IJARSCT

ISSN (Online) 2581-9429

International Journal of Advanced Research in Science, Communication and Technology (IJARSCT)

Impact Factor: 5.731

Volume 12, Issue 4, December 2021

Kinetic and Mechanistic study of Oxidative Transformation of Mandelic acid by Pyridiniumdichromate in DMF-Water Medium

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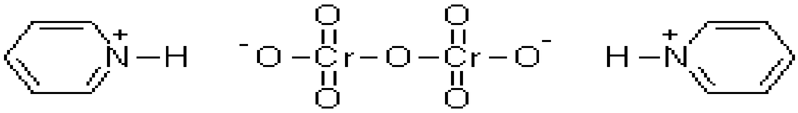
Abstract: *Oxidation of mandelic acid by Pyridinium dichromate was studied in the presence of perchloric acid in DMF-H_2O medium at 40 ºC. The kinetics of the reaction was followed spectrophotometrically at λ max = 355 nm. The reaction is unit dependence on each of PDC, [H^+] and [substrate]. Michaelis-Menten type kinetics was observed. The reactions were studied at different temperature [30, 35, 40, 45, 50 ºC] and activation parameters were computed.*

Keywords: Chromium, Michaelis-Menten, Oxidation of Mandelic acid, Pyridinium dichromate, Spectrophotometrically

I. INTRODUCTION

Vauquelin was a French chemist found Chromium in 1798[1]. This is located in group VI-B of the periodic table, it is a transition element having a ground state electronic configuration of (Ar) $3d^5$ $4s^1$. Recently, oxidation processes have fascinated a lot of researchers, especially with respect to selective and environmentally friendly Chromium (VI) reagents. Chromium (VI) is employed for oxidation of organic compounds and it is reduced to lower oxidation states.[2] The new reagent Pyridiniumdichromate (PDC) prepared is soluble in water, it is economic, stable, non-hygroscopic and easy to prepare in good yield (97%). The structural formula is represented as shown in Scheme 1 It is more stable and easily stored as compared to other Cr (VI) reagents.; we are particularly interested to see the mechanism of the oxidation of Mandelic acid by PDC in acidic DMF-Water medium.



Scheme 1: Pyridinium dichromate

II. MATERIAL AND METHODS

Pyridiniumdichromate was prepared by the method of Corey[3], and its purity was checked by iodometrically and melting point. Mandelic acids (A.R.grade) were used as supplied and purity was checked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout in the investigation. The rate measurements were carried out at 40ºC in $HClO_4$ under the condition [Mandelic acid] >> [PDC], in the solvent system of 50 % (v/v) DMF-H_2O.The progress of the reaction was followed by measuring the absorbance of PDC at 355 nm in one cm cell placed in the compartment of spectrophotometer. The kinetics run were followed for more than 70-80% completion of the reaction and first order kinetics were observed.

DOI: 10.48175/IJARSCT-2392

III. STOICHIOMETERY AND PRODUCT ANALYSIS

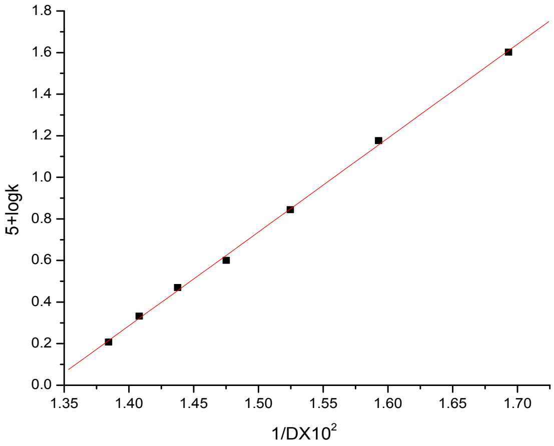
To determine the stoichiometry of a reaction a known slight excess of oxidant was added to a known amount of mandelic acid, by keeping all other condition of reaction is constant and after some hours the residual of oxidant was determined spectrophotometrically at 355nm. The product of oxidation was benzaldehyde and was identified by its 2, 4-dinitro phenyl hydrazine derivative. The stoichiometry of the reaction was found to correspond to the equation:
[Oxidant] [Mandelic acid]= [Benzaldehyde]

IV. EFFECT OF SUBSTRATE

The effect of mandelic acid concentration on the reaction rate was studied at constant [PDC], [$HClO_4$], temperature and DMF % [Table 1]. The reaction rate is increased with increasing of mandelic acid concentrations. When the logarithms of k_{obs} values were plotted against the logarithms of the [mandelic acid], (Figure 1) a linear plot was obtained. The plot of 1/kobs versus 1/[mandelic acid], was found to be linear with small positive intercept, Kinetic and mechanistic study of oxidative transformation of mandelic acid by indicates that Michaelis–Menten type kinetics is followed with respect to mandelic acid but the value of intercept is very small indicates that intermediate complex may be highly reactive so concentration will be very small at any time.

V. EFFECT OF DIELECTRIC CONSTANT

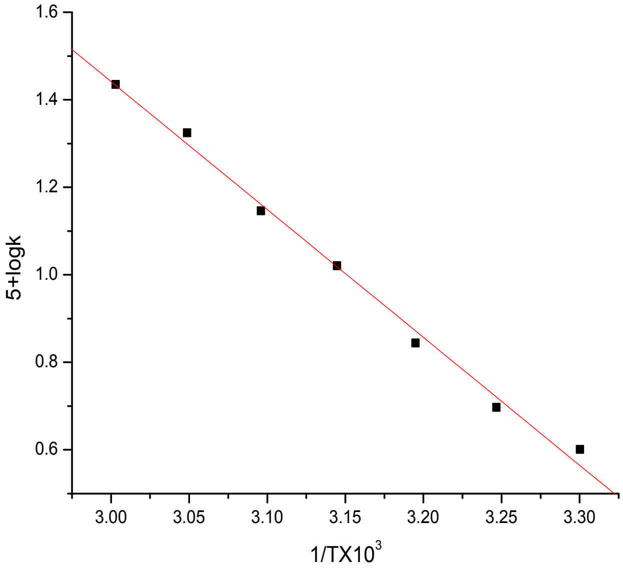
The influence of variation of dielectric constant of the medium was carried out by the changing DMF (% v/v) in the reaction medium, keeping other conditions remaining constants and the reaction rate was affected considerably. The rate of reaction increased with an increasing volume percentage of DMF [Table 1]. In the present investigation a plot of $\log k_{obs}$ vs. 1/D (Graph1) shows a straight line with a positive slope, clearly supporting that there is involvement of positive ion-dipole in the rate determining.



Graph 1

VI. EFFECT OF TEMPERATURE

The reaction was studied at different temperatures (303-333 K), keeping other experimental conditions constant. The rate constant of the reaction was found to increase with increasing temperature [Table 2]. From the Arrhenius plot of log k_{obs}versus 1/T (Graph 2) , activation energy and other thermodynamic parameters were calculated [Table 3]. The entropy of activation is negative as expected for bimolecular reaction. The complex formation is proved by the plot of 1/kobs against 1/ [mandelic acid]. It has been pointed out that if entropy of activation is negative and small the reaction will be slow.



Graph 2

VII. EFFECT OF PERCHLORIC ACID

In order to study the effect of [H^+] on the rate of the reaction, kinetic runs were carried out keeping the concentrations of all other reactants are constant and varying the [H^+] with $HClO_4$. From an inspection of the data present in [Table 1], it may be seen that the rate of the reaction increases with increase in [H^+]. When the logarithms of k_{obs} values were plotted against logarithms of the corresponding [H^+], a linear plot with a positive slope was obtained and indicate that first order reaction with respect to the hydrogen ion concentration.

Table 1: Effect of [Substrate], [$H^{+]}$, and Solvent [PDC]= 2 X 10^{-4}M T = 313 K

[Substrate] M	[$HClO_4$] X 10M	DMF % (v/v)	K X 10^5
0.002	3.3	50	6.98
0.003	3.3	50	10.14
0.004	3.3	50	13.92
0.005	3.3	50	17.56
0.006	3.3	50	21.32
0.007	3.3	50	24.56
0.002	3.3	50	6.98
0.002	5.2	50	11.56
0.002	6.6	50	14.82
0.002	8.5	50	19.56
0.002	9.9	50	23.56
0.002	11.1	50	26.12
0.002	3.3	30	2.95
0.002	3.3	20	2.15
0.002	3.3	10	1.61

Temperature	**KX 10^{-5}**
303	3.99
308	4.98
313	6.98
318	10.48
323	13.99
328	21.1
333	27.22

Table 2: Effect of Temperature (Substrate) 2X10-3M, [HClO4] 3.3X10-1M DMF 50% (v/v), [PDC] = 2 X 10-4 M T = 313 K

Substrate	**log A**	**Energy of activation ΔE kJ mol-^{1}**	**Entropy of activation ΔSJ mol^{-1}K^{-1}**	**Enthalpy of activation ΔH kJ mol**	**Free energy of activation ΔG kJ mol-1**
Mandelic acid	9.36	55.95	-69.69	53.34	21.86

Table 3: Thermodynamic Parameters

VIII. CONCLUSION

At room temperature the reaction between mandelic acid and oxidants are very slow in the low perchloric acid concentration in DMF-water medium. The oxidation of mandelic acid by oxidants are first order with respect to [oxidants], [mandelic acid] and [$HClO_4$]. The reaction was studied at different temperatures. In the temperature range of 303-333 K, Arrhenius equation is valid. The negative value of entropy indicates that the complex is more ordered than reactant.

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