



Research Article

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Kinetics of oxidation of isoamyl alcohol by zinc dichromate

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ABSTRACT

The kinetics of oxidation of isoamyl alcohol (IAA) by zinc dichromate (ZDC) has been studied in 40% acetic acid 60% water medium in the presence of perchloric acid at 303K. The reaction is first order each in zinc dichromate, isoamyl alcohol and hydrogen ion concentration. The rate of oxidation increases with decrease in dielectric constant of solvent suggests ion-dipole interaction. Increase in ionic strength by the addition of sodium perchlorate has no effect on the rate constant. There is no polymerization with acrylonitrile and absence of free radical was proved. 3-methyl-1-butanol has been identified as a product of oxidation. The rate of the reaction has been conducted at four different temperatures and activation parameters were calculated. From the observed kinetic results, a suitable mechanism with rate law has been proposed.

Keywords: Isoamyl alcohol, kinetics: oxidation and zinc 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]. Firouzabadi[8] showed that the chromium(VI) based oxidant viz, ZDC is a versatile and mild, efficient, stable reagent for the oxidation of organic compounds including alcohols, oximes, olefins, and aromatic hydrocarbons in aprotic organic solvents at room temperature. The literature survey reveals that the kinetics of oxidation of isoamyl alcohol by zinc dichromate has not yet been studied. Hence, in the present investigation, the oxidation of isoamyl alcohol by zinc dichromate in aqueous acetic acid medium and the correspondent mechanistic aspects are reported.

EXPERIMENTAL SECTION

Analar Grade of isoamyl alcohol was distilled and used. The zinc dichromate was prepared by literature method[9]. Acetic acid was purified[10] 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.

Kinetic Measurements

The kinetic studies were carried out under pseudo first order conditions in 40% acetic acid 60% water medium with the concentration of the isoamyl alcohol in large excess compared to that of the oxidant. All reactant solutions were placed in thermostated water bath for one hour to attain a temperature of 30 °C. Appropriate quantities of the reagent solutions were mixed in a 250cm³ conical flask already placed in the thermostated bath. The reaction rate was followed by measuring the decrease in absorbance at 470nm for up to 80% of the reaction by systronics UV-Visible spectrophotometer. The reaction was completed when the zinc dichromate solution turned from yellow to green. The reactions were followed by determining the concentration of the unreacted ZDC, for known intervals of time.

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 $\pm 2\%$

Stoichiometry and product analysis

The reaction mixture containing an excess of oxidant over isoamyl alcohol were kept at room temperature in the presence of perchloric acid for 24 h. Estimation of the unreacted oxidant showed that one mole of isoamyl alcohol consumed one mole of the oxidant.

Isoamyl alcohol(0.1mol) in acetic acid and ZDC(0.1mol) in water were mixed with perchloric acid and kept at room temperature for one day to ensure completion of the reaction. Then the reaction mixture was extracted with chloroform. The chloroform layer was then dried over anhydrous sodium sulphate and then evaporation of the chloroform layer gave the liquid product. From the infrared, GC-MS spectral data, it was conformed that the product obtained was 3-methyl-1-butanol.

RESULTS AND DISCUSSION

Oxidation of isoamyl alcohol by zinc dichromate has been conducted in 40 % acetic acid and 60% water medium at 303 K under pseudo – first order conditions and the observed results were discussed. The order of the reaction with respect to zinc dichromate was found to be unity as shown by the linearity of log absorbance verses time plot. (Table I). At constant concentration of substrate and perchloric acid, the increase in concentration of zinc dichromate did not affect the rate of reaction(Table I) The linear constancy in the value of k_1 irrespective of the concentration of the zinc dichromate confirms the first order dependence on zinc dichromate. The varying the concentration of isoamyl alcohol at 303 K and keeping all other reactant concentration as constant and the rates were measured (Table 1). The rate of oxidation increased progressively on increasing the concentration of isoamyl alcohol indicating first order dependence with substrate. The plot of $\log K_{obs}$ versus $\log [\text{isoamyl alcohol}]$ gave the slope of 0.90($r=0.999$), shows that the oxidation reaction was first order with respect to isoamyl alcohol.

The reaction was followed with different concentrations of perchloric acid and keeping all the concentrations as constant and rate were measured. The rate of the reaction increases with the increasing the concentration of H^+ . A plot of $\log K_{obs}$ versus $\log [H^+]$ gave a straight line with a slope of 0.89 which indicates first order with respect to hydrogen ion concentration. The change in ionic strength by the addition of sodium perchlorate has no effect on the rate constant (Table I) indicating the involvement of neutral molecule in the rate determining step.

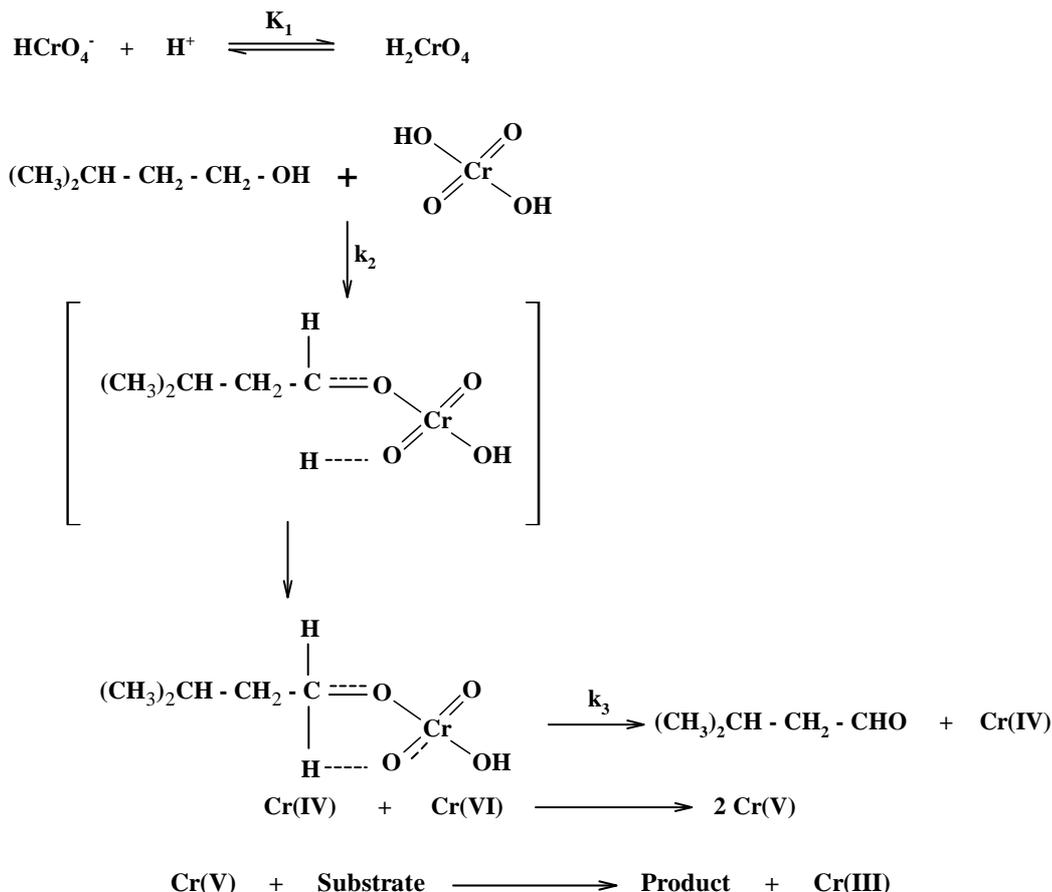
The effect of solvent composition on the reaction rate was studied by varying the concentration of acetic acid 40% - 55%. The reaction rate increases with the increase in the proportion of acetic acid in the medium (Table I), when the acetic acid content increases in the medium, the acidity of the medium increased where has the dielectric constant of the medium is decreased suggesting ion-dipole interaction[11,12]. The clear mixture containing isoamyl alcohol and zinc dichromate when allowed to stand with a drop of acrylonitrile[13] no turbidity is formed suggesting the non involvement of free radicals in this reaction.

The rate constants were measured at four different temperature and the activation parameters were computed from a plot of $\ln K_2/T$ versus $1/T$ of the Eyring's equation[14] and it was found to be linear. The negative value 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. The rate constant and thermodynamic parameters are tabulated in Table II.

Mechanism and Rate law

The order with respect both ZDC and Isoamyl alcohol was first order. The addition of sodium perchlorate or acrylonitrile had an insignificant effect on the rate of the reaction. The rate of the reaction decreases with addition of Al(III) indicate that the reaction proceed by three electron transfer process. The observed stoichiometry for the reaction was 1:1 and the oxidation product is 3-methyl-1-butanol. Based on the experimental results, a probable mechanism and rate law for the oxidation of isoamyl alcohol by zinc dichromate is given below in scheme I.

Mechanism



Scheme I

Rate Law:

The above mechanism leads to the following rate law

$$\text{Rate} = \frac{-d[\text{ZDC}]}{dt} = K_1 k_2 k_3 [\text{ZDC}] [\text{Sub}] [\text{H}^+]$$

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

Table I: Rate constant for the oxidation of isoamyl alcohol by zinc dichromate at 303K

[IAA] x 10 ¹ mol dm ⁻³	[ZDC] x 10 ³ mol dm ⁻³	[HClO ₄] x 10 ¹ mol dm ⁻³	% of acetic acid	[NaClO ₄] x 10 ⁴ mol dm ⁻³	[AlCl ₃] x 10 ² mol dm ⁻³	K x 10 ⁴ (s ⁻¹)
2.0 - 4.0	4.0	0.5	40	0.0	0.0	1.48 - 3.08
2.0	4.0 - 5.5	0.5	40	0.0	0.0	1.48 - 1.29
2.0	4.0	0.5 - 2.0	40	0.0	0.0	1.48 - 4.60
2.0	4.0	0.5	40 - 55	0.0	0.0	1.48 - 2.89
2.0	4.0	0.5	40	0.0 - 10.0	0.0	1.48 - 1.53
2.0	4.0	0.5	40	0.0	0.0 - 1.5	1.48 - 0.95

Table II: Dependence of rate constant on temperature and activation parameters

$$[\text{ZDC}] = 4.0 \times 10^{-3} \text{ mol dm}^{-3} \quad [\text{IAA}] = 2.0 \times 10^{-1} \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 10^{-1} \text{ mol dm}^{-3} \quad \text{Solvent} = 40\% \text{ CH}_3\text{COOH} - 60\% \text{ H}_2\text{O}$$

Temperature (K)	k ₁ x 10 ⁴ (s ⁻¹)	Activation Parameters
303	1.48	ΔH# = 36.09 kJmol ⁻¹
308	1.53	ΔS# = -289.4 JK ⁻¹ mol ⁻¹
313	2.09	ΔG# = 123.79 kJmol ⁻¹
318	2.99	E _a = 38.617 kJmol ⁻¹ at 303 K

CONCLUSION

The reaction is first order each in [substrate], [oxidant] and [H⁺]. The stoichiometry was found to be one mole of isoamyl alcohol consuming one mole of zinc dichromate. The main product of the reaction was found to 3-methyl-1-

butanal. The negative values of ΔS^\ddagger 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.

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