International Journal of Research in Engineering, Science and Management
Volume-2, Issue-5, May-2019
www.ijresm.com | ISSN (Online): 2581-5792

Kinetics of Oxidation of Methyl Salicylate by N-Chloro-3-Methyl-2, 6-Diphenyl Piperidin-4-One in Ethanol in Acid Medium

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***Abstract*: To study the "kinetics of oxidation of Methyl salicylate by N-chloro-3-methyl 2, 6-diphenyl piperidin-4-one'' in sulphuric acid medium. The influence of oxidant, acid, substrate, solvent &salt (NH_4Cl, NaCl, KCl, $ZnSO_4$) variation on the rate of the reaction has also been studied. The rate constant is calculated from the linear plot of log a/a-x Vs time. The order with respect to the oxidant, acid and substrate are found to be fractional.**

***Keywords*: Methyl salicylate, Halonium cation, NCMDP, Nucleophile.**

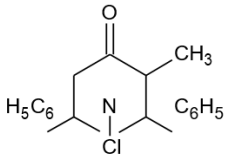
1. Introduction

Chemical kinetics deals with study of rates of chemical processes and with how the rate depends on factors such as concentration and temperature. Chemical kinetics also includes investigations of how different experimental conditions can influence the speed of a chemical reaction and yield information about the reaction mechanism and transition states, as well as the construction of mathematical models that can describe the characteristics of a chemical reaction. A kinetic study can disprove a mechanism but it cannot establish a mechanism with certainty.

A. Oxidation kinetics

Oxidation reactions are those which involve the loss of electrons and hence increase in oxidation number. Kinetics of oxidation of various compounds like alcohols, aldehydes, ketones and hydroxyl acids have been carried out extensively in solution phase using various oxidizing agents like Mn(III), Mn(VII), V(V), Cr (VI) and hydrogen peroxide. Apart from the above, the N-Halogen compounds have proved themselves as effective oxidants since they give different reactive species during oxidation.

The N-Halogen compound can act as a source of Halonium cation, Hypohalite ion and N- anion which act both as a base and a Nuleophile. N-Halo compounds can also be used for Halogenation and dehydrogenation studies. N-Halo compounds have been used as an oxidizing agents for the oxidation of aldehyde, ketone, hydroxyl acid. The structure of NCMDP is given as



2. Experimental work

The kinetics of oxidation of methyl salicylate by NCDMP in 75% ethanol water mixture in the presence of H_2SO_4 was studied iodo metrically at regular intervals of time. The preparation and purification of reagents used and the kinetic procedure that was adopted to follow the reaction are described in this section.The glass apparatus used for the experiments were well cleaned with a solution of chromic acid and rinsed thoroughly with doubly distilled water and dried in air oven.

A. Thermostat

A precision thermostat with an accuracy of ± 0.01^0C was used as a constant temperature bath to carry out all the kinetic variations. The thermostat was a cylindrical glass tank filled with distilled water which was stirred and heated electrically.

B. Preparation of 3 -methyl – 2,6 -diphenylpiperidine – 4- one

The procedure adopted was that of Noller and Baliah. They proposed that piperdione derivatives with substituents in the 1, 2, 3, 5 and 6 positions can be prepared by the Mannich condensation between aldehyde and ketone and ammonium acetate. Dry ammonium acetate (39g) was dissolved in glacial acetic acid (150ml) and the solution was mixed with Benzaldehydge (10g) and ethyl methyl ketone (36g). The mixture was just heated to boil and allowed to stand at room temperature overnight. The reaction mixture was diluted with ether (250ml) and treated with conc. Hydrochloric acid (25ml). The precipitated hydrochloride was collected and washed with ethanol-ether mixture (1:5). The hydrochloride thus obtained was suspended in acetone and neutralized with aqueous ammonia. Dilution with water gave the free base, which melted at 95-96^0C after recrystallization from benzene petroleum ether mixture.

C. Preparation of n -chloro -3- methyl- 2,6 -diphenyl piperidi -4 -one

3 -methyl -2,6-diphenylpipieridin-4- one hydrochloride were dissolved in ethanol. Chlorine gas is produced when conc. HCl is added to potassium permanganate. The chlorine gas which is produced is passed through the solution for about 30 minutes. On dilution with excess amount of water, the compound was thrown out which on recrystallization from ethanol showed the melting point 190-191^{0}C.

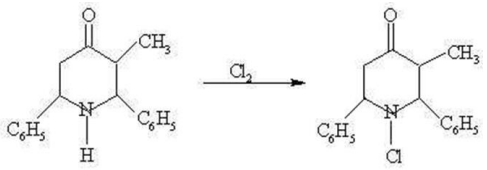


Fig. 2. Preparation of NCMDP

D. Kinetic measurements

The reactions were carried out in aqueous ethanol (75%) medium in presence of sulphuric acid. In all the kinetic runs the total volume of the reaction mixture was taken to be constant to 30ml. known volumes of the solution of the substrate, sulphuric acid, water and alcohol were mixed in a flask to bring the percentage of alcohol to the desired value and thermostated. A precision thermostat with an accuracy of 0.010C was used as a constant temperature bath to carry out all the kinetic variations. The reaction was started by pipetting about a convenient volume of the NCMDP and delivering it into the flask containing the reaction mixture. A stop watch was started when the pipette was halfway empty. At different intervals of time, 2ml aliquots of reaction mixture were removed and transformed into a conical flask containing 1ml of 1% starch 5ml of 10% KI. This reaction mixture was titrated against standard sodium thiosulphate 0.0002M solution. This will estimate the unreacted NCMDP present in the reaction mixture.

3. Results and discussion

The kinetics of oxidation of Methyl salicylate by N-Chloro-3-methyl-2,6-diphenyl piperidin-4- one in 75%ethanol in acid medium has been studied. The results are discussed under the following topics.

A. Effect of varying oxidant concentration on the Rate of the Reaction

The effect of oxidant on the rate of the reaction was studied by carrying out the reaction in presence of different concentrations (0.001M-0.005M) of oxidant by keeping all other concentration constant. The values of rate constants were presented in the Table 1. The rate of reaction is decreased with increase in concentration of oxidant. The order of the reaction with respect to oxidant concentration is fractional, as shown in Table 2, Fig. 1.

Table 1
Effect of varying [Oxidant]
[MS] =0.01 M [H+] =1.0 M

NCMDP (10^{-3}M)	K_{obs} ($10^{-4}s^{-1}$)
1.0	2.3800
1.5	1.5200
2.0	1.4400
2.5	1.3500
3.0	1.0542

Table 2
Order with respect to oxidant

4+logC	4+logK
1.00	4.3765
1.17	4.1818
1.30	4.1583
1.39	4.1303
1.47	4.0229

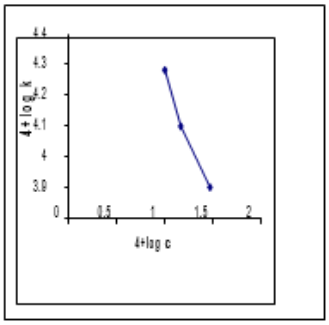


Fig. 1. Oxidant concentration

B. Effect of varying acid concentration on the rate of reaction

The effect of oxidant on the rate of the reaction was studied by carrying out the reaction in presence of different concentrations of acid (0.6M-1.6M) by keeping all other concentration constant. The values of rate constants were presented in the Table 3. The rate of reaction is slightly increased with increase in concentration of sulphuric acid. Increase in rate is due to the presence of H+ Ion in the reaction mixture. The order of the reaction with respect to acid concentration is fractional, shown in Table 4, Fig. 2.

Table 3
Effect of varying [H^+] [MS] =0.01 M

T=35°C H_2SO_4 (10^3M)	K_{obs} ($10^{-4}s^{-1}$)
0.6	1.5400
0.8	1.6000
1.0	2.2300
1.4	2.4600
1.6	2.5100

Table 4

Effect of varying [H^+]

[MS] =O.01M

T=35°C

Order with respect to [H^+]

Substrate	K_{obs} ($10^{-4}s^{-1}$)
0.010	3.8300
0.015	3..3300
0.020	3.0700
0.025	2.9400
0.030	2.2600

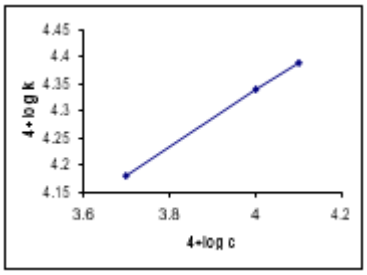


Fig. 2. Acid concentration

C. Effect of varying substrate concentration on the rate of the reaction

The Effect of oxidant on the rate of the reaction was studied by carrying out the reaction in presence of different concentrations of substrate (0.01M-0.03M) by keeping all other concentration constant. The values of rate constants were presented in the Table 5. The rate of reaction is decreased with increase in concentration of substrate. This is due to high concentration of substrate fails to react with oxidant at low concentration. The order of the reaction with respect to substrate concentrations shown in Table 6, Fig. 3.

TABLE 5

Effect of varying [MS]

[MS] =0.01 M

T =35°C

Substrate	K_{obs} ($10^{-4}s^{-1}$)
0.010	3.8300
0.015	3..3300
0.020	3.0700
0.025	2.9400
0.030	2.2600

TABLE 6

Order with respect to substrate

4+logC	4+logK
2.0	4.5831
2.17	4.5224
2.30	4.4871
2.39	4.4683
2.47	4.3541

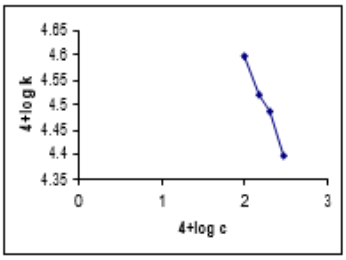


Fig. 3. Substrate concentrations

D. Effect of solvent variation on the rate of reaction.

The Effect of solvent on the rate of the reaction was studied by carrying out the reaction in presence of different percentage of ethanol by keeping all other concentration constant. The rate constants were calculated from the linear plot of log a/a-x versus time. The values of rate constants were presented in the Table 7. The rate of reaction was not altered by increasing polarity of the solvent. There is no dipole-dipole interaction during the course of the reaction; it's shown in Table 7.

TABLE 7

Effect of varying Solvent

[MS] =0.01M

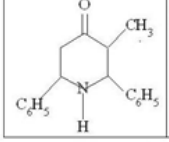
[NCMDP] =0.001M [H^+] =1.0M

% of Ethanol	K_{obs} [$10^{-4}s^{-1}$]
70	1.5400
65	1.5400
60	1.0900
55	1.5400
50	1.4300

E. IR spectral data

The IR spectra of the synthesized compounds were recorded in NICOLET 200 FT-IR using KBr pellets. The spectrum is obtained by plotting the % Transmittance against Wave number cm^{-1}.

IR SPECTRAL DATA OF THE SYNTHESIZED COMPOUNDS

COMPOUND	IR DATA
	N-H Stretching at 2972 cm^{-1} C=O Stretching at 1702 cm^{-1} C-H Stretching at 1415 cm^{-1}

IR SPECTRA OF THE PRODUCT

COMPOUND	IR DATA
HCHO	C=O stretching at 1722 cm^{-1}
$C_6H_4(0H)COOH$	Broad OH band appears at 3118 cm^{-1}

4. Conclusion

The kinetic study of oxidation by NCMDP on Methyl Salicylate shows that the rate of oxidation decreases with increase in concentration of oxidant and substrate. The rate of oxidation increases with increase in acid strength and does not alter with increase in solvent polarity.

References

[1] K. Ganapathy, and S. Kabilan, "Kinetics of oxidation of some ortho, meta, and para substituted S-phenylmercaptoacetic Acids by N-Chloro-3-Methyl-2,6-Diphenyl piperidin-4-one in buffered ethanol-water," in International Journal of Chemical kinetics, vol. 21, no. 6, pp. 423-430, June 1989.