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Kinetic Studies on The Oxidation of 1-Phenyl Ethanol and Its *para*-Substituted Derivatives by Potassium Dichromate in Aqueous Acetic Acid Medium

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Kinetics of oxidation of 1-phenyl ethanol by potassium dichromate in aqueous acetic acid medium containing sulphuric acid have been carried out. The rate of reaction was found to be first order with respect of both [substrate] and [oxidant]. The rate was found to increase with increasing percentage of acetic acid and [sulphuric acid]. The rate was found to be increased by the presence of electron donating substituents and retarded by electron withdrawing groups. Various thermodynamic parameters were calculated using Arrhenius and Frying equation using the data obtained from temperature studies. Based on the observations suitable mechanism has been proposed. Radical formation was ruled out using acrylonitrile.

Key Words: Kinetic oxidation, 1-Phenyl ethanol, Potassium dichromate.

INTRODUCTION

Several inorganic oxidizing agents like hypochlorite[1], chromic acid, chromates, permanganate[2], dichromate[3], chlorate[4], *etc*. have been reported for the oxidation of organic compounds. The kinetics and mechanism of oxidation of 1-phenyl ethanol in aqueous acetic acid medium using acidic dichromate has been carried out in present study. It was reported[5] that Cr(VI) in aqueous solution exists as a pH dependent mixture of species like $HCrO_4^-$ and $HCr_2O_7^-$. The active species was reported to be $HCrO_4^-$. This anion reacts with the alcohol forming the chromate ester which decomposes giving the product.

EXPERIMENTAL

1-Phenyl ethanol (E. Merck) was used. AnalaR grade potassium dichromate, sodium thiosulphate and potassium iodide were also used. Iodometric method was employed for the estimation. Double distilled water was used for preparing solutions. Acetic acid was purified by standard procedure.

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The product analysis was carried out by taking known amount of 1-phenyl ethanol and potassium dichromate in aqueous medium containing mineral acid and acetic acid. The reaction mixture was stirred for 6 h and the resulting mixture was treated with ether and the product separated and identified and confirmed as acetophenone by 2,4-dinitrophenylhydrazine test. The stoichiometric analysis was carried out using known amount of 1-phenyl ethanol and known excess amount of potassium dichromate in 10 % aqueous acidic medium. The unreacted potassium dichromate estimated iodometrically and a 3:1 ratio between the (carbinol) and (dichromate) was observed.

Kinetic studies were carried out under pseudo first order condition keeping [substrate] >> [oxidant]. The investigations were carried out by changing [oxidant], [substate] [H_2SO_4], percentage of acetic acid and [salt], at varying temperatures. The progress of the reaction was followed iodometrically.

RESULTS AND DISCUSSION

The kinetic data obtained by changing [oxidant] and [substrate] shows a first order dependence of rate of reaction on both (Table-1). The rate was found to be increased with increasing percentage of acetic acid and [H_2SO_4] (Tables 2 and 3). This shows the involvement of a protonated species in the reaction. Addition of salt shows no effect on the rate of reaction which ruled out the interaction between the ionic species. Free radical mecahnism was ruled out by the failure of polymerization of acrylonitrile added into the reaction mixture. These observations suggest a mechanism through ion-dipole interaction[6]. The large negative value of entropy of activation suggests the formation of a complex chromate ester as transient intermediate. The negative value of Hammett's ρ value indicate the chance for C–H bond cleavage the rate of which is found to be increased by electron donating groups and decreased by electron withdrawing groups. The Hammett

TABLE-1
EFFECT OF [SUBSTRATE] AND [OXIDANT] ON THE RATE OF OXIDATION OF 1-PHENYL ETHANOL

[Substrate] × 10^2	[Oxidant] × 10^3	k_{obs} × 10^4 (s^{-1})	k_2 × 10^3 (dm^3 mL^{-1} s^{-1})
4	1	2.698	6.74
4	2	2.682	6.71
4	3	2.752	6.88
4	4	2.706	6.76
2	1	1.305	6.53
3	1	1.949	6.49
4	1	2.698	6.74
5	1	3.197	6.39

TABLE-2
EFFECT OF [ACETIC ACID] ON THE RATE OF OXIDATION OF 1-PHENYL ETHANOL
[Substrate] × 10^2: 4 mol dm^{-3}; Temp. 308 K; [Oxidant] × 10^3: 1 mol dm^{-3}

HOAc (%)	Dielectric constant	$k_{obs} \times 10^4$ (s^{-1})
10	68	2.698
20	61	4.713
30	54	9.707
40	47	14.430

TABLE-3
EFFECT OF [H_2SO_4] IN THE RATE OF OXIDATION OF 1-PHENYL ETHANOL
[Substrate] × 10^2: 4 mol dm^{-3}; Temp. 308 K; [Oxidant] × 10^3: 1 mol dm^{-3}

[H_2SO_4] × 10	$k_{obs} \times 10^4$ (s^{-1})	Correlation coefficient
2.5	2.322	0.9999
5.0	2.698	0.9999
7.5	3.180	0.9994
1.0	4.414	0.9999

plot is given in Fig. 1. Free energy of activation was found to be almost equal for 1-phenyl ethanol and its substituted derivatives and hence suggests the same mechanism for the oxidation (Table-4). Based on the above data the following mechanism is suggested.

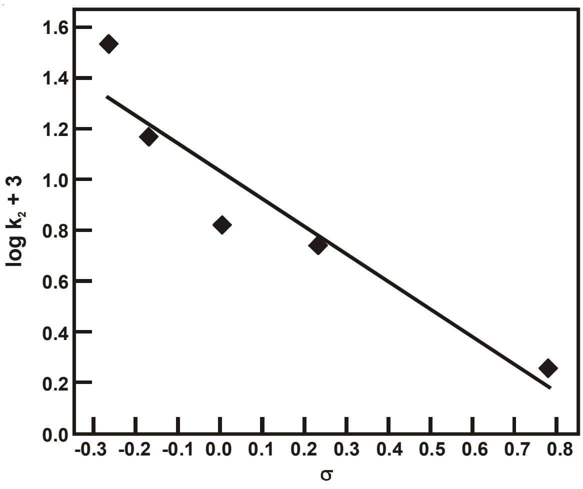
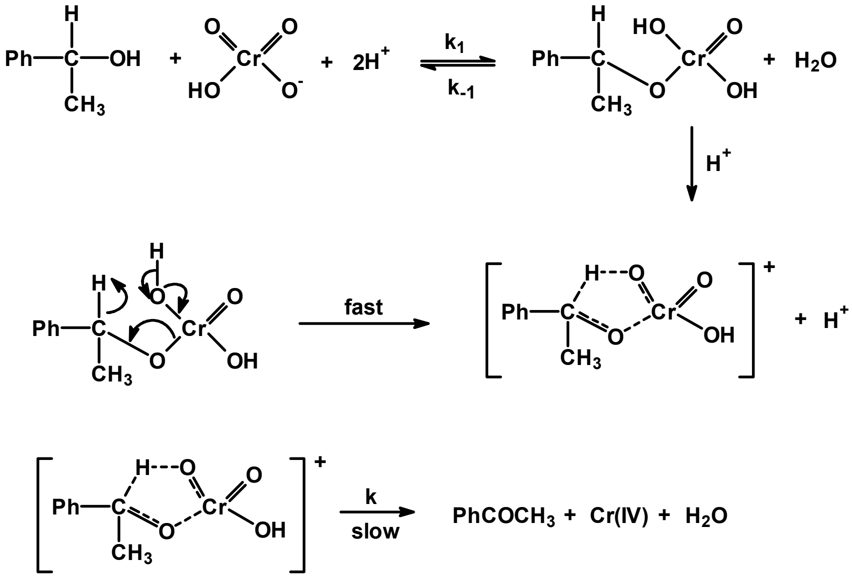


Fig. 1. Hammett plot for the oxidation of 1-phenyl ethanol in aq. HOAc

TABLE-4
ACTIVATION PARAMETERS FOR THE OXIDATION FOR 1-PHENYL ETHANOL AND ITS SUBSTITUTED DERIVATIVES IN 10 % AQ. ACETIC ACID MEDIUM

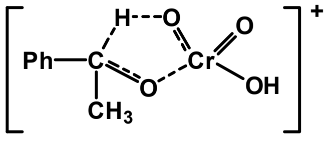
Alcohols	$k_2 \times 10^3$ (dm^3 mol^{-1} s 303)	Ea (kJ mol^{-1})	$\Delta H^{\#}$ (kJ mol^{-1})	$-\Delta S^{\#}$ (J mol^{-1} K)	$\Delta G^{\#}$ (kJ mol^{-1})
1-Phenyl ethanol	6.630	44.870	42.460	63.53	61.709
p-Chloro-1-phenyl ethanol	5.570	36.670	34.210	76.02	51.244
p-Nitro-phenyl ethanol	1.813	82.114	74.374	15.73	69.607
p-Methyl-1-phenyl ethanol	14.870	51.930	49.460	50.63	64.800
p-Methoxy-1-phenyl ethanol	34.140	31.470	29.100	76.82	52.370



$$3Cr(IV) \longrightarrow Cr(VI) + 2Cr(III)$$

Hence the rate law is $\frac{dx}{dt} = k[X]$

where X =



$$[X] = \frac{k_1[PhCHOHCH_3][HCrO_4^-]}{k_{-1}}$$

$$\frac{dx}{dt} = k\frac{k_1[PhCHOHCH_3][HCrO_4^-]}{k_{-1}}$$

$$= k_2[PhCHOHCH_3][HCrO_4^-]$$

where $k_2 = \dfrac{k\ k_1}{k_{-1}}$

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