Kinetics and Mechanism of Oxidation of Ethyl Benzoate by N-Chloro-3-Methyl-2, 6 Diphenyl Piperidine-4-Ones in Acid Medium

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Abstract: *Kinetic study on the Oxidation of ethyl benzoate by N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one in ethanol in acid medium has been carried out. The reaction follows first order kinetics, each in Ethyl benzoate, NCMDP and H^+. The rate increased with increase in $[H^+]$ with fractional order. The effect of various anions on the rate of oxidation was found to be in the order $SO_4^{2-} > Cl^-$. The effect of temperature on the rate of oxidation was studied by varying temperatures from 311K–325K. Based on the kinetic results and the product analysis, a suitable mechanism has been proposed for the reaction of NCMDP with Ethyl benzoate. The synthesized N-chloro-3-methyl-2,6- diphenylpiperidine-4-one and the product obtained were characterized by IR Spectra.*

Keywords: Oxidation, ethyl benzoate, kinetics

1. Introduction

Kinetic studies on the oxidation of acids, cyclohexnol, allylalcohol, dimethyl sulpoxide and substituted aniline by N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one have been reported.[1-5] The N-halogen compounds can act as a source of halonium cation, hypohalite ion. N-anion which acts both as a base and a nucleophile.[6] N-halo compounds can also be used for halogenation and dehydrogenation studies. Ethyl benzoate oxidation by N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one is slow in acid medium. The nature of the active oxidizing species and the mechanism depends on the native of the halogen atom.

2. Experimental Work

Ethyl Benzoate used was commercially available (BDH). ARgrade Con.HCl, $Na_2S_2O_3$, KI, $K_2Cr_2O_7$ were used. Ethanol was kept over CaO (lime) over night.Then it was filtered and distilled. Distilled ethanol and double distilled water were used for the entire experiment.

The oxidant N-chloro-3-methyl-2, 6- diphenylpiperidine-4-one was prepared in two stages. The procedure adopted was that of Noller and Baliah[7] for the first stage preparation of 3-methyl-2, 6- diphenylpiperidine-4-one through Mannich Condensation between an aldehyde and ketone in presence of Ammonium acetate (Fig.1). The procedure of Ganapathy and Vijayan[8] was followed for the second stage of the preparation of NCMDP (Fig.2). The synthesized compounds were characterized by IR spectra.
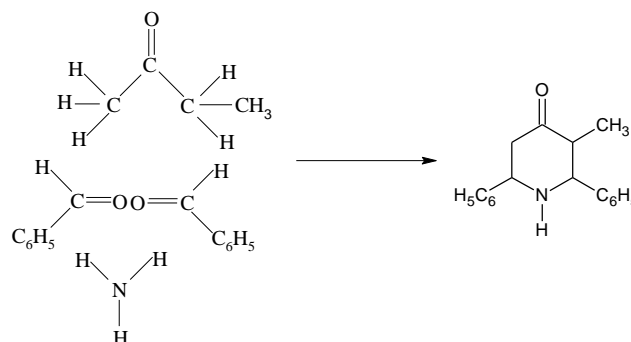

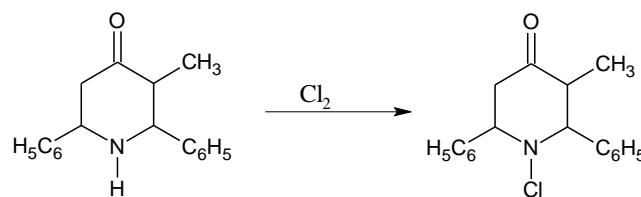**Figure 1:** Preparation of 3-methyl-2, 6- diphenylpiperidine-4-one

Figure 2: Preparation of **NCMDP**

The kinetic measurements were made under first order condition by maintaining equal concentration of the substrate and oxidant while all the other reagents were kept constant. Known quantity of the substrate, sulphuric acid, water and alcohol were mixed in a flask and thermostated in a precision thermostat of 0.01° C accuracy. The reaction was initiated by adding a convenient volume of the oxidant to the above mixture. Aliquots were removed at definite time intervals and the unreacted NCMDP was estimated Iodimetrically.

A known excess of NCMDP was allowed to react with methyl benzoate in H_2SO_4 medium for the completion of the reaction. The reaction mixture was also analysed for the product.

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3. Results and Discussion

Product Analysis

The reaction mixture was tested with Schiff's base and the immediate formation of pink colour showed the presence of aldehyde. The other product was found to be Benzoic acid. The obtained aldehyde and benzoic acid are characterized by IR spectra.

Effect of Varying [NCMDP]

With the oxidant in excess (0.001-0.005M) at constant [HCl],[EB], The plots of log [NCMDP] vs. Time were linear showing first order dependence with respect to the oxidant concentration The rate of reaction is decreased with increase in concentration of oxidant, as shown in Table(1).

Effect of varying [H^+]

The rate was found to increase with increase in concentration of H^+ and the order was found to be fractional as shown in Table (2)

Effect of Ionic Strength of the Medium

Effect of variation of [Cl^-] on the rate

Variation of ionic strength of the medium by adding NaCl&KCl (0.001-0.005M) keeping all other concentration constant.[Cl^-] in KCl had no effect on the rate.But .[Cl^-] in NaCl slightly increased the rate of reaction,as shown in Table (3).

Effect of variation of [SO_4^{2-}]

Variation of ionic strength of the medium by adding $ZnSO_4$ &Na_2SO_4 (0.001-0.004M) keeping all other concentration constant.[SO_4^{2-}] in both $ZnSO_4$ &Na_2SO_4 slightly increased the rate of the reaction, as shown in Table (4).

Effect of varying Temperature

The reaction was studied at different temperatures in the range of 311-325K.The enthalpy of activation and ehergy of activation are calculated from the Eyring plot of $logK/T \times 10^{-4}$ vs $1/T \times 10^{-4}K^{-1}$ and Arrehenius plot of logk vs 1/T as shown in Table (5).

Energy of activation= -193.88 KJ/mol

Enthalpy of activation= 164.7901 KJ/mol

Effect of dielectric constant of the medium

The reaction was carried out at different composition ethanol (50-70٪).thw rate of the reaction is increased with increase the composition of ethanol, as shown in table (6).

Table 1: Effect of Varying Oxidant Concentration on the Rate of Reaction

NCMDP (10^3M)	K_{obs} ($10^{-4}s^{-1}$)
1.0	2.180
1.5	1.740
2.0	1.430
2.5	1.230
3.0	1.040

Table 2: Effect of Varying [H^+] On the Rate of Reaction

[H^+] M	K_{obs} ($10^{-4}s^{-1}$)
0.6	2.350
0.8	2.430
1.0	2.470
1.2	2.640
1.4	3.060

Table 3: Effect of Varying Cl^- Ion on the Rate of Reaction

KCl M	K_{obs} ($10^{-4}s^{-1}$)	NaClM	K_{obs} ($10^{-4}s^{-1}$)
0.001	1.540	0.001	1.980
0.002	1.450	0.002	2.080
0.003	1.650	0.003	2.190
0.004	1.660	0.004	2.280
0.005	1.490	0.005	2.900

Table 4: Effect of Varying So_4^{2-} Ion on the Rate of Reaction

Na_2SO_4M	K_{obs} ($10^{-4}s^{-1}$)	$ZnSO_4$ M	K_{obs} ($10^{-4}s^{-1}$)
0.001	1.460	0.001	1.980
0.002	1.600	0.002	2.670
0.003	1.750	0.003	2.760
0.004	2.150	0.004	2.810

Table 5: Activation Parameters on the Rate of Reaction

Temperature	$1/T \times 10^{-4}K^{-1}$	$logK_{obs}$	$\dfrac{logK_{obs} \times 10^{-4}}{T}$
311	32.15	0.1335	4.2926
314	31.84	0.1875	5.9713
317	31.54	0.3909	12.331
321	31.15	0.4265	13.286
325	30.76	0.5132	15.790

Table 6: Effect of Dielectric Constant on the Rate of Reaction

% Of Ethanol	K_{obs} [10^{-4} s^{-1}]
50	1.090
55	1.110
60	1.280
65	1.760
70	1.850

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