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OXIDATION STUDY OF 4-METHOXYBENZYL ALCOHOL BY CR (VI) OXIDANTS IN PARTIAL AQUEOUS MEDIUM- A COMPARATIVE STUDY

Chemistry

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ABSTRACT

Oxidation of 4-Methoxybenzyl alcohol by different Cr (VI) oxidants [PDC and PCC] has been studied in acetic acid-H2O medium in the presence of PTSA spectrophotometrically. The reactions are found first order with respect to both the oxidants, [H^+], and [substrate].Michaelis-Menten type kinetics is observed. The reaction rate decreases with increasing volume percentage of acetic acid in reaction mixture. The reaction was studied at different temperature [298-318 K] and activation parameters were computed. The oxidation product was identified as Cr (III) and corresponding aldehyde. The oxidation rate order was found with respect to the oxidants are: PCC > PDC

KEYWORDS

Oxidation, 4-Methoxybenzyl alcohol, PTSA, PCC and PDC.

1. INTRODUCTION

4-Methoxybenzyl alcohol (Anisyl alcohol) is used as a fragrance and flavouring. It occurs naturally but is produced by reduction of anisaldehyde.

Kinetics and mechanism of the oxidation of substituted benzyl alcohols by pyridinium chlorochromate studied by Banerji[1] et al. The oxidation of benzyl alcohol by pyridinium chlorochromate is first order with respect to both the oxidant and the alcohol.

Kinetics and mechanism of oxidation of substituted benzyl alcohols by polymer supported chromic acid was studied by Jawanjal and Hilage[2]. The reactions between substituted benzyl alcohols were found to proceed through ester formation.

Oxidation of benzyl alcohol by pyridinium dichromate in acetonitrile, using the para/meta ratio of substituent effects was recently studied by Kabilan et al[3]. Rate constants were measured for the oxidation reaction of benzyl alcohol and twenty-five ortho-, meta- and para-monosubstituted derivatives.

Banerji[4] studied the kinetics and mechanism of the oxidation of substituted benzyl alcohols by pyridinium chlorochromate. The oxidation of benzyl alcohol by pyridinium chlorochromate is first order with respect to both the oxidant and the alcohol.

Oxidation of benzyl alcohol and cyclohexanol along with some aliphatic primary and secondary alcohol in 30% dioxane and water (v/v) medium was studied using PDC as oxidant by Hiran et al.[5].

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 [6].

2. MATERIALS AND METHODS:

Oxidants Pyridiniumchlorochromate [7] and Pyridiniumdichromate [8] were prepared by the method describe in the literature. The purity of the oxidants was checked by spectral analysis. 4-Methoxybenzyl alcohol (A.R.grade) was used as supplied. All other chemicals used in this investigation were of analytical reagent grade.

The rate measurements were carried out at 303 K in PTSA under the condition [substrate] >>[oxidants], in the solvent system of 50-50 % (v/v) Acetic acid-H_2O. The reaction was initiated by mixing a calculated amount of thermostatted oxidant in to the reaction mixture. The progress of the reaction was followed by measuring the absorbance of oxidants at 380 nm in one cm cell placed in the thermostatted compartment of Systronics VISISCAN -167 spectrophotometer.

The kinetics run were followed for more than 60-70% completion of the reaction and good first order kinetics were observed.

3. RESULTS AND DISCUSSION:

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 alcohol by keeping all other condition of reaction is constant and after some hours the residual of oxidant was determined spectrophotometrically at 380 nm. The product of oxidation was corresponding aldehyde and was identified by its 2, 4-dinitro phenyl hydrazine derivative.

3.2 Effect of Oxidants:

Under experimental condition, the first -order rate constants are independent of the initial concentration of the oxidants when varied in the range (0.5 – 4.0) X 10^{-3} mol/dm^{-3} at 303K. The reactivity of oxidation of alcohol towards the oxidants was found to be PDC < PCC.

3.3 Effect of Substrate:

The reaction rate is increase with increasing of alcohol concentration with both the oxidants. A plot of log k against log [subs] gives a straight line [fig-1] with respect to three oxidants. This revealed that the rate of oxidation is first order with respect to substrate. It has been found that the plot of (1/k) versus (1/ [subs]) is straight line with small intercept, indicates that Michaelis- Menten type kinetics is observed with PDC and PCC. The variation of the rate of oxidation of alanine with oxidants can be expresses as-

$$d\,[\text{oxidants}]\,/\,dt = k\,[\text{alcohol}]\,[\text{oxidants}]\,/\,K_M + [\text{alcohol}]$$

3.4 Effect of [H^+] ion:

Keeping all other reactants constant and varying the [H^+] with PTSA 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^+], linear plots with a positive slope was obtained and indicate that first order reaction with respect to the hydrogen ion concentration. Under the present experimental conditions (2-7 x10^{-3} mol dm^{-3} [H^+]), the protonated chromium (VI) is presumed to be the reactive species since the rate increases with increase in [H^+].

3.5 Effect of solvent composition:

The influence of variation of dielectric constant of the medium was carried out by the changing acetic acid (% v/v) in the reaction medium, keeping other conditions remaining constants and the reaction rate was affected considerably. The rate of reaction decreased with an increasing volume percentage of acetic acid [table 1], suggesting that a low dielectric medium favors the oxidation. A plot of log k against 1/D is linear with a positive slope for alcohol under study. This indicates an ion-dipole type of interaction in the rate –determining step.

3.6 Effect of Temperature:

The reaction was studied at different temperatures (298-318 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, activation energy and other thermodynamic parameters was 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. The complex formation is proved by the plot of 1/k_{obs} against 1/ [alcohol]. It has been pointed out that if entropy of activation is negative and small the reaction will be slow.

4. Conclusion:

At room temperature the reaction between substrate and oxidants are very slow in the low PTSA concentration in acetic acid-water medium. The oxidation of 4-Methoxybenzyl alcohol by oxidants are first order with respect to [oxidants], [substrate] and [PTSA]. The reaction was studied at different temperatures. In the temperature range of 298-318 K, Arrhenius equation is valid. The negative value of entropy indicates that the complex is more ordered than reactant. The description of the mechanism is consistent with all experimental evidence. Among two Cr (VI) oxidants alcohol oxidized faster with PCC.

TABLE NO. 1 Effect of [Substrate], [H^+] and Solvent [PDC] = 2 x 10^{-3} M T = 303 K

[Subs] x10^2 M	[PTSA] x 10^3	Acetic acid % v/v	k_{obs} x 10^4	
			PDC	PCC
2	3.	50	5.26	6.41
3	3	50	7.57	9.23
4	3	50	10.29	12.55
5	3	50	12.14	14.81
6	3	50	15.42	18.81
7	3	50	18.11	22.09
2	2	50	3.99	4.74
2	3	50	5.25	6.24
2	4	50	6.67	7.93
2	5	50	7.87	9.36
2	6	50	9.11	10.84
2	7	50	11.02	13.11
2	3.	30	4.28	5.09
2	3	40	5.25	6.24
2	3	50	6.41	7.62
2	3	60	7.82	9.30
2	3	70	9.54	11.35

TABLE NO. 2[SUBSTRATE]= 2 X 10^{-2} M [PTSA] =3 X 10^{-3} M [Oxidant] = 2 x 10^{-3} M [Acetic acid]= 50 %

Temperature In K	k_{obs} x 10^4	
	PDC	PCC
298	**4.28**	**5.09**
303	**5.25**	**6.24**
308	**6.41**	**7.62**
313	**7.82**	**9.30**
318	**9.54**	**11.35**

TABLE NO. 3 THERMODYNAMIC PARAMETERS [Alcohol]= 2 X 10^{-2} M [PTSA] =3 X 10^{-3} M [Oxidant] = 2 x 10^{-3} M [Acetic acid] = 50 %

Oxidants	log A	$\Delta E_a^{\#}$ kJ mol^{-1}	$\Delta S^{\#}$ J $mo^{l-1}K^{-1}$	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}
PDC	6.36	31.40	-127.13	28.88	69.88
PCC	5.77	27.57	-138.23	25.05	69.38

Fig-1 Variation of rate with substrate concentration by different oxidants

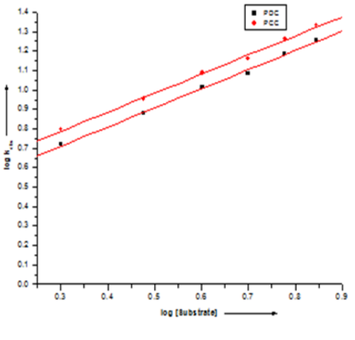
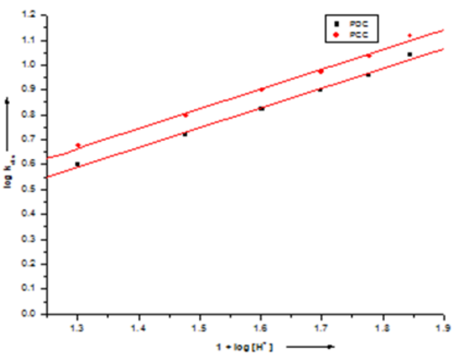


Fig-2 Variation of rate with [H+] by different oxidants



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