ORIGINAL RESEARCH PAPER

Volume-7 | Issue-1 | January-2018 | PRINT ISSN No 2277 - 8179

INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

COMPARATIVE STUDY OF OXIDATION OF BENZYL ALCOHOLS BY DIFFERENT CR (VI) OXIDANTS IN ACETIC ACID- H2O MEDIUM

Chemistry

Akshi Bansal* Research Scholar, Pacific academy of Higher Education and Research University, Udaipur *Corresponding Author

B. K. Dangarh Asstt. Prof. of Chemistry, Govt. P. G. College, Neemuch, M.P.

ABSTRACT

A comparative study of oxidation of Benzyl alcohol by different Cr (VI) oxidants [PCC and PDC] has been studied in acetic acid -H_2O 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] & the activation parameters were computed. The oxidation product was identified as Cr (III) and Benzaldehyde. The oxidation rate order was found with respect to the oxidants are: PCC > PDC

KEYWORDS

Oxidation, Benzyl alcohol, PTSA, Oxidants.

1. INTRODUCTION

Benzyl alcohol is used in paint strippers, especially when combined with compatible viscosity enhancers to encourage the mixture to cling to painted surfaces. It is a precursor to a variety of esters, used in the soap, perfume, and flavor industries.

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.

Jain et al.[2] studied the kinetics of oxidation of some aliphatic primary and secondary alcohols viz. ethanol, propan-1-ol, propan-2-ol, butan-1-ol, butan-2-ol and 2- methyl butanol by pyridinium chlorochromate (PCC) in water and perchloric acid medium.

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 B.L. Hiran and Kailashchand[3].

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[4].

2. MATERIALS AND METHODS

Oxidants Pyridiniumchlorochromate [5] and Pyridiniumdichromate [6] were prepared by the method describe in the literature. The purity of the oxidants was checked by spectral analysis. Benzyl 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 alanine, 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.

The stoichiometry of the reaction was found to correspond to the equation:

$$\underset{\text{[Oxidant]}}{2Cr(VI)} + 3C_6H_5CH_2OH + 3H_2O \rightarrow \underset{\text{[Benzaldehyde]}}{3C_6H_5CHO} + 2Cr(III) + 6H^+$$

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 Benzyl alcohol towards the oxidants was found to be PDC < PCC.

3.3 Effect of Substrate

The effect of substrate concentration on the reaction rate was studied at constant [Oxidants], [PTSA], and temperature [table 1]. 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 reaction proceeds through the formation of a complex between the oxidant and substrate.

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 Pyridine

It has been observed that there no effect of addition of pyridine on rate of reaction, indicating that oxidants are not hydrolyzed in the reaction. Further this shows stability of oxidants in the conditions understudy.

3.7 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[fig-2], 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/kobs 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 alcohol and oxidants are very slow in the low PTSA concentration in acetic acid-water medium. The oxidation of benzyl 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 benzyl alcohol oxidized faster with PCC.

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

[Subs] x10^2 M	[PTSA] x 10^3	Acetic acid % v/v	k_{obs} x 10^4	
			PDC	PCC
2	3.	50	2.47	3.01
3	3	50	4.69	5.72
4	3	50	7.98	9.73
5	3	50	12.71	15.50
6	3	50	17.67	21.55
7	3	50	23.82	29.06
2	2	50	1.55	1.89
2	3	50	2.47	3.01
2	4	50	3.64	4.44
2	5	50	5.05	6.16
2	6	50	6.70	8.17
2	7	50	8.94	10.90
2	3.	30	8.98	10.95
2	3	40	4.79	5.84
2	3	50	2.47	3.01
2	3	60	1.32	1.61
2	3	70	0.67	0.82

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	**1.65**	**2.01**
303	**2.47**	**3.01**
308	**3.34**	**4.07**
313	**4.58**	**5.58**
318	**6.08**	**7.41**

TABLE NO. 3 THERMODYNAMIC PARAMETERS [Benzyl 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-}1K^{-1}	$\Delta H^\#$ kJ mol^{-1}	$\Delta G^\#$ kJ mol^{-1}
PDC	9.34	50.73	-69.50	48.21	71.78
PCC	8.47	44.99	-86.55	42.47	71.12

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

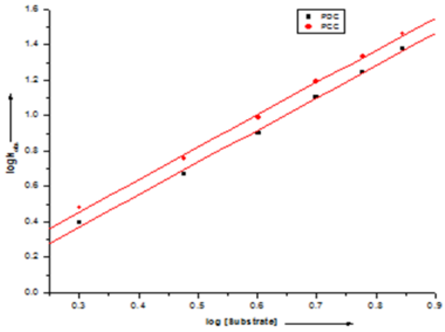
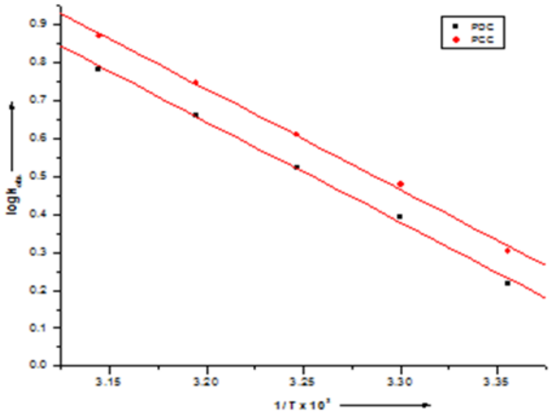


Fig-2 Variation of rate with Temperature by different oxidants



REFERENCES:

1. Banerji K. K.: J. Chem. Soc., Perkin Tran.; (1978), 2, 639-641.
2. Jain S., Hiran B.L. and Bhatt C.V.: E-J. Chem.; (2009), 6 (1) 237-246.
3. Kailash chand: Ph.D. Thesis, M.L.S. University Udaipur, India (2009).
4. Motwani Kirti, Dangarh B.K.and Shorgar Neetu : International Journal of Scientific Research ; (2017), 6 (10) 583-584.
5. Core E.J. and Suggs W.T.; Tetrahedron Lett., 31, 2647, (1975).
6. Corey E.J. and Shmidt G.; Tetrahedron Lett., 399, (1979).