KINETICS OF SODIUM TUNGSTATE CATALYZED OXIDATION OF MALEIC ACID BY HYDROGEN PEROXIDE

Abdul HalimA-K Mohammed, and Safaa Rasheed Yasin
Chemical Engineering Department – College of Engineering – University of Baghdad – Iraq

ABSTRACT

Kinetics of oxidation of maleic acid by hydrogen peroxide catalyzed by Sodium tungstate, have been studied. Rate of oxidation exhibits 1.6 order dependence on concentration of hydrogen peroxide, first order dependence on concentration of maleic acid and 0.6 order on concentration of Sodium tungstate dihydrate. The effect of temperature on the reaction rate also was studied and the activation energy obtained was 59.121 kJ.mole^{-1}.

INTRODUCTION

Murray and Taylor[1] studied the kinetics of maleic acid oxidation by potassium chlorate using osmium tetroxide as a catalyst where meso-tartaric acid is obtained from this reaction. They found that the overall reaction is kinetically of second order, first with respect to the acid and first with respect to the catalyst. The absence of the effect of variation, first, in the concentration of the chlorate at constant acid and catalyst concentration and second in the water concentration shows these to be of zero order.

The effect of temperature was studied over the range 9-95°C. The energies of activation calculated by the Arrhenius equation for each successive ten-degree interval and then averaged is 55.647 kJ.mol^{-1}.

Panigrahi and Misro[2] studied the kinetics of oxidation of maleic acid by sodium periodate using osmium tetroxide as a catalyst where meso-tartaric acid is obtained from this reaction. They studied the dependence of the rate equation on the concentrations of periodate (IO_4^-), maleic acid, osmium tetroxide ($O_sO_4^-$) and alkali used in the reaction. They found that the reaction have zero order nature with respect to oxidant concentration, first order dependence with respect to the maleic acid concentration, and first order dependence with respect to the osmium tetroxide concentration. The dependence of reaction rate on alkali concentration is of a definite value till a certain alkali concentration beyond which dependence on alkali concentration tends to zero.

In this work kinetics of Sodium tungstate catalyzed oxidation of maleic acid by hydrogen peroxide was studied. cis-Epoxy succinic acid is produced from this reaction which is hydrolyzed to dl- tartaric (racemic) acid at reflux temperature and at pH lower than 4[3,4,5].

EXPERIMENTAL

Materials

- Maleic anhydride ($C_4H_2O_3$) manufactured by *Riedel Haen AG* with a purity of 99.5%.
- Hydrogen peroxide (H_2O_2) with a concentration of 47 wt.%.
- Sodium tungstate dihydrate ($Na_2WO_4.2H_2O$) manufactured by May and Baker Ltd. with a purity of 99% was used to catalyze epoxidation of maleic acid.

Procedure

The required quantity of maleic anhydride was added to the aqueous solution of sodium tungstate catalyst and the solution was then heated to 50-55°C to dissolve all the maleic anhydride added. Then the solution was filtered to remove any solid impurities, and then charged through the dropping funnel into the reaction flask. A measured quantity of 47% hydrogen peroxide was added to the stirred mixture. The desired temperature was maintained for a specified length of time by using a hot water bath. It was found advantageous to use stirrer speeds lower than 120 rpm to avoid unnecessary loss of oxygen. Figure (1) shows the laboratory experimental unit used in this work.

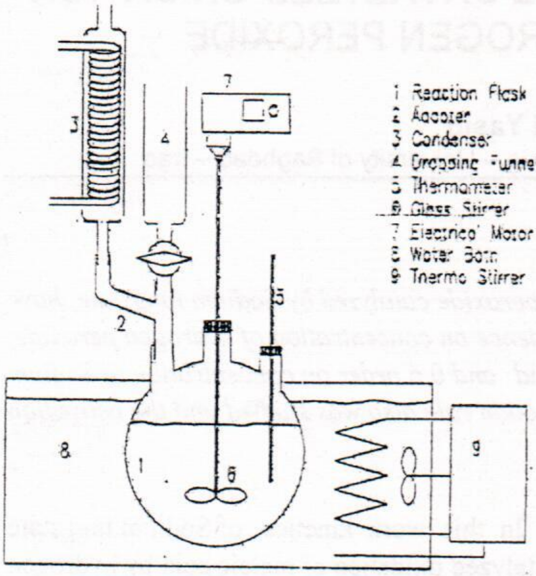


Fig. (1) Laboratory experimental unit

Kinetic Run

Sample of about 1ml of the reaction mixture was withdrawn at regular time intervals and weighed in 100ml conical flask. The reaction was immediately quenched by pouring distilled water 10-20 ml. containing 2 ml. of glacial acetic acid and 1-2 g of potassium iodide. The liberated iodine was titrated against 0.1 N sodium thiosulphate solution until the color of the solution was changed to yellow, then 1ml of starch solution was added and the titration was continued until the blue color disappeared.

Weight percent $H_2O_2 = V*N*1.7007/W$

RESULTS AND DISCUSSION

Determination of the Order of Reaction

For determination the order of reaction, equations of zero, first, and second order reaction were used[6]:

for zero order reaction,

$$[H_2O_2]=[H_2O_2]-k_o t \qquad (1)$$

for first order reaction,

$$\ln\{[H_2O_2]_o/[H_2O_2]\}=k_1 t \qquad (2)$$

for second order reactioin,

$$\{1/[H_2O_2]\}=\{1/[H_2O_2]\}+k_2 t \qquad (3)$$

Plot of $[H_2O_2]$ and $\{1/[H_2O_2]\}$ versus time for equation (1) and (3) respectively, are non-linear as shown in figures (2) and (3), while plot of $\ln\{[H_2O_2]_o/[H_2O_2]\}$ versus time for equation (2) is linear as shown in figure (4). This proves that the epoxdation reaction follows the first order nature. The rate constant calculated by equation (1) and figure (4) is shown in table (1) using hydrogen peroxide concentration of 3.39 g.mol/liter and sodium tungstate concentration of 0.0100712 g.mol/liter at temperature of 70°C.

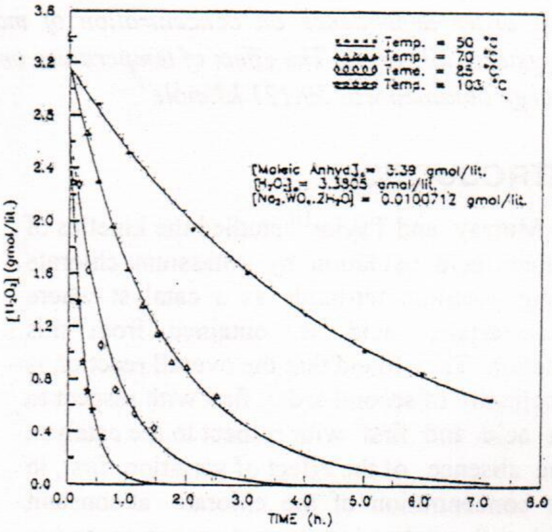


Fig. (2) Test of zero order reaction

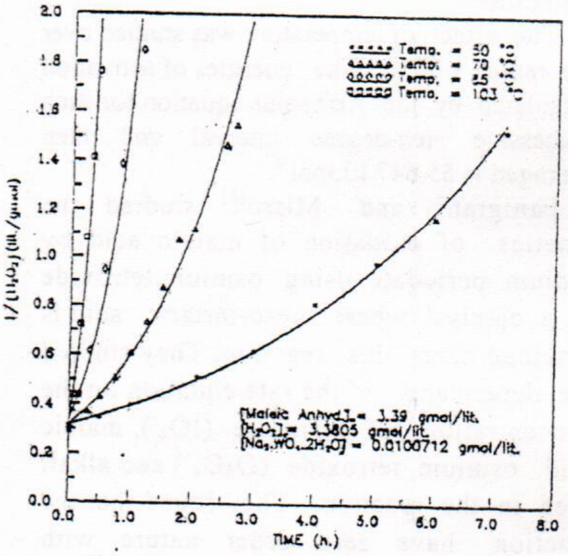


Fig. (3) Test for second order reaction

Dependence of Rate Constant on Hydrogen Peroxide Concentration

The rate constant k_1 was found to increase with decrease in hydrogen peroxide concentration at constant concentrations of maleic an hydride and sodium tungstate dihydrate catalyst, as shown from figure (5).

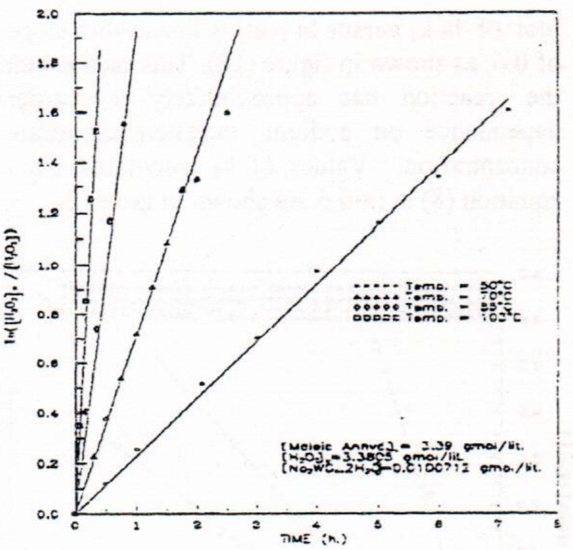


Fig. (4) Test for first order reaction

Table (1), Calculation of rate constant

Elapsed time (h)	$[H_2O_2]$ g.mol/liter	$Ln([H_2O_2]_o/[H_2O_2])$	K_1
0	$[H_2O_2]_o$=3.38	0	---
0.3	2.6854	0.2302	0.7673
0.5	2.3076	0.3818	0.7636
0.75	1.9685	0.5408	0.7211
1.0	1.6394	0.7237	0.7237
1.25	1.3585	0.9116	0.7293
1.50	1.1410	1.0861	0.7241
1.75	0.9314	1.2891	0.7366
2.00	0.8917	1.3326	0.6663
2.50	0.6815	1.6015	0.6406

Mean of k_1= 0.7197,By-graph (slope from figure (4)) = 0.7205

Temp. = 70°C, $[H_2O_2]_o$ = 3.3805 g.mol/liter, [Maleic anhyd.]=3.39 g.mol/liter, $[Na_2WO_4.2H_2O]$ = 0.0100712 g.mol/liter

The dependence of reaction rate on hydrogen peroxide concentration was found by using the following equation[2]:

$$k_3=k_1[H_2O_2]^n \qquad (4)$$

or

$$\ln k_1= \ln k_3 - n \ln[H_2O_2] \qquad (5)$$

plot of ln k_1 versus ln$[H_2O_2]$ is linear with slope of 1.6, as shown from figure (6). This proves that the reaction has approximately 1.6 order dependence on $[H_2O_2]$. Values of k_3 calculated from equation (4) at n=1.6 are shown in table (2).

Dependence of Rate Constant on Maleic Anhydride Concentration

The rate constant k_1, was found to increase with increase in maleic an hydride concentration at constant concentrations of hydrogen peroxide and sodium tungstate, as shown from figure (7). The dependence of reaction rate on maleic anhydride concentration was found by using the following equations[1,2]:

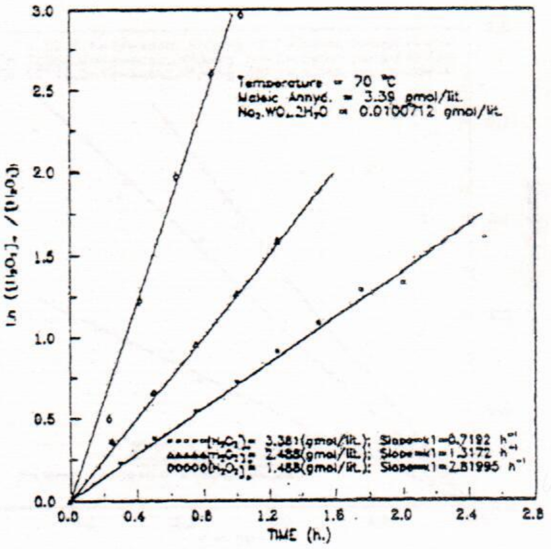


Fig. (5) Effect of hydrogen peroxide concentration on reaction rate constant (k_1)

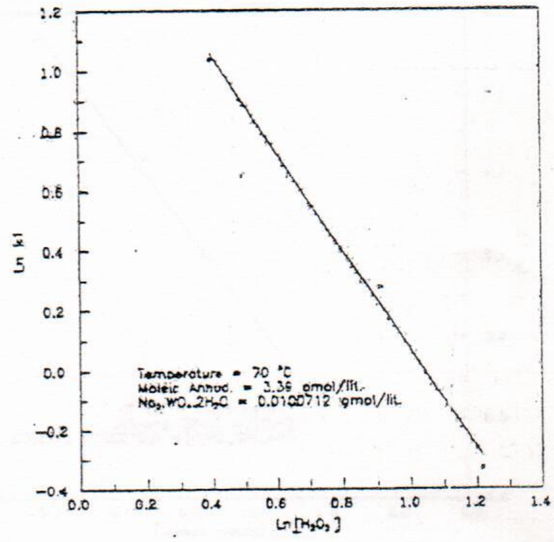


Fig. (6) Calculation the order of hydrogen peroxide concentration

$$k_4 = k_1[H_2O_2]^{1.6}/[\text{maleic}]^n = k3/[\text{maleic}]^n \qquad (6)$$

or

$$\ln k_3 = \ln k_4 + n \ln[\text{maleic}] \qquad (7)$$

plot of ln k_3 versus ln[maleic anhyd.] is linear with unit slope, as shown in figure (8). This shows the reaction rate has first order dependence on maleic anhydride concentration. Values of k_4 calculated from equation (6) at n=1 are shown in table (2).

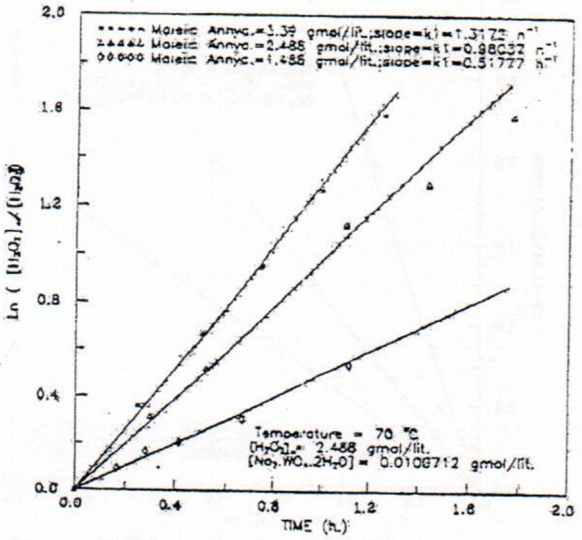


Figure (7) Effect of maleic anhydride concentration on reaction constant (k_1)

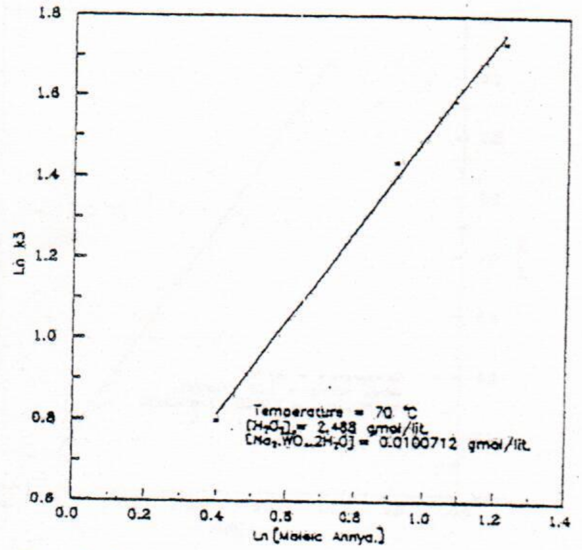


Fig. (8) Calculation the order of maleic anhydride concentration

Dependence of Rate Constant on Sodium Tungstate Dihydrate Concentration

The rate constant k_1, increases with increase in sodium tungstate dihydrate concentration at constant concentrations of maleic anhydride and hydrogen peroxide, as shown from figure (9). The dependence of reaction rate on catalyst concentration was found by using the following equations[1,2]:

$$k_5=k_1[H_2O_2]^{1.6}/[\text{maleic}]^1[\text{cat}]^n=k_4/[\text{cat}]^n \quad (8)$$

or

$$\ln k_4=\ln k_5 + n \ln [\text{cat}] \quad (9)$$

plot of $\ln k_4$ versus $\ln$ [cat] is linear with slope of 0.6, as shown in figure (10). This means that the reaction has approximately 0.6 order dependence on sodium tungstate dihydrate concentration. Values of k_5 calculated from equation (8) at n=0.6 are shown in table (2).

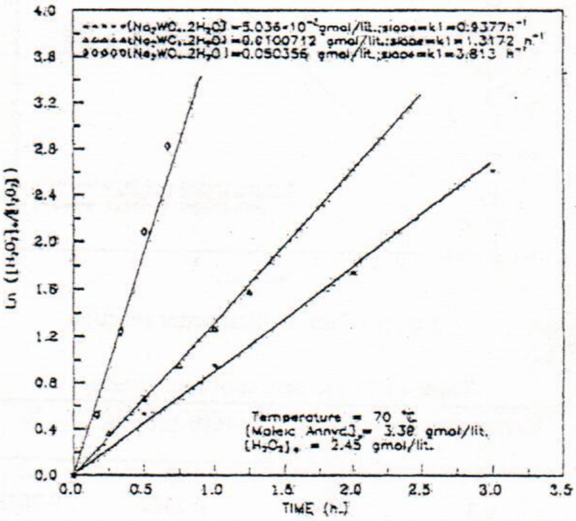


Fig. (9) Effect of catalyst (sodium tungstate dihydrate) concentration on reaction rate constant.

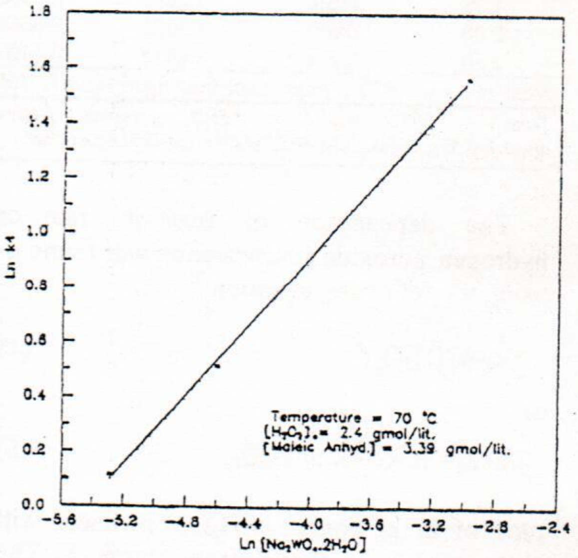
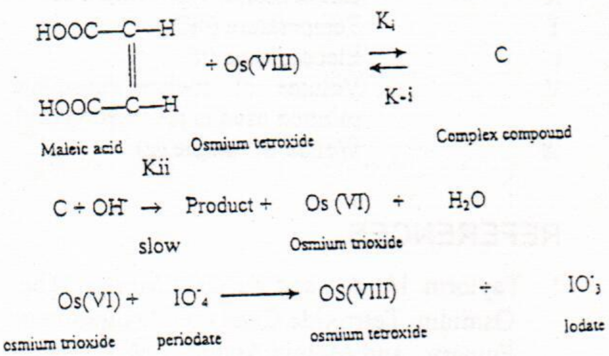


Fig. (10) Calculation the order of catalyst (sodium tungstate dihydrate) concentration.

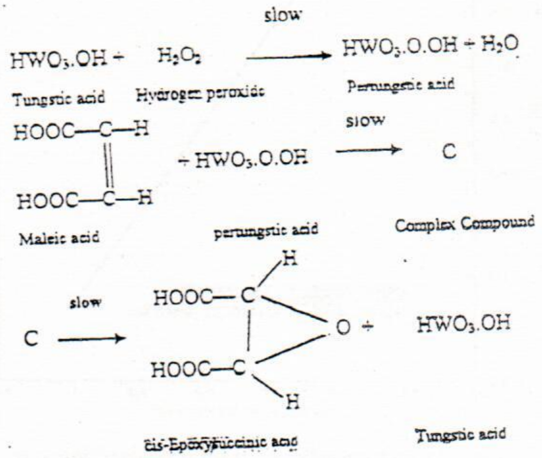
This value, i.e. 0.6 order, is different from the value (1st order) obtained by Panigrahi and Misro[2], and Murry and Taylor[1]. This may be due to the differences in the mechanism of osmium tetroxide used by these authors.

The difference in the mechanism between osmium tetroxide catalyst and sodium tungstate catalyst also affect the dependence of reaction rate on oxidant concentration. In this work, the dependence of reaction rate on oxidant (hydrogen peroxide) concentration is 1.6 order, while the dependence in the case of osmium tetroxide[1,2] is zero order.

The following steps are envied for maleic and osmium tetroxide $O_S(VIII)$[2]:



In the above mechanism, osmium tetroxide reacts directly with maleic acid to form a complex compound. The reaction step of osmium trioxide $O_S(VI)$ with periodate (IO_4^-) is fast, because the dependence of reaction rate on oxidant (periodate) concentration is zero order. For tungstate acid, the following mechanism can be proposed:



The dependence of reaction rate on hydrogen peroxide concentration (1.6 order) means that the reaction of hydrogen peroxide with tungstate acid is slow step.

Table (2) Dependence of rate constant on concentrations of maleic acid, hydrogen peroxide, and catalyst at 70°C.

Run No.	[Maleic Anhyd.] g.mole/liter	$[H_2O_2]_o$ g.mole/liter	$[Na_2WO_4.2H_2O$ g.mole/liter	K_1 h^{-1}	K_3 $(g.mole/liter)^{1.6}.h^{-1}$	K_4 $(g.mole/liter)^{0.6}.h^{-1}$	K_5 h^{-1}
1	3.39	3.381	0.010712	0.7192	5.0504	1.4898	23.5114
2	3.39	2.488	0.010712	1.3172	5.6626	1.6704	26.3616
3	3.39	1.488	0.010712	2.81995	5.3261	1.5711	24.7945
4	1.4883	2.488	0.010712	0.51777	2.2259	1.4956	23.6030
5	2.4880	2.488	0.010712	0.98037	4.2145	1.6939	26.7325
6	3.390	2.488	0.010712	1.3172	5.6626	1.6704	26.3616
7	3.39	2.400	$5.030*10^{-3}$	0.9377	3.8054	1.1225	26.8494
8	3.39	2.488	0.010712	1.3172	5.6626	1.6704	26.3616
9	3.39	2.476	0.0503564	3.813	16.2656	4.7981	28.8295

Effect of Temperature on the Reaction Rate

The effect of temperature on the rate of reaction was studied as shown in figure (4). The rate of reaction is increased as the temperature of the reaction solution is increased. The effect of temperature was studied for the temperature of 50, 70, 85, and 103°C and the values of the rate constants are shown in table (3). The energy of activation was calculated by using the Arhenius equation[1,6]:

$$k_1 = F \exp(-E/RT) \qquad (10)$$

Table (3) Effect of temperature on maleic acid oxidation

Temp. °C	k_1 (h^{-1})	1/(T+273) (1/°K)	ln k_1
50	0.2377	$3.095*10^{-3}$	-1.4367
70	0.7192	$2.914*10^{-3}$	-0.3296
85	2.1795	$2.792*10^{-3}$	0.7791
103	4.9901	$2.66*10^{-3}$	1.6075

$[H_2O_2]_o$=3.3805 g.mol/liter, [maleic anhyd.]$_o$=3.39 g.mol/liter, $[Na_2WO_4.2H_2O]$=0.0100712 g.mol/liter

Figure (11) shows a plot of ln k_1 versus (1/Temp.°C+273))*10^3. Linear equation was obtained with slope of (E/R), and the energy of activation was calculated as 59.121 kJ.mol^{-1}. Similar energy of activation (55.647 kJ.mol^{-1}) has also been reported by Taylor[1] for potassium chlorate oxidation of maleic acid catalyzed by osmium tetroxide.

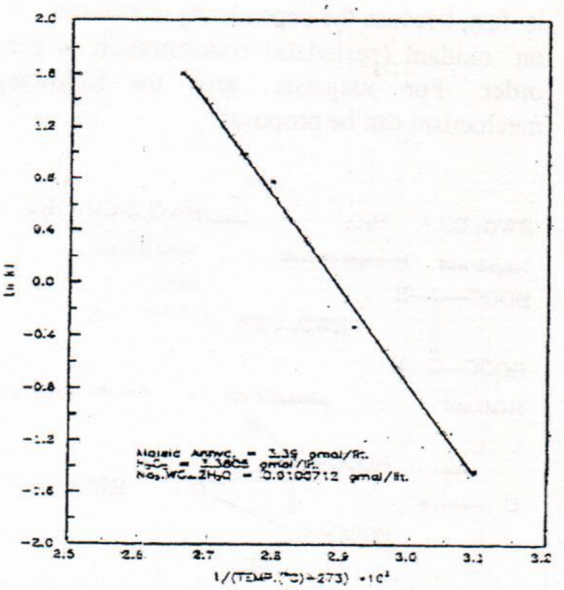


Fig. (11) Effect of temperature on reaction rate

NOMENCLATURE

E	Activation energy (J/g.mol)
F	Frequency factor
$[H_2O_2]_o$	Initial concentration of H_2O_2 (g.mol/liter)
k_o	Zero order reaction rate constant ($g.mol.liter^{-1}.h^{-1}$)
k_1	First order reaction rate constant (h^{-1})
k_2	Second order reaction rate constant ($liter.mol^{-1}.h^{-1}$)
k_3	Reaction rate constant, independent on concentration of H_2O_2 $(g.mol/liter)^{1.6}h^{-1}$
k_4	Reaction rate constant independent on concentrations of H_2O_2 and maleic acid $(g.mol/liter)^{0.6}h^{-1}$
k_5	Reaction rate constant independent on concentrations of H_2O_2, maleic acid , and sodium tungstate catalyst (h^{-1}).
[maleic anhyd.]$_o$	Initial concentration of maleic anhyd. in the reaction solution (g.mol/liter)
$[Na_2WO_4.2H_2O]$	Concentration of sodium tungstate dihydrate catalyst in the reactio solution (g.mol/liter)
N	Normality of sodium thiosulfate solution used in the titration
R	Gas constant, 8.314 J/mol.°K
T	Temperature (°K)
t	Elapsed time (h)
V	Volume of sodium thiosulfate solution used in the titration (ml)
W	Weight of sample (g)

REFERENCES

1. Taylorm H. A. and Zelikoff Murry, "The Osmium Tetroxide Catalyzed Oxidation of Fumaric and Maleic Acids", J. Am. Chem. Soc., Vol. 72, P. 5039, 1950.
2. Panigrahi, G. P. and Misro, P. K., "Kinetics and Mechanism of Os(VIII)-Catalyzed Oxidation of Unsaturated Acids by Sodium Periodate", Indian J. Chem., Vol. 16A, P. 201, 1978.
3. Church, J. M. and Blumberg, R., "Synthesis of Tartaric Acid", Ind. Eng. Chem., Vol. 43, P. 1780, 1951.
4. Bewsey, J. A., "Synthetic Tartaric Acid and the Economics of Foods Acidulants", Chemistry and Industry (London), Vol. 3, P. 119, 1977.
5. Payne, G. B. and Williams, P. H., "Sodium Tungstate Catalyzed Epoxidation of Unsaturated Acids", J. Org. Chem.. Vol. 24, P. 54, 1959.
6. Smith, J. M., "Chemical Engineering Kinetics", 3rd ed., New York , McGraw-Hill, 1981.