Kinetic and mechanistic studies on the hypochlorite oxidation of 1-phenyl ethanol and its para substituted derivatives in aqueous acetic acid medium

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Abstract: Kinetic studies of the oxidation of 1-phenyl ethanol and some of its para substituted derivatives by hypochlorite have been studied in aqueous acetic acid medium. The reaction showed first order dependence on both [1-phenyl ethanol] and [hypochlorite]. The reaction did not induce the polymerisation of added acrylonitrile and rules out the involvement of any radical intermediate in the reaction. The rate of reaction found to increase with increase in dielectric constant of the medium. The order of reactivity among the studied alcohols is p - CH_3 > - H > p – Cl > p – NO_2. Plots of log k_2 versus Hammett's substituent constant (σ) has been found to be linear with a negative slope indicating an electron deficient carbon centre in transition state. Thermodynamic parameters were determined and a suitable mechanism is proposed in concordance with the obtained results.

Key words : 1-phenyl ethanol, para substituted 1-pheny ethanols, Hypochlorite, kinetics, mechanism.

Introduction

Oxidation reactions are very important in synthetic organic chemistry today. Various substrates which are commercially important are prepared by the oxidation reactions of substrates[1-2]. Various oxidizing agents are used in which permanganate[3-5], chromate[6-8], hypochlorite[9-11] and bromate[12-14] are very important in oxidative conversions.

The present report deals with the kinetics of the oxidation of 1-phenyl ethanol and para substituted1-phenyl ethanols by hypochlorite in aqueous acetic acid medium. Stoichiometry of the reaction, product analysis and effect of concentration of added substrate, oxidant and salt, effect of polarity of the medium, effect of substituents and effect of temperature on the rate of oxidation were carried out. Based on the results obtained, various activation parameters were computed. Structure – activity relationship was also studied by plotting the Hammett plot. A suitable mechanism is proposed based on the experimental observations.

Experimental

Analar grade sodium hypochlorite (E Merck, India) was used and its solution was prepared in doubly distilled water. Acetic acid (E Merck, India) was purified by refluxing with sodium hypochlorite for three hours and distilled[15-16]. 1-phenyl ethanol used was of analar grade (Merck KGaA, Germany). p-chloro, p-nitro and p-

methyl 1-phenyl ethanols were prepared by the reduction of the corresponding ketones using sodium borohydride and purified under vacuum distillation.

Kinetic measurements were carried out under conditions where [1-phenyl ethanol] >> [hypochlorite]. The progress of the reaction was followed by titrating aliquots of the reaction mixture with standard sodium thiosulphate at regular intervals of time. The experiments were repeated and pseudo-first order rate constants, k_{obs} were computed from the linear least square plots of log [hypochlorite] versus time.

Results and Discussion

Stoichiometry of the reaction was determined under the condition [NaOCl] >> [Carbinol] till the completion of reaction. It was found that one mole of hypochlorite is equivalent to one mole of 1-phenyl ethanol.

$$C_6H_5CHOHCH_3 + NaOCl \rightarrow C_6H_5COCH_3 + H_2O + NaCl$$
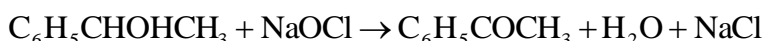
The product of oxidation of 1-phenyl ethanol was identified as acetophenone from the formation of its 2,4-dinitrophenylhydrazone (DNP). The yield of product is very high (>90%) and the product was charactrerised by its melting point. The melting point of 2,4-dinitrophenylhydrazone of product was found to be $145 \pm 2\ ^0C$ where this matches with that of 2,4-dinitrophenylhydrazone of pure acetophenone. The oxidation of 1-phenyl ethanol by hypochlorite in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile and rules out the involvement of any radical intermediate in the reaction.

The oxidation reaction was carried out with different initial [hypochlorite] and [carbinol] in 20% aqueous acetic acid medium at 298.5 K. The effect of [oxidant] and [substrate] on oxidation of 1-phenyl ethanol is given in table 1. The logarithmic plot of [hypochlorite] versus time was found to be linear at various [hypochlorite] and these results prove that the reaction is first order with respect to [hypochlorite]. This was further confirmed from the constant values of specific rates (k_{obs}) for the different [hypochlorite] for a given [carbinol]. The effect of [carbinol] on reaction rate was followed by taking different initial [carbinol] and the observed rate constant increased with [carbinol] in a linear fashion. Moreover, the second order rate constants (k_2) were found to be constant which indicates the first order dependence of the reaction with respect to the [carbinol]. The first order dependence on the [carbinol] was further confirmed by the plot of log k_{obs} versus log [carbinol] which is linear with a unit slope.

Table 1: Effect of [oxidant] and [substrate] on the rate of oxidation of 1-phenyl ethanol
Temperature - 298.5 K   Medium - 20% aq. HOAc (v/v)

$[ClO_4^-]$ x 10^3 (mol dm^{-3})	[carbinol] x 10^2 (mol dm^{-3})	k_{obs} x 10^3 (s^{-1})	k_2 x 10^2 (dm^3 mol^{-1} s^{-1})
2	4	5.28	13.20
3	4	5.16	12.90
3.5	4	5.12	12.80
4	4	5.24	13.10
2	2	2.54	12.70
2	3	3.80	12.67
2	3.5	4.48	12.80
2	4	5.28	13.20

The effect of dielectric constant of the medium on 1-phenyl ethanol oxidation was carried under pseudo first order condition, by varying the acetic acid percentage and is given in table 2. The reaction rate is found to increase with the increase in dielectric constant of the medium. (Decrease in percentage of acetic acid in aqueous acetic acid medium). This indicates the involvement of an anion and a dipole in the rate determining step of the reaction which is according to Amis equation[17].

Table 2: Effect of dielectric constant of the medium on the rate of oxidation.
$[ClO_4^-] \times 10^3 = 2.0$ mol dm^{-3} [carbinol] $\times 10^2 = 4.0$ mol dm^{-3}
Temperature - 298.5 K

Acetic acid : water	Dielectric constant	$k_{obs} \times 10^3$ (s^{-1})	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})
20 : 80	61	5.28	13.20
30 : 70	53	4.41	11.04
40 : 60	47	5.12	12.79
50 : 50	39.8	2.95	7.38

The effect of added salt on the rate of oxidation was studied by varying the [NaCl] and is given in table 3. The rate constant is found to be almost constant with different concentrations of NaCl which ruled out the involvement of the reaction between two charged ions in the rate determining step. The reaction may be due to the interaction between an ion and a dipole or between two dipolar entities[18-19].

Table 3: Effect of [NaCl] on the rate of oxidation.
$[ClO_4^-] \times 10^3 = 2.0$ mol dm^{-3} [carbinol] $\times 10^2 = 4.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v)   Temperature - 298.5 K

[NaCl] $\times 10^2$ mol dm^{-3}	$k_{obs} \times 10^3$ (s^{-1})	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})
1	4.98	12.45
2	4.79	11.98
3	4.85	12.12

The effect of substituents on the rate of oxidation of carbinols has been studied and is found in the order p - CH$_3$ > - H > p – Cl > p – NO$_2$.   These results are presented in table 4. The electron-releasing substituents accelerate the oxidation process while the electron-withdrawing substituents retard the process.

Table 4: Effect of substituents on the rate of oxidation
$[ClO_4^-] \times 10^3 = 2.0$ mol dm- 3   [carbinol] $\times 10^2 = 4.0$ mol dm^{-3}
Medium - 20% aq. HOAc (v/v)   Temperature - 298.5 K

| Substrate	$k_{obs} \times 10^3$ (s^{-1})	$k_2 \times 10^3$ (dm^3 mol^{-1} s^{-1})
p-nitro	0.51	1.26
p-chloro	1.24	3.10
H	5.28	13.20
p-methyl	23.99	59.98

The effect of temperature on the rate of oxidation of 1-phenyl ethanol using hypochlorite in 20% aq. HOAc (v/v) were studied in the temperature range 298.5 K to   308.5 K. The values of various thermodynamic parameters were calculated and presented in table 5.

Table 5: Activation parameters for the oxidation of benzyl alcohols
Medium - 20% aq. HOAc   Temperature - 298.5 K

Substrate	$k_2 \times 10^3$ (dm^{3}mol^{-1} s^{-1})	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (JK^1 mol^{-1})	$\Delta G^{\#}$ (kJ mol^{-1})
1-phenyl ethanol	5.28	34.81	29.61	189.49	86.56

Based on the evidences obtained experimentally, the proposed mechanism is as explained below. A hydrogen abstraction mechanism which leads to the formation of free radicals is negated in view of the failure to initiate the polymerisation of added acrylonitrile. The reaction was found to show first order kinetics with

respect to [oxidant] and [substrate]. The effect of [salt] on the rate of oxidation was studied. The effect of polarity of the medium on the rate of oxidation of 1-phenyl ethanol was investigated by varying the acetic acid percentage in the reaction mixture. It has been observed that the reaction rate increases with increase in percentage of acetic acid (decrease in dielectric constant of the medium) suggesting more polar solvents may require larger reaction time. The plot of log k_2 versus 1/D, where D is the dielectric constant of the medium is linear (r = 0.9978) with a negative slope. This implies the occurrence of an interaction between a dipole and a negative ion and indicates the probable involvement of OCl⁻ species in the reaction. The addition of salt did not change the reaction rate which rules out the involvement of the reaction between two charged ions in the rate determining step. The value of entropy of activation, $\Delta S^{\#}$ is negative indicating a large surrendering of disorder in the transition state and this is in agreement with the prediction of the formation of intermediate. The influence of substituents at the para position of the benzene ring of 1-phenyl ethanol was studied and found that electron-releasing susbtituents accelerate the oxidation process while the electron-withdrawing groups retard the process. The electron-releasing substituents accelerate the reaction rate by the electron transfer by assisting the breakage of C-H bond by transmission of electron across C-C bond in the direction of chlorine. The electron-withdrawing groups retard this electron transfer and thus reducing the reaction rate. The Hammet plot of log k_2 with σ, where σ is the susbtituent constant is linear with a negative slope (negative value for reaction constant, ρ) indicates an electron deficient carbon centre in transition centre.
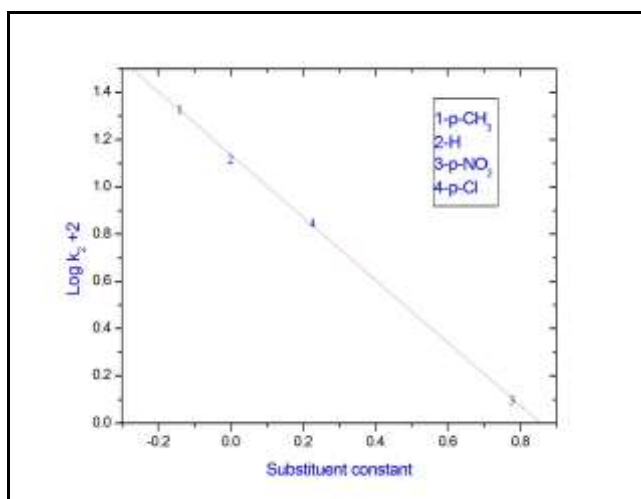

Fig.1: Hammett plot for the oxidation of benzyl alcohols.

Based on the above facts the mechanism of the oxidation of carbinols by hypochlorite ions may be suggested as follows. Alcohol reacts with hypochlorite in acetic acid medium giving carbinol-hyopochlorite complex by the elimination of water by a fast equilibrium step. This complex undergoes a slow rate determining decomposition involving the cleavage of C-H bond and O-Cl bond.

A suitable rate expression for the oxidation of 1-phenyl ethanols using hypochlorite in consistent with the above observations can be given as
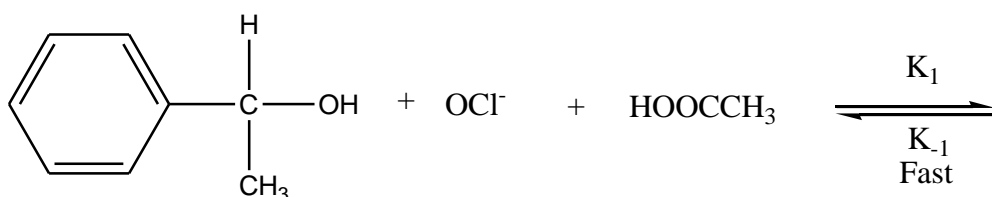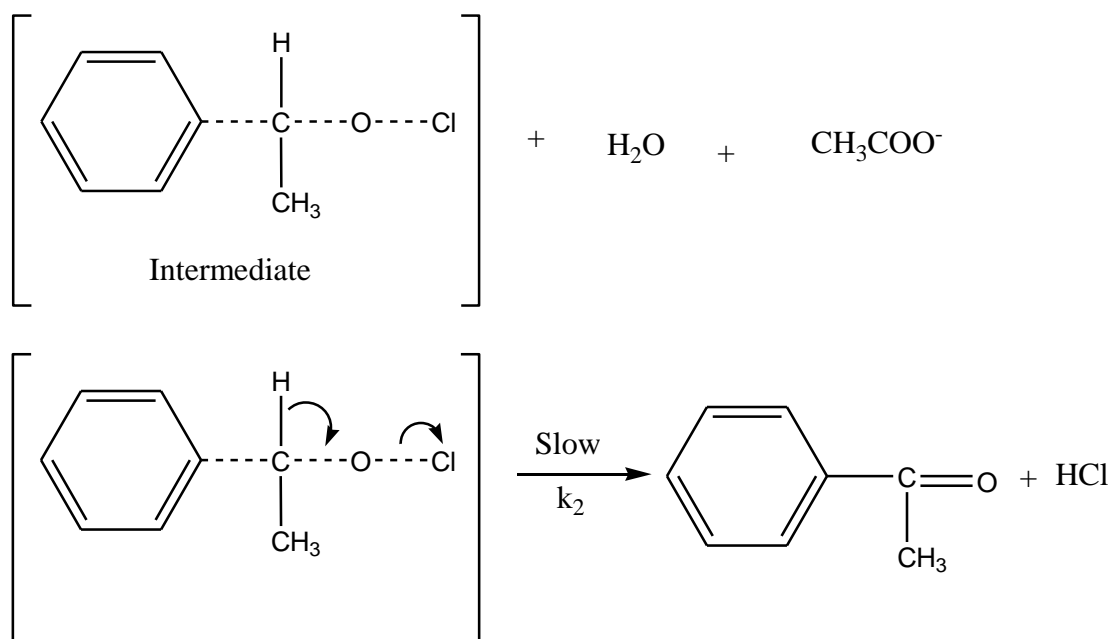
$$\text{Rate} = -\frac{d[OCl^-]}{dt} = -\frac{d[PhCHOHCH_3]}{dt} = k_2[PhCHCH_3OCl]$$

Applying steady state approximation to the intermediate,

$$\frac{d[PhCHCH_3OCl]}{dt} = 0$$

$$K_1[PhCHOHCH_3][OCl^{-1}] - K_{-1}[PhCHCH_3OCl] - k_2[PhCHCH_3OCl^-] = 0$$

$$[PhCHCH_3OCl^-] = \frac{K1[PhCHOHCH_3][OCl^-]}{K_{-1} + k2}$$

$$\text{Rate} = \frac{K_1k_2[PhCHOHCH_3][OCl^-]}{K_{-1} + k_2}$$

(Since $K_{-1} \ggg k_2$, k_2 can be neglected from denominator)

$$\text{Rate} = Kk_2[PhCHOH][OCl^{-}]$$

(Where $K=K_1/K_{-1}$)

The oxidation of 1-phenyl ethanol and para substituted derivatives by hypochlorite in aqueous acetic acid medium gave corresponding acetophenones as the product. A suitable mechanism involving the formation of a carbinol-hypochlorite complex in a fast pre-equilibrium step and then the disproportionation of the complex in a subsequent slow step involving the cleavage of C-H bond and O-Cl bond forming the product was proposed.

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