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OXIDATION OF POLY (VINYL ALCOHOL) BY CHROMIC ACID IN PRESENCE OF MODERATELY STRONG ACID; A KINETIC AND MECHANISTIC APPROACH

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ABSTRACT

Kinetics and mechanism of oxidation of Poly (Vinyl Alcohol) (PVA), a synthetic polymer by Chromic Acid in presence of moderately strong acid (Monochloroacetic Acid) has been studied spectrophotometerically. The reaction was found to be acid catalyzed. Kinetics of oxidation of Monochloroacetic Acid by Chromic Acid observed first order reaction. Both kinetics and spectrophotometeric results indicates the formation of intermediate complex. The complex finally decomposes to give reaction product keto derivatives. A mechanism for the reaction is proposed based on the experimental observations. Kinetic parameters such as dielectric constant, temperature coefficient and pH values are calculated.

Keywords; Oxidation, Ostwald isolation, Kinetics, Reaction Mechanism, Poly (Vinyl Alcohol), Chromic Acid, Monochloroacetic Acid

I.INTRODUCTION

The science of macromolecule behavior in solution is a rapidly developing field with regard to their wide application in the preparation of colloidal and nano-size metal particles[22]. Stabilizers (polymers, surfactants and complexing agents) have a significant effect on orientation and interaction of metal particles[8]. It has been established that the most important role of the stabilizing polymer is to protect the nano partical from coagulation. Poly (Vinyl Alcohol) (PVA) is one of the favoured macromolecule for carrying out synthesis of polymer-nano particles composite[5]. Preparation of colloidal and none-metal particles depends upon the reduction of metal salt by suitable reducing agent as well as the presence of stabilizers[2].The compounds of Chromium (VI) pose serious dangers to biological systems, whereas those of Chromium (III) are relatively non-toxic. Chromic Acid in acidic media has been used extensively as a part a potent oxidant for studying the kinetics of many organic substrates. In some cases the mechanistic approach has been on intermediate complex formation and in others the results have been interpreted by a free radical mechanism in the absence of kinetic or spectrometric evidence. The mechanisms suggested by various authors are not uniform, indicating that a wide variety of mechanisms are possible depending on the nature of the reactive

species of Chromic Acid as well as the reductant substrates.PVA and its oxidation product (Poly Vinyl Ketone (PVK)) have reducing and complexing properties respectively, towards various transition metal ions. It has been established that the secondary – OH groups in the macromolecule skeleton are responsible for the oxidation of PVA by Chromic Acid. The oxidation product PVK has a high tendency to chelate with most of known polyvalent metal ions; it can be used as a chelating agent for removal of undesired poisonous toxic heavy metal cations from the environment, soil and wastewater etc.

II. MATERIALS AND METHOD

All the chemicals were of AnalaR grade, Poly (Vinyl Alcohol) (PVA) (Merck) was used without further purification. (Merck), Chromium Trioxide (CrO_3) (Qualigens), moderately strong acid i.e., Monochloroacetic Acid ($CH_2ClCOOH$) (Merck) and all other chemicals were used of highest purity available commercially. Carbon dioxide free deionized and doubly distilled water was used as solvent for preparation of stock solutions of PVA. Poly (Vinyl Alcohol) solution was prepared as descried literature method[12]. All other solutions were prepared in double distilled water. These stock solutions stored in dark bottles away from light to avoid the photo reduction. Solutions of oxidant and reaction mixtures containing known quantities of substrates and oxidant solutions were separately thermally equilibrated at desired temperature ($25 \pm 0.1\ ^oC$). The reaction was initiated by mixing the requisite amounts of the oxidant with the reaction mixture. The course of the reaction was followed by recording the decrease of absorbance (Optical Density - O.D.) of Cr (VI) by spectrophotometerically.

The possibility of formation of free radicals was examined by adding Acrylonitrile to the partially oxidized reaction mixture. There is no polymerization is occurred, so the reaction does not proceed by a free radical mechanism.

III.PRODUCT ANALYSIS

Under the kinetics conditions, the results show that PVA react with Chromic Acid to form an intermediate compound. Intermediate compound finally decompose slowly to give reaction product Poly (Vinyl Ketone) PVK. Separation of PVK oxidation product as a chelating agent takes place by mixing the Poly (Vinyl Alcohol) PVA with Chromic Acid .The reaction mixture was stirred for 24 hours at room temperature to complete oxidation of the alcoholic group of the substrate. The solution was treated overnight with excess of freshly prepared saturated 2,4-dinitrophenylhydrazine in 2M Hydrochloric Acid. The mixture was cool down for 24 hours, after that formed precipitate was filtered. The crude product was crystallized from Methanol, dried, weighted and placed into desicator for analysis. The Ketone was identified by infra red spectrum of the precipitate. It is well known that one-OH group of secondary alcohols oxidized in to carbonyl group (C=O) with the same number of Carbon atoms. Therefore, n - number of –OH group of Poly (Vinyl Alcohol) are responsible for the oxidation which leads to the formation of n - number of Keto-derivatives with the same number of Carbon atoms.

It was also observed that the Ketone does not undergo further oxidative degradation under our kinetic experimental conditions because a spot test[6] for carboxylic acid was negative.

In the oxidation of Poly (Vinyl Alcohol) PVA by Chromic Acid in presence of moderately strong acid[4] i.e. Monochloroacetic Acid (MCA) some of the kinetic runs performed by keeping the concentration of Chromic Acid and Poly (Vinyl Alcohol) constant at 0.0065 M and 0.0350 M respectively while the concentration of Monochloroacetic Acid had varied from 0.0250 M to 0.2000 M respectively. Dielectric constant of the reaction mixture decreases quite naturally, value of dielectric constant is determined and average value of dielectric constant is found to be order of 1.553.

Values of rate constant; pH and dielectric constants at 37°C are tabulated in table no.01 and temperature coefficient of all the runs in table no. 02.

Table No-01

S. No.	Concentration of MCA (M)	Rate Constant K x 10^{-3} min^{-1}	pH values	H^+ Concen-tration x10^{-2}	Dielectric Constant
1.	0.0000	2.6573	2.05	0.891	1.688*
2.	0.0250	4.9081	1.80	1.585	1.574
3.	0.0500	5.4108	1.74	1.800	1.571
4.	0.0750	5.8845	1.68	2.089	1.568
5.	0.1000	6.4230	1.62	2.399	1.561
6.	0.1250	6.9173	1.58	2.630	1.555
7.	0.1500	7.4038	1.54	2.884	1.548
8.	0.1750	7.9385	1.50	3.162	1.542
9.	0.2000	8.4375	1.47	3.388	1.534

*Not included in average

Table No-02

S. No	Concentrati-on of MCA (M)	Rate constants Kx10^{-3}at 27°C	Rate constants Kx10^{-3} at 37°C	Rate constants Kx10^{-3} at 47°C	Temperature Coefficient	
					k_{37} / k_{27}	K_{47} / k_{37}
1.	0.0000	1.3890	2.6573	5.2083	1.91	1.96
2.	0.0250	2.5300	4.9081	9.6690	1.94	1.97

3.	0.0500	2.7466	5.4108	10.6052	1.97	1.96
4.	0.0750	2.9720	5.8845	11.4748	1.98	1.95
5.	0.1000	3.2604	6.4230	12.5891	1.97	1.96
6.	0.1250	3.5292	6.9173	13.6271	1.96	1.97
7.	0.1500	3.7583	7.4038	14.4374	1.97	1.95
8.	0.1750	4.0093	7.9385	15.6388	1.98	1.97
9.	0.2000	4.2830	8.4375	16.7063	1.97	1.98

Fig. No-01

Variation of rate constant with the concentration of Monochloroacetic Acid cf Table No. - 01

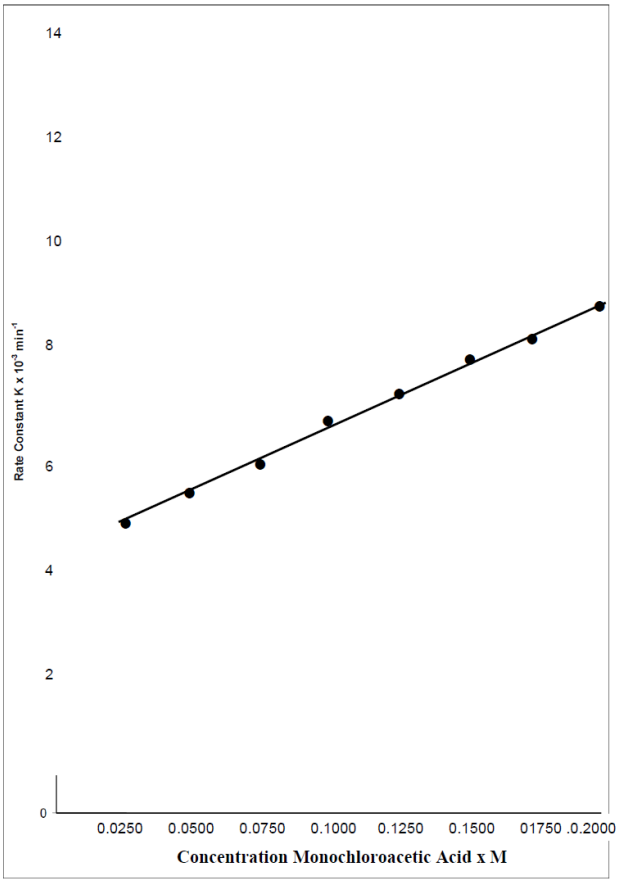
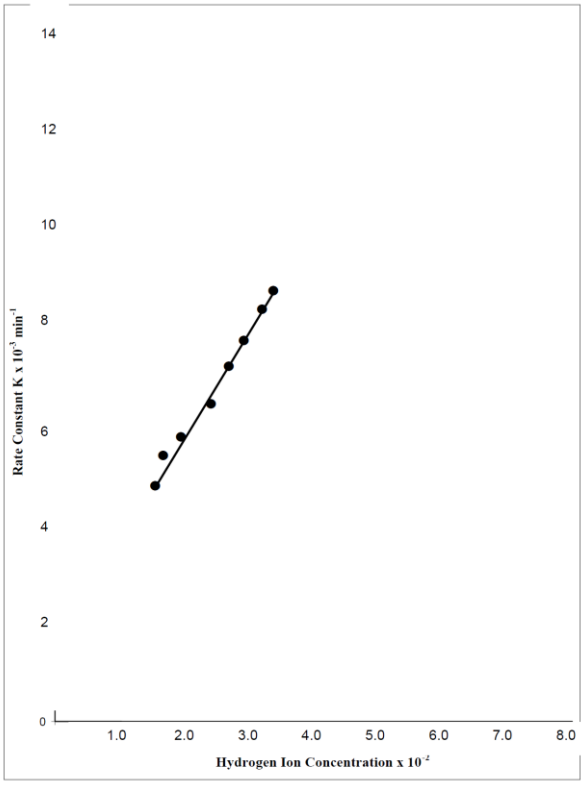


Fig. No.-02

Variation of rate constant with the Hydrogen ion concentration cf Table No. - 01



IV.RESULTS AND DISCUSSION

The kinetics of oxidation of Poly (Vinyl Alcohol) PVA by Chromic Acid in presence of moderately strong acid (Monochloeoacetic Acid) has been studied. The substrate (MCA) was varied in the range of 0.0250M to 0.2000M at 37^{o}C and keeping all other reactant concentration as constant and the rate were measured in Table No.01.Ostwald's[23] isolation method was used to determine the order of reaction. The rate of oxidation increased progressively on increasing the concentration of MCA, indicating first order dependence with substrate. The Fig.No.01 and 02 (both plots are linear) shows that oxidation reaction was first order dependence with respect to substrate, oxidant and Hydrogen ion concentration. The enhancement of the reaction rate with an increase in the amount of Monochloroacetic Acid generally may be attributed to two factors viz,(i) the increase in acidity accruing at constant Hydrogen ion concentration and (ii) the decrease in dielectric constant with an increase in the MCA content. The magnitude of this effect could be analyzed by suggesting that, a decrease in the dielectric constant of the medium would favour the dichromate form over the chromate form. The reaction is catalyzed by hydrogen ion. Increases in the rate shows positive catalysis which has been explained in several ways, the most important of these are, fast formation of the activated complex and less stability of an intermediate catalyst compounds, breaking of chain reaction, regenerancy of both the positive catalyst and the reactant from the intermediate compound and catalytic side reaction of decomposition. In the oxidation of PVA, it is observed that pH value of the reaction mixture do not change much by increasing the concentration of MCA. The effect of temperature was studied in the presence of MCA. Values of temperature coefficient tabulated in Table no.02.On the basis of table no.2, it is clear that the temperature coefficient is fairly constant as it is equal to two, so the

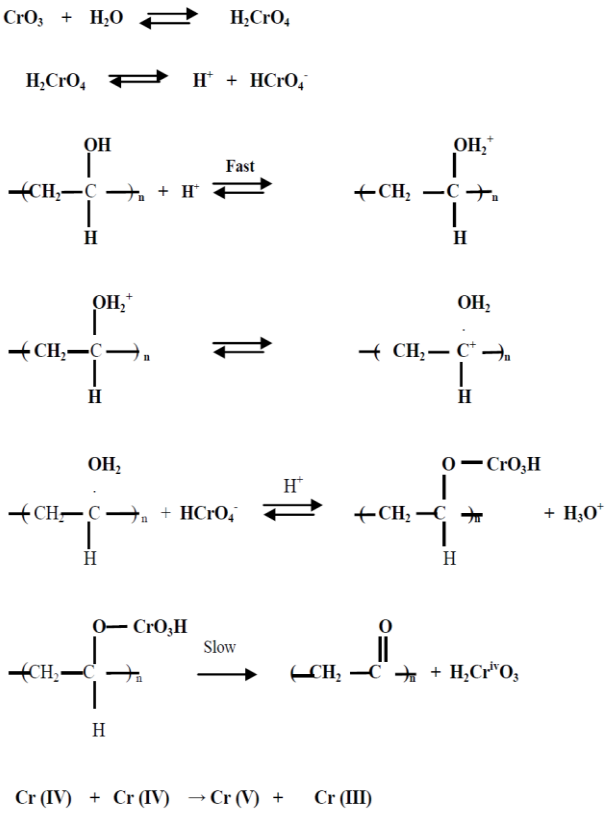
temperature effect is purely thermal. Hence, the reaction is normal, homogeneous and adheres to Arrhenius[3] equation.

Rate laws; The kinetic equation proposed for this reaction is given below;

$$\frac{-\,d\,[(HCrO_4^-)(MCA)]}{dt} = K\,[Cr\,(VI)]\,[MCA]\,[H^+]$$

The reaction was found to be first – order dependence with respect to oxidant and substrate. The reaction exhibited Michaelis- Menton[21] type kinetics with respect to substrate.

V.MECHANISM



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