its role as oxidant, the oxidation of some organic substrates, different sets of reactions have been studied. With this idea the oxidation of Propane -1,2 –diol has been carried out by osmium tetroxide in aqueous alkaline medium. Explanation of results has been shown as was found by the study[8].

Keywords: *Osmium tetroxide, catalyst, Rate of reaction, Rate constant, Effect of temperature, hexacynoferrate (**III**) ion.*

INTRODUCTION:

The oxidation of diols[1,2] is of great interest because of unusual oxidation pattern. Diols can react as alkoxide ions or as such. This peculiar behaviour of diols was inferred from kinetics observation[9]. Manifold variations of diol concentration show that the reaction velocity initially increases with diol concentration, reaches a maximum, and then decreases at still higher concentration. This decreases in reaction velocity is attributed to the formation of a 1:2, Osmium – diol complex[10].

It was also observed that the reaction is first order in Hydroxide ion at lower OH^- concentrations, but tends towards zero order at higher OH^- Ion Concentration[11].

The variation of Osmium tetroxide and hexacyno ferrate (**III**) u first order and zero order

kinetics, respectively, for the entire course of reaction. In order to explain the actual path of the reaction, two reaction schemes have been proposed[12].

The final oxidation products have been identified by chromatography. In Propane -1,2-diol, Oxalic acid has been confirmed as the final oxidation product[13].

Experimental:

1. **Material Employed :-**

Chemical were used A.R. Grade. The Osmium tetroxide (osmic acid) used was 1.00 gram ample (Johnson Matthey & Co. Ltd.) The stock solution of Os (VIII) was prepared by dissolving the above sample in sodium hydroxide solution of known strength. The stock solution of diols were prepared by weighing approximate quantities of sample. The solution were finally standardized against potassium dichromate solution, prepared from Analar (B.D.H.) grade sample[14].

2. **Mixing Of Reactants (Stopped-Flow Technique) :-**

This technique is an extension of conventional spectrophotometry, based on rapid mixing of two reactants.[3] Temperature control is essential, since kinetics of the most chemical reaction are strongly temperature dependent. For this reason in the "cantebury'' design the mixing cell is immersed in the thermostatics bath maintained with the help of two automatically controlled heaters.

Stopped-flow spectrometry covers a time scale of 10^{-3} to 2×10^{2} second. The lower limit is set by the mixing time of the reactant and by observing cell volume. The mixing time is not so easily defined and depends markedly on viscosity of the sample. It has been shown that efficient mixing can be obtained with reagent of viscosities 20 times greater than water in suitable condition.[4]

It is necessary to transform the kinetic trace in to optical density, according to the definition-

$$D = \log V0/Vt$$

After the completion of reaction the [Os(VI)] produced was determined spectro photo metrically. In all instances the reaction stoichiometry was found to be 4:1. Thus the reaction may be represented as-

Diol + 4 Os(VIII) → 4 Os (VI) + other products

The organic products were identified by paper and thin layer chromatography.[5]

Determination of The order of The Reaction With Respect To Osmium Tetroxide In The Oxidation Of Propane -1,2-Diol In Aqueous Alkaline Medium :-

The order of reaction with respect to osmium tetroxide, its concentration was varied keeping the concentration of all the other reactants constant. The ionic strength of the medium was kept constant with the help of standard solution of potassium chloride. Results obtained are presented in the individual tables from 2.1 to 2.5. From the experimental graph the value of voltage i.e. Vt have been calculated at different intervals of time. It is given in first and second columns of each table

From these two data the value of optical density "D'' and first order velocity constant K_1 has been calculated accordingly[6]. The last column of each table contains the value of calculated first order velocity constant K_1. The average value of K_1 also given below each table. In order to further verify the order with respect to osmium tetoxide log D0 /Dt against time has been plotted and from the slop of these straight line the value of K_1 has been calculated[7].

Table 2.1

$[O_sO_4]$	$= 1.965 \times 10^{-4}$ M	Temp.	$= 35^0$C
[Propane- 1,2 –diol	$= 2.0 \times 10^{-3}$M	Volt F.S.	=0.2 V
[NaOH]	= 0.15 M	Sweep Time	= 2 sec.
[KCl]	= 0.35 M	u	= 0.50M

Time (sec.)	Voltage	Log V_0/V_t =D	Log D_0/D_t	K_1 (sec^{-1})
0.00	4.926	0.006476	0.0000	0.0000
0.02	4.931	0.006035	0.03063	3.5169
0.04	4.935	0.005683	0.05673	3.2662
0.06	4.940	0.005243	0.09173	3.5108
0.08	4.944	0.004892	0.12182	3.5069
0.10	4.949	0.004453	0.16265	3.7459
0.12	4.954	0.004014	0.2077	3.9867
0.14	4.957	0.003751	0.23716	3.9013
0.16	4.961	0.003401	0.2797	4.0259
0.18	4.964	0.003138	0.31465	4.0258

Average K_1 $= 3.723$ sec^{-1} , Graphical $K_1 = 3.869$ sec^{-1}

Table 2.2

$[O_sO_4]$	$= 3.93 \times 10^{-4}$ M	Temp.	$= 35^0$C
[Propane- 1,2 –diol	$= 2.0 \times 10^{-3}$M	Volt F.S.	=0.2 V
[NaOH]	= 0.15 M	Sweep Time	= 2 sec.
[KCl]	= 0.35 M	u	= 0.50M

Time (sec.)	Voltage	Log V_0/V_t =D	Log D_0/D_t	K_1 (sec^{-1})
0.00	4.815	0.01637	0.0000	0.0000
0.02	4.826	0.01547	0.02456	2.8278
0.04	4.835	0.01457	0.05059	2.9126
0.06	4.845	0.01367	0.7828	3.0046
0.08	4.855	0.01278	0.10752	3.0951
0.10	4.865	0.01188	0.13923	3.2065
0.12	4.875	0.01099	0.17305	3.3211
0.14	4.880	0.01055	0.19079	3.1385
0.16	4.890	0.009661	0.22903	3.2971
0.18	4.905	0.008330	0.2934	3.3785
0.20	4.916	0.007358	0.2722	3.1341
0.22	4.920	0.007005	0.29353	3.07268
0.24	4.924	0.006652	0.21598	3.03211

Average K_1 = 3.339 sec^{-1}, Graphical K_1 = 3.316 sec^{-1}

Table 2.3

$[O_sO_4]$	= 5.895 X 10^{-4} M	Temp.	= 35^0C
[Propane- 1,2 –diol	= 2.0 X10^{-3}M	Volt F.S.	=0.5 V
[NaOH]	= 0.15 M	Sweep Time	= 2 sec.
[KCl]	= 0.35 M	u	= 0.50M

Time (sec.)	Voltage	Log V_0/V_t =D	Log D_0/D_t	K_1 (sec^{-1})
0.00	4.785	0.01908	0.0000	0.0000
0.02	4.800	0.01773	0.03209	3.6959
0.04	4.810	0.01682	0.05498	3.1655
0.06	4.825	0.01547	0.09131	3.5049
0.08	4.835	0.01457	0.11735	3.3781
0.10	4.845	0.01368	0.14471	3.3329
0.12	4.855	0.01278	0.17428	3.3446
0.14	4.865	0.01189	0.20562	3.3825

0.16	4.870	0.01144	0.22234	3.2003
0.18	4.880	0.01055	0.25755	3.2953
0.20	4.885	0.01011	0.27626	3.1812

Average K_1 = 3.348 sec^{-1}, Graphical K_1 = 3.316sec^{-1}

Table 2.4

$[O_sO_4]$	= 7.86 X 10^{-4} M	Temp.	= 35^0C
[Propane- 1,2 –diol	= 2.0 X10^{-3}M	Volt F.S.	=0.5 V
[NaOH]	= 0.15 M	Sweep Time	= 2 sec.
[KCl]	= 0.35 M	u	= 0.50M

Time (sec.)	**Voltage**	**Log V_0/V_t =D**	**Log D_0/D_t**	**K_1 (sec^{-1})**
0.00	4.805	0.01728	0.0000	0.0000
0.02	4.820	0.01592	0.03560	4.0994
0.04	4.830	0.01502	0.6087	3.5048
0.06	4.845	0.01368	0.10146	3.8943
0.08	4.860	0.01233	0.14658	4.2997
0.10	4.870	0.011441	0.17902	4.1242
0.12	4.875	0.01099	0.19655	3.7720
0.14	4.885	0.010105	0.23301	3.8329
0.16	4.890	0.009661	0.25252	3.6347
0.18	4.900	0.008774	0.29435	3.7659
0.20	4.905	0.008331	0.31685	3.6485
0.22	4.910	0.007889	0.34052	3.5646

Average K_1 = 3.824 sec^{-1}, Graphical K_1 = 3.782sec^{-1}

Table 2.5

$[O_sO_4]$	= 9.825 X 10^{-4} M	Temp.	= 35^0C
[Propane- 1,2 –diol	= 2.0 X10^{-3}M	Volt F.S.	=1.0 V
[NaOH]	= 0.15 M	Sweep Time	= 2 sec.
[KCl]	= 0.35 M	u	= 0.50 M

Time (sec.)	Voltage	Log V_0/V_t =D	Log D_0/D_t	K_1 (sec^{-1})
0.00	4.810	0.01682	0.0000	0.0000
0.02	4.825	0.01547	0.03633	4.1834
0.04	4.835	0.01457	0.06237	3.5909
0.06	4.850	0.01323	0.010426	4.0018
0.08	4.860	0.01233	0.13486	3.8821
0.10	4.865	0.01189	0.15064	3.4693
0.12	4.875	0.010995	0.18463	3.5434
0.14	4.880	0.01055	0.20257	3.3323
0.16	4.895	0.009217	0.26124	3.7602

Average K_1 = 3.719 sec^{-1}, Graphical K_1 = 3.627 sec^{-1}

Table 2.6

Effect of variation of osmium tetroxide concentration on the reaction rate in the oxidation of Propane -1,2 –diol.

[Propane- 1,2 –diol = 2.0 $X10^{-3}$M Temp. = 35^0C

[NaOH] = 0.15 M

[KCl] = 0.35 M u = 0.50 M

$[O_SO_4]X10^4M$	K_1 (sec^{-1})		Volt F.S.(v)	SweepTime (sec)
	Calculated	Graphical		
1.965	3.722	3.689	0.1	2
3.930	3.339	3.316	0.2	2
5.895	3.348	3.316	0.5	2
7.860	3.824	3.782	0.5	2
9.325	3.719	3.627	0.5	2

[Propane- 1,2 –diol = 2.0 $X10^{-3}$M $[O_SO_4]$ X 10^{-4}M

[NaOH] = 0.15 M (1) - 1.965

[KCl] = 0.35 M (2) – 3.930

Temp. = 35^0C

On Y-axis log (D_0 /D_t) x 10^2 And On X-Axis Time (sec)

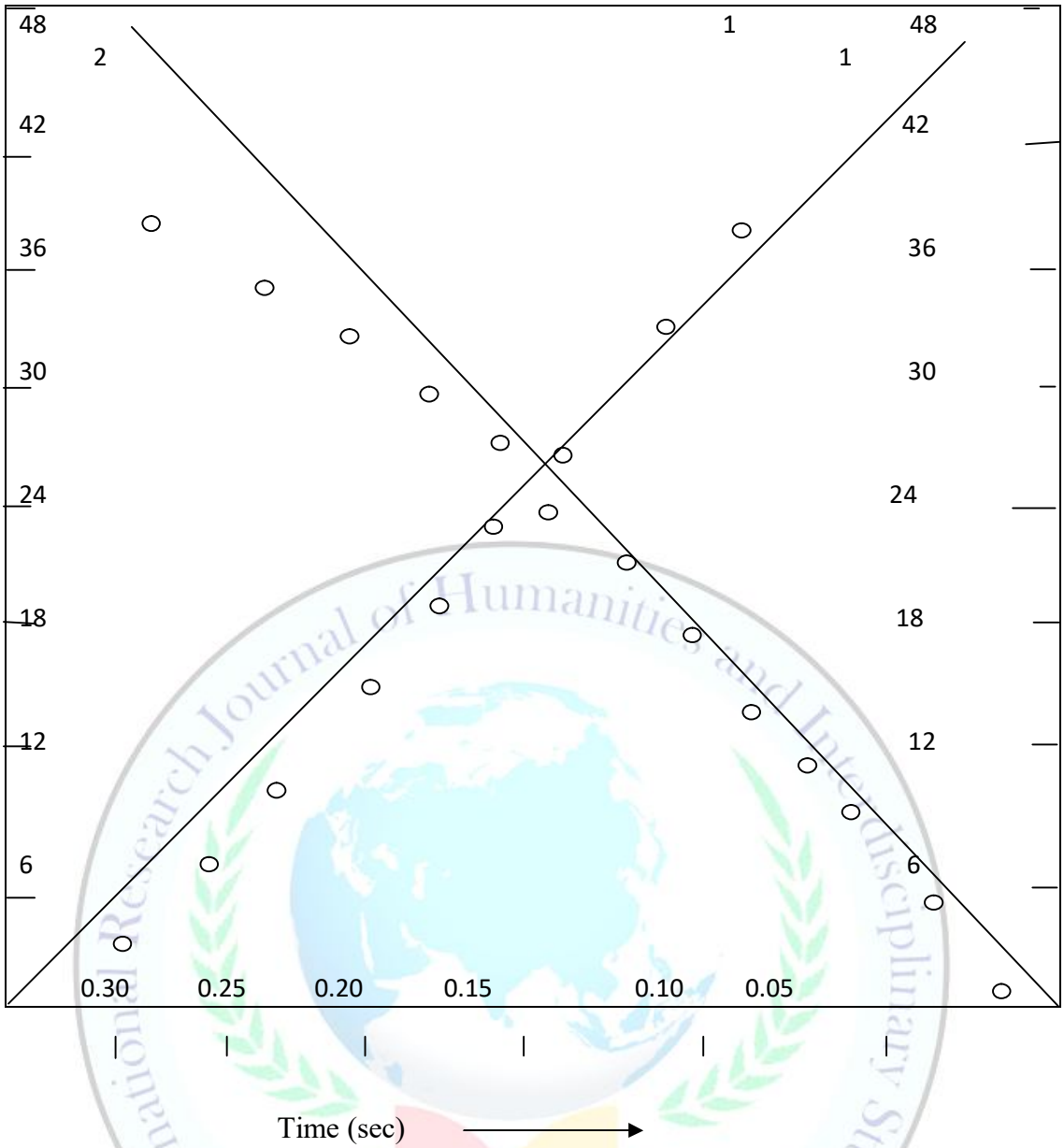

Fig.1 Individual plots of log (D_0 /D_t) vs Time for the oxidation of Propane -1,2 –diol

[Propane- 1,2 –diol = 2.0 X10^{-3}M [O_SO_4] X 10^{-4}M

[NaOH] = 0.15 M (3) - 5.895

[KCl] = 0.35 M (4) – 7.86

Temp. = 35^0C (5) - 9.825

On Y-axis log (D_0 /D_t) x 10^2 And On X-Axis Time (sec)

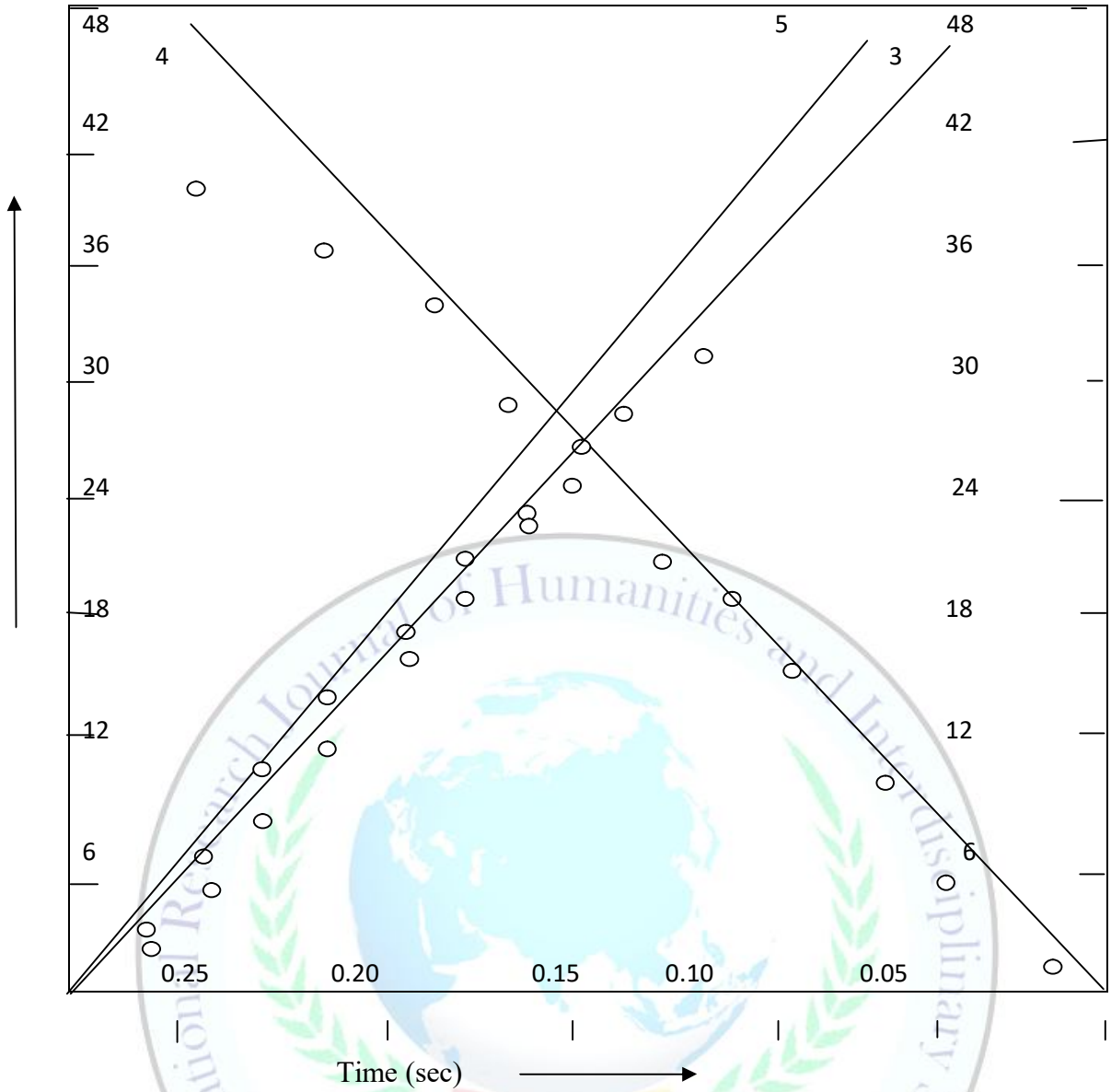

Fig.2 Individual plots of log (D_0 /D_t) vs Time for the oxidation of Propane -1,2 –diol.

Result and Discussion:-

The value k, kK, K and K_1 obtained from different plots for the oxidation of diols by osmium tetroxide in aqueous alkaline medium are-

Diol	K(sec^{-1})	kK	K × 10^{-3}	K_1 × 10^{-5}
Propane -1,2-diol	2.38	3541	1.48	2.65

A close examination of above table shows that the value of rate constant of disproportion "k" are practically constant.

The plot of $1/K_1$ V_S[S] is shown below-

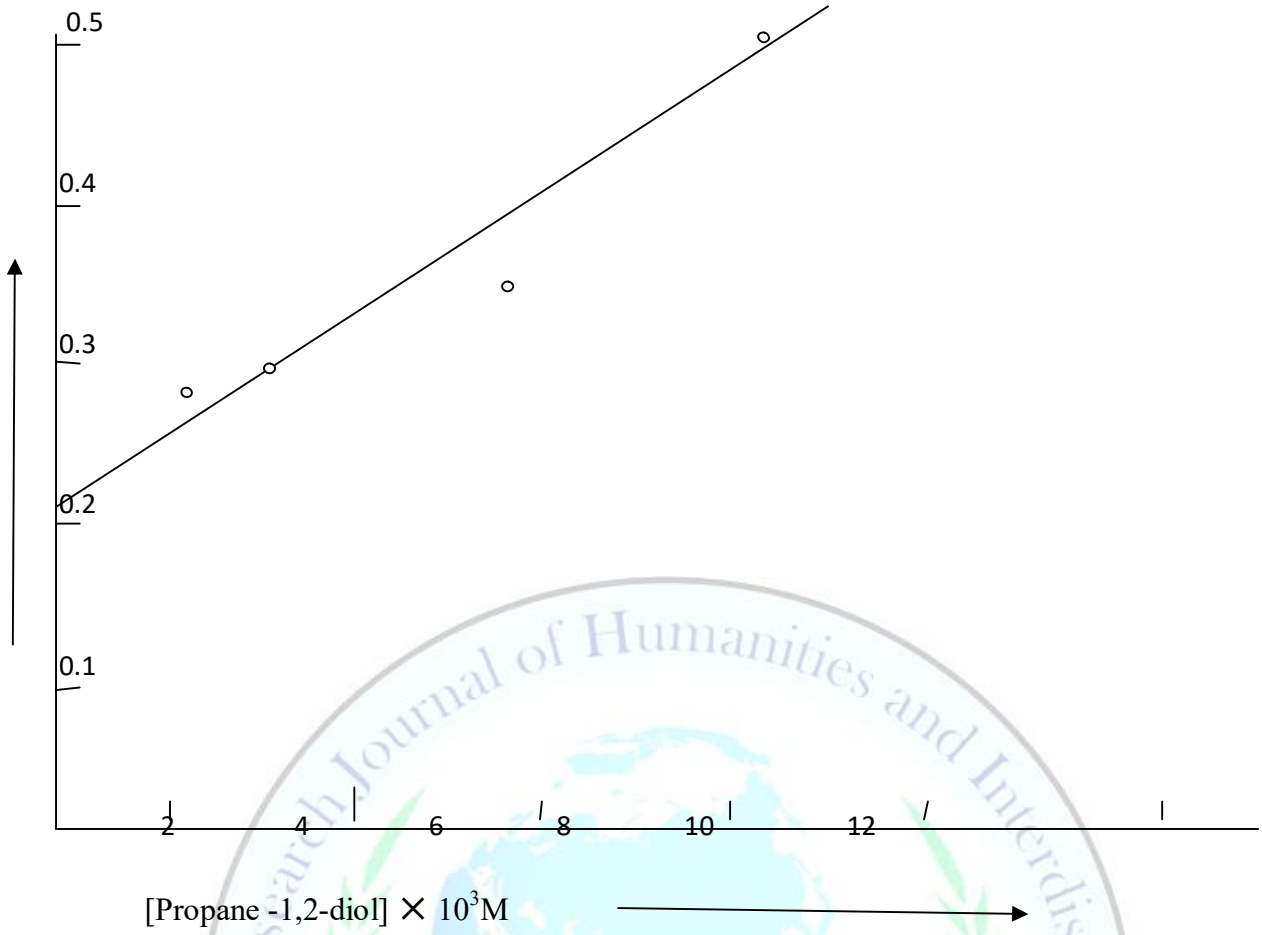

Fig. Plot of $1/K_1$ $V_S[S]$ for Propane -1,2-diol

The rate law which clearly explain first order kinetics with respect to osmium tetra oxide concentration are-

$$\frac{-d\,[O_S(VIII)]}{dt} = \frac{2kK[O_S(VIII)]_T\,[G]}{1+K[G]+KK_1[G]^2}$$

The results obtained with respect to substrate and hydroxide ions are also quite clear from above equation.

The equation clearly explain the first order kinetics with respect to diol at low concentration are-

$$K_1 = 2.\,kK[G]$$

The experimental data were subjected to statistical regression analysis. Theoretical values were obtained by using equation developed from the proposed reaction mechanism. The result is Lactic Acid.

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