


ORIGINAL RESEARCH PAPER
Chemistry
Kinetic and Mechanistic study of Oxidative Transformation of Citric acid by Pyridiniumdichromate in DMF-Water Medium
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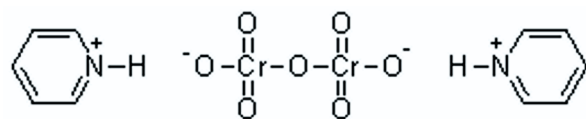
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ABSTRACT

Oxidation of citric acid by PDC was studied in the presence of perchloric acid in DMF- H₂O medium at 40 C. The kinetics of the reaction was followed spectrophotometrically at $\lambda_{\max} = 355 \text{ nm}$. The reaction is unit dependence on each of PDC, [H⁺] and [substrate]. Michaelis-Menten type kinetics was observed with different alpha hydroxy acids. The reactions were studied at different temperature [30, 35, 40, 45, 50 C] and activation parameters were computed.

I. INTRODUCTION

Chromium compounds have been widely used in aqueous and non- aqueous medium for the oxidation of a variety of organic compounds [1-3]. Chromium compounds especially Cr (VI) reagents have been proved to be versatile reagents capable of oxidizing almost all the oxidizable organic functional groups. The study of both very slow and very fast reactions can pose severe experimental problems. 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. A number of new Cr (VI) reagents like Tripropylammonium fluorochromate [4], Pyridiniumfluorochromate[5], Tetrabutylammoniumchlorochromate[6] and tetraethyl ammonium chlorochromate [7] have been used to study the kinetics and mechanism of various organic compounds. The ultimate goal of our study is to build our knowledge based on the oxidation behavior of citric acids with PDC. Kinetics of oxidation of methionine [8], oximes [9], unsaturated acids [10], cysteine [11], and alcohols [12] by pyridiniumchlorochromate were reported. Our literature survey reveals that the oxidation of alpha hydroxy acids by different oxidants has received limited attention; we are particularly interested to see the mechanism of the oxidation of citric acid by PDC in acidic DMF-Water media.



Pyridinium dichromate
Scheme 1

II. Materials And Methods

Pyridiniumdichromate was prepared by the method of Corey [13], and its purity was checked by iodometrically and melting point. Citric 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 40°C in HClO₄ under the condition [citric acid] >> [PDC], in the solvent system of 50 % (v/v) DMF-H₂O. 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 60-70% completion of the reaction and first order kinetics were observed.

3.1 Stoichiometry and product analysis

To determine the stoichiometry of a reaction a known slight excess of oxidant was added to a known amount of citric 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 Acetone and was identified by its 2, 4-dinitro phenyl hydrazine derivative. The stoichiometry of the reaction was found to correspond to the equation:


Effect of Substrate

The effect of Citric acid concentration on the reaction rate was studied at constant [PDC], [HClO₄], temperature and DMF % [Table 1]. The reaction rate is increased with increasing of Citric acid concentrations. When the logarithms of k_{obs} values were plotted against the logarithms of the [Citric acid], (Figure 1) a linearplot was obtained. The plot of $1/k_{\text{obs}}$ versus $1/[\text{Citric acid}]$, was found to be linear with small positive intercept, Kinetic and Mechanistic study of Oxidative Transformation of Citric acid by indicates that Michaelis-Menten type kinetics is followed with respect to Citric 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.

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]. A lot of theories have been given to quantitative explanation [14, 15] for the effect of dielectric constant (D) of the reaction medium on the kinetics of liquid phase reaction. For the limiting case of a zero angle of approach between two dipoles or ion-dipole system, Amis [16] had shown that in a linear plot of $\log k_{\text{obs}}$ vs. $1/D$. The positive slope indicates a positive ion-dipole reaction, while a negative slope indicates the involvement of two dipoles or a negative ion-dipole reaction. In the present investigation a plot of $\log k_{\text{obs}}$ vs. $1/D$ shows a straight line with a positive slope, clearly supporting that there is involvement of positive ion-dipole in the rate determining.

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 $\log k_{\text{obs}}$ versus $1/T$, activation energy and other thermodynamic parameters were calculated [Table 3]. The entropy of activation is negative as expected for bimolecular reaction. The negative value also suggests the formation of a cyclic intermediate from non-cyclic reactants in the rate determining step [17]. The complex formation is proved by the plot of $1/k_{\text{obs}}$ against $1/[\text{Citric acid}]$. It has been pointed out [18] that if entropy of activation is negative and small the reaction will be slow.

Effect of Perchloric acid

In order to study the effect of $[\text{H}^+]$ on the rate of the reaction, kinetic runs were carried out keeping the concentrations of all other reactants are constant and varying the $[\text{H}^+]$ 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 $[\text{H}^+]$. When the logarithms of k_{obs} values were plotted against logarithms of the corresponding $[\text{H}^+]$, 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], $[\text{H}^+]$, and Solvent [PDC]=1 X 10^3 MT = 313 K

[Substrate] X 10^3 M	[HClO ₄] X 10^1 M	DMF % (v/v)	KX 10^{-5}
2	3.3	50	6.9
3	3.3	50	8.89
4	3.3	50	11.15
5	3.3	50	4.85
6	3.3	50	16.9
7	3.3	50	19.91
2	3.3	50	6.9
2	5.2	50	10.93
2	6.6	50	13.95
2	8.5	50	17.12
2	9.9	50	20.98
2	11.1	50	22.98
2	3.3	30	11.89
2	3.3	20	3.01
2	3.3	10	1.01

Table 2 Effect of Temperature (Substrate) 2×10^3 M, [HClO₄] 3.3×10^1 M, DMF 50% (v/v), [PDC]= 2×10^4 MT = 313 K

Temperature	KX 10-5
303	3.12
308	4.5
313	6.9
318	10.37
323	12.18
328	18.77
333	22.59

Table No.3: Thermodynamic Parameters

Substrate	log A	Energy of activation ΔE kJ mol ⁻¹	Entropy of activation ΔS^\ddagger mol ⁻¹ K ⁻¹	Enthalpy of activation ΔH^\ddagger kJ mol ⁻¹	Free energy of activation ΔG^\ddagger kJ mol ⁻¹
Citric acid	4.88	35.1	-155.3	32.5	48.6

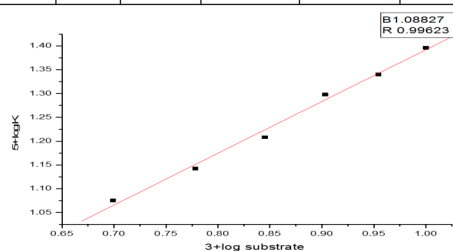


Figure 1

CONCLUSION

At room temperature the reaction between citric acid and oxidants are very slow in the low perchloric acid concentration in DMF-water medium. The oxidation of citric acid by oxidants are first order with respect to [oxidants], [citric acid] and $[\text{HClO}_4]$. 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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