



Research Article

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Kinetics of oxidation of mandelic acid by imidazolium dichromate in acetic acid medium

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ABSTRACT

The kinetics of oxidation of mandelic acid by Imidazolium dichromate has been studied in 50% acetic acid – water (v/v) medium in the presence of perchloric acid at 303K. The reaction is the First order with Respect to [oxidant], and Fractional order with respect to [substrate] and [acid]. Hence, Michaelis menten types of kinetics has been observed. 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 studied at five different temperatures and the activation parameters were calculated. The oxidation of mandelic acid resulted in the formation of corresponding oxoacid has been identified as the product of oxidation. From the observed kinetic results a suitable mechanism with rate data has been proposed.

Keywords: Mandelic 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[1-3] Chromium especially Cr(VI) reagents have been proved to be versatile Reagents and capable of oxidizing almost all the oxidisable organic functional groups [4-6]. Numerous Reagents and experimental procedures have been developed to carry out this transformation [7], in particular reagents containing chromium (VI) Reactive Species are widely used for the oxidation of alcohol to carbonyl compounds[8,9]. Imidazolium dichromate has been used as a mild selective oxidant in synthetic organic chemistry[10]. Oxidations of mandelic acid by other Pyridinium and quiniolinium halochromate [11] have been reported. These seems to be no report on the oxidation of α -hydroxy acid by IDC in the acetic acid medium and no report on its mechanism. Hydroxy acid may be oxidized either as alcohol yielding corresponding Oxo acids[12].

EXPERIMENTAL SECTION

Materials And Methods:

E.Merck Mandelic acid is recrystallized and its melting point is checked. The solutions are prepared in distilled acetic acid in AR grade perchloric acid was used Imidazolium dichromate was prepared[13] by literature method. Acetic acid was purified[14] by standard method and the fraction distilling at 118^oC was collected. All other chemicals used were of AR grade. The solutions were prepared in triple distilled water.

Kinetic Measurements:

The Reaction was carried out under Pseudo first order conditions [MA] \gg [IDC] in 50% (v/v) aqueous acetic acid containing perchloric acid. The course of the reaction was followed colorimeter at 470nm 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 with in $\pm 1\%$

Stoichiometry and Product Analysis:

The reaction mixture containing an excess oxidant over mandelic acid were kept at room temperature in the presence of perchloric acid for 24 hours. Estimation of the unchanged oxidant showed that one mole of mandelic acid consumed one mole of the oxidant. The product oxoacid was identified by spot test and IR, GC-MS spectral data.

RESULTS AND DISCUSSION

Oxidation of mandelic acid by Imidazolium dichromate has been conducted in 50% acetic acid and 50% water medium at 303k 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 one as shown by the linearity of log absorbance against time. (Table 1)

Table 1. Rate Constant for the oxidation of mandelic acid by IDC at 303k

[MA] x 10 ² mol dm ⁻³	[IDC] x 10 ³ mol dm ⁻³	[HClO ₄] x 10 ¹ mol dm ⁻³	[NaClO ₄] x 10 ⁴ mol dm ⁻³	[ACOH- H ₂ O] (%v/v)	[AlCl ₃] x 10 ⁴ mol dm ⁻³	K _{obs} x 10 ⁴ S ⁻¹
2.0-4.0	3.0	1.0	-	50	-	4.62 – 5.43
2.0	3.0-4.5	1.0	-	50	-	4.62 – 4.21
2.0	3.0	1.0 – 4.0	-	50	-	4.62 – 13.01
2.0	3.0	1.0	0-10.0	50	-	4.62 – 4.69
2.0	3.0	1.0	-	45-65	-	3.46 – 6.94
2.0	3.0	1.0	-	50	0-7.5	4.62 – 1.91

The concentration of Imidazolium dichromate was varied in the range 3.0×10^{-3} to 4.5×10^{-3} mol dm⁻³ at 303k 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 Imidazolium dichromate confirms the first order dependence on Imidazolium dichromate.

The mandelic acid varied in the range 2.0×10^{-2} to 4.0×10^{-2} mol dm⁻³ at 303K and keeping all other reactant concentration as constant and the rates were measured (Table 1). The rate of oxidation increased with very slightly on increasing the concentration of mandelic acid, indicating fractional order dependence with substrate. The plot of log k_{obs} versus log [MA] gave a straight line with a slope of 0.51, shows that the oxidation reaction was fractional order with respect to mandelic acid. The double reciprocal plot of $1/k$ versus $1/s$ gave a straight line with a definite intercept indications the michaelis – menten type of kinetics in this reaction.

The perchloric acid concentration was varied in the range 1×10^{-1} to 4×10^{-1} mol dm⁻³ and keeping the other concentrations as constant and rate constant were measured (Table 1). The increase in [HClO₄] in the oxidation reaction very slightly increases the rate of the reaction and shows a direct fractional order dependence on [HClO₄] a plot of log K against log [H⁺] is linear.

The change in ionic strength by the addition of sodium perchlorate has no effects on the rate constant indicating the involvement of a neutral molecule in the rate determining step.

The effect of varying solvent composition on the reaction rate was studied by varying the concentration of acetic acid 45% - 65%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table 1) is suggesting the involvement of ion-dipole interaction [15-17]

The reaction does not induce polymerization of acrylonitrile indicating the absence of free radical pathway [18-19]. The reaction rate decreases with increasing the concentration of Al³⁺ ions confirming the involvement of three electron process in this reaction.

Effect of Varying Temperature:

The rate constant were measured at five different temperature and the activation parameters were computed from a plot of $\ln k_2 / T$ against $1/T$ of the Eyring's equation[20].

Table 2 Activation Parameters for the oxidation of mandelic acid by Imidazolium dichromate

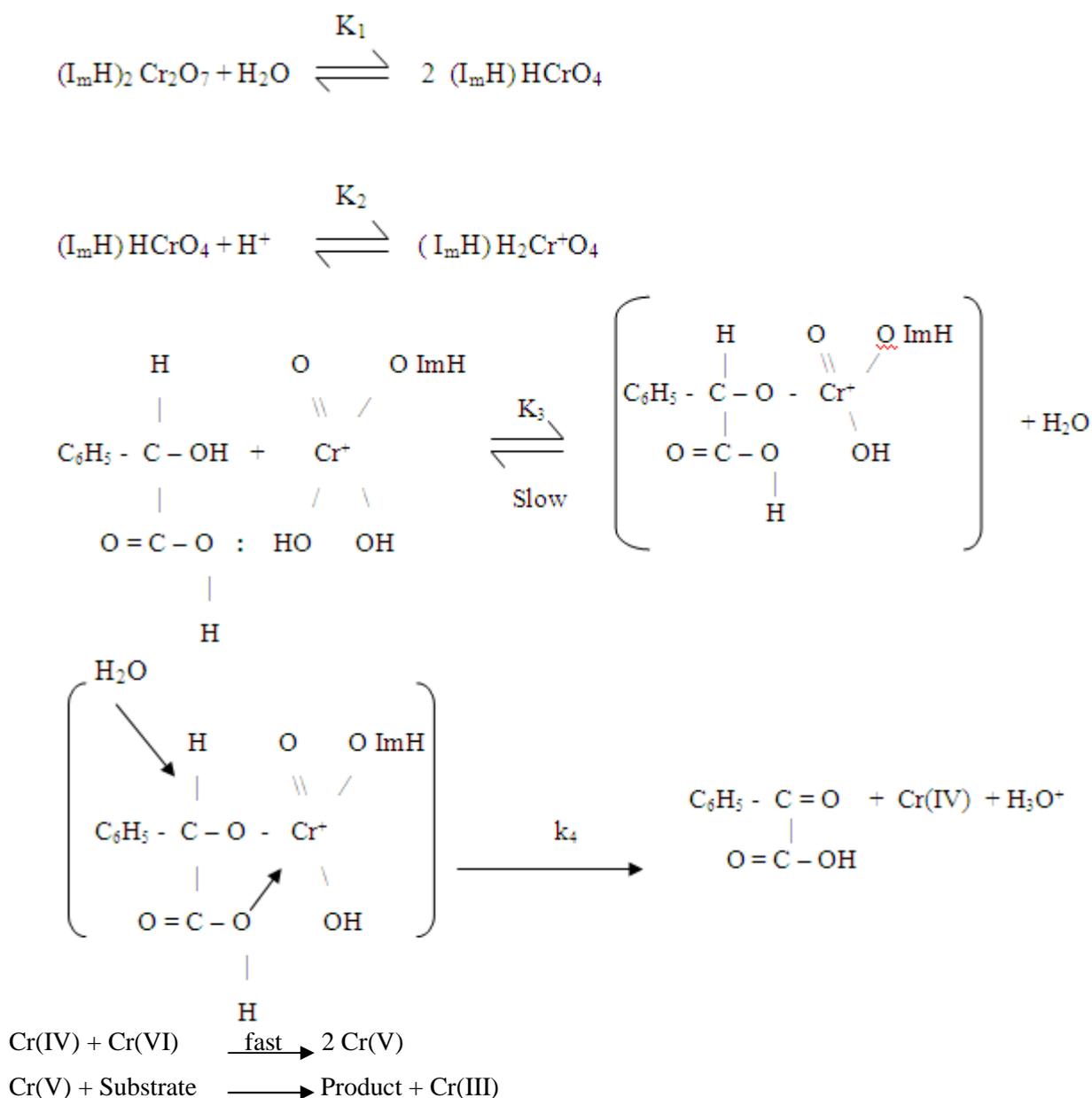
S. No	Substrate	[IDC] = 3.0 x 10 ⁻³ mol dm ⁻³ [MA] = 2.0 x 10 ⁻² mol dm ⁻³					[HClO ₄] = 1.0 x 10 ⁻¹ mol dm ⁻³ 50% Acetic acid 50% water medium			
		10 ⁴ k _{obs} s ⁻¹					ΔH [#] (kJmol ⁻¹)	-ΔS [#] (JK ⁻¹ mol ⁻¹)	ΔG [#] (kJmol ⁻¹) at 303 K	E _a (kJmol ⁻¹) at 303 K
1	Mandelic acid	4.62	7.54	10.45	11.02	12.39	35.64	256.53	113.37	38.16

The negative value of entropy of activation ΔS[#] 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:

In view of these observation, a probable mechanism for the oxidation can be given as shown in scheme 1.

The dichromate ion is known to exist in solution as the dimeric species above 0.05 mol dm⁻³. At lower concentrations it exists in the monomeric forms as HCrO₄⁻, H₂CrO₄, and H₃CrO₄⁺. The reaction is showing first order dependence on the oxidant and fractional order with respect to substrate.



Im = Imidazolium

Scheme -1

The above mechanism leads to the following rate law

$$\text{Rate} = \frac{-d[\text{IDC}]}{dt} = k_4 \text{ complex}$$

By Applying steady state approximation for the complex

The rate law is given below.

$$\frac{-d[\text{IDC}]}{dt} = \frac{K_1 K_2 K_3 k_4 [\text{S}] [\text{IDC}] [\text{H}^+]}{1 + K_1 [\text{IDC}] + K_2 [\text{H}^+] + K_3 [\text{S}]}$$

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

CONCLUSION

The main product of the reaction were found to be oxoacid. The reaction is first order in oxidant and fractional order with substrate. The stoichiometry was found to be one mole of mandelic acid consuming one mole of imidazolium dichromate. The negative value of ΔS^\ddagger provides a support for the formation of a rigid activated complex.

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REFERENCES

- [1] Muzart *J Chem Rev.*, **1992**,113.
- [2] Sayyed Hussain, S.R.Gour, Mazahar Farooqui, *Der Chemica Sincia.*, **2011**, 2(1), 61.
- [3] Sangita Sharma, Jayesh Ramani, Jasmin Bhalodia, Falguni Thakkar, *Der Chemica Sincia.*, **2011**, 2(4),140.
- [4] B Richter and J Masnovi, *J Chem Soc Chem Commun.*, **1988**,1,35.
- [5] A Kothari, S Kothari and K K Banerji, *Indian J Chem.*, **2005**, 44A, 2039.
- [6] S A Chimatadar, M S Salunke and S T Nandibewoor, *Indian J Chem.*, **2006**, 45A, 388.
- [7] M Hudlicky, Oxidation inorganic chemistry/reductions in organic chemistry, Vol.1, 2nd Ed., Washington:ACS Monograph, **1990**,186.
- [8] L Fieser, M Fieser M, Reagents for organic synthesis, New York : John Wiley and Sons, **1967**, 144.
- [9] G Caineil, G Cardillo, Chromium oxidation in organic chemistry, Springer-Verlag, New York, **1984**.
- [10] S. Sheik Mansoor and Shyed Shafi, *E.Journal of chemistry* **2009**, 6(S1), S522-S528
- [11] A. Sopa R, Agrawal S, and Banerji K K, Proc Indian Acad Sci., (*Chem Sci.*,) **1991**.
- [12] Banerji. K K, *J Chem Res(S)* , **1978**, 193.
- [13] S. Kim, Lhim. D.C, *Bull Chem, SDoc.JPn.*, **1986**, 59, 3297.
- [14] A. Weissberger., E.S. Prabhakar., "Organic Solvents physical properties and Methods of purifications" 2nd ed., Inter science publisher Ltd., London, **1963**, 170.
- [15] J E Quinlan, E S Amis, *J Am Chem Soc* (**1955**) 77, 4187-4191.
- [16] E S Amis, Solvent effects on reaction rates and mechanism, academic press, New York, **1966**, 42.
- [17] S. Parimala Vaijayantyi, N. Mathiyalagan., *Der Chemica Sincia.*, **2011**, 2(3), 41.
- [18] J S Littler, W Awaters, *J Chem. Soc.*, **1959**, 1299.
- [19] Krantik Patil., *Der Chemica Sinica.*, **2011**, 2(6), 245.
- [20] A A Frost, R G Pearson, kinetics and Mechanism. Wiley Eastern New Delhi, **1970**.