Chapter-III

Detailed study of oxidation of substituted alcohols

The present chapter includes the detail study of oxidation of following alcohols.

1]4-Chlorobenzyl alcohol

2] Benzyl alcohol

3]4-Methoxybenzyl alcohol

The oxidation of these alcohols is explained, regarding the variations in,

1] Concentration of alcohol

2] Concentration of polymeric reagent

3] Solvent

4] Temperature

5] % of crosslinking in polymeric reagent

A] Standard kinetic run:

At the beginning, preliminary experiments were carried out in order to decide the range of concentration of polymeric reagent, concentration of alcohol, suitable solvent and temperature at which the reaction proceeds satisfactorily.

It was found that, the reaction proceeds with a measurable velocity at 45°C using $15x10^{-3}$ ml of benzyl alcohol in 5 ml of 1;4 Dioxane and 140 mg of polymeric reagent (Chromium(VI)oxide supported on Ambersep 900.

The kinetic data and plots of optical density versus time is shown in Chart1 (140 mg, 15 $x10^{-3}$ml alcohol at 45°C in 1:4 Dioxane)

The observed rate constant k was calculated from graphs. The results in the chart 1 shows that the equation,

$$k = \text{Slope (for graphical method)}$$

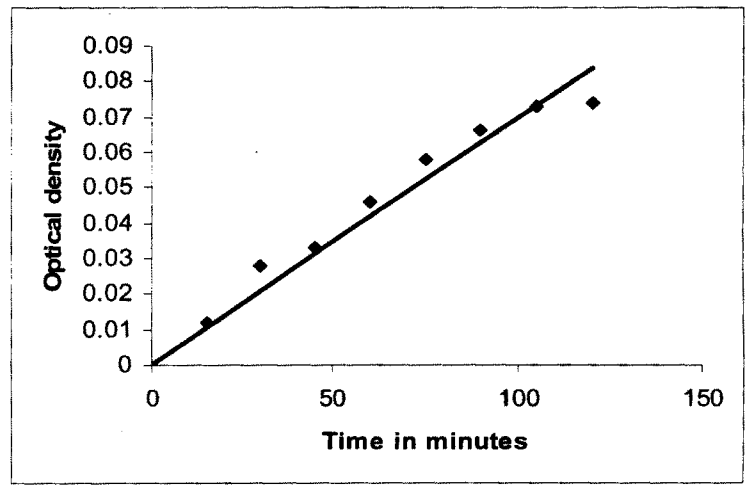
is quite valid as the graphically determined values of k are almost constant. The optical density versus time plots is linear passing through origin. These facts lead to conclude that the reaction may follow zero order kinetics under experimental conditions.

Chart 1

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.028
3	45	0.033
4	60	0.046
5	75	0.058
6	90	0.066
7	105	0.073
8	120	0.074



Mean k = Slope = 7.61 $x10^{-4}$ min^{-1}

B] Effect of change in alcohol concentration:

In order to observe the effect of concentration of alcohol on rate of reaction, it was necessary to study the reaction at different initial concentration of substrate alcohol. For this purpose the concentration of substrate was varied according to molar concentration of alcohols as follows and the kinetic runs obtained are embodied in following charts accordingly.

Alcohols	Charts
4-Chlorobenzyl alcohol	2,3,4,5
Benzyl alcohol	6,7,8,9
4-Methoxybenzyl alcohol	10,11,12,13

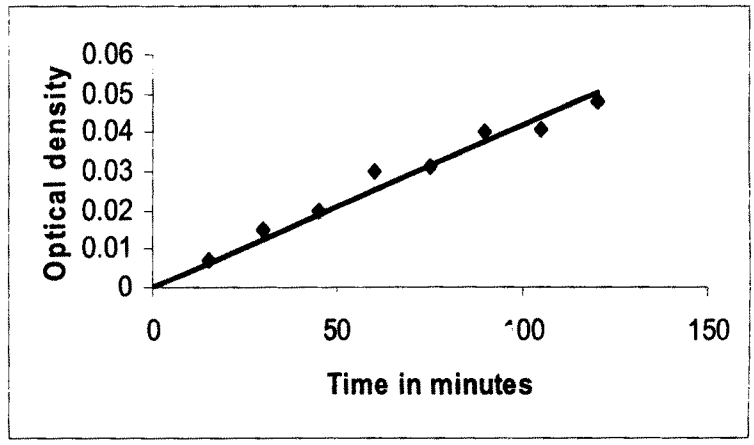
Chart 2

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Chlorobenzyl alcohol 13.4 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.011
3	45	0.019
4	60	0.028
5	75	0.031
6	90	0.037
7	105	0.048
8	120	0.050



Mean k = Slope = 4.00×10^{-4} min.$^{-1}$

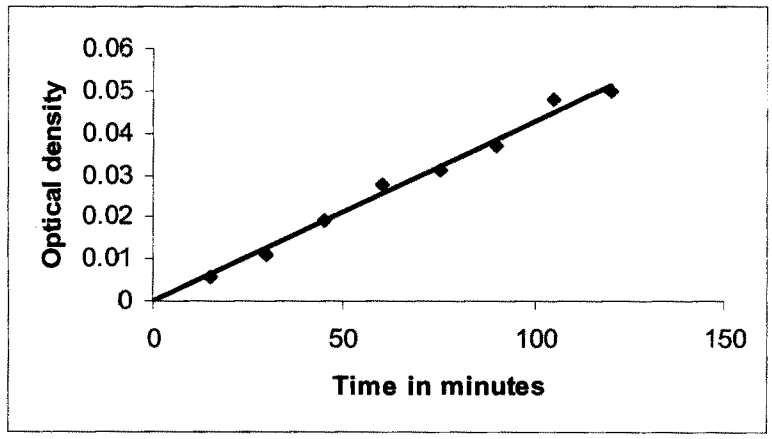
Chart 3

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.011
3	45	0.019
4	60	0.028
5	75	0.031
6	90	0.037
7	105	0.048
8	120	0.050



Mean k = Slope = 4.11×10^{-4} min.$^{-1}$

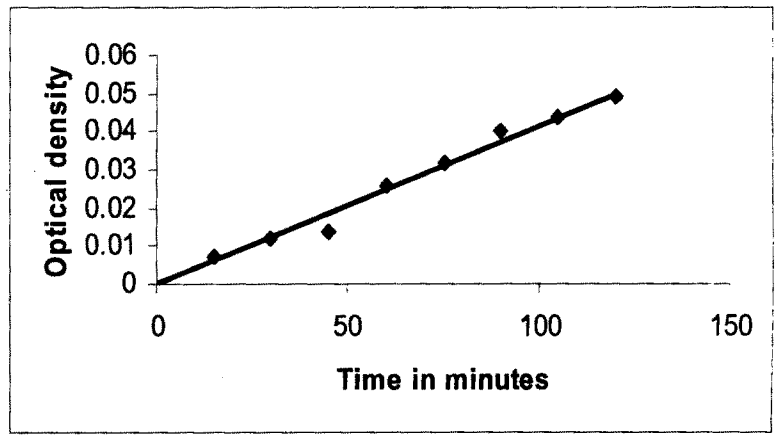
Chart 4

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Chlorobenzyl alcohol 27.0 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.011
3	45	0.019
4	60	0.028
5	75	0.031
6	90	0.037
7	105	0.048
8	120	0.050



Mean k =Slope = 4.16×10^{-4} min.$^{-1}$

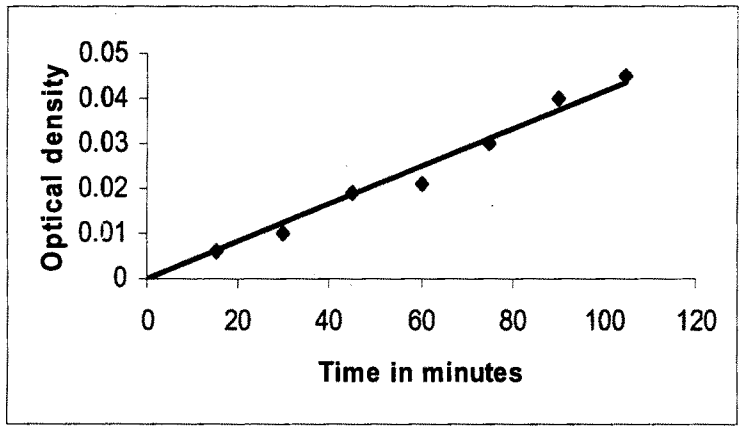
Chart 5

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Chlorobenzyl alcohol 33.6 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.010
3	45	0.019
4	60	0.021
5	75	0.030
6	90	0.040
7	105	0.045
8	120	0.049



Mean k = Slope = 4.00×10^{-4} min.$^{-1}$

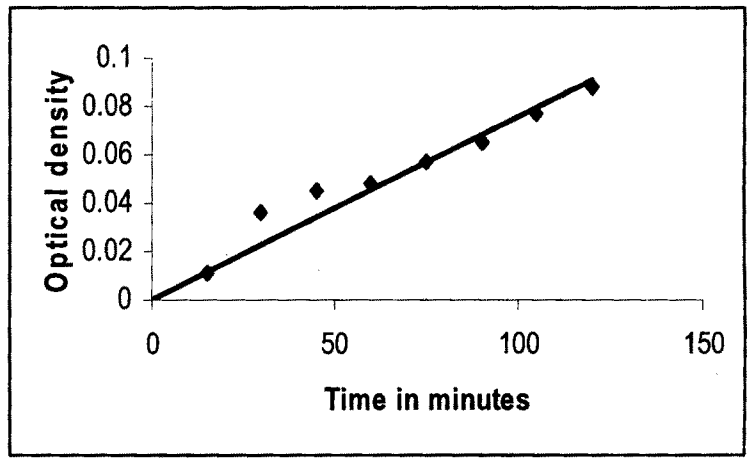
Chart 6

Effect of change in concentration of alcohol on rate of reaction

Substrate	Benzyl alcohol 10 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation table:

No.	Time in minutes	Optical density
1	15	0.011
2	30	0.036
3	45	0.045
4	60	0.048
5	75	0.057
6	90	0.065
7	105	0.077
8	120	0.088



Mean k = Slope = 7.72 $x10^{-4}$ min^{-1}

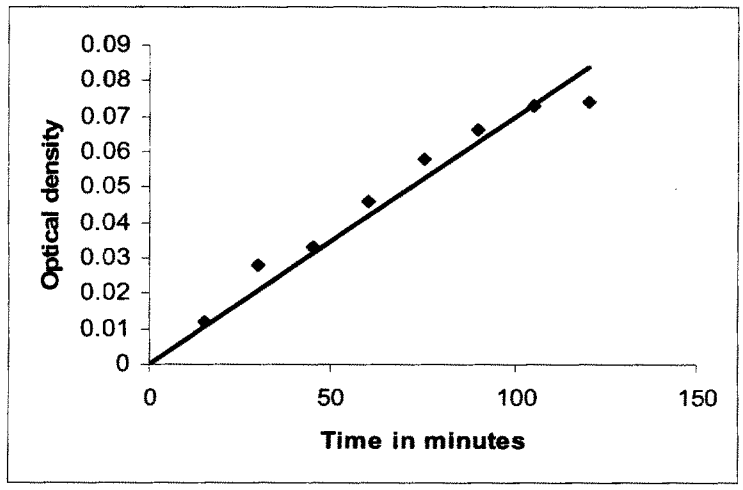
Chart 7

Effect of change in concentration of alcohol on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.028
3	45	0.033
4	60	0.046
5	75	0.058
6	90	0.066
7	105	0.073
8	120	0.074



Mean k = Slope = $7.61x10^{-4}$ $min.^{-1}$

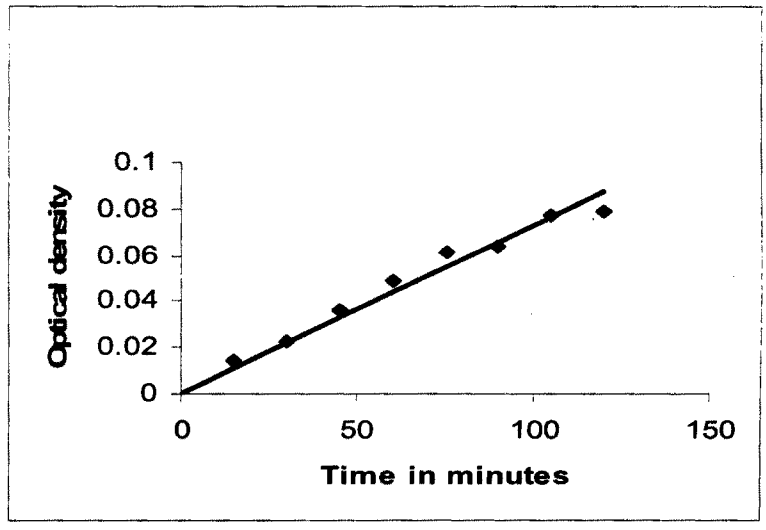
Chart 8

Effect of change in concentration of alcohol on rate of reaction

Substrate	Benzyl alcohol 20 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.014
2	30	0.023
3	45	0.036
4	60	0.049
5	75	0.061
6	90	0.064
7	105	0.077
8	120	0.079



Mean k=Slope = 7.50 $x10^{-4}$ $min.^{-1}$

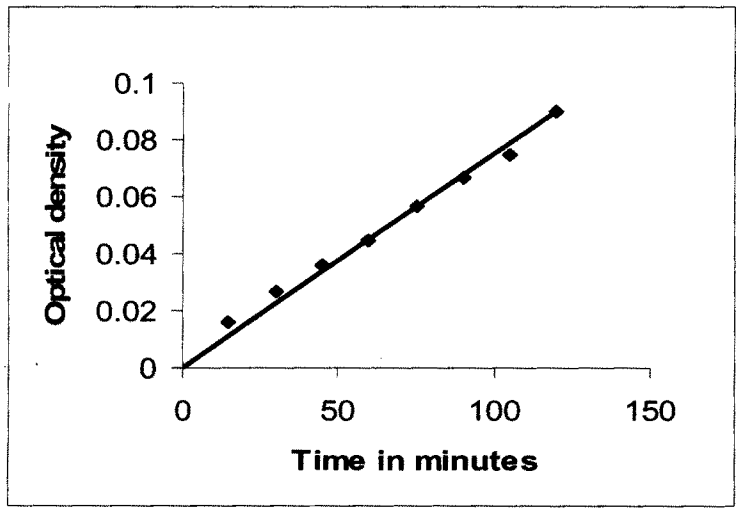
Chart 9

Effect of change in concentration of alcohol on rate of reaction

Substrate	Benzyl alcohol 25 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.016
2	30	0.027
3	45	0.036
4	60	0.045
5	75	0.057
6	90	0.067
7	105	0.075
8	120	0.090



Mean k = Slope = 7.50 $x10^{-4}$ $min.^{-1}$

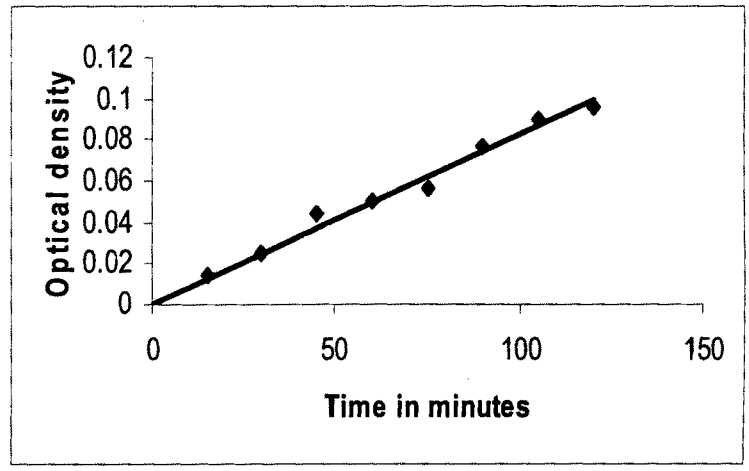
Chart 10

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Methoxybenzyl alcohol 13.0×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.015
2	30	0.025
3	45	0.045
4	60	0.051
5	75	0.056
6	90	0.077
7	105	0.090
8	120	0.096



Mean k =Slope = 8.69×10^{-4} min^{-1}

Chart 11

Effect of change in concentration of alcohol on rate of reaction

Substrate 4-Methoxybenzyl alcohol 18.2×10^{-3} ml

Oxidant concentration 140 mg

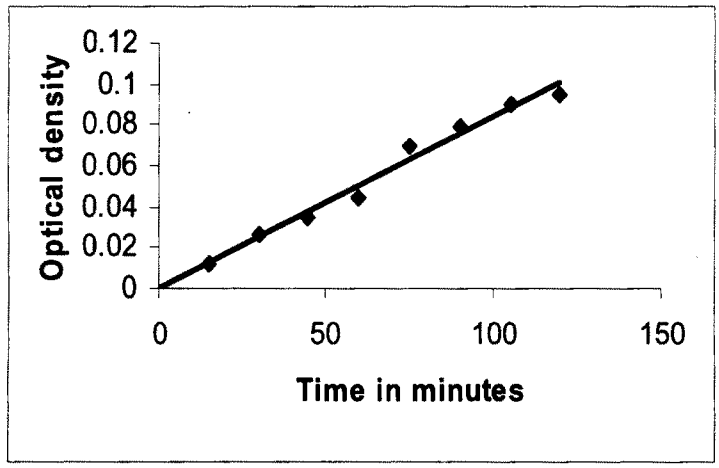
Temperature 45°C

Solvent 1:4 Dioxane, 5 ml

λmax 273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.026
3	45	0.035
4	60	0.044
5	75	0.070
6	90	0.079
7	105	0.090
8	120	0.095



Mean k = Slope = 8.63×10^{-4} min^{-1}

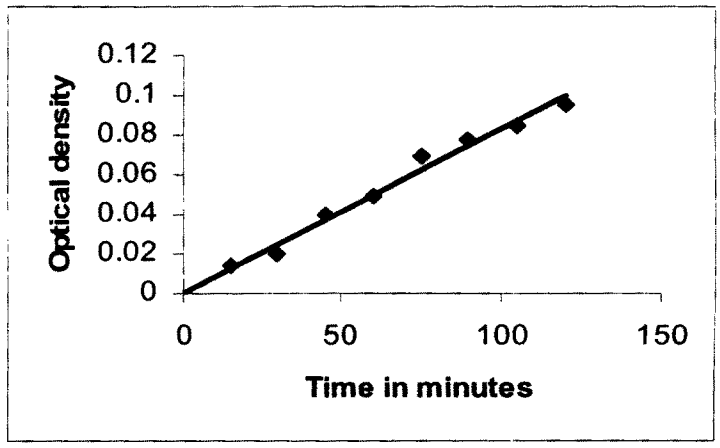
Chart 12

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Methoxybenzyl alcohol 24.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.014
2	30	0.020
3	45	0.040
4	60	0.050
5	75	0.069
6	90	0.078
7	105	0.085
8	120	0.095



Mean k =Slope = 8.57×10^{-4} min.$^{-1}$

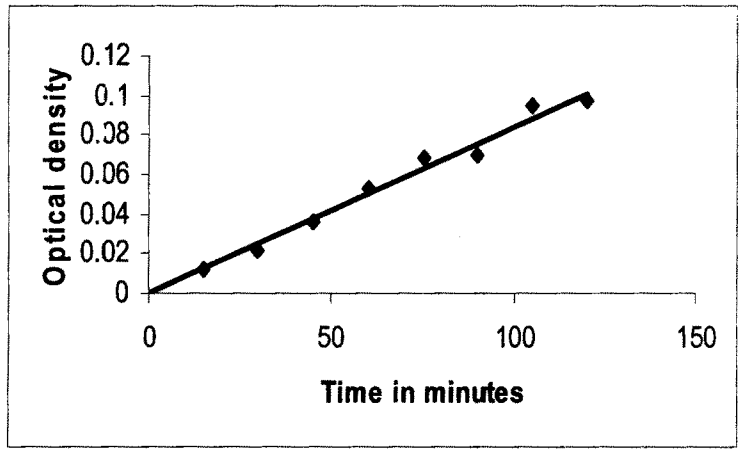
Chart 13

Effect of change in concentration of alcohol on rate of reaction

Substrate	4-Methoxybenzyl alcohol 30.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.022
3	45	0.036
4	60	0.053
5	75	0.068
6	90	0.070
7	105	0.095
8	120	0.097



Mean k=Slope = 8.94×10^{-4} min.$^{-1}$

From the kinetic data and graphical representation of these runs, it is observed that optical density against time plots in the above mentioned charts are linear passing through origin .The value of k at different intervals of time, calculated graphically are almost constant, hence the zero order kinetic behaviour of reaction is retained at different initial concentration of alcohol. Therefore the zero order rate constant is independent of initial concentration of alcohol.

Table 1

Rate constant for change in alcohol concentration:

4-Chlorobenzyl alcohol	Alcohol conc. mg ⟶	13.4	20.2	27.0	33.6
	k x 10^{-4} min^{-1} ⟶	4.0	4.11	4.11	4.0
Benzyl alcohol	Alcohol conc. x10^{-3} ml ⟶	10	15	20	25
	k x 10^{-4} min^{-1} ⟶	7.72	7.61	7.50	7.50
4-Methoxybenzyl alcohol	Alcohol conc. x10^{-3} ml ⟶	13.0	18.2	24.2	30.2
	k x 10^{-4} min^{-1} ⟶	8.69	8.63	8.57	8.94

C] Effect of change in resin concentration:

In order to investigate the effect of concentration of resin on the rate of reaction, and also to determine the order of reaction with respect to resin concentration, the reaction was carried out using different initial concentrations of resin [120-180 mg] at 45°C and at constant molar concentrations of alcohol,

keeping the solvent [1:4 Dioxane] as well as concentration of solvent [5 ml] unchanged for alcohols. The kinetic data and plots of these runs are represented in following Charts

Alcohols	Charts
4-Chlorobenzyl alcohol	14,15,16,17
Benzyl alcohol	18,19,20,21
4-Methoxybenzyl alcohol	22,23,24,25

From data it is observed that,

* The value of k at different interval of time, calculated graphically, is almost constant.
* The optical density versus time plot in each case is linear passing through zero.
* The mean value of k for all the kinetic runs with different concentrations of resin for each alcohol is also constant.

Hence it can be concluded that, the observed rate constants of the reaction under investigation are insensitive to the different concentration of resin. Hence rate constant of reaction under investigation are independent of concentration of alcohol and also resin [polymeric reagent].

Table 2

Rate constant for change in polymeric reagent concentration:

Alcohols	Oxidant Conc. in mg			
	120	140	160	180
	$k \times 10^{-4}$ min^{-1}			
4-Chlorobenzyl alcohol	4.13	4.11	4.19	4.16
Benzyl alcohol	7.72	7.61	7.69	7.50
4-Methoxybenzyl alcohol	8.63	8.63	8.69	8.69

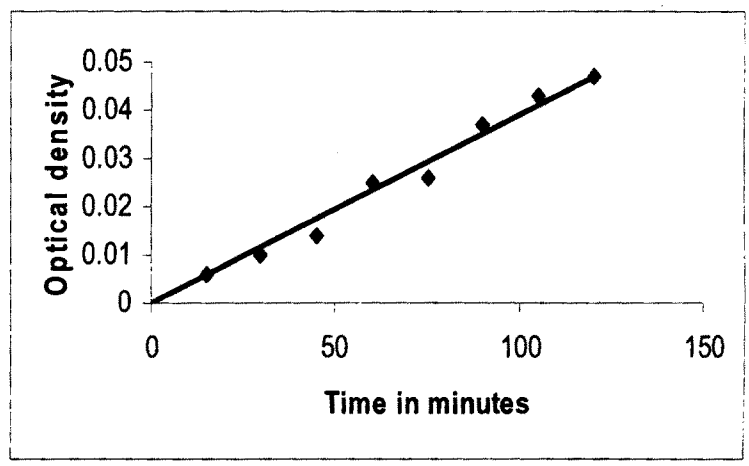
Chart 14

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	120 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.010
3	45	0.019
4	60	0.021
5	75	0.030
6	90	0.040
7	105	0.045
8	120	0.049



Mean k = Slope = 4.13 x10^{-4} min.$^{-1}$

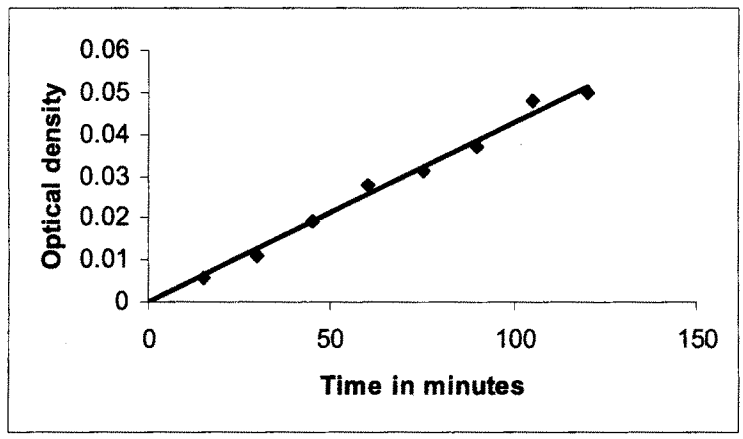
Chart 15

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.011
3	45	0.019
4	60	0.028
5	75	0.031
6	90	0.037
7	105	0.048
8	120	0.050



Mean k = Slope = 4.11 x10^{-4} min.$^{-1}$

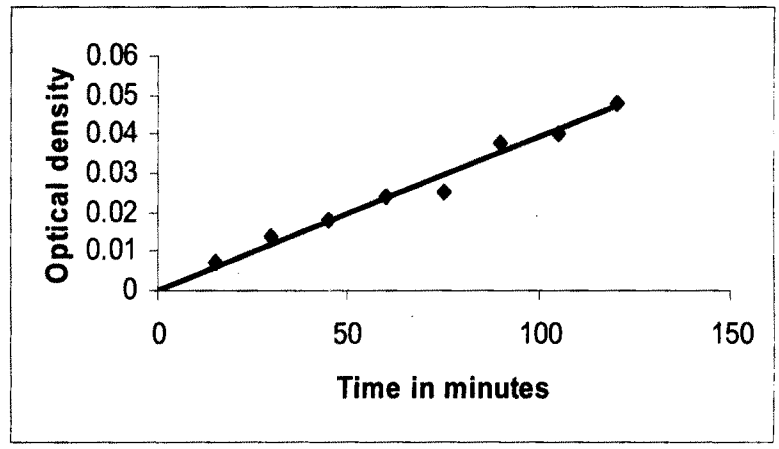
Chart 16

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	160 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.007
2	30	0.014
3	45	0.018
4	60	0.024
5	75	0.025
6	90	0.038
7	105	0.040
8	120	0.048



Mean k =Slope = 4.19×10^{-4} min^{-1}

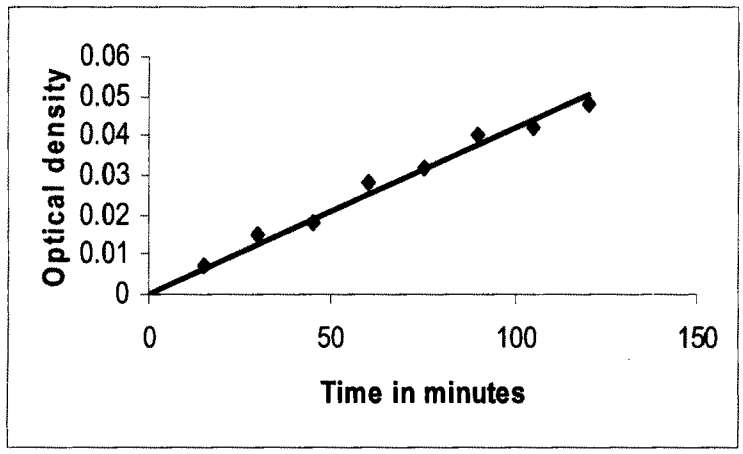
Chart 17

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	180 mg
Temperature	45°C
Solvent	1:4Dioxane, 5ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.007
2	30	0.015
3	45	0.018
4	60	0.028
5	75	0.032
6	90	0.040
7	105	0.042
8	120	0.048



Mean k = Slope = 4.16×10^{-4} min.$^{-1}$

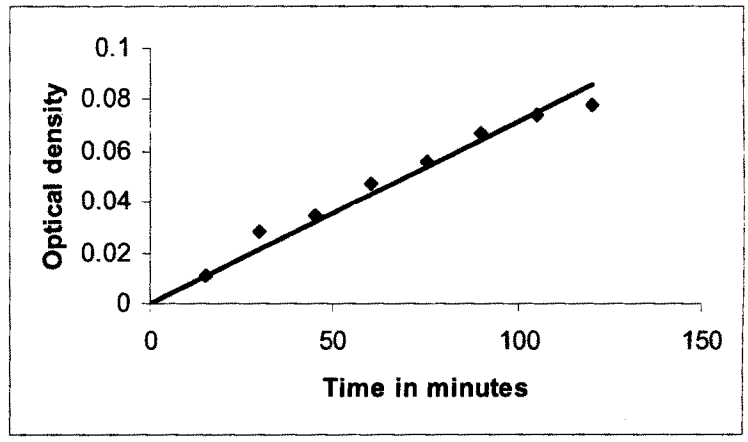
Chart 18

Effect of polymeric reagent concentration on rate of reaction

Substrate	Benzyl alcohol 15 x10^{-3} ml
Oxidant concentration	120 mg
Temperature	45°C
Solvent	1:4Dioxane, 5ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.011
2	30	0.028
3	45	0.035
4	60	0.047
5	75	0.056
6	90	0.067
7	105	0.074
8	120	0.078



Mean k = Slope = 7.72 x10^{-4} min.$^{-1}$

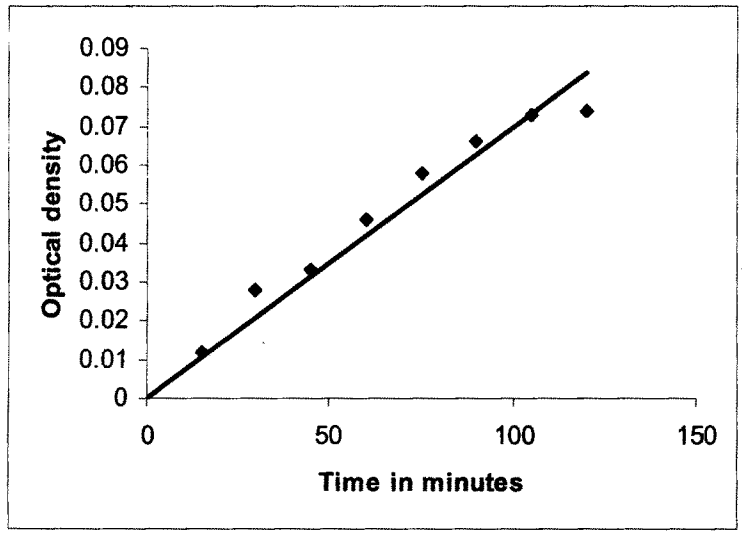
Chart 19

Effect of polymeric reagent concentration on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.028
3	45	0.033
4	60	0.046
5	75	0.058
6	90	0.066
7	105	0.073
8	120	0.074



Mean k = Slope = 7.61 $x10^{-4}$ $min.^{-1}$

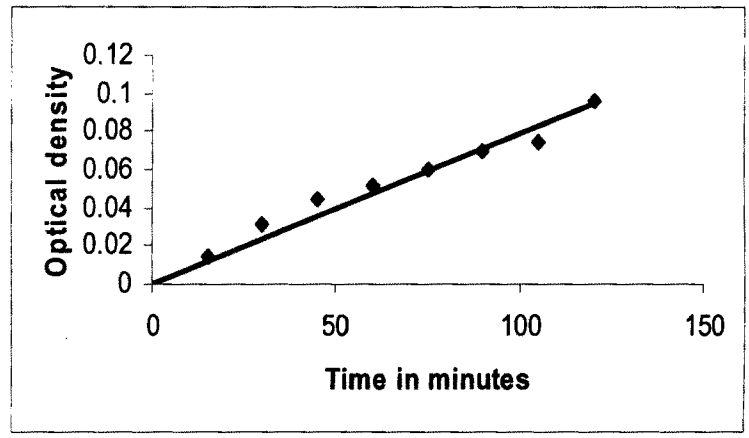
Chart 20

Effect of polymeric reagent concentration on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	160 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.014
2	30	0.031
3	45	0.044
4	60	0.052
5	75	0.060
6	90	0.070
7	105	0.075
8	120	0.096



Mean k=Slope = 7.69 $x10^{-4}$ $min.^{-1}$

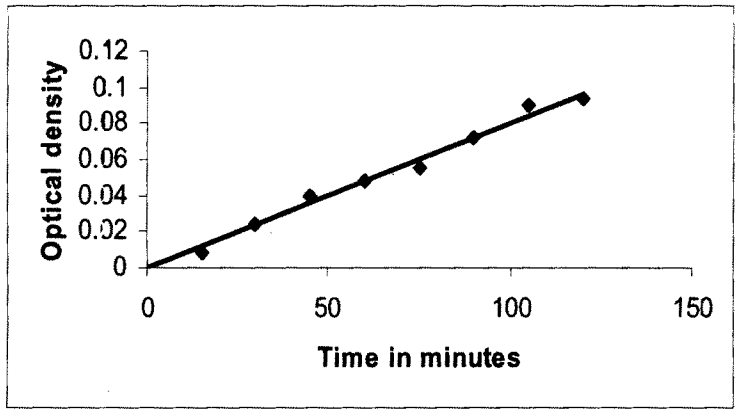
Chart 21

Effect of polymeric reagent concentration on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	180 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.009
2	30	0.024
3	45	0.040
4	60	0.048
5	75	0.055
6	90	0.072
7	105	0.090
8	120	0.094



Mean k =Slope =7.50 $x10^{-4}$ $min.^{-1}$

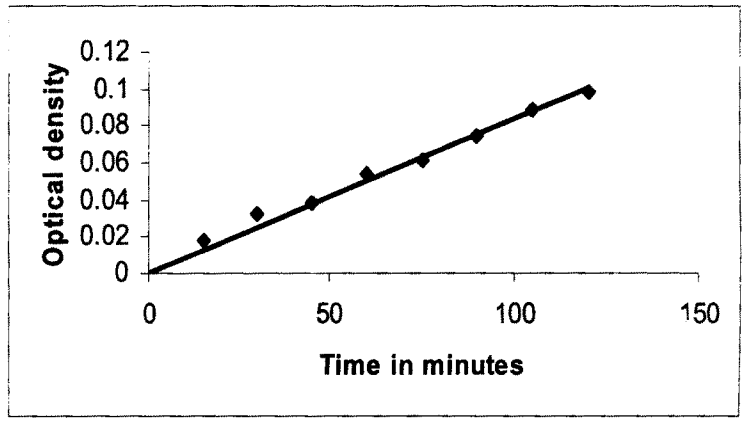
Chart 22

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	120 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.018
2	30	0.033
3	45	0.038
4	60	0.054
5	75	0.061
6	90	0.074
7	105	0.089
8	120	0.099



Mean k = Slope = 8.63×10^{-4} min.$^{-1}$

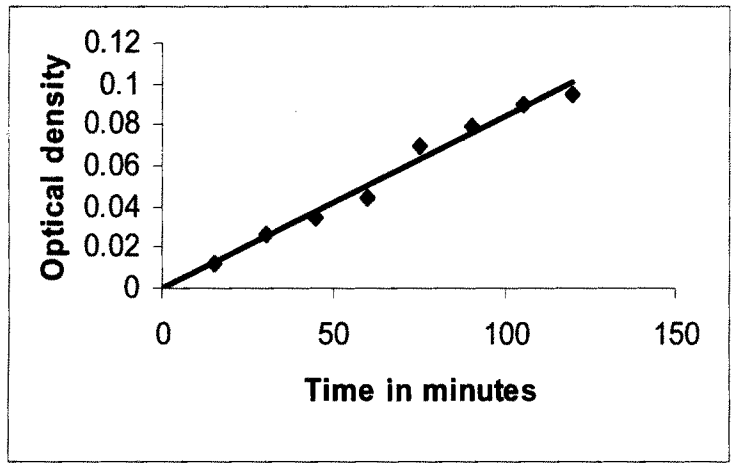
Chart 23

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.026
3	45	0.035
4	60	0.044
5	75	0.070
6	90	0.079
7	105	0.090
8	120	0.095



Mean k = Slope = 8.63×10^{-4} min^{-1}

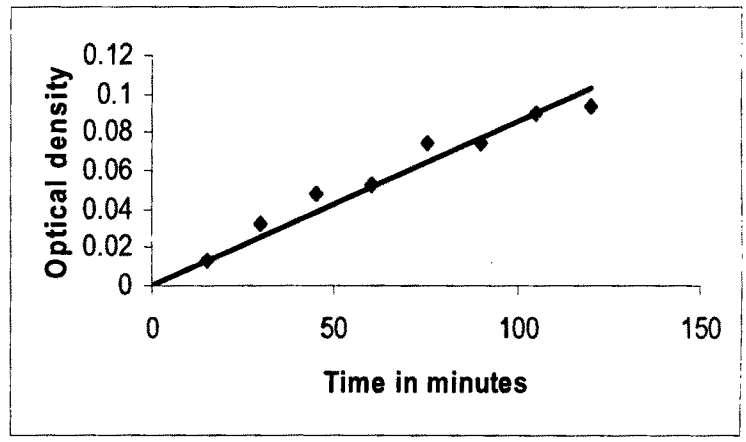
Chart 24

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	160 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.013
2	30	0.032
3	45	0.048
4	60	0.053
5	75	0.074
6	90	0.075
7	105	0.090
8	120	0.094



Mean k = Slope = 8.69×10^{-4} min.$^{-1}$

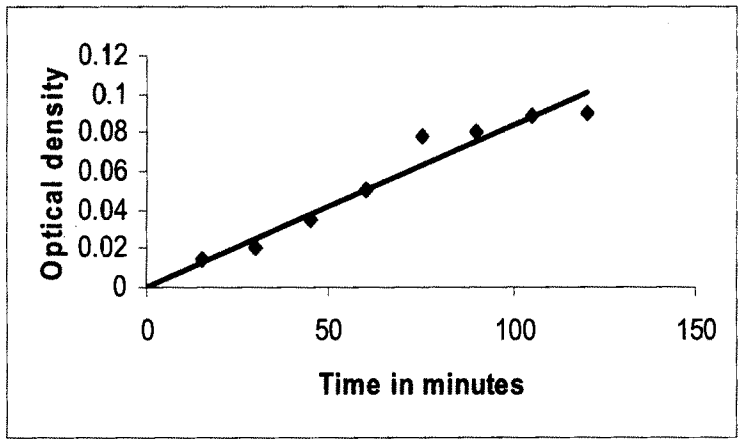
Chart 25

Effect of polymeric reagent concentration on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3}ml
Oxidant concentration	180 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.015
2	30	0.020
3	45	0.035
4	60	0.050
5	75	0.078
6	90	0.081
7	105	0.089
8	120	0.090



Mean k =Slope = 8.69×10^{-4} min.$^{-1}$

D] Effect of change in solvent:

The effect of change in solvent was studied by carrying out the reaction in different solvents like 1:4Dioxane, CCl_4, Chloroform, Cyclohexane.

The kinetic data and optical density versus time plots are represented in charts

Alcohols	Charts
4-Chlorobenzyl alcohol	26,27,28,29,
Benzyl alcohol	30,31,32,33,
4-Methoxybenzyl alcohol	34,35,36,37

A Careful study of observation shows that the rate of reaction increases as the dielectric constant of solvent increases. [Table 3]

Table 3

Rate constants for change in solvents:

Solvent	Dielectric constant	Alcohols		
		4-Chloro benzyl alcohol	Benzyl alcohol	4-Methoxy benzyl alcohol
		$k \times 10^{-4}$ min^{-1}		
Cyclohexane	2.0	3.46	5.76	6.40
CCl_4	2.2	3.86	6.81	6.92
1:4Dioxane	2.2	4.11	7.61	8.63
Chloroform	4.8	6.47	8.26	11.0

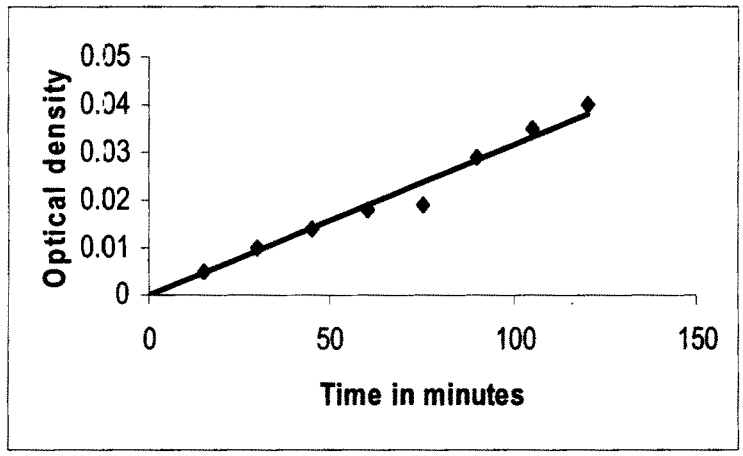
Chart 26

Effect of Change of Solvent on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Cyclohexane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.005
2	30	0.010
3	45	0.014
4	60	0.018
5	75	0.019
6	90	0.029
7	105	0.035
8	120	0.040



Mean k = Slope = 3.46×10^{-4} min^{-1}.

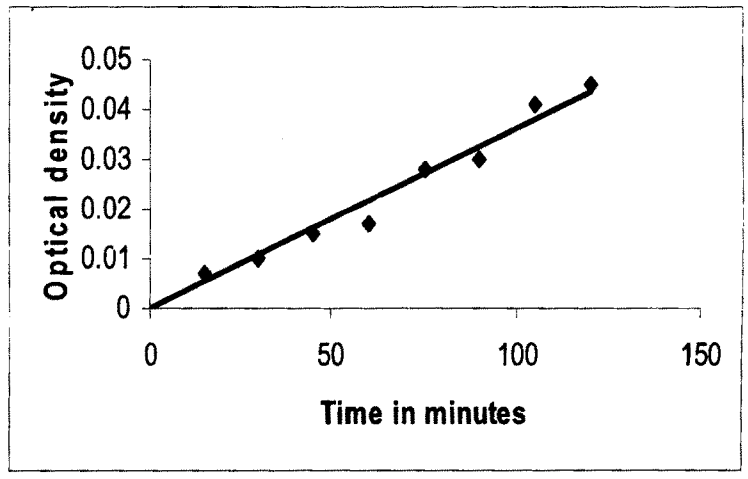
Chart 27

Effect of change of solvent on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	CCl_4 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.007
2	30	0.010
3	45	0.015
4	60	0.017
5	75	0.028
6	90	0.030
7	105	0.041
8	120	0.045



k = Slope = 3.84×10^{-4} min.$^{-1}$

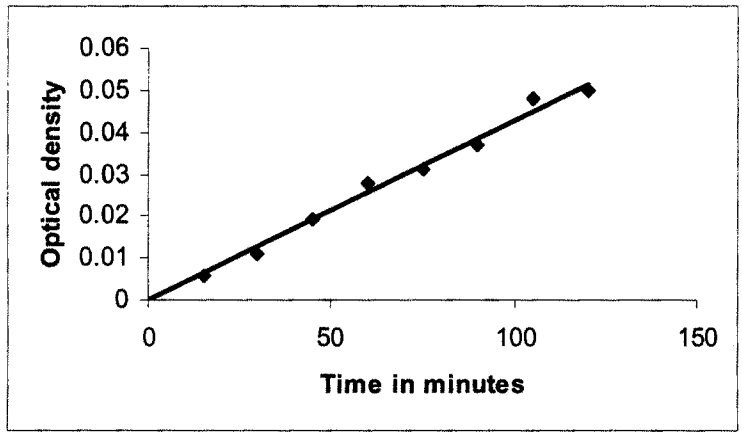
Chart 28

Effect of change in solvent on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.006
2	30	0.011
3	45	0.019
4	60	0.028
5	75	0.031
6	90	0.037
7	105	0.048
8	120	0.050



Mean k = Slope = 4.11 x10^{-4} min.$^{-1}$

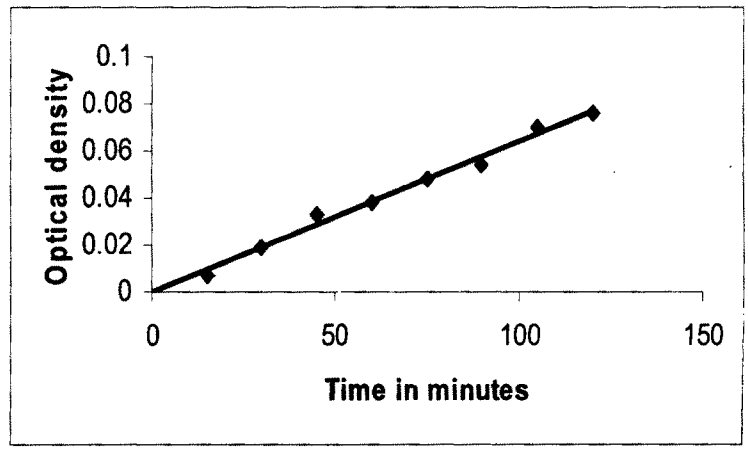
Chart 29

Effect of change of solvent on rate of reaction

Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Chloroform, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.007
2	30	0.019
3	45	0.033
4	60	0.038
5	75	0.048
6	90	0.054
7	105	0.070
8	120	0.076



Mean k = Slope =6.47 x10^{-4} min.$^{-1}$

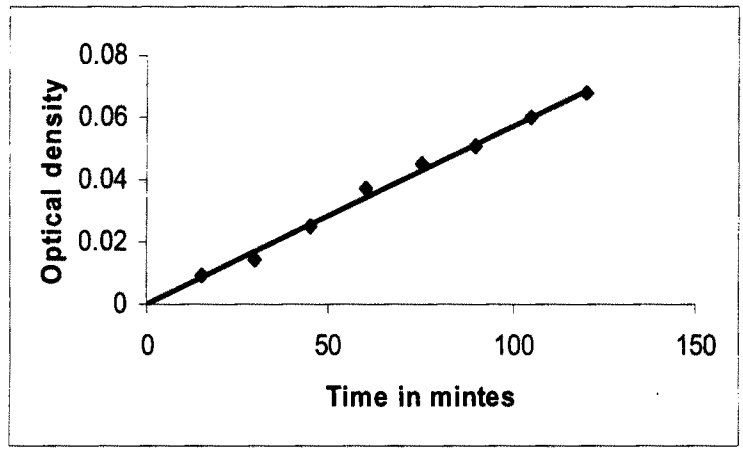
Chart 30

Effect of change in solvent on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Cyclohexane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.009
2	30	0.014
3	45	0.025
4	60	0.038
5	75	0.045
6	90	0.051
7	105	0.060
8	120	0.068



Mean k = Slope = 5.76 $x10^{-4}$ min^{-1}

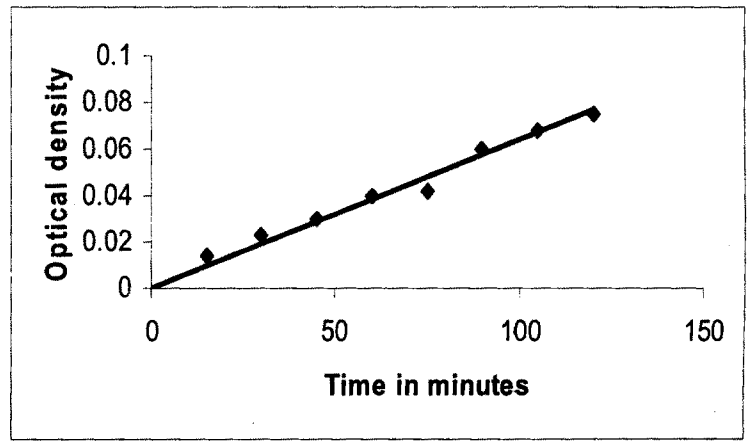
Chart 31

Effect of change in solvent on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	CCl_4, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.014
2	30	0.023
3	45	0.030
4	60	0.040
5	75	0.042
6	90	0.060
7	105	0.068
8	120	0.075



Mean k =Slope = 6.81 x 10^{-4} min^{-1}

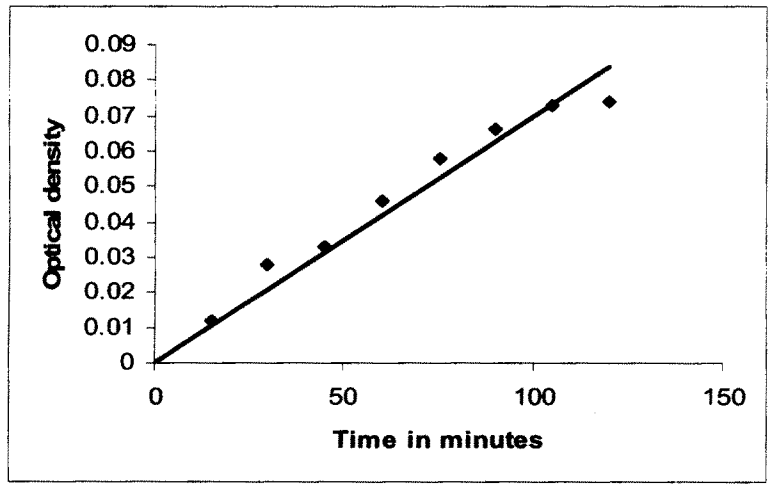
Chart 32

Effect of change in solvent on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.028
3	45	0.033
4	60	0.046
5	75	0.058
6	90	0.066
7	105	0.073
8	120	0.074



k =Slope = 7.61 x 10^{-4} min^{-1}

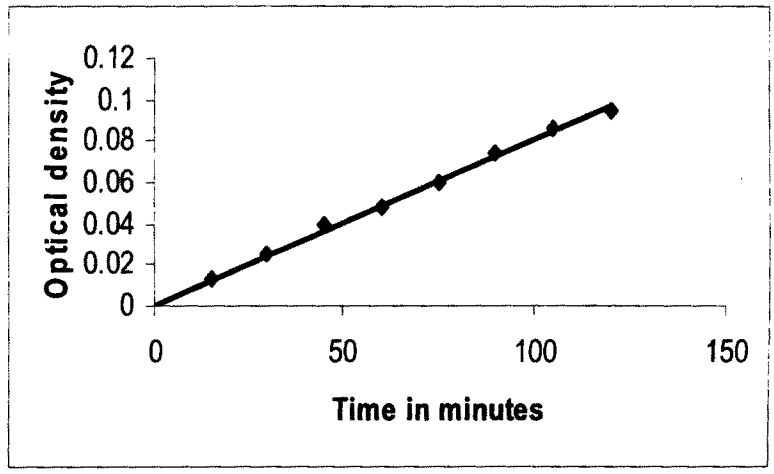
Chart 33

Effect of change in solvent on rate of reaction

Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Chloroform, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.013
2	30	0.025
3	45	0.040
4	60	0.048
5	75	0.060
6	90	0.074
7	105	0.087
8	120	0.095



Mean k = Slope = 8.26 $x10^{-4}$ $min.^{-1}$

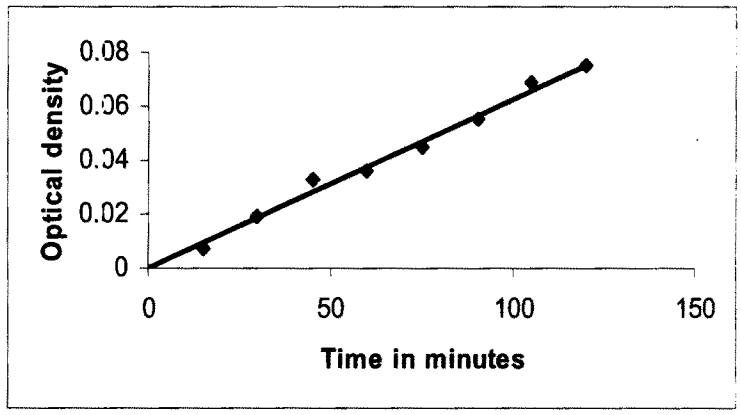
Chart 34

Effect of change in solvent on the rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Cyclohexane, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.025
2	30	0.037
3	45	0.062
4	60	0.074
5	75	0.086
6	90	0.099
7	105	0.110
8	120	0.115



Mean k =Slope = 6.40×10^{-4} min.$^{-1}$

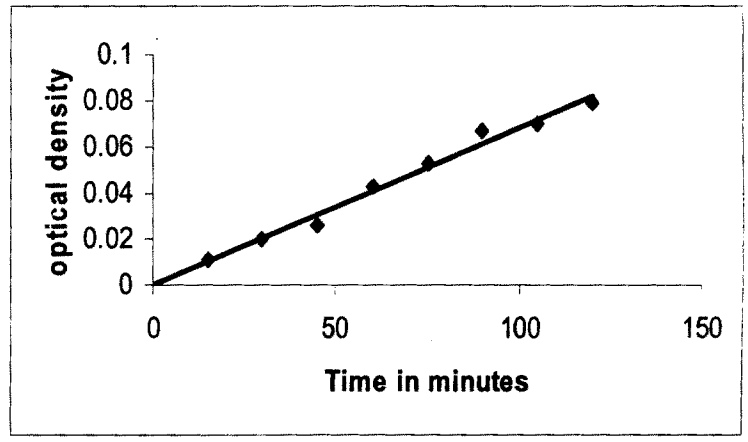
Chart 35

Effect of change in solvent on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	CCl_4 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.011
2	30	0.020
3	45	0.026
4	60	0.043
5	75	0.053
6	90	0.067
7	105	0.070
8	120	0.079



Mean k = Slope = 6.92×10^{-4} min.$^{-1}$

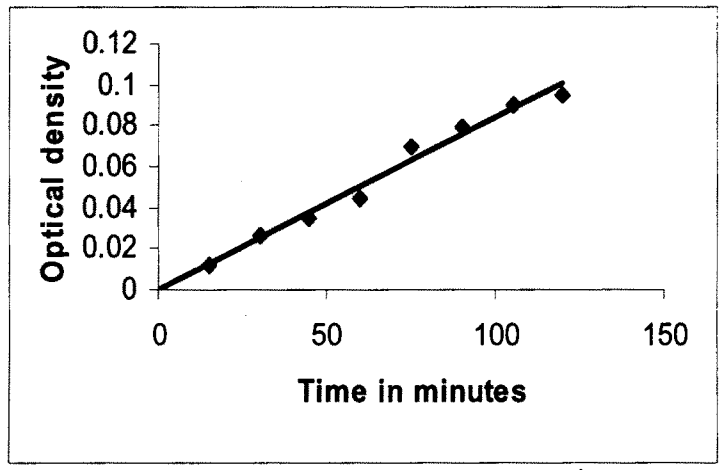
Chart 36

Effect of change in solvent on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	1:4 Dioxane, 5ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.012
2	30	0.026
3	45	0.035
4	60	0.044
5	75	0.070
6	90	0.079
7	105	0.090
8	120	0.095



Mean k = Slope = 8.63×10^{-4} min^{-1}

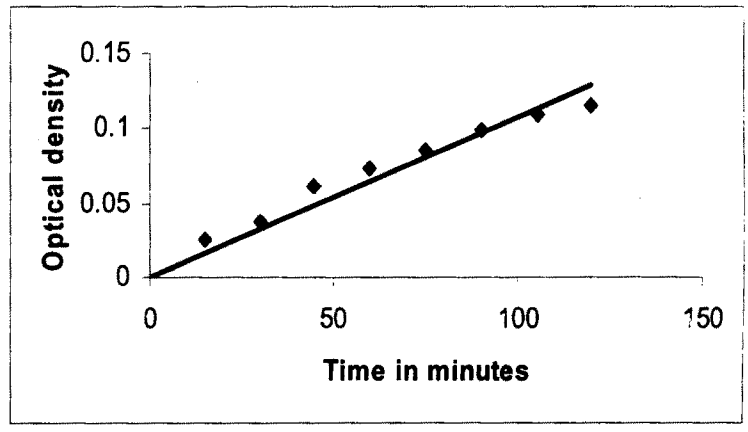
Chart 37

Effect of change in solvent on rate of reaction

Substrate	4-Methoxybenzyl alcohol 18.2×10^{-3} ml
Oxidant concentration	140 mg
Temperature	45°C
Solvent	Chloroform, 5 ml
λmax	273 nm

Observation Table:

No.	Time in minutes	Optical density
1	15	0.025
2	30	0.037
3	45	0.062
4	60	0.074
5	75	0.086
6	90	0.099
7	105	0.110
8	120	0.115



Mean k = Slope = 11.0×10^{-4} min.$^{-1}$

E] Effect of temperature:

To investigate the effect of temperature on the rate of reaction, the reaction was carried out at four different temperatures,(40°, 45°, 50° and 55°C).The kinetic data and graphical representation of these experiments of alcohols, at different temperature are summarized in charts

Alcohol	Charts
4-Chlorobenzyl alcohol	38, 38[A]
Benzyl alcohol	39, 39[A]
4-Methoxybenzyl alcohol	40, 40[A]

The rate constants of the above alcohols are represented in Table 4

Table 4

Rate constants for change in temperature:

Alcohols	Temperatures			
	40°C	45°C	50°C	55°C
	$k \times 10^{-4}$ $min.^{-1}$			
4-Chlorobenzyl alcohol	3.33	4.11	5.76	9.41
Benzyl alcohol	5.31	7.61	8.50	15.00
4-Methoxybenzyl alcohol	6.55	8.63	11.5	15.45

A tabulated result shows that the reaction rate depends on temperature and it increases with increase in temperature.

The values of observed rate constants at different temperatures were used to determine various thermodynamics parameters like temperature coefficient, energy of activation [Ea], frequency factor [A],enthalpy of activation[$\Delta H^{\#}$] ,entropy of activation [$\Delta S^{\#}$],free energy of activation[$\Delta G^{\#}$].

Chart 38

Effect of temperature on rate of reaction

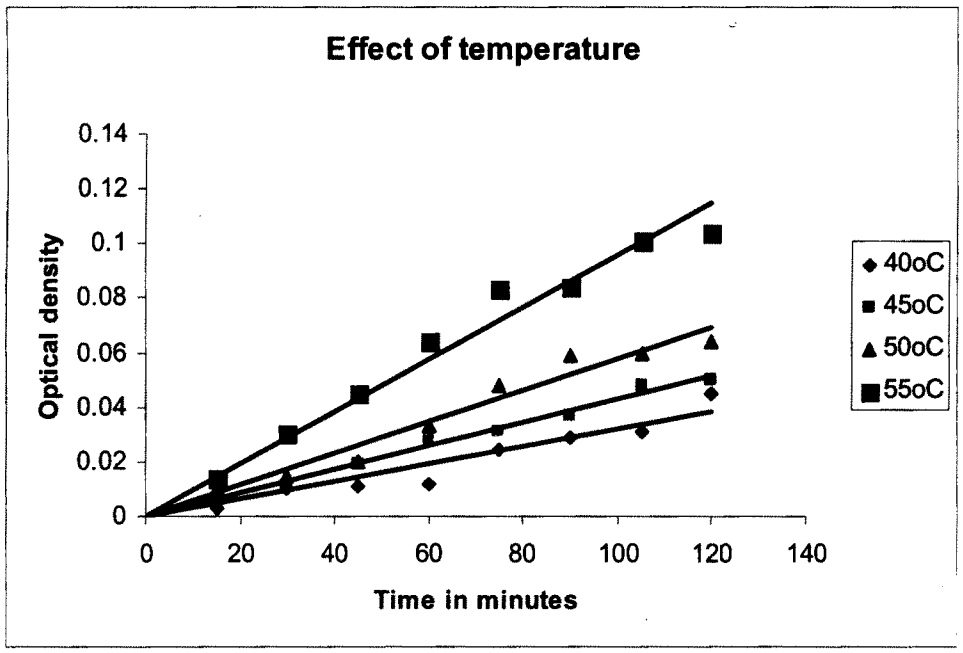
Substrate	4-Chlorobenzyl alcohol 20.2 mg
Oxidant concentration	140 mg
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table

No.	Time in minutes	Optical density			
		40°C	45°C	50°C	55°C
1	15	0.003	0.006	0.010	0.014
2	30	0.010	0.011	0.015	0.030
3	45	0.011	0.019	0.020	0.045
4	60	0.012	0.028	0.033	0.064
5	75	0.024	0.031	0.048	0.083
6	90	0.029	0.037	0.059	0.084
7	105	0.031	0.048	0.060	0.101
8	120	0.045	0.040	0.064	0.104

Chart 38[A]

Effect of temperature on rate of reaction



No.	Temperature °C	k x10^{-4} min^{-1}
1	40	3.33
2	45	4.11
3	50	5.76
4	55	9.41

Chart 39

Effect of temperature on rate of reaction

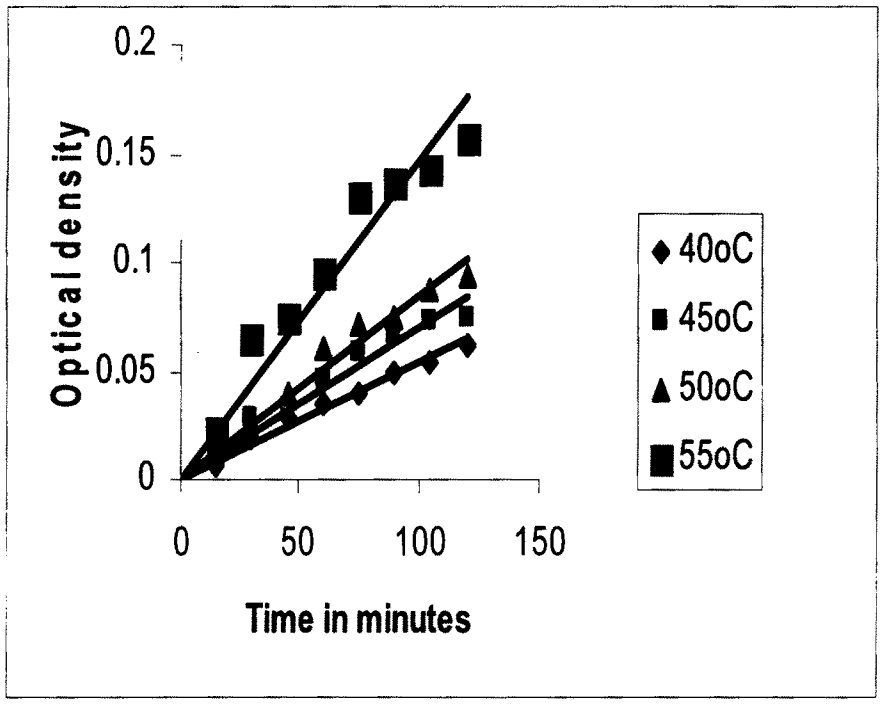
Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant Concentration	140 mg
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density			
		40°C	45°C	50°C	55°C
1	15	0.007	0.012	0.013	0.023
2	30	0.019	0.028	0.023	0.065
3	45	0.029	0.033	0.040	0.074
4	60	0.035	0.046	0.061	0.096
5	75	0.040	0.058	0.072	0.130
6	90	0.049	0.066	0.074	0.136
7	105	0.054	0.073	0.087	0.143
8	120	0.062	0.074	0.093	0.157

Chart 39[A]

Effect of temperature on rate of reaction



No.	Temperature °C	k x$10^{-4}$$min^{-1}$
1	40	5.31
2	45	7.61
3	50	8.50
4	55	15.0

Chart 40

Effect of temperature on rate of reaction

Substrate 4-Methoxybenzyl alcohol 18.2×10^{-3} ml

Oxidant Concentration 1:4Dioxane, 5 ml

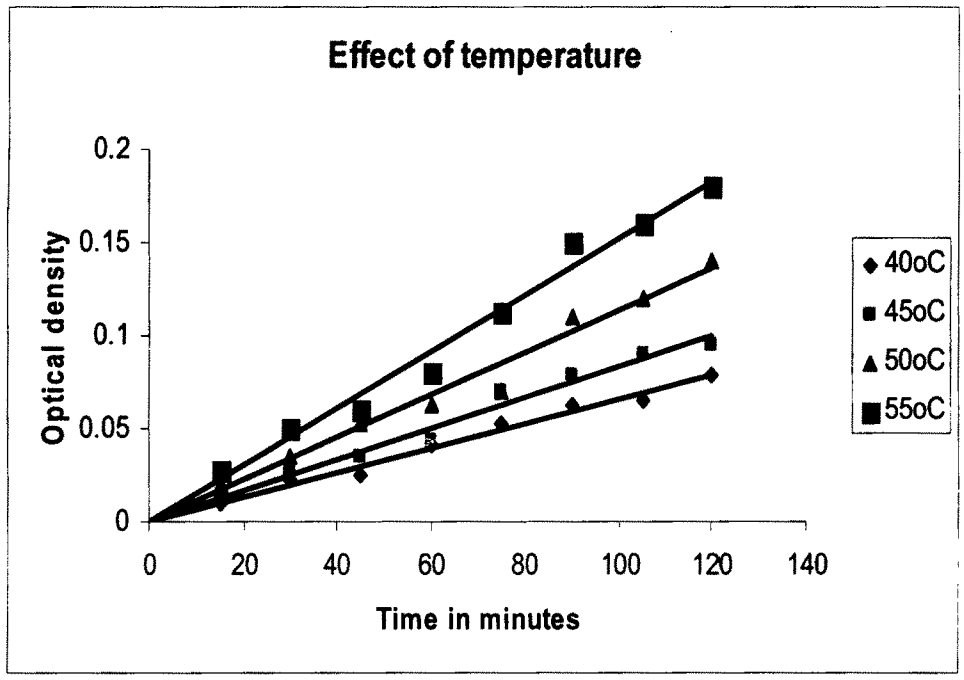
λmax 248 nm

Observation Table:

No.	Time in minutes	Optical Density			
		40°C	45°C	50°C	55°C
1	15	0.010	0.012	0.020	0.028
2	30	0.022	0.026	0.035	0.050
3	45	0.025	0.035	0.052	0.060
4	60	0.041	0.044	0.062	0.080
5	75	0.053	0.070	0.070	0.112
6	90	0.063	0.079	0.110	0.150
7	105	0.065	0.090	0.120	0.160
8	120	0.079	0.095	0.140	0.180

Chart 40[A]

Effect of temperature on rate of reaction



No.	Temperature°C	k x10^{-4} min^{-1}
1	40	6.55
2	45	8.63
3	50	11.50
4	55	15.45

Temperature coefficient:

The reaction of zero order rate constants for rise in temperature by 10°C are calculated in two pairs of temperature. The mean values of temperature coefficients of reactions are as follows.

Table 5

Temperature coefficient

No.	Alcohols	Temperature coefficient
1	4-Chlorobenzyl alcohol	2.00
2	Benzyl alcohol	1.78
3	4-Methoxybenzyl alcohol	1.77

Energy of activation [Ea]:

Applicability of Arrhenius equation,

$$\ln k = \ln A - Ea/RT$$

In present work it was verified by plotting log k against 1/T.The plots for various alcohols are depicted as,

Alcohols	Charts
4-Chlorobenzyl alcohol	41
Benzyl alcohol	42
4-Methoxybenzyl alcohol	43

The value of energy of activation were determined from the slopes of the plots using the relation,

$$Ea = \text{Slope} \times 2.303\ R$$

The plots were linear with negative slope, indicating that the reaction under investigation obey Arrhenius law throughout the temperature range that was used.

The graphical values of energy of activation are in Table 6

Table 6

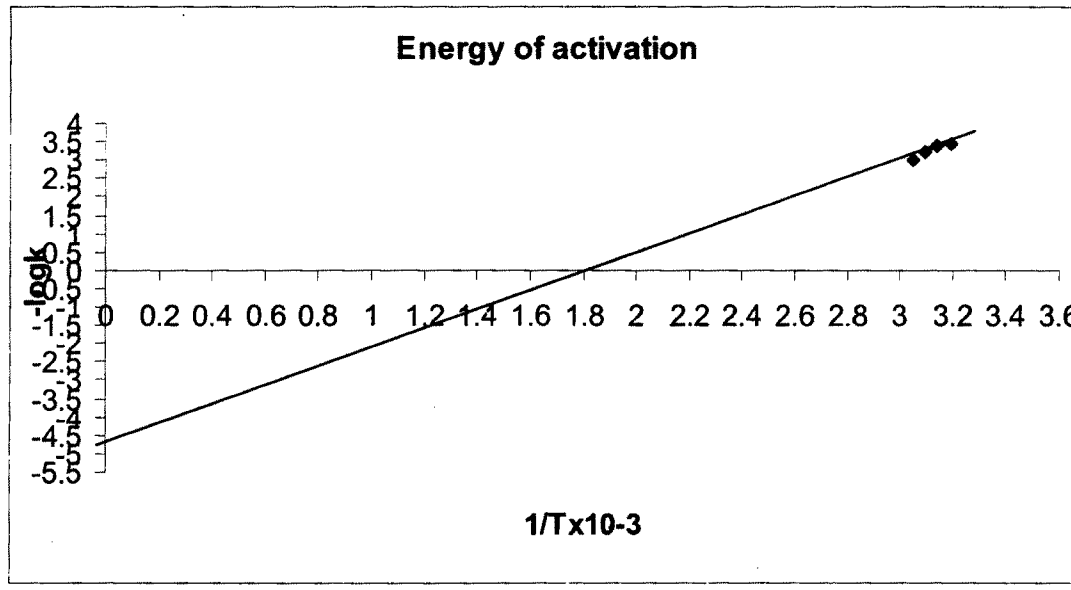
Energy of activation

No.	Alcohols	Energy of activation Kcal
1	4-Chlorobenzyl alcohol	12.07
2	Benzyl alcohol	12.04
3	4-Methoxybenzyl alcohol	11.04

Chart 41

Energy of activation of 4-Chlorobenzyl alcohol

$1/T \times 10^{-3}$	-log k
3.1948	3.4775
3.1444	3.3861
3.0959	3.2395
3.0487	3.0263

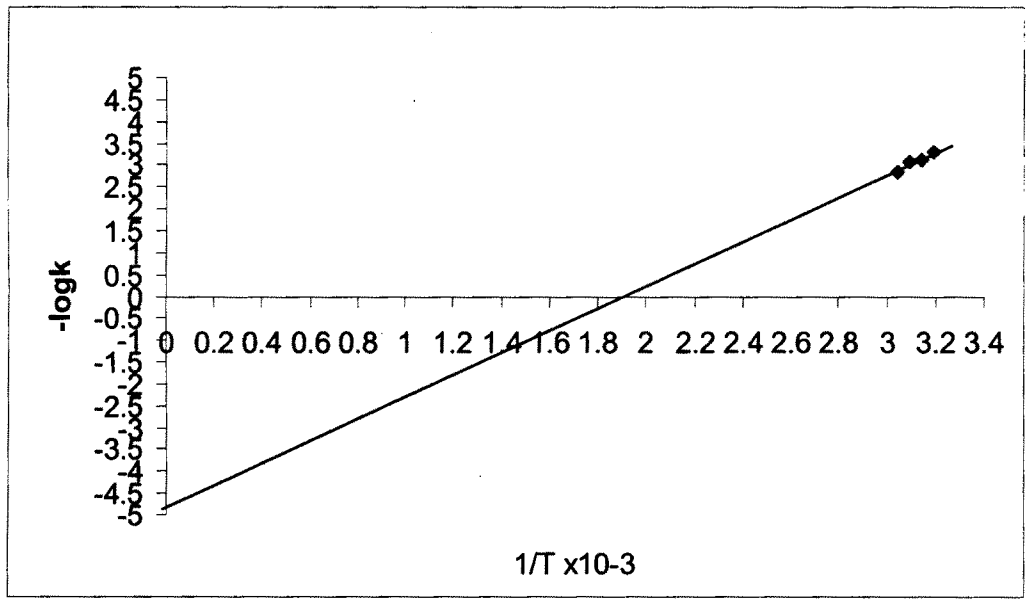


Energy of activation (Ea): 12.07 Kcal

Chart 42

Energy of activation of Benzyl alcohol

$1/Tx10^{-3}$	-log k
3.1948	3.2749
3.1186	3.1186
3.0959	3.0705
3.0487	2.8239

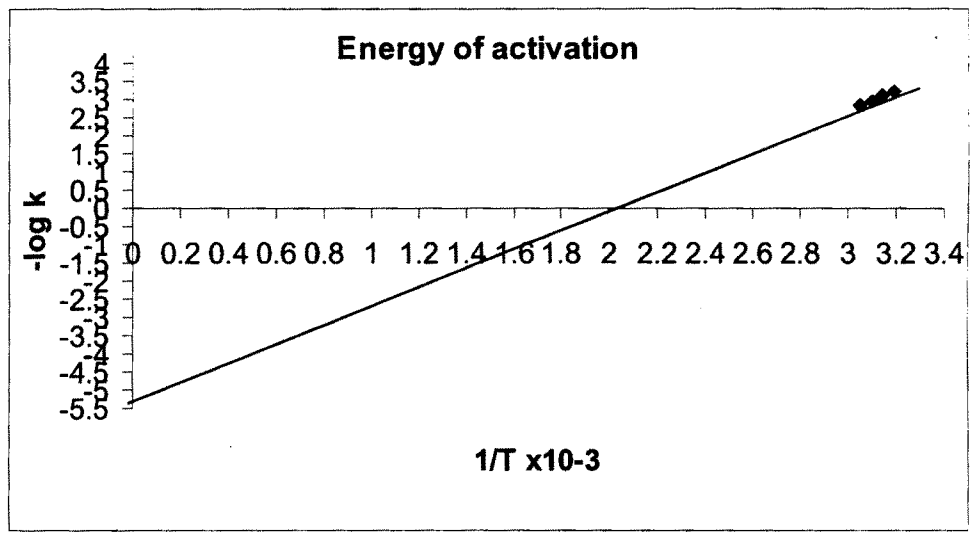


Energy of activation (Ea) : 12.04 Kcal

Chart 43

Energy of activation of 4-Methoxybenzyl alcohol:

$1/T \times 10^{-3}$	-log k
3.1948	3.1837
3.144	3.0639
3.0959	2.9393
3.0487	2.8110



Energy of activation (Ea) = 11.44 Kcal

Frequency factor:

The frequency factor of the reaction was determined by Arrhenius law which predicts that, the intercept of log k against 1/T plot on y axis gives the value of log A .The intercept was evaluated and hence value of A was deduced. The value of frequency factor are depicted in Table 7

Table 7

Frequency factor:

No	Alcohols	Frequency factor x 10^4
1	4-Chlorobenzyl alcohol	5.01
2	Benzyl alcohol	8.91
3	4-Methoxybenzyl alcohol	11.22

Enthalpy of activation:

The standard Eyring equation,

$$k_r = (KT/h)\, e^{\Delta S\#/R}\, e^{-\Delta H\#/RT}$$

can be written as,

$$\log[k/(KT/h)] = \Delta S^{\#}/2.303\ R - \Delta H^{\#}/2.303RT$$

log[k/(KT/h)] plotted against 1/T,when linear plots were obtained.These plots are represented in charts,

Alcohols	Charts
4-Chlorobenzyl alcohol	44
Benzyl alcohol	45
4-Methoxybenzyl alcohol	46

The enthalpy change for the formation of an activated complex has been calculated from the values of the slope using the relation,

$$\Delta H^{\#} = \text{Slope} \times 2.303\ R$$

The values of enthalpy of activation are compiled in Table 8

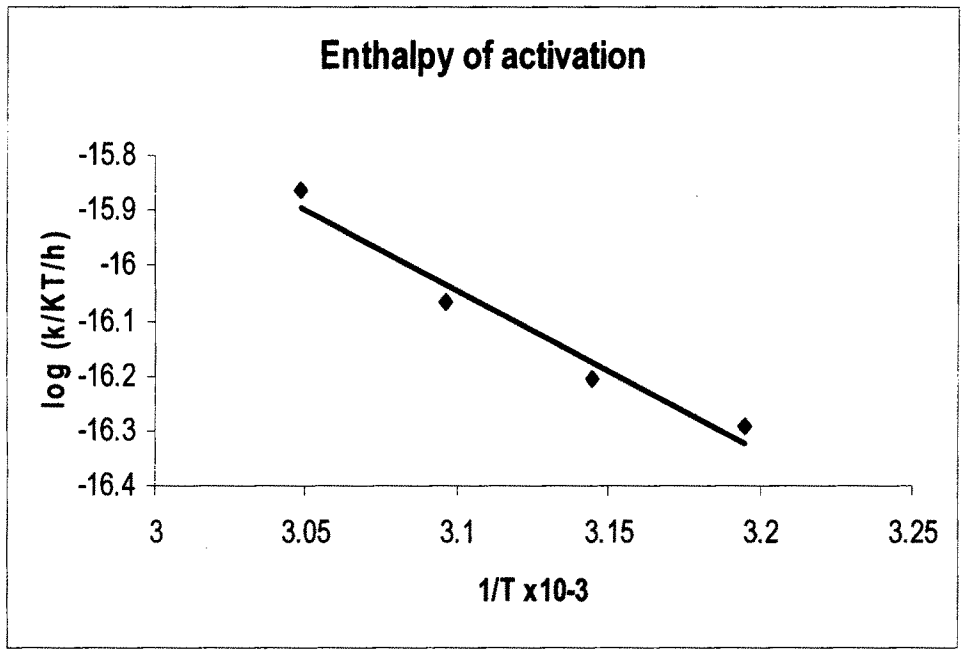
Table 8 Enthalpy of activation

No.	Alcohols	$\Delta H^{\#}$ Kcal mol^{-1}
1	4-Chlorobenzyl alcohol	16.85
2	Benzyl alcohol	13.55
3	4-Methoxybenzyl alcohol	11.44

Chart 44

Enthalpy of activation of 4-Chlorobenzyl alcohol ($\Delta H^{\#}$)

$1/T \times 10^{-3}$	log (k/KT/h)
3.1948	-16.2919
3.1444	-16.2074
3.0959	-16.0676
3.0487	-15.8610

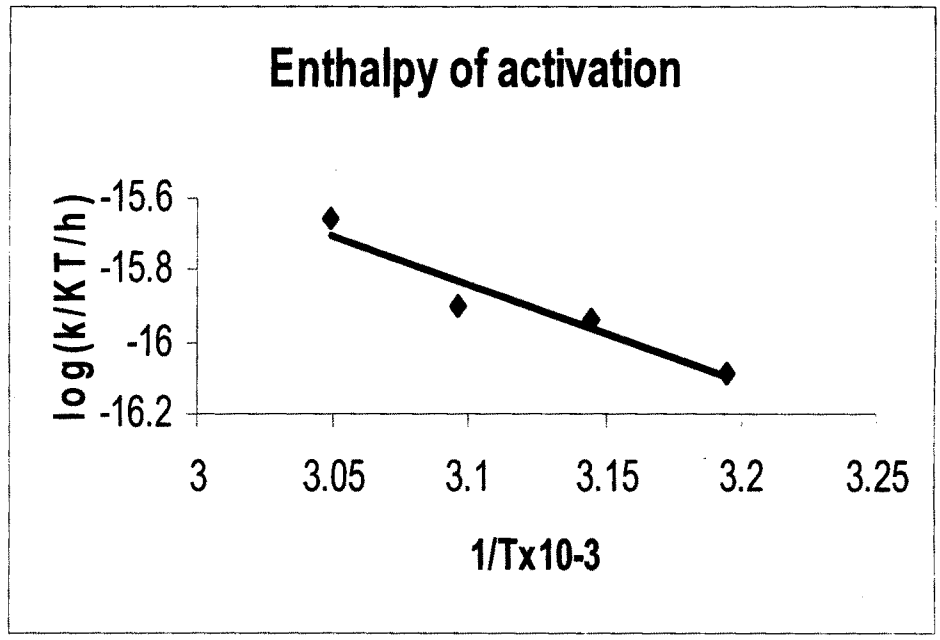


Enthalpy of activation ($\Delta H^{\#}$) = 16.85 Kcal mol^{-1}

Chart 45

Enthalpy of activation of Benzyl alcohol

$1/T \times 10^{-3}$	log (k/KT/h)
3.1948	-16.0892
3.1444	-15.9398
3.0959	-15.8986
3.0487	-15.6586

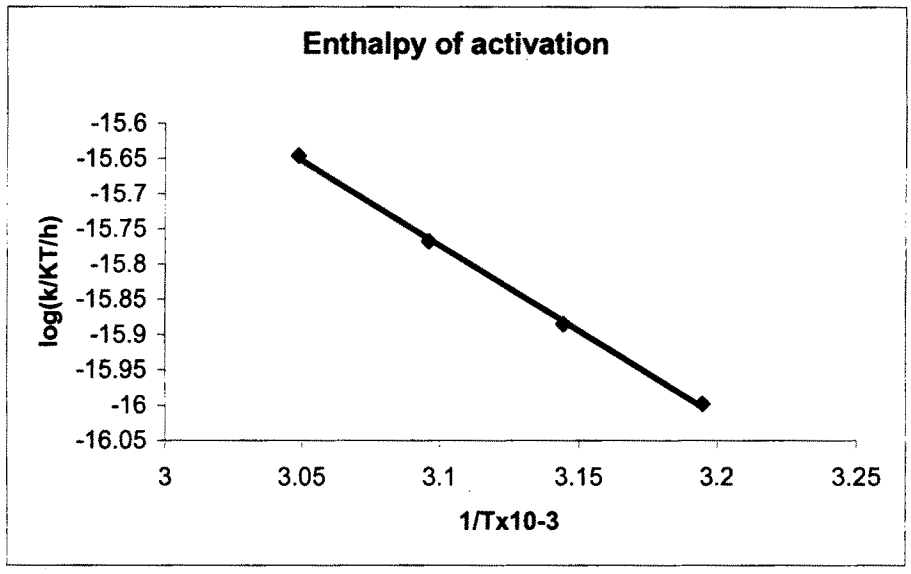


Enthalpy of activation ($\Delta H^{\#}$) =13.55 Kcal mol^{-1}

Chart 46

Enthalpy of activation of 4-Methoxybenzyl alcohol:

$1/T \times 10^{-3}$	log (k/KT/h)
3.1948	-15.9981
3.144	-15.8852
3.0959	-15.7673
3.0487	-15.6457



Enthalpy of activation= $\Delta H^{\#} = 11.44$ Kcal mol^{-1}

Entropy of activation ($\Delta S^{\#}$):

The value of $\Delta H^{\#}$ obtained by graphical method is used to calculate entropy of activation at each temperature by applying the equation.

$$\log [k/(KT/h)] = \Delta S^{\#}/2.303 - \Delta H^{\#}/2.303\ RT$$

The mean values of $\Delta S^{\#}$ are compiled in Table 9

Table 9

Entropy of activation

No	Alcohols	$\Delta S^{\#}$ e.u.
1	4-Chlorobenzyl alcohol	-21.04
2	Benzyl alcohol	-30.42
3	4-Methoxybenzyl alcohol	-36.71

Free energy of activation ($\Delta G^{\#}$):

The free energy of activation ($\Delta G^{\#}$) is related to rate constant k of the reaction by equation.

$$k_r = (KT/h)\ e^{-\Delta G\#/RT}$$

This can be rearranged to get the expression.

$$\log k = \log (KT/h) - \Delta G^{\#}/2.303\ RT$$

The free energy of activation is calculated at each temperature using the above equation and mean value is determined. These results were confirmed by verification of equation.

$$\Delta G^{\#} = \Delta H^{\#} - T\Delta S^{\#}$$

Where $\Delta H^{\#}$ = Enthalpy of activation

$\Delta S^{\#}$ = Entropy of activation

The values of free energy of activation for alcohols under study are compiled in Table 10

Table 10

Free energy of activation

No	Alcohols	$\Delta G^{\#}$ Kcal.mol^{-1}
1	4-Chlorobenzyl alcohol	23.61
2	Benzyl alcohol	23.20
3	4-Methoxybenzyl alcohol	22.91

F] Effect of % of cross linking on the rate of reaction:

All those reactions which are catalysed homogeneously by acid or base, have been carried out in presence of cationic or anionic ion exchange resins. The structural factors of resin such as effect of pore size, solvent, crosslink density, adsorption, and diffusion and distribution phenomenone are found to vary from resin to resin. While studying the effect of % of crosslinking on rate of reaction, a variation in rate of reaction was observed[1-5].

The effect of % of cross linking in the polymeric resin [oxidant] was studied between 4%, 6%, and 6.5%(cross linked with DVB).It was found that zero order rate constant increases as the % of cross linking in polymeric resin

decreases. This is complied in Table 11. Due to increased cross linked density, there is steric interference at the catalytic site.

The kinetic data and plots of optical density versus time are represented in following charts

Alcohols	Charts
4-Chlorobenzyl alcohol	47, 47[A]
Benzyl alcohol	48, 48[A]
4-Methoxybenzyl alcohol	49, 49[A]

Table 11

Effect of % of crosslinking on rate of reaction

Alcohols	$k \times 10^{-4}$ min^{-1}		
	4%	6%	6.5%
4-Chlorobenzyl alcohol	5.00	4.11	3.84
Benzyl alcohol	9.00	7.61	4.09
4-Methoxybenzyl alcohol	11.00	8.63	5.41

Chart 47

Effect of change in % of crosslinking on rate of reaction

Substrate 4-Chlorobenzyl alcohol 20.2 mg

Oxidant concentration 140 mg

Temperature 45°C

Solvent 1:4Dioxane, 5 ml

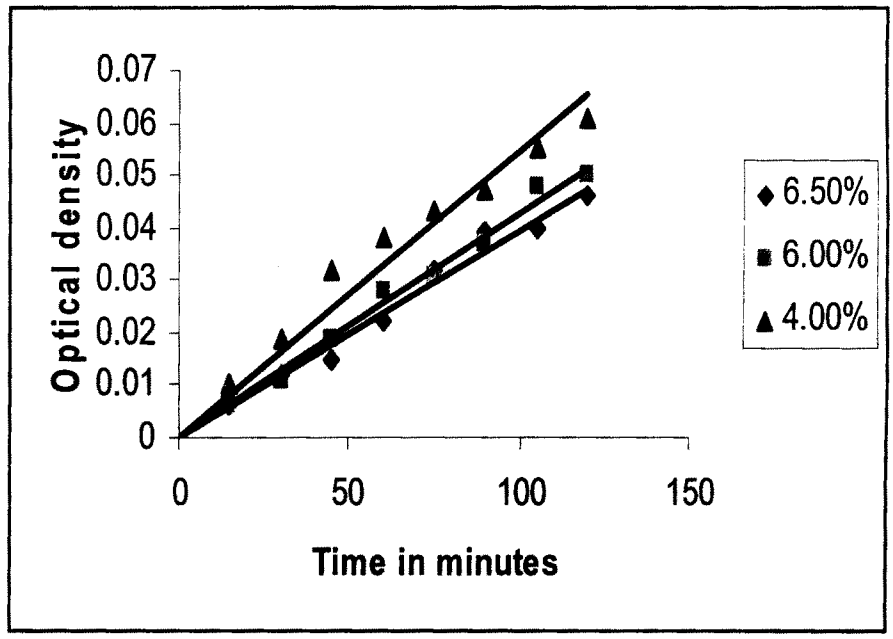
λmax 248 nm

Observation Table:

No.	Time in minutes	Optical density		
		4%	6%	6.5%
1	15	0.010	0.006	0.006
2	30	0.019	0.011	0.012
3	45	0.032	0.019	0.015
4	60	0.038	0.028	0.022
5	75	0.043	0.031	0.032
6	90	0.047	0.037	0.039
7	105	0.055	0.048	0.040
8	120	0.061	0.050	0.046

Chart 47[A]

Effect of change in % of crosslinking on rate of reaction



N0.	% of crosslinking	k x10^{-4} min^{-1}
1	4	5.00
2	6	4.11
3	6.5	3.84

Chart 48

Effect of change in % of crosslinking on rate of reaction

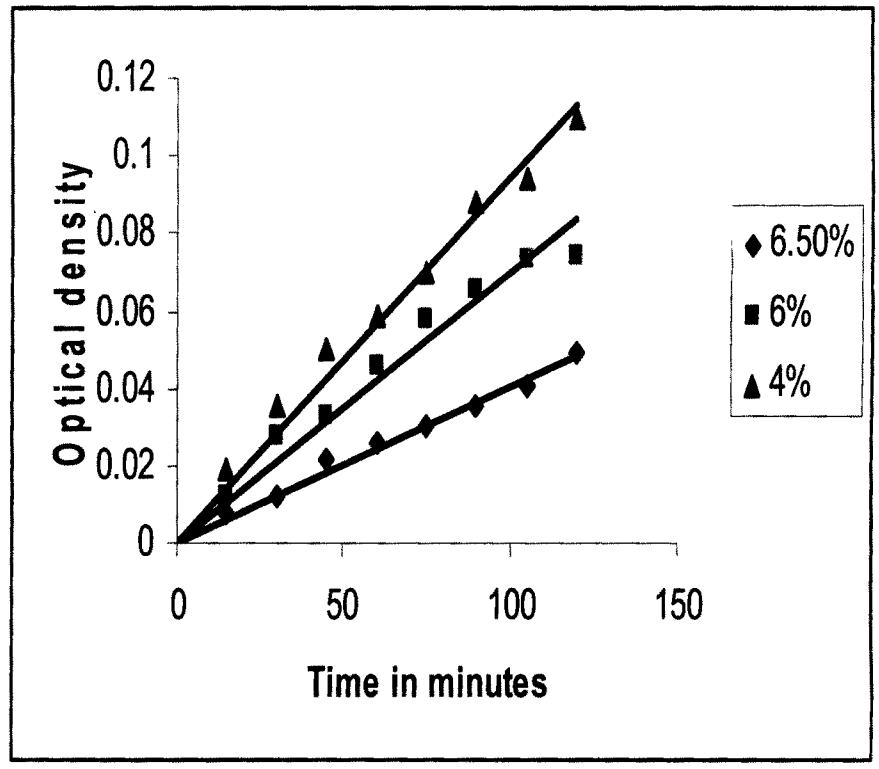
Substrate	Benzyl alcohol 15 $x10^{-3}$ ml
Oxidant Concentration	140 mg
Temperature	45°C
Solvent	1:4Dioxane, 5 ml
λmax	248 nm

Observation Table:

No.	Time in minutes	Optical density		
		4%	6%	6.5%
1	15	0.019	0.012	0.008
2	30	0.035	0.028	0.012
3	45	0.050	0.033	0.022
4	60	0.059	0.046	0.026
5	75	0.070	0.058	0.030
6	90	0.088	0.066	0.035
7	105	0.094	0.073	0.041
8	120	0.110	0.047	0.049

Chart 48[A]

Effect of change in % of crosslinking on rate of reaction



NO.	% of cross linking	k $x10^{-4}$ min^{-1}
1	4	9.00
2	6	7.61
3	6.5	4.09

Chart 49

Effect of change in % of cross linking on the rate of reaction

Substrate 4-Methoxybenzyl alcohol $18.2x10^{-3}$ ml

Oxidant concentration 140 mg

Temperature 45°C

Solvent 1:4 Dioxane, 5 ml

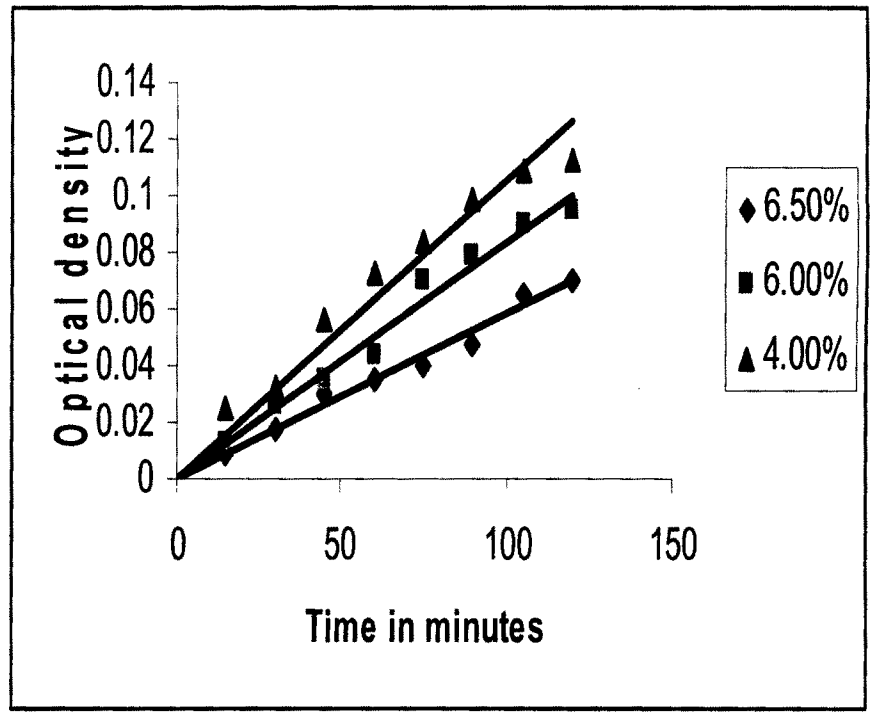
λmax 273 nm

Observation Table:

No.	Time in minutes	Optical density		
		4%	6%	6.5%
1	15	0.025	0.12	0.009
2	30	0.033	0.026	0.018
3	45	0.060	0.035	0.030
4	60	0.072	0.044	0.035
5	75	0.084	0.070	0.040
6	90	0.099	0.079	0.048
7	105	0.109	0.090	0.065
8	120	0.0112	0.095	0.070

Chart 49[A]

Effect of change in % of cross linking on the rate of reaction



No.	% of cross linking	k x10^{-4} min^{-1}
1	4	11.0
2	6	8.63
3	6.5	5.41

References

1. R.W.Fumer,*J.Org.Chem.*,**27**(1962)4115.
2. V.J.Frilette,E.B.Mower,M.K.Rubin,*J.Catalysis*,**3**(1964)25.
3. M.B.Bochner,S.M.Greber,W.R.Vieth, A.J.Rodger,*Ind.Eng.Chem.* Fund., **4**(1965)314.
4. H.M.Heath,Jr,B.C.Gates.A.I.*Chem.Eng.J.*,**18**(1972)32.
5. E.R.Gillard,H.J.Bixler,J.O.Connell,*Ind.Eng.Chem.Fund.*,**10**(1971)185.