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Determination Of The Order of Reaction With Respect To Osmium Tetroxide In The Oxidation Of Butane-1, 3-Diol In Aqueous Alkaline Medium

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ABSTRACT:

The present experiment were perform with Butane -1, 3 Diol used as reducing agent. In this case the concentration of osmium tetroxide was varied keeping the concentration of other reactants constant. Ionic strength of medium was also kept constant with the help of a standard solution of potassium chloride. Table from 1.1 to 1.5 show the individual runs at different concentrations of osmium tetroxide. The value of K_1 ,given in the last column of each table, clearly indicate that the order of the reaction with respect to osmium tetroxide is unity because the value of K_1 calculated in each table are uniform the beginning to the end of the reaction. The average K_1values are given below the table.

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-

$$\text{Diol} + 4\,\text{Os(VIII)} \rightarrow 4\,\text{Os (VI)} + \text{other products}$$

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 1.1 to 1.5. 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 1.1

$[O_sO_4]$	= 1.965 X 10^{-4} M	Temp.	= 35^0C
[Butane- 1,3 –diol	= 2.0 X10^{-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	4.620	0.03433	0.0000	0.0000
0.02	4.640	0.03245	0.02446	2.8165
0.04	4.665	0.03012	0.05682	3.2713
0.06	4.690	0.02779	0.09179	3.5230
0.08	4.710	0.02595	0.12154	3.4987
0.10	4.730	0.02411	0.15348	3.5346
0.12	4.745	0.02273	0.17907	3.4367
0.14	4.760	0.02136	0.20607	3.3899
0.16	4.775	0.01999	0.23486	3.3805
0.18	4.790	0.01863	0.26546	3.3964
0.24	4.825	0.01547	0.34618	3.3219

Average K_1 = 3.417 sec^{-1}, Graphical K_1 = 3.455 sec^{-1}

Table 1.2

$[O_sO_4]$	= 3.93 X 10^{-4} M	Temp.	= 35^0C
[Butane- 1,3 –diol	= 2.0 X10^{-3}M	Volt F.	=0.1 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	4.929	0.006211	0.0000	0.0000
0.02	4.933	0.005859	0.025338	2.9177
0.04	4.936	0.005549	0.04895	2.8181
0.06	4.941	0.005155	0.08093	3.1065
0.08	4.945	0.004804	0.11156	3.2115
0.10	4.949	0.004453	0.14451	3.3280
0.12	4.954	0.004014	0.18958	3.6384
0.14	4.958	0.003663	0.2293	3.7724
0.16	4.962	0.003313	0.27294	3.9286
0.18	4.966	0.002963	0.32143	4.1125
0.20	4.969	0.002701	0.36164	4.1642
0.22	4.972	0.002439	0.40595	4.2496
0.24	4.974	0.002264	0.43828	4.2057
0.28	4.979	0.001828	0.53118	4.3689

Average K_1 = 3.678 sec^{-1}, Graphical K_1 = 3.401 sec^{-1}

Table 1.3

[O_sO_4] = 5.895 X 10^{-4} M Temp. = 35^0C
[Butane- 1,3 –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	4.590	0.03716	0.0000	0.0000
0.02	4.625	0.03386	0.04038	4.6508
0.04	4.650	0.03152	0.07149	4.1160
0.06	4.675	0.02919	0.10484	4.0242

0.08	4.690	0.02779	0.12619	3.6326
0.10	4.710	0.02595	0.15594	3.5913
0.12	4.730	0.02411	0.18788	3.6057
0.14	4.745	0.02273	0.2135	3.5117
0.16	4.755	0.02182	0.2312	3.3281
0.18	4.770	0.02045	0.2594	3.3187
0.20	4.780	0.01954	0.2792	3.2144

Average K_1 = 3.699 sec^{-1}, Graphical K_1 = 3.685 sec^{-1}

Table 1.4

$[O_sO_4]$ = 7.86 X 10^{-4} M Temp. = 35^0C

[Butane- 1,3 –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	4.585	0.03763	0.0000	0.0000
0.02	4.615	0.03479	0.03408	3.9243
0.04	4.640	0.03245	0.6432	3.7032
0.06	4.660	0.03058	0.09009	3.4582
0.08	4.685	0.02826	0.12436	3.5801
0.10	4.705	0.02641	0.15377	3.5412
0.12	4.720	0.02503	0.17707	3.3983
0.14	4.745	0.02273	0.21893	3.6015
0.16	4.760	0.02136	0.2459	3.5399

0.18	4.775	0.01999	0.2747	3.5146
0.20	4.790	0.01863	0.3053	3.5158
0.22	4.800	0.01773	0.3268	3.4213
0.24	4.810	0.01682	0.3497	3.3557

Average K_1 = 3.546 sec^{-1}, Graphical K_1 = 3.454 sec^{-1}

Table 1.5

$[O_sO_4]$ = 9.825 X 10^{-4} M Temp. = 35^0C

Time (sec.)	Voltage	Log V_0/V_t =D	Log D_0/D_t	K_1 (sec^{-1})
0.00	4.650	0.03152	0.0000	0.0000
0.02	4.675	0.02919	0.03335	3.8405
0.04	4.695	0.02733	0.061946	3.5666
0.06	4.720	0.02503	0.010012	3.8431
0.08	4.735	0.02365	0.12476	3.5914
0.10	4.755	0.02182	0.15973	3.6786
0.12	4.770	0.02045	0.18789	3.6059
0.14	4.785	0.01909	0.21778	3.5825
0.16	4.800	0.01773	0.2499	3.5967

[Butane- 1,3 –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

0.18	4.810	0.01682	0.27276	3.4898
0.20	4.825	0.01547	0.3091	3.5592
0.22	4.835	0.01457	0.3551	3.5081
0.24	4.845	0.01368	0.3685	3.4785
0.26	4.855	0.01278	0.3921	3.4727

Average K_1 = 3.601 sec^{-1}, Graphical K_1 = 3.455 sec^{-1}

Table 1.6

Effect of variation of osmium tetroxide concentration on the reaction rate in the oxidation of Butane -1, 3– diol.

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

[NaOH] = 0.15 M Volts F.S. = 0.5v

[KCl] = 0.35 M u = 0.50 M

$[O_sO_4]X10^4$ M	K_1 (sec^{-1})		Volt F.S.(v)	SweepTime (sec)
	Calculated	Graphical		
1.965	3.417	3.455	0.5	2
3.930	3.678	3.401	0.1	2
5.895	3.699	3.685	0.5	2
7.860	3.546	3.454	0.5	2
9.825	3.601	3.455	0.5	2

[Butane- 1,3 –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 (3) -5.895

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

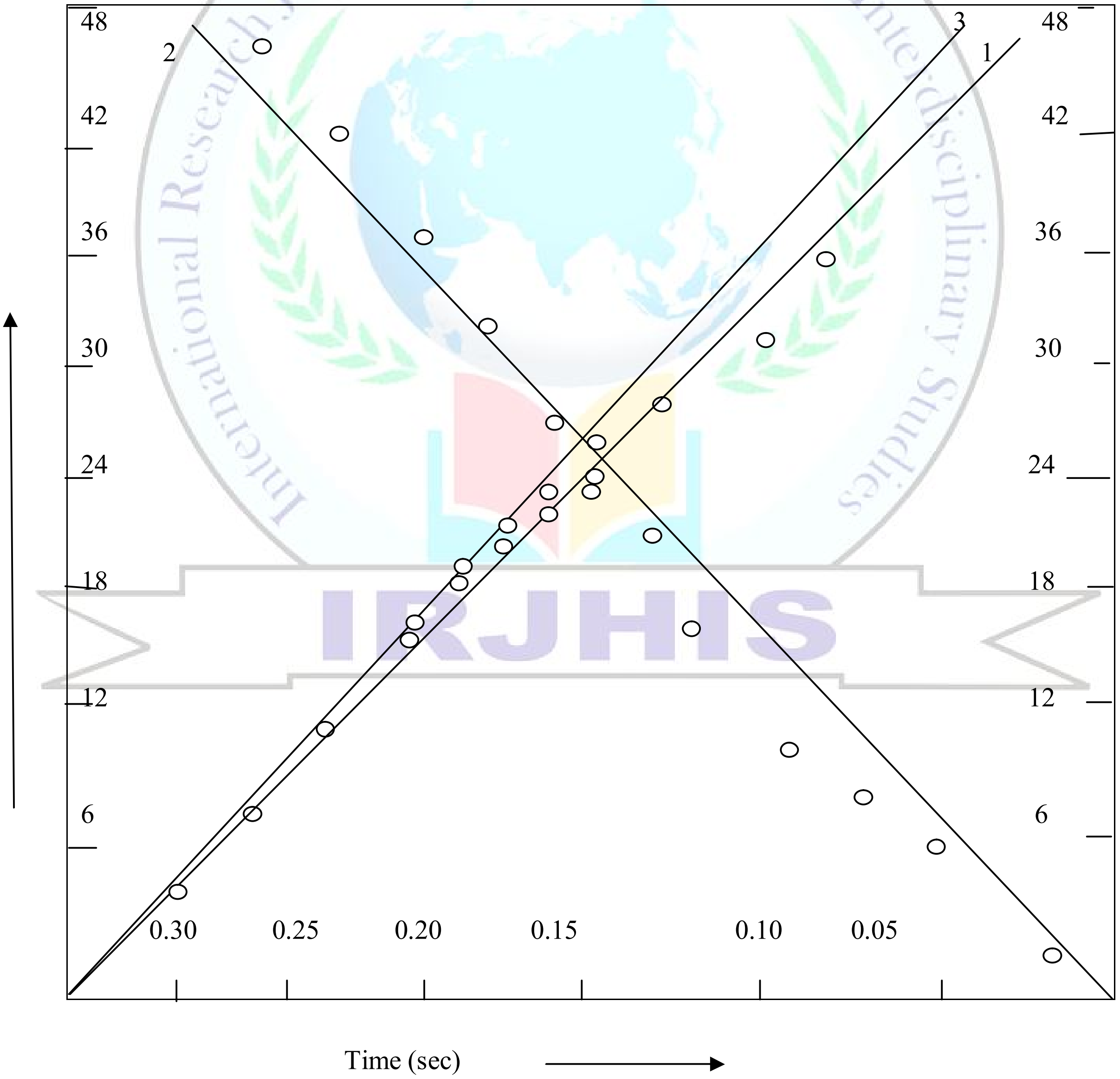

Fig.1.1 Individual plots of log (D_0 /D_t) vs Time for the oxidation of Butane -1,3 –diol

[Butane- 1,3 –diol = 2.0×10^{-3}M [OsO_4] X 10^{-4}M

[NaOH] = 0.15 M (4) – 7.86

[KCl] = 0.35 M (5) - 9.825

Temp. = 35^0C

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

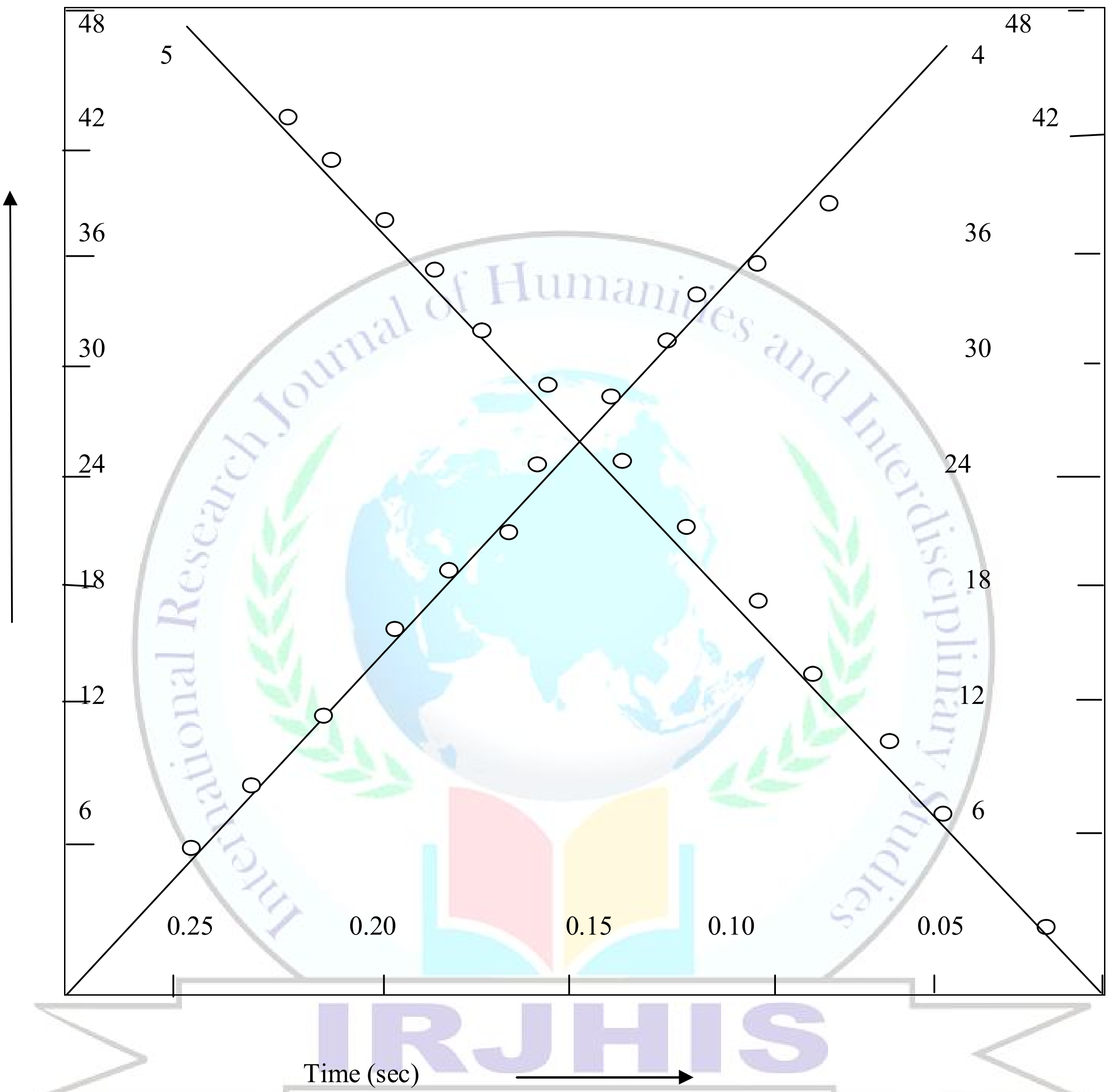

Fig.1.2 Individual plots of log (D_0 /D_t) vs Time for the oxidation of Butane -1,3 –diol.

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 $\times 10^{-3}$	$K_1 \times 10^{-5}$
Butane-1,3-diol	2.44	3375	1.38	1.80

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-

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

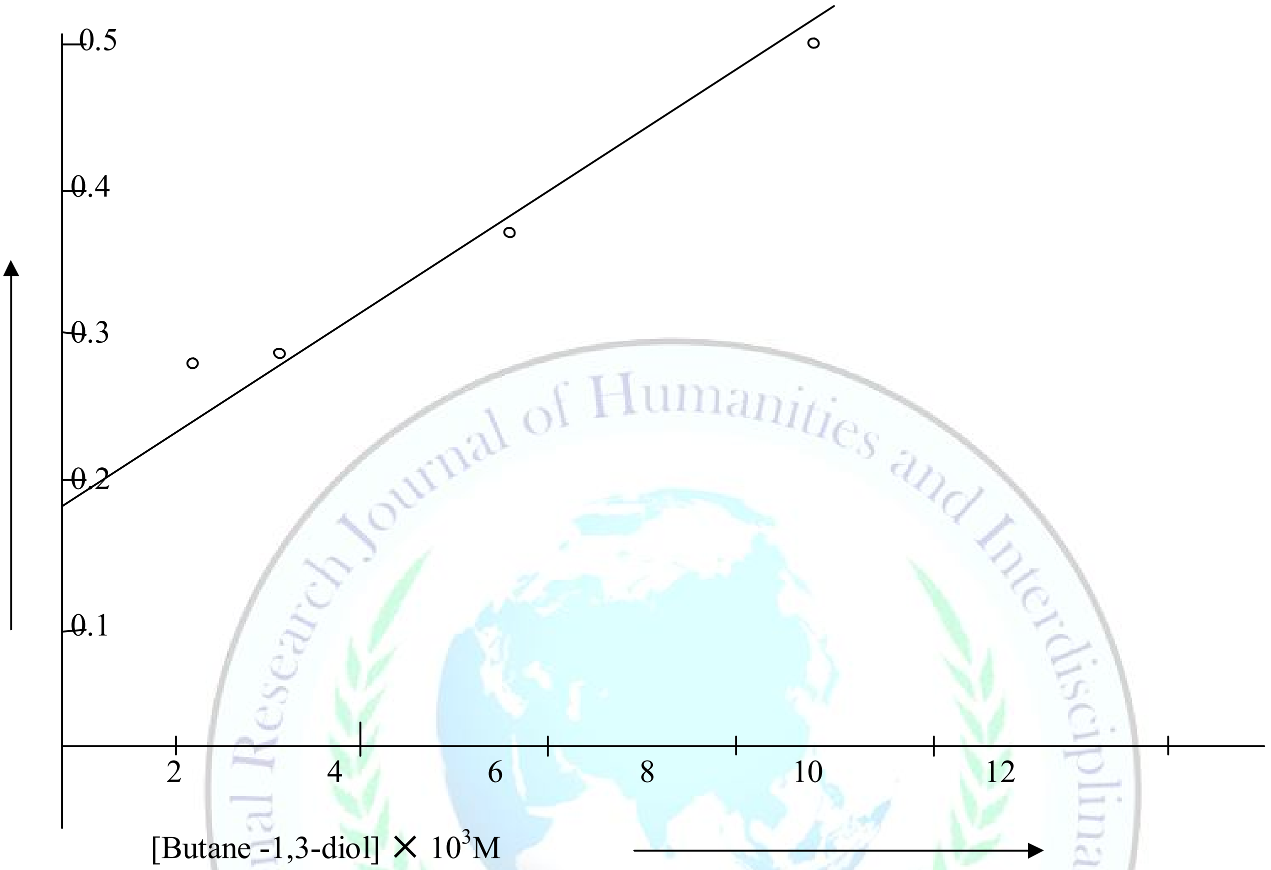

Fig.1.3 Plot of $1/K_1$ $V_S[S]$ for Butane -1,3-diol

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 3-hydroxy Butanoic Acid.

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