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OXIDATIVE TRANSFORMATION OF PROPAN-1-OL WITH PCC IN ACETONITRILE

Chemistry

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ABSTRACT

Kinetic mechanism was investigated for oxidative transformation of propan-1-ol is done by pcc in acetonitrile. PTSA was used as donner of [H+] and reaction was carried out at 308 °C temperature. Rate of reaction was examined for various concentration of PTSA, substrate. Reaction rate was also accomplished for different solvent compositions. The change in dielectric constant can vary the rate. All experiments were operated at 360 nm optical density. Thermodynamic parameters were evaluated and a mechanism was proposed. Propan-1-ol gives corresponding aldehyde after oxidation.

KEYWORDS

PCC, oxidation, reaction rate, propan-1-ol etc.

Introduction-

Oxidation reactions are paid too much attention by scientists because of its importance in various life processes. Alcohols are a substance for invention from years because its uses and applications at various places. So, oxidation of alcohols is investigated many times. Cr based oxidizing reagents have proved as remarkable for oxidizing alcohols as PCC, PDC, QDC, QxDC, MDC and many more. PCC was developed by Correy[1], it was uses by although its was reported in 1899 but firstly used in 1975[2]. Commercially PCC is used as good oxidizing regents. Oxidation of tertiary alcohols by pyridinium chlorochromate (PCC) studied by Lauren A. Beihoffer et.al. [3] Oxidation of alcohols by pcc generally carried out in Dichloromethane[4,5,6]. Oxidation of alcohols by pcc generally carried out in Dichloromethane. A typical PCC oxidation involves addition of an alcohol to a suspension of PCC in dichloromethane.[6][7][8] Oxidative transformation of alcohol by PCC[7], Dl-alanine by QDC8, DL-alanine and Glycine by PDC[9], L-isoleucine and L-valine by PCC[10], glycine and alanine by PDC[11] was investigated.

Material and Method: -

All regents were A.R. grade which we use for analysis. Propanol was used with 99.99% pure. PTSA was used as a source of [H^+]. All experiments were carried out at 308 k temperature. Optical density was 360 nm for each analysis. Purity of alcohol was checked by melting point- 97°C. PCC was synthesized by method given by Correy and Suggs. Orange substance (PCC) was collected over sintered glass funnel dried for 1 Hour in vacuum. Purity was checked by m.p. All solutions were made in acetonitrile. PCC is highly soluble in DMF, DMSO and many other solvents. All glass wares were of borosil. Thermostat and magnetic stirrer was maintained the temperature.

Kinetic measurements: -

Beer Lambert's law was followed by reaction mixture of Oxidant, Alcohol in Non-Aqueous solvent in acidic medium. So, plot between absorbance v/s Oxidant gives a straight line. Concentration of PCC was taken ten times more than alcohol so reaction order observed pseudo first order. The was carried out at constant temperature by thermostat in glass stopper. Reaction mixture was prepared by dissolving required amount of substance in acetonitrile. Same solvent for used for PTSA and PCC. All reaction required solutions were kept in a thermostatic bath for maintain a constant temperature 308K (±0.1) for reaction. Alcohol, PTSA and acetonitrile was kept at constant temperature and required amount of PCC was added in this solution of initiate the reaction. The optical density of the reaction mixture was fixed by spectrophotometer at 360 nm by using **Systronic VISISCAN 167** spectrophotometer.

Product analysis and stoichiometry: -

Product analysis was investigated under kinetic conditions. Excess volume of alcohol over PCC was taken in a typical experiment, and kept for reaction completion. Moles of PCC consumed were determined by difference in absorbance before and after completion of reaction. After completion of reaction this reaction mixture was treated with 2,4-dinitrophenylhydrazine. A yellow-orange precipitate obtained which was filtered, washed, dried and weighed. From the weight of the precipitate, moles of carbonyl compound (product) were determined and hence stoichiometry was confirmed. 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. No variation in rate was observed for stabilizing free acrylonitrile in nitrogen atmosphere. It proves that free radicals are absent in is reaction.

Effect of oxidant concentration: -

The order of reaction observed first with PCC i.e. plot between log absorbance versus time gives straight line for more than 80% reaction. Further the value of k_{obs} is independent of the initial concentrations of PCC.

Effect of substrate concentration: -

The rate of oxidation enhanced with the concentration of alcohol. Plot between log k_{obs} versus log [substrate] observed as a straight line. Plot of 1/k_{obs} versus1/[Substrate] gave linear line passing through origin or negligible intercepts near to zero suggest that the rate does not follow Michalis-Mentane type kinetics.

Effect of PTSA concentration: -

The effect of hydrogen ion on rate of oxidative transformation was observed for varying concentration of H^+ and keeping concentration of another reactants constant. Since there is no effect of ionic strength on reaction rate therefore ionic strength was not kept constant in this experiment. Enhancing the concentration of acid increases the rate it suggests the formation of protonated PCC in the rate determining step. The plot of log kobs against log [H^+] obtains linear.

Effect of solvent composition: -

Rate of oxidative transformation enhanced with increasing the percentage composition of benzene in acetonitrile. In other words, rate of oxidation increases with decrease in dielectric constant. 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 increase the ratio of benzene, dielectric constant decrease so that rate of reaction enhanced.

Effect of temperature: -

Rate of oxidation of 1-propanol was investigated at various temperature, the reaction follows Arrhenius equation. Energy of activation was calculated by slopes of straight line obtained plotting log k versus1/T. Suggests the activation parameters for butan-1-ol are calculated.

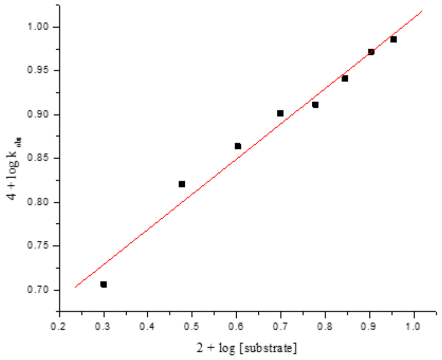
TABLE NO.:1
Effect of [substrate], [H^+] and Solvent

[PCC]=2×10^{3}M T=308K

Substrate × 10^2 Mol dm^{-3}	[PTSA] × 10^2 Mol dm^{-}1	Solvent Acetonitrile + Benzene	Propan-1-ol
2.0	3.0	0	4.33
3.0	3.0	0	5.65
4.0	3.0	0	7.02
5.0	3.0	0	8.21
6.0	3.0	0	9.67
7.0	3.0	0	10.69
8.0	3.0	0	11.16
9.0	3.0	0	11.96
2.0	2.0	0	3.53
2.0	3.0	0	4.33
2.0	4.0	0	7.01
2.0	5.0	0	9.85
2.0	6.0	0	11.01
2.0	3.0	0	4.33
2.0	3.0	10	6.74
2.0	3.0	20	7.46
2.0	3.0	30	8.12
2.0	3.0	40	9.7

Thermodynamic parameters

Substrate	Thermodynamic parameter				
	E_a KJ mol^{-1}	Log A	ΔS J mol^{-1}K^{-1}	ΔH KJ mol^{-1}	ΔG KJ mol^{-1}
Propan-1-ol	40.02	6.89	-98.63	37.46	67.84



Plot of substrate variation

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