



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Oxidation of phenoxyacetic acid by imidazolium dichromate

K. G. Sekar*¹ and M. Vellaisamy²

¹Department of Chemistry, National College, Tiruchirappalli, Tamilnadu, India

²Department of Chemistry, Rajah Serfoji Government College, Thanjavur, Tamilnadu, India

ABSTRACT

The kinetics of oxidation of phenoxyacetic acid by imidazolium dichromate in presence of oxalic acid has been studied in 50% acetic acid- water medium at 313 K. The order with respect to phenoxyacetic acid and Imidazolium dichromate were both one and fractional order with respect to oxalic acid and perchloric acid. The decrease in dielectric constant of the medium increases the rate of the reaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile. The reaction has been conducted at four different temperatures and activation parameters were calculated. *p*-benzoquinone has been identified as the product of oxidation. A suitable mechanism and rate law in consonance with the observed facts is proposed.

Key words: Phenoxyacetic acid, oxidation, kinetics, imidazolium dichromate

INTRODUCTION

Chromium compounds have been used in aqueous and non aqueous medium for the oxidation of a variety of organic compounds [1]. Chromium especially Cr(VI) reagents have been proved to be versatile reagents and capable of oxidizing almost all the oxidisable organic functional groups [2-4]. Numerous reagents and experimental procedures have been developed to carry out this transformation [5], in particular reagents containing chromium(VI) reactive species are widely used for the oxidation of alcohols to carbonyl compounds [6-7]. Imidazolium dichromate has been used as on mild selective oxidant in synthetic organic chemistry [8]. A survey of the literature shows that some systematic studies were carried out on the oxidation reaction of phenoxyacetic acid by various oxidants [9-15]. The literature survey reveals that the kinetics and mechanism of oxidation of phenoxyacetic acid by IDC has not yet been studied. In the present investigation, the oxidation of phenoxyacetic acid by IDC in aqueous acetic acid medium in the presence of oxalic acid with perchloric acid and the corresponding mechanistic aspects has also been discussed.

EXPERIMENTAL SECTION

The phenoxyacetic acid was prepared and purified by Koelsch [16]. Imidazolium dichromate was prepared [17] by literature method and its purity was checked by an iodometric method. Acetic acid was purified [18] by standard method and the fraction distilling at 118 °C was collected. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

The reaction was carried out under pseudo-first order conditions [PAA] \gg [IDC] in 50% (v/v) aqueous acetic acid containing oxalic and perchloric acid. The course of the reaction was followed photoelectric colorimetrically at 470 nm for upto 80% of the reaction the pseudo-first order rate constants k_1 computed from the linear plots of log absorbance *versus* time by the least squares method, were reproducible within $\pm 3\%$.

Stoichiometry and Product Analysis

The reaction mixture containing an excess of oxidant over phenoxyacetic acid were kept at room temperature in the presence of oxalic acid and perchloric acid for 24 h. Estimation of the unchanged oxidant showed that one mole of phenoxyacetic acid consumed one mole of the oxidant. It was extracted with ether and the residue that separated during solvent evaporation was analysed. The product, *p*-benzoquinone was identified by IR spectral data.

RESULTS AND DISCUSSION

Oxidation of phenoxy acetic acid by imidazolium dichromate has been conducted in 50% acetic acid - 50% water medium at 313 K under pseudo-first order conditions and the observed results were discussed.

The order of the reaction with respect to imidazolium dichromate was found to be unity as shown by the linearity of log absorbance against time plot (Table 1). The pseudo first order rate constants were found to be independent of initial concentration of imidazolium dichromate.

The concentration of imidazolium dichromate was varied in the range 1.0×10^{-4} to 3.0×10^{-4} mol dm⁻³ and keeping all other reactant concentrations as constant and the rates were measured (Table 1). The linear constancy in the value of k_1 irrespective of the concentration of the imidazolium dichromate confirms the first order dependence on imidazolium dichromate.

The phenoxyacetic acid concentration was varied in the range 1.0×10^{-2} to 5.0×10^{-2} mol dm⁻³ at 313 K and keeping all other reactant concentration as constant and the rates were measured (Table 1). A plot of log k against log [S] was linear with a slope of unity. The rate of oxidation increased progressively on increasing the concentration of phenoxyacetic acid, indicating first order dependence with substrate.

The perchloric acid concentration was varied in the range of 0.5×10^{-1} to 2.5×10^{-1} mol dm⁻³ and keeping the other concentrations as constant and rate were measured (Table 1). The rate of the reaction increases with increasing the concentration of [H⁺]. The plot of log k versus log [H⁺] gave a straight line with a slope (0.51) indicating fractional order with respect to [H⁺].

The reactions were carried out with the varying concentration of oxalic acid from 3.5×10^{-2} to 17.5×10^{-2} mol dm⁻³ while keeping the other concentrations of other reagent constant. The plot of log k_1 versus log [oxalic acid] gave a straight line with slope (0.53) indicating fractional order dependence with oxalic acid.

The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant indicating the involvement of a neutral molecule in the rate determining step. The effect of solvent composition on the reaction rate was studied by varying the solvent composition of 50-65%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table 1). When the acetic acid content increases in the medium, the acidity of the medium is increased where as the dielectric constant of the medium is decreased suggesting ion-dipole interaction [19-20].

The clear mixture containing phenoxyacetic acid and imidazolium dichromate when allowed to stand with a drop of acrylonitrile [21] no turbidity is formed suggesting the non involvement of free radical in the reaction. The reaction rate decreases with increasing the concentration of Mn²⁺ ions confirming the involvement of two electron process in the reaction [22].

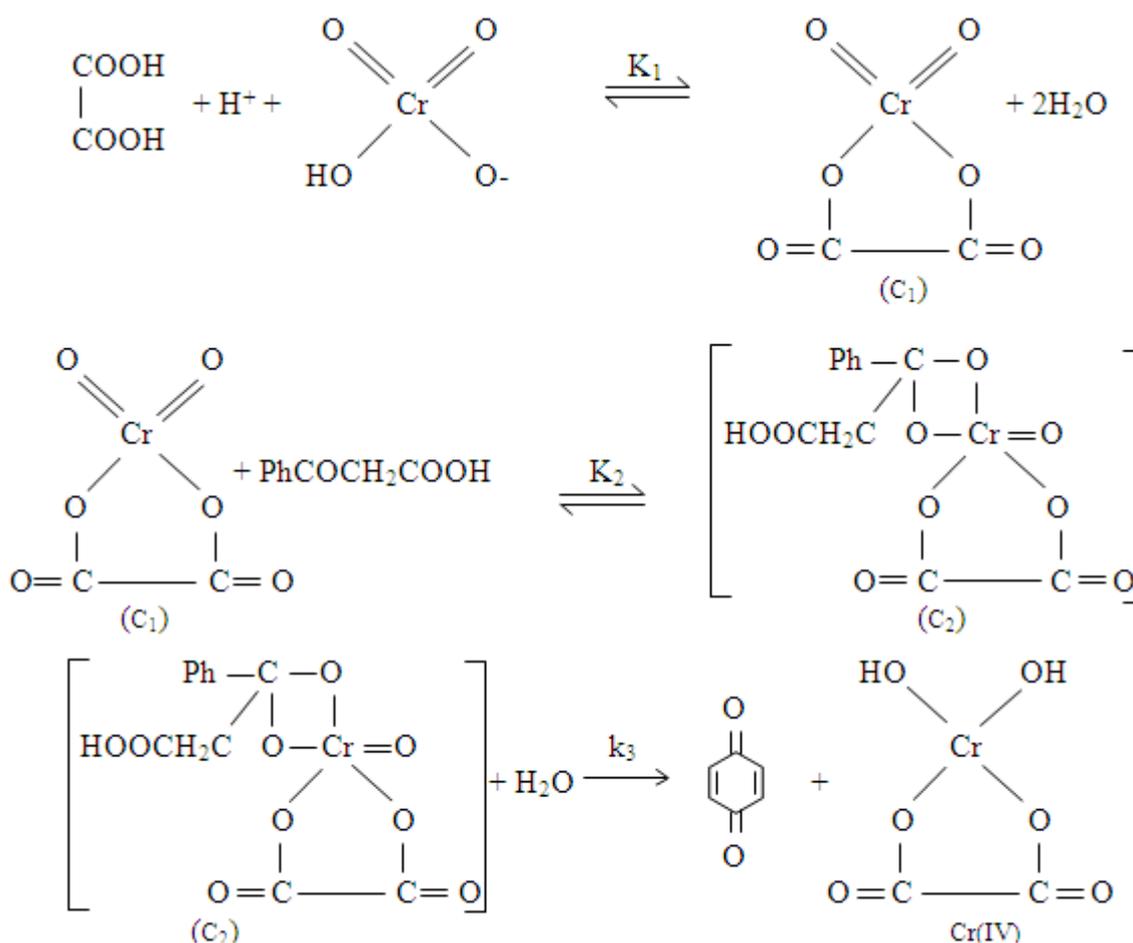
The rate constants were measured at four different temperatures and the activation parameters (Table 2) were computed from a plot of $\ln k_2/T$ against $1/T$ of the Eyring's equation [23]. The negative values of entropy of activation ΔS^\ddagger indicates a polar transition state with extensive charge separation which promote high degree of solvation of the transition state compared to the reactants.

Mechanism and Rate law

From the experimental results, it is observed that the kinetics of oxidation of phenoxyacetic acid with Cr(VI) in 50% acetic acid – water, follows first order each in [oxidant], [substrate] and fractional order in [oxalic acid], [H⁺] Added Mn (II) salt suppressed the rate, indicating the involvement of a two electron process in the rate determining step.

Based on the observations a probable mechanism is given in scheme - I.

Mechanism:



Rate Law:

The above mechanism leads to the following rate law

$$\begin{aligned} \frac{-d[\text{IDC}]}{dt} &= k_3 C_2 = k_3 K_2 [S] [C_1] \\ &= \frac{K_1 K_2 k_3 [S][\text{ox}][\text{IDC}][\text{H}^+]}{1 + K_1[\text{ox}] + 1 + K_1[\text{H}^+]} \\ &= \frac{K_1 K_2 k_3 [S][\text{ox}][\text{IDC}][\text{H}^+]}{\{1 + K_1[\text{ox}]\} \{1 + K_1[\text{H}^+]\}} \\ k_{\text{obs}} &= \frac{K_1 K_2 k_3 [S][\text{ox}][\text{H}^+]}{1 + K_1[\text{ox}] + K_1[\text{H}^+]} \end{aligned}$$

The proposed mechanism and the derived rate law fit well to the experimental observations.

Table 1. Rate constant for the oxidation of phenoxyacetic acid by imidazolium dichromate at 313 K.

[PAA] x 10 ² (M)	[IDC] x 10 ⁴ (M)	[HClO ₄] x 10 ¹ (M)	[H ₂ C ₂ O ₄] x 10 ³ (M)	[NaClO ₄] x 10 ⁴ (M)	[AcOH-H ₂ O] (% v/v)	[MnSO ₄] x 10 ⁴ (M)	k ₁ x 10 ⁴ (s ⁻¹)
1.0 - 5.0	1.5	1.0	7.0	-	50	-	5.52 - 35.69
2.0	1.0 - 3.0	1.0	7.0	-	50	-	12.27 - 12.58
2.0	1.5	0.5 - 2.5	7.0	-	50	-	8.31 - 18.62
2.0	1.5	1.0	7.0 - 21.0	-	50	-	12.37 - 22.39
2.0	1.5	1.0	7.0	0-7.5	50	-	12.36 - 12.18
2.0	1.5	1.0	7.0	-	50 - 65	-	12.36 - 17.14
2.0	1.5	1.0	7.0	-	50	0 - 7.5	12.36 - 8.96

Table 2 Dependence of rate constant on temperature and activation parameters

[IDC] = 1.5 × 10 ⁻⁴ mol dm ⁻³	[Phenoxyacetic acid] = 2.0 × 10 ⁻² mol dm ⁻³
[HClO ₄] = 1.0 × 10 ⁻¹ mol dm ⁻³	[Oxalic acid] = 7.0 × 10 ⁻² mol dm ⁻³
AcOH - H ₂ O (v/v) = 50 : 50	

Temperature (K)	k ₁ x 10 ⁴ (s ⁻¹)	Activation Parameters
303	9.13	ΔH [#] = 22.40 kJmol ⁻¹
313	12.36	ΔS [#] = -196.98 JK ⁻¹ mol ⁻¹
323	16.71	ΔG [#] = 94.21 kJmol ⁻¹ at 313 K
333	22.34	E _a = 25.00 kJmol ⁻¹ at 313 K

CONCLUSION

The reaction is first order each in [substrate], [oxidant] and fractional order with respect to oxalic acid, [H⁺]. The stoichiometry was found to be one mole of phenoxyacetic acid consuming one mole of imidazolium dichromate. The main product of the reaction was found to be *p*-benzoquinone. The negative values of ΔS[#] provided support for the formation of a rigid activated complex. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

Acknowledgement

The authors are thankful to the authorities of National College (Autonomous), Tiruchirappalli for providing facilities and encouragement.

REFERENCES

- [1] Muzart. J, *J Chem Rev.*, **1992**, 113.
- [2] Richter. B and Masnovi. J, *J. Chem. Soc. Chem. Commun.*, **1988**, 1, 35.
- [3] Kothari. A, Kothari. S and K. K. Banerji, *Indian J. Chem.*, **2005**, 44A, 2039.
- [4] Chimatadar. S.A, Salunke. M.S and Nandibewoor. S.T, *Indian J. Chem.*, **2006**, 45A, 388.
- [5] Hudlicky. M, *Oxidations in Inorganic Chemistry/Reductions in Organic Chemistry*, Vol. 1, 2nd Ed., Washington: ACS Monograph, ACS, **1990**, 186.
- [6] Fieser. L and Fieser. M, *Reagents for Organic Synthesis*, New York: John Wiley and Sons, **1967**, 144.
- [7] Cainelli. G and Cardillo. G, *Chromium Oxidation in Organic Chemistry*, Springer-Verlag, New York, **1984**.
- [8] Shiek Mansoor. S and Shyed Shafi, *E. J. Chem.*, **2009**, 6(S1), S522.
- [9] Baliah. N and Gurusurthy. R, *Indian J. Chem.*, **1981**, 620.
- [10] Gurusurthy. R and Gopalakrishnan. M, *Indian J. Chem.*, **1986**, 25A, 476.
- [11] Gurusurthy. R, Sathiyarayanan. K and Gopalakrishnan. M, *Bull. Chem. Soc. Jpn.*, **1992**, 65, 1096.
- [12] Nagarajan. S and Gopalakrishnan. M, *Oxid. Commun.*, **1995**, 18(2), 162.
- [13] Elango. K.P and Karunakaran. K, *Oxid. Commun.*, **1996**, 19(1), 44.
- [14] Sekar. K.G and Anbarasu. K, *Oxid. Commun.*, **2011**, 34(2), 314.
- [15] Palaniappan. A.N, Udayakumar. R, Srinivasan and C. Raju, *Der Chemica Sinica*, **2012**, 3(3), 708.
- [16] Koelsch. C.F, *J. Am. Chem. Soc.*, **1931**, 53, 304.
- [17] Kim. S and Lhim. D.C, *Bull. Chem. Soc. Jpn.*, **1986**, 59, 3297.
- [18] Weissberger. A, Prabhakar. E.S, *Organic Solvents Physical Properties and Methods of Purifications*, 2nd Ed., Inter Science Publisher Ltd., London, **1963**, 170.
- [19] Quinlan. J.E and Amis. E.S, *J. Am. Chem. Soc.*, **1955**, 77, 4187.
- [20] Amis. E.S, *Solvent Effects on Reaction Rates and Mechanism*, Academic Press, New York, **1966**, p.42.
- [21] Littler. J.S and Waters. W.A, *J. Chem. Soc.*, **1959**, 1299.
- [22] Banfi. S, Cavazzini. M, Pozzi. G, Barkanova. S.V and Kaliya. O.L, *J. Chem. Soc. Perkin Trans.*, **2000**, 2, 879.
- [23] Frost. A.A and Pearson. R.G, *Kinetics and Mechanism*, Wiley Eastern, New Delhi. **1970**, p.99.