KINETICS OF OXIDATION OF MALEIC MONO ANILIDE BY N-CHLORO-3-METHYL-2,6-DIPHENYL PIPERIDINE-4-ONE IN ACID MEDIUM

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In the present investigation the kinetics of oxidation of maleic mono anilide by N-chloro-3- methyl-2-6 diphenyl piperidin-4 – one has been carried out in the solvent 70% ethanol-water mixture under acidic condition. The N-chloro-3- methyl-2-6 diphenyl piperidin-4 – one cannot be used as an oxidant since it is unstable in basic medium. The kinetic study was carried out under pseudo first order conditions that is keeping the concentration of substrate maleic mono anilide in excess over the concentration of oxidant, N-chloro-3-methyl-2-6 diphenyl piperidin-4 – one .The progress of the reaction was followed by estimating the unreacted N-chloro-3- methyl-2-6 diphenyl piperidin-4 – one by iodometric method. The acidic medium is maintained by hydrochloric acid.

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1. Introduction

The kinetics of oxidation of various substrates by N-halo compounds has gained importance for the past few decades. Of the many N-halo compounds [1-4], chloramines –T [5], N-Bromosuccinimide [6-9] (NBS), N-Chloro Benz amide [10] (NCB), N-chloro saccharin[11], N-bromo acetamide[12] (NBA) and N-chloro benzotriazol [13] are a few notable oxidants. The kinetics of oxidation of various organic substrates such as primary and secondary alcohols [14, 15], α -hydroxyl acids [16], dim ethyl NCPulphoxide [17] and phenyl methyl sulphoxide by chloramines – T has been studied by several workers. Recently a new oxidant, namely N-chloro-3-methlyl-2-6-diphenyl piperidin-4- one (NCP) has been reported by Ganapathy & Vijayan [18] . Though NCP resembles other N-halo compounds in properties, it has some merits over the others. NCP is a mild oxidizing and Chlorinating agent, and liberates iodine instantaneously and quantitatively from an acidified iodide ions. So NCP can be employed as a good agent to standardize thio sulphate solution. NCP oxidation continues to be the topic of great interest for organic chemists as evidenced by the development of new techniques and procedures reported in current literature. The NCP cannot be used as an oxidant, since it is unstable in basic medium. The behaviour of N-chloro piperidones in basic medium was studied by Vijayan & Krishnamurthy [19]. In basic medium it undergoes substitution reaction or elimination reaction followed by rearrangement. The N-chloro piperidones yielded many new compounds on reaction with base, of which N-hydroxy piperidone is one and it has been characterized by spectroscopic studies. Various substrates were employed to study the kinetics of oxidation using NCP. In this present investigation the kinetics of oxidation of maleic mono anilide (MMA) by NCP has been carried out.

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2. Experimental methods

Preparation of N-Chloro-3 methyl-2, 6-diphenyl piperidin-4 – one: (NCP)

N – Chloro – 3 – methyl –2, 6-diphenyl piperidin-4 – one was prepared by chlorination of 3 – methyl-2, 6-diphenyl piperidin-4 – one

Preparation of 3 –methyl –2, 6-diphenyl piperidin-4 – one:

The procedure adopted was that of Noller and Baliah [20]. A solution of dry ammonium acetate (20g) in alcohol (50 ml) was mixed with benzaldehyde (50 ml) and 2-butanone (20ml). The mixture was just heated to boil and allowed to stand at room temperature overnight. Then the reaction mixture was treated with concentrated hydrochloric acid (30ml). The precipitated hydrochloride was washed with ethanol-water mixture. It was recrystallised from aqueous ethanol and it melted at 224 – 225^{o}C.

Preparation of N-chloro-3- methyl-2-6 diphenyl piperidin-4 – one (NCP):

The piperidine hydrochloride was dissolved in 60-70% ethanol water mixture by warming. Free chlorine gas was passed through it for about half an hour. Chlorine gas was prepared by adding potassium permanganate to concentrated hydrochloric acid. Excess of water was added liberally to precipitate the chlorinated compound and the precipitate was filtered and washed well with water. After repeated recrystallisation from ethanol, the compound melted at 149-150^{o}C.

2.1. Kinetics of oxidation

NCP- (N-Chloro-3 methy-2, 6-diphenylpiperidin-4 – one) was purified by crystallization to constant melting point (m.p.150^{0}C) and dried in vacuum before use. The rectified spirit was refluxed with sulphuric acid and distilled. The alcohol was then refluxed over silver nitrate and potassium hydroxide and fractionated through a dufton column. All other chemicals used were of AR grade. Doubly distilled water was used throughout the kinetic measurements.

2.2. Kinetic Procedure

The rate of the reaction was followed iodometrically. All measurements were made at 25^{0} C. The reaction medium was ethanol-water (70% v/v) mixture. The reaction was initiated by adding known volume of NCP solution. Aliquots were withdrawn from the reaction mixture at various intervals of time and added to excess of potassium iodide solution. The liberated iodine was titrated against standardized sodium Thiosulphate solution using starch as an indicator. Thiosulphate solution was standardized using NCP. NCP has been used as a primary standard oxidant, since it is a stable crystalline solid and it liberates iodine almost instantaneously from acidified iodide ions. The pseudo first order rate constants were computed from the slope of the plot of log (a-x) versus time. The rate of the reaction at various concentrations of oxidant, maleic methyl anilide (MMA) and acid.

3. Results and discussion

After the discovery of N – chloro –3 – methyl – 2, 6 – diphenylpiperidin – 4 – one (NCP) by Vijayan and Ganapathy [18], several chemists [21] studied the behaviour of the above compound by carrying out the kinetic investigations using it as an oxidant. NCP has been used as an oxidant in the kinetic and mechanistic study of oxidation of allyl alcohol[18],cyclohexanoneoxime[33],tetrahydrothiopyranone[18], anilines[22], phenols[23], hydroxylamine[24], sodium bi sulphite [25],dimethyl sulphoxide, etc..In the present study, the kinetics of oxidation of maleic mono anilide (MMA) by NCP was carried out in the solvent 70% ethanol – water mixture under acidic condition. The kinetic study was carried out under pseudo first order conditions that is keeping the concentration of substrate (MMA) in excess over the concentration of oxidant, NCP.The progress of the reaction was followed by estimating the unreacted NCP by iodometric method. The acidic medium is maintained by hydrochloric acid.

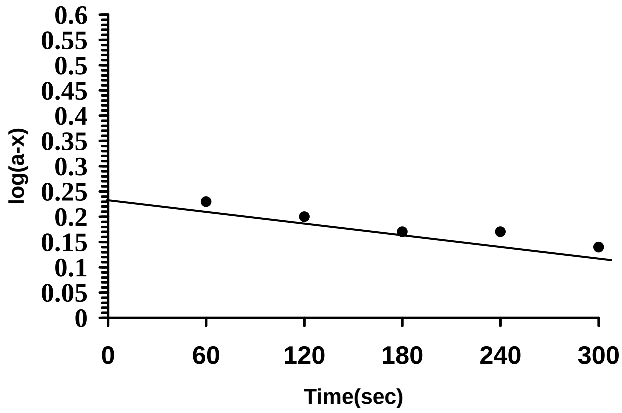
3.1. Kinetic data. Effect of varying [NCP]

Table.1.Effect of Varying Concentration of NCP (0.000625M)

[NCP]	= 0.000625M	[MMA]	= 0.01M
SOLVENT	= 75% Ethanol – water	TEMPERATURE	= 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	2.6	1.58×10^{-3}
2.	120	2.5	1.05×10^{-3}
3.	180	2.4	1.14×10^{-3}
4.	240	2.3	1.03×10^{-3}
5.	300	2.2	1.13×10^{-3}

r = 0.25, Calculated Value $k_1 = 1.21 \times 10^{-3}$, k_1 from graph = 1.25×10^{-3}



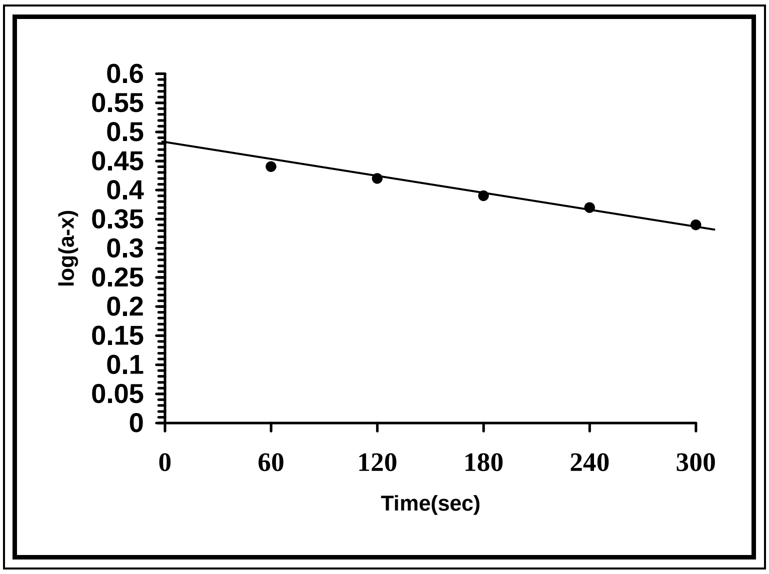
Plot .1. Time Vs log (a-x) [concentration of NCP 0.000625M]

Table.2. Effect of Varying Concentration of NCP (0.00125M)

[NCP]	= 0.00125M	[MMA]	= 0.01M
SOLVENT	=75% Ethanol – water	TEMPERATURE	= 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	2.6	1.58×10^{-3}
2.	120	2.5	1.05×10^{-3}
3.	180	2.4	1.14×10^{-3}
4.	240	2.3	1.03×10^{-3}
5.	300	2.2	1.13×10^{-3}

r = 0.47, Calculated Value $k_1 = 1.18 \times 10^{-3}$, k_1 from graph = 1.11×10^{-3}



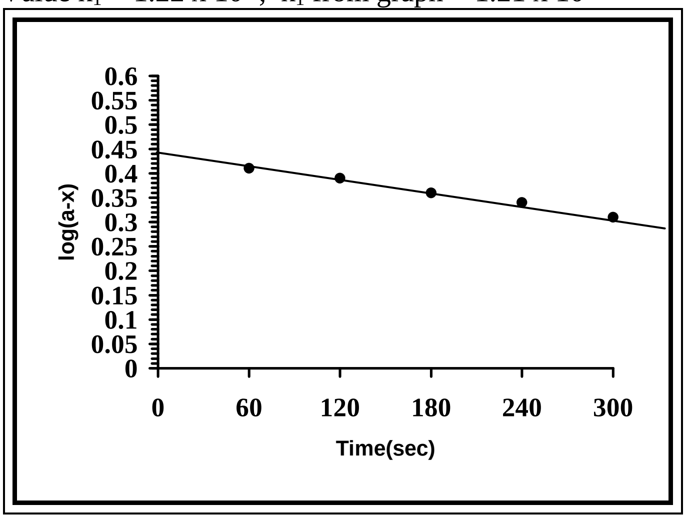
Plot.2. Time Vs log (a-x) [concentration of NCP 0.00125M]

Table.3. Effect of varying concentration of NCP (0.001875M)

[NCP] = 0.001875M [MMA] = 0.01M
SOLVENT = 75% Ethanol – water TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	2.5	$1.58x10^{-3}$
2.	120	2.4	$1.13x10^{-3}$
3.	180	2.2	$1.23x10^{-3}$
4.	240	2.1	$1.12x10^{-3}$
5	300	2.0	$1.06x10^{-3}$

r = 0.44, Calculated Value $k_1 = 1.22 \times 10^{-3}$, k_1 from graph = 1.21×10^{-3}



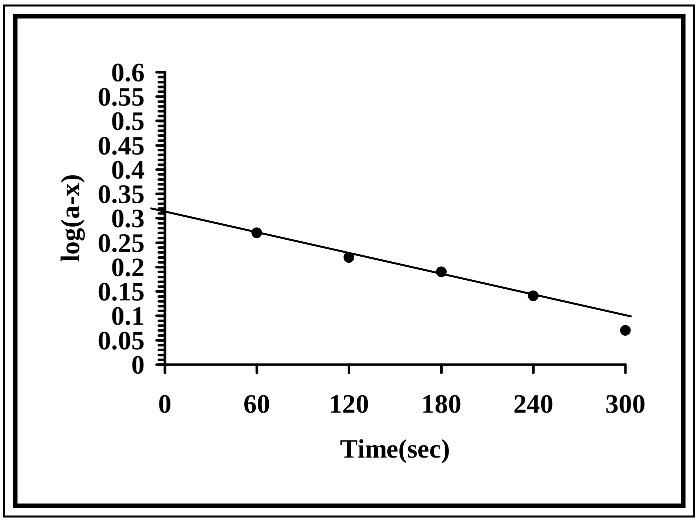
Plot.3. Time Vs log (a-x) [concentration of NCP 0.001875M]

Table.4. Effect of varying concentration of NCP (0.0025M)

[NCP] = 0.0025M [MMA] = 0.01M
SOLVENT = 75% Ethanol – water TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.8	$1.32x10^{-3}$
2.	120	1.6	$1.64x10^{-3}$
3.	180	1.5	$1.09x10^{-3}$
4.	240	1.4	$1.01x10^{-3}$
5.	300	1.2	$1.15x10^{-3}$

r = 0.31 Calculated Value $k_1 = 1.24 \times 10^{-3}$ k_1 from graph = 1.30×10^{-3}



Plot.4. Time Vs log (a-x) [concentration of NCP 0.0025M]

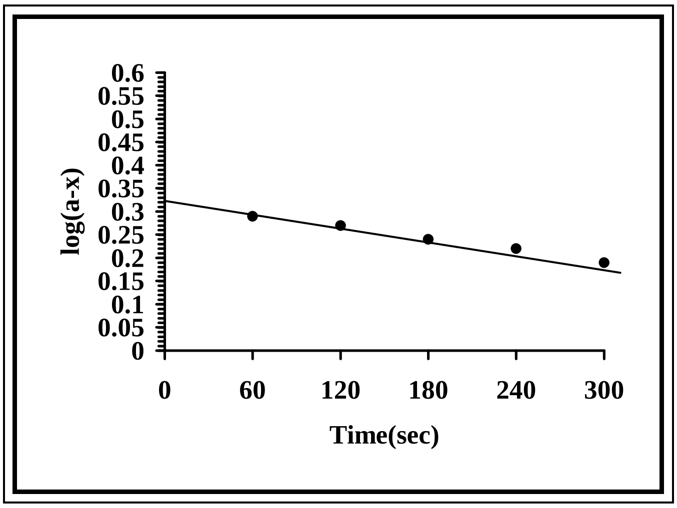
3.2. Effect of varying [MMA]

Table.5. Effect of Varying Concentration 0f MMA (0.01M)

[NCP] = 0.00125M [MMA] = 0.01M
[ACID] = 0.0005M SOLVENT = 75%
Ethanol – water TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.9	$1.50x10^{-3}$
2.	120	1.8	$1.20x10^{-3}$
3.	180	1.7	$1.12x10^{-3}$
4.	240	1.6	$1.09x10^{-3}$
5.	300	1.5	$1.08x10^{-3}$

r = 0.31, Calculated Value k_1 = 1.19 x 10^{-3} , k_1 from graph = 1.05x 10^{-3}



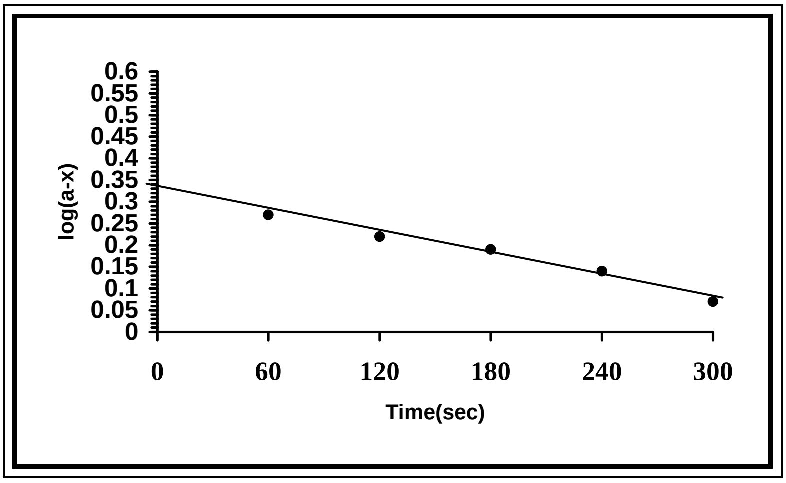
Plot.5. Time Vs log (a-x) [Concentration Of MMA 0.01M]

Table.6. Effect Of Varying Concentration Of MMA (0.015M)

[NCP] = 0.00125M [MMA] = 0.015M
[ACID] = 0.0005M SOLVENT = 75%
Ethanol – water TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.8	$1.32x10^{-3}$
2.	120	1.6	$1.64x10^{-3}$
3.	180	1.5	$1.09x10^{-3}$
4.	240	1.4	$1.01x10^{-3}$
5.	300	1.2	$1.14x10^{-3}$

r = 0.34 Calculated Value $k_1 = 1.24 \times 10^{-3}$, k_1 from graph = 1.21×10^{-3}



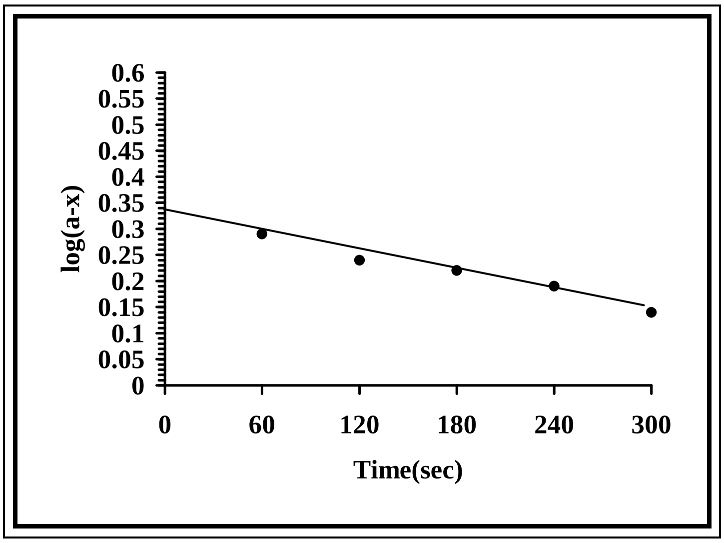
Plot.6 .Time Vs log (a-x) [concentration of MMA 0.015M]

Table.7. Effect of Varying Concentration of MMA (0.02M)

[NCP] = 0.00125M [MMA] = 0.02M
[ACID] = 0.0005M SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.9	$1.34x10^{-3}$
2.	120	1.7	$1.60x10^{-3}$
3.	180	1.6	$1.40x10^{-3}$
4.	240	1.5	$1.30x10^{-3}$
5.	300	1.4	$1.29x10^{-3}$

r = 0.34, Calculated Value k_1 = 1.38 x 10^{-3}, k_1 from graph = 1.30 x 10^{-3}



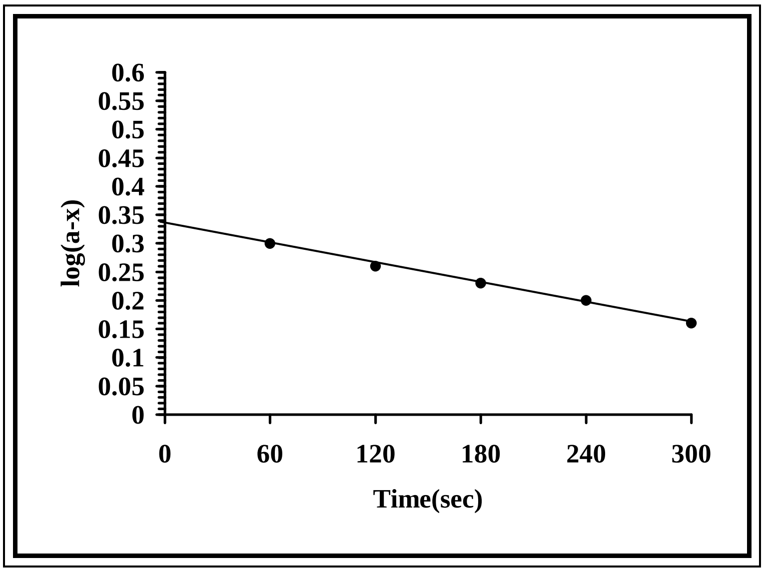
Plot.7. Time Vs log (a-x) [concentration of MMA 0.02M]

Table.8. Effect of Varying Concentration of MMA (0.025M)

[NCP] = 0.00125M [MMA] = 0.025M
[ACID] = 0.0005M SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.9	$1.90x10^{-3}$
2.	120	1.8	$1.40x10^{-3}$
3.	180	1.7	$1.25x10^{-3}$
4.	240	1.5	$1.46x10^{-3}$
5.	300	1.4	$1.29x10^{-3}$

r = 0.34 Calculated Value k_1 = 1.48 x 10^{-3}, k_1 from graph = 1.32 x 10^{-3}



Plot.8. Time Vs log (a-x) [concentration of MMA 0.025M]

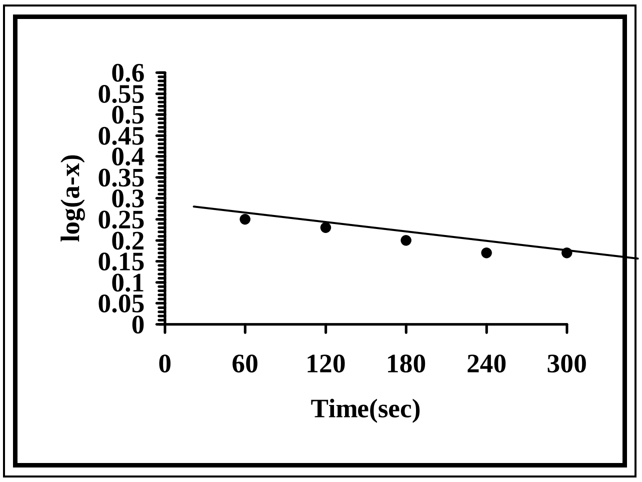
3.3. Effect of varying [ACID]

Table.9. Effect of Varying Concentration of Acid (0.0005M)

[NCP] = 0.00125M [MMA] = 0.01M
[ACID] = 0.0005M SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.8	$0.90x10^{-3}$
2.	120	1.7	$0.92x10^{-3}$
3.	180	1.6	$0.95x10^{-3}$
4.	240	1.5	$0.98x10^{-3}$
5.	300	1.5	$0.78x10^{-3}$

r = 0.27 Calculated Value k_1 = 0.91 x 10^{-3} , k_1 from graph = 0.95 x 10^{-3}



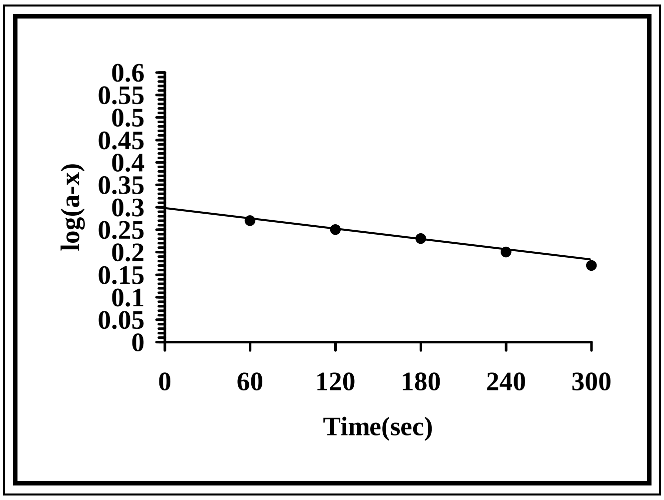
Plot.9. Time Vs log (a-x) [concentration of ACID 0.0005M]

Table.10. Effect of Varying Concentration of Acid (0.0010M)

[NCP] = 0.00125M [MMA] = 0.01M
[ACID] = 0.0010M SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.9	$1.18x10^{-3}$
2.	120	1.8	$1.04x10^{-3}$
3.	180	1.7	$1.01x10^{-3}$
4.	240	1.6	$1.02x10^{-3}$
5.	300	1.4	$1.18x10^{-3}$

r = 0.30 Calculated Value $k_1 = 1.08 \times 10^{-3}$, k_1 from graph = 1.07×10^{-3}



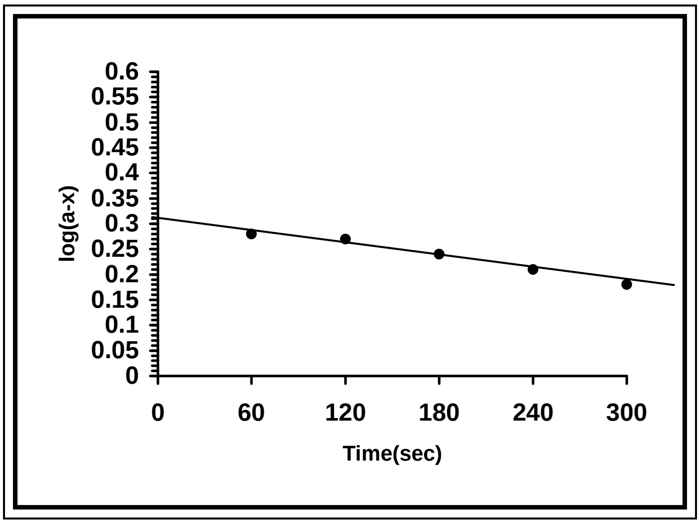
Plot.10. Time Vs log (a-x) [concentration of ACID 0.0010M]

Table.11. Effect of Varying Concentration of Acid (0.0015M)

[NCP] = 0.00125M [MMA] = 0.01M
[ACID] = 0.0015M SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.9	$1.18x10^{-3}$
2.	120	1.8	$1.04x10^{-3}$
3.	180	1.7	$1.01x10^{-3}$
4.	240	1.6	$1.01x10^{-3}$
5.	300	1.5	$1.02x10^{-3}$

r = 0.31 Calculated Value $k_1 = 1.05 \times 10^{-3}$, k_1 from graph = 1.10×10^{-3}



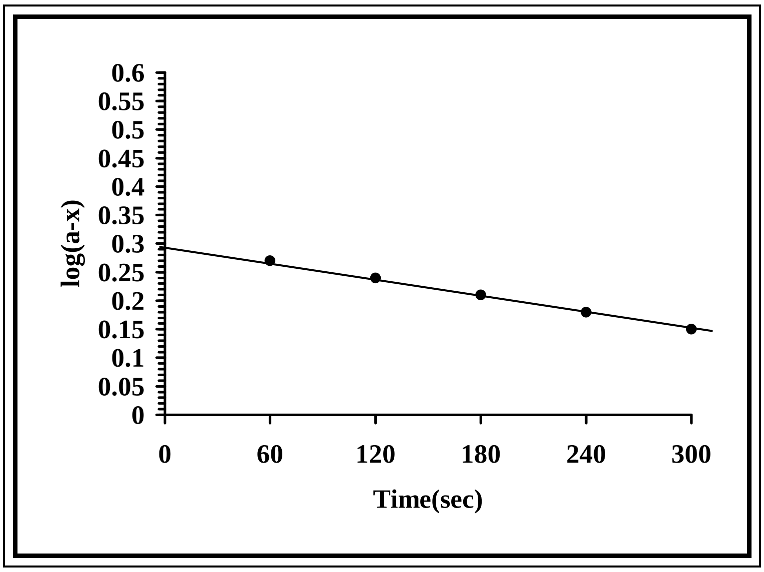
Plot.11.Time Vs Log (a-x) [Concentration of ACID 0.0015M]

Table.12. Effect of Varying Concentration of Acid (0.0020M)

[NCP] = 0.00125M
[ACID] = 0.0020M
[MMA] = 0.01M
SOLVENT = 75% Ethanol – water
TEMPERATURE = 25^0C

S.No	Time (Sec)	Volume of thio (ml)	Rate Constant (k_1) (sec^{-1})
1.	60	1.8	$1.67x10^{-3}$
2.	120	1.7	$1.31x10^{-3}$
3.	180	1.6	$1.21x10^{-3}$
4.	240	1.5	$1.17x10^{-3}$
5.	300	1.4	$1.17x10^{-3}$

r = 0.29, Calculated Value $k_1 = 1.30 \times 10^{-3}$, k_1 from graph = 1.23×10^{-3}



Plot.12. Time Vs log (a-x) [concentration of ACID 0.0020M]

3.4 Effect of varying concentration of NCP

The reaction was studied by varying the concentration of NCP keeping the concentrations of substrate, maleic mono anilide (MMA), acid and solvent constant.

Table .13. Variation of [NCP]

[MMA] = 0.01 M [ACID] = 0.0005M
SOLVENT = 75%Ethanol – water TEMPERATURE = 25^0C

S.No	Concentration of NCP (M)	Rate constant (k_1) (sec^{-1})
1	0.000625	$1.18x10^{-3}$
2	0.00125	$1.19x10^{-3}$
3	0.001875	$1.21x10^{-3}$
4	0.0025	$1.22x10^{-3}$

3.5 Effect of varying concentratiom of MMA

The pseudo first order rater constants were measured at different concentrations of [MMA]. The concentrations of NCP and acid were maintained at [0.0005M] and [0.01M] respectively.

Table. 14. Variation of [MMA]

[NCP] = 0.00125M [ACID] = 0.0005M
Solvent = 75% Ethanol and water Temperature = 25^{0}C

S.No	Concentration of substrate (M)	Rate constant (k_1) (sec^{-1})
1.	0.01	1.19x10^{-3}
2.	0.015	1.24x10^{-3}
3.	0.02	1.38x10^{-3}
4.	0.025	1.48x10^{-3}

3.6 Effect of varying concentration of acid

The rate constant was studied by varying the concentration of the acid at constant concentration of NCP, and MMA, solvent.

Table. 15. Variation Of [Acid]

SOLVENT = 75% Ethanol – water Temperature= 25^{0}C [NCP] = 0.00125 [MMA] = 0.01M

S.No	Concentration of Acid (M)	Rate constant (k_1) (sec^{-1})
1.	0.0005	9.11x10^{-4}
2.	0.0010	1.08x10^{-4}
3.	0.0015	1.05x10^{-4}
4.	0.0020	1.30x10^{-4}

4. Conclusions

In the present work, 3-methyl-2, 6-diphenyl piperidine -4-one, N-choloro-3-methyl-2, 6 diphenyl piperidin-4-one (NCP) and maleic mono anilide (MMA) were prepared. The kinetic study of oxidation of MMA by NCP in acid medium under pseudo first order conditions has been carried out. The reaction is total second order, first order with respect to oxidant and first order with respect to MMA. Acid is catalyzing the reaction; the increase in the concentration of acid increases the rate constant of the reaction but not linearly.

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