Oxidation of Methanol and Ethanol By Pyridinium Chlorochromate –Kinetics and Mechanism

Chemistry

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ABSTRACT

Kinetics of oxidation of some alcohols viz. methanol and ethanol by pyridinium chlorochromate (PCC) have been studied in acetonitrile medium in the presence of PTSA at 308K temperature. The reaction shows first order dependence with respect to concentration of substrate and [H+]. The rate of oxidation increases with decrease in dielectric constant of solvent. All experiments were perform at 360nm optical density. Activation parameter have been evaluated . A mechanism consistent with experiments observation has been proposed.

KEYWORDS

Oxidation, alcohols, PCC, etc.

Introduction:

The oxidation of primary alcohols to carboxylic acids is an important oxidation reaction in organic chemstry. The most common oxidants are PCC, PDC, and other Cr(VI) complexes.PCC is known as correy's[1] reagent is very useful oxidizing agent for oxidation of alcohol. It is used as an oxidant for oxidation of alcohols[2-4], amino acids[5-6], aldehydes[7-10], L-cysteine and aniline[11] etc. Oxidation of alcohol by PCC[12], Dl-alanine by QDC[13], DL-alanine and Glycine by PDC[14], L-isoleucine and L-valine by PCC[14], glycine and alanine by PDC[16] was studied. In this paper we describe kinetics of oxidation of methanol and ethanol By PCC in acetonitrile medium. PCC is orange yellow salt which converts in green colored sustains after reduction. As the number of carbon increases rate of oxidation increases.

Material and Method:

All chemicals were used of A.R. grade. Purity of alcohol was checked by b.p. PCC is prepared by improved method of Correy and Suggs described. Its purity was checked by m.p. Standard PCC solution was prepared in acetonitrile. All calibrated borosil glassware were used for experiments. Electronic thermostate was used for maintain particular temperature.

Kinetic measurements:

The solution of oxidant, alcohol in non-aqueous solvent in acidic medium follow Beer Lambert's law i.e. absorbance v/s Oxidant is a straight line. The reaction condition are arranged as pseudo first order. The reaction was carried in thermostate in glass stopper at constant temperature. Reaction was initiated by adding rapidly pre-determined volume of PCC solution in above reaction mixture. The optical density of the reaction mixture was measured at 360 nm by using Systronics VISISCAN 167 spectrophotometer.

Product analysis and stoichiometry:

Product analysis was carried out under kinetic conditions. The whole reaction mixture (after completion of reaction) was treated with 2,4-dinitrophenylhydrazine. A yellow-orange precipitate obtained which was filtered, washed, dried and weighed. Conformation of carbonyl (aldehyde/ketone) compound was done by melting point, IR and nitrogen percentage analysis of precipitate obtained. Cr(III) was confirmed by visible spectra of the reaction solution after completion of reaction. The stoichiometric equation is:

$$3RR'CH(OH) + 2Cr(VI) + H_3O^+ \longrightarrow RR'C = O + 2 Cr(III) + H_2O + 7H^+$$

There was no change in rate or absorbance on addition of stabilizer free acrylonitrile in nitrogen atmosphere. This confirms absence of free radical.

Effect of oxidant concentration:

The reactions are of first order with respect to PCC i.e. log absorbance versus time is straight line for more than 80% reaction. Further the value of k_{obs} is independent of the initial concentrations of PCC. (Table:-1)

Effect of substrate concentration:

The rate of oxidation increased on increasing the concentration of alcohols . Plot of log k_{obs} versus log [substrate] is a straight line (Table:-1). Plot of $1/k_{obs}$ versus $1/$[Substrate] gave linear line passing with very small intercepts nearly zero suggests that the rate does not obey Michalis Mentane type kinetics.

Effect of PTSA concentration:

The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying [H+]. A steady increase in oxidation rate with increase in the acidity of the medium suggests the formation of protonated PCC in the rate determining step. The plot of log kobs against log [H+] is linear therefore order of reaction is one with respect to [H+].

Effect of solvent composition :

At constant [H+] the rate of oxidation increases with increase in percentage of solvent composition [table 3].In other words a decrease in rate with increase in dielectric constant of solvent is observed. This is due to polar character of the transition state as compared to the reactants. The logarithm of the rate constant of a reaction between ions should vary linearly with the reciprocal of the dielectric constant if reaction involves ion-dipole type of interaction. As we increases the ratio of benzene, dielectric constant decrease so that rate of reaction increases.

Effect of temperature:

The rates of oxidation of alcohols were observed at various temperature and the reactions obey Arrhenius equation. Energy of activation was calculated by slopes of straight line obtained plotting log k versus $1/T$. Suggests the activation parameters for Ethanol and Methanol are calculated.

Discussion:

Kinetics of oxidation of Methanol and Ethanol by PCC was investigated at particular concentrations of the reactants. At low concentrations of PCC and when substrates are in large excess, the reaction is found to be first order in respect of PCC. Plot of log k_{obs} vs log [Substrate] gave a straight-line with slope ≈1 showed first order dependence over substrate. The thermodynamic parameters are mentioned in Table 5. The entropy of activation is negative as expected for a bimolecular reaction. The rate of oxidation increases with increase in PTSA concentration, increment in temperature ,and by decreasing the dielectric constant of solvent. Rate of Oxidation of Methanol is lower than Ethanol in every condition. This is in accordence with mol and no of carbon atom.

Energy of activation suggests C-H bond breaking in rate determining step and negative entropy of activation indicates formation of cyclic from non-cyclic or more polar than reactants structure formation. A study increase in the oxidation rate with an increase in the acidity of the medium suggests the formation of protonated PCC in the rate-determining step. The plot of log k against log [H+] is linear with a slope

of nearly one suggesting that one protons may involve in the rate-determining step.

The Mechanism of Chromate Oxidations:
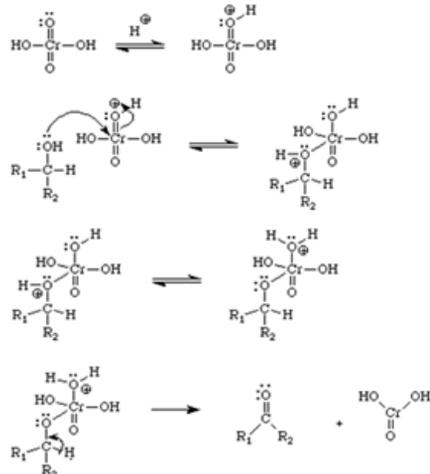
TABLE NO.:1 Effect of [substrate], [H$^+$] and Solvent [PCC]=2×10^{3}M T=308K

Substrate × 10^2 Mol dm^{-3}	[PTSA] × 10^2 Mol dm^{-1}	Solvent Acetonitrile + Benzene	k$_{obs}$ × 10^4,sec^{-1}	
			Methanol	Ethanol
2.0	3.0	0	2.51	4.99
3.0	3.0	0	3.41	6.62
4.0	3.0	0	3.97	7.30
5.0	3.0	0	4.57	7.97
6.0	3.0	0	5.05	8.16
7.0	3.0	0	5.37	8.73
8.0	3.0	0	5.44	9.37
9.0	3.0	0	5.65	9.68
2.0	2.0	0	1.16	3.87
2.0	3.0	0	2.51	5.60
2.0	4.0	0	3.92	6.69
2.0	5.0	0	5.65	7.66
2.0	6.0	0	6.20	8.42
2.0	3.0	0	2.51	3.88
2.0	3.0	10	3.6	5.48
2.0	3.0	20	4.07	6.31
2.0	3.0	30	4.70	7.32
2.0	3.0	40	5.67	8.31
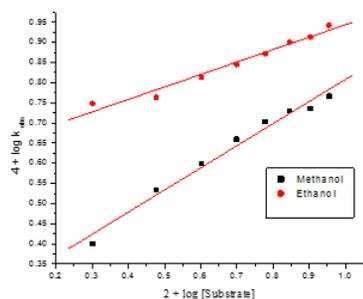
Figure1: Effect of Substrate Concentration

Table:2- Variation of rate with temperature [Alcohol]=2×10^{-2}M, [PTSA]=3×10^{-2}M, [PCC]=2×10^{-3}M

Temperature K	k obs × 10^4,sec^{-1}	
	Methanol	Ethanol
298	33.6	50.0
303	51.1	89.7
308	65.5	101.0
313	103.2	135.9
318	122.5	173.0

Table:3- Thermodynamic Parameters for various substrate

Substrate	Thermodynamic parameters				
	E$_a$ KJ mol^{-1}	log A	ΔS J mol^{-1}K^{-1}	ΔH KJ mol^{-1}	ΔG KJ mol^{-1}
Methanol	51.89	6.89	-98.63	37.4	67.84
Ethanol	45.76	7.92	-97.86	43.2	73.19

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