ORIGINAL RESEARCH PAPER
Volume-6 | Issue-9 | September-2017 | ISSN No 2277 - 8179 | IF : 4.176 | IC Value : 78.46
INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

# KINETICS AND MECHANISM OF OXIDATIVE TRANSFORMATION OF SOME ALCOHOLS BY PYRIDINIUMCHLOROCHROMATE IN ACETONITRILE

**Chemistry**

**Kirti Motwani** Research scholar Pacific University, Udaipur
**B K Dangarh** Asst. Professor, Govt. P.G. College, Neemuch (M.P.)
**Neetu Shorgar** Asst. Professor, Pacific University, Udaipur(Raj.)

## ABSTRACT

The present paper describe the kinetic study of oxidation of butan-1-ol and butan-2-ol by Pyridiniumchlorochromate at 308K spectophotometrically in acetonitrile. The reaction shows first order dependence with respect to [PCC],[Substrate] and [H+]. The rate of oxidation increases with decrease in dielectric constant of solvent. Activation parameter have been evaluated. A mechanism consistent with experimental observation has been proposed.

## KEYWORDS

Kinetics, alcohol, PCC, PTSA.

### Introduction:-

Selective oxidation of primary alcohols to aldehydes can be easily accomplished by using chromium (τI) reagents. The convenient reagent for this conversion is pyridiniumchlorochromate1. It is used as an oxidant for oxidaion of alcohols2-4, amino acids5-6, aldehydes7-10, and aniline11 etc. Oxidation of alcohol by PCC12,Dl-alanine by QDC13,DL-alanine and Glycine by PDC14,L-isoleucine and L-valineby PCC14, glycine and alanine by PDC16 was studied. In this paper we describe kinetics of oxidation of butan-1-ol and butan-2-ol by PCC in acetonitrile.

### Material and Methods:-

All chemicals were used of A.R. grade. Alcohols are used V/V 99.99% and acetonitrile was used as non –aqueous solvent. PTSA is used for acidic medium. Purity of alcohol checked by B.P. PCCis prepared by improved method of Corey and Suggs. It's purity was checked by m.pt.. Standard PCC solution was prepared in acetonitrile The solution of oxidant, alcohol in non-aqueous solvent in acidic medium follow Beer Lambert's law i.e. plot of absorbance v/s oxidant is a straight line. The reaction condition are arranged as pseudo first order. The reaction mixture was prepared by mixing the required amount of substrate , PTSA, acetonitrile, and allowed it in a thermostatic bath for maintained at constant temperature(308K ±0.1°) for reaction. Reaction was initiated by adding rapidly predetermined volume of PCC solution in above reaction mixture. The optical density of the reaction mixture was measured by spectrophotometer at 360 nm by using Systronics VISISCAN 167 spectrophotometer.

### Product analysis and stoichiometry:-

Product analysis was carried out under kinetic conditions. After completion of reaction, whole reaction mixture 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 points, and IR. Cr(III) was confirmed by visible spectra of the reaction solution after completion of reaction. The stoichiometric equation is:

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

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

### 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 kobs 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 kobs versus log [substrate] is a straight line, i.e. first order with respect to substrate. Plot of 1/kobs versus1/[Substrate] gave linear line passing through origin or very small intercepts nearly zero suggest that the rate does not obey Michalis Mentan type kinetics. [Table-1]

### Effect of $[H^+]$concentration

The effect of hydrogen ion concentration on the rate of the oxidation was studied by varying $[H^+]$ while keeping the concentration of other reactants constant. Since there is no effect of ionic strength on reaction rate therefore ionic strength was not kept constant. 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 the order of reaction with $[H^+]$ is one.

### Effect of solvent composition :-

At constant $[H^+]$ the rate of oxidation increases with increase in percentage of benzene in acetonitrile. 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 that's why 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 versus1/T table-2. The activation parameters for both th4e alcohols are calculatedtable-3.The rate constant were measures with the range of 298-318K.

### Discussion:-

The kinetics of butan-1-ol and butan-2-ol was studied in acetonitrile. The rate of oxidation increases by increasing substrate concentration and taking PCC, PTSA constant. The reaction is found to be first order in respect of PCC. Plot of log kobs vs. log [Substrate] gave a straight-line with slope ≈1 showed first order dependence over substrate. The rate of reaction also increases with increasing PTSA concentration and temperature. The rate of reaction decreases with increasing dielectric constant of solvent by varying the solvent by mixing.

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 kobs against log $[H^+]$ is linear with a slope of nearly one suggesting that one protons may involve in the rate-determining step.

Above description conclude that rate of reaction will vary with every condition change. The position of alcohol group can give a change in the rate of oxidation as observed in the experiment.

## Mechanism:

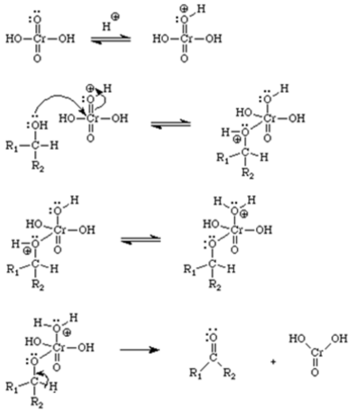

**TABLE-1 Effect of [substrate], $[H^+]$ and Solvent [PCC]=$2\times10^3$ M T=308K**

| Substrate × 102 M | [PTSA] × 102 M | % 0f Benzene | kobs × 104sec-1 | |
|---|---|---|---|---|
| | | | Butan-1-ol | Butan-2-ol |
| 2.0 | 3.0 | 0 | 4.33 | 4.45 |
| 3.0 | 3.0 | 0 | 5.65 | 6.42 |
| 4.0 | 3.0 | 0 | 7.02 | 7.72 |
| 5.0 | 3.0 | 0 | 8.21 | 9.32 |
| 6.0 | 3.0 | 0 | 9.67 | 9.98 |
| 7.0 | 3.0 | 0 | 10.69 | 10.89 |
| 8.0 | 3.0 | 0 | 11.16 | 11.78 |
| 9.0 | 3.0 | 0 | 11.96 | 12.38 |
| 2.0 | 2.0 | 0 | 3.53 | 3.32 |
| 2.0 | 3.0 | 0 | 4.33 | 4.45 |
| 2.0 | 4.0 | 0 | 7.01 | 7.42 |
| 2.0 | 5.0 | 0 | 9.85 | 10.36 |
| 2.0 | 6.0 | 0 | 11.01 | 11.86 |
| 2.0 | 3.0 | 0 | 4.33 | 4.45 |
| 2.0 | 3.0 | 10 | 6.74 | 7.04 |
| 2.0 | 3.0 | 20 | 7.46 | 7.74 |
| 2.0 | 3.0 | 30 | 8.12 | 8.61 |
| 2.0 | 3.0 | 40 | 9.7 | 11.16 |

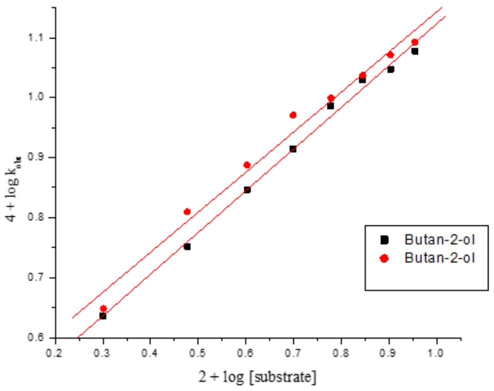

**Figure1: Effect of Substrate Concentration**

Table:2- **Variation of rate with temperature**

[Alcohol]=2×10-$^2$M, [PTSA]=3×10-$^2$M, [PCC]=2×10-$^3$

| Temperature K | $k_{obs}$ × $10^4$sec-$^1$ | |
|---|---|---|
| | Butan-1-ol | Butan-2-ol |
| 298 | 56.4 | 64.4 |
| 303 | 82.4 | 83.0 |
| 308 | 112.7 | 115.9 |
| 313 | 143.8 | 156.1 |
| 318 | 211.2 | 219.5 |

**Table:3- Thermodynamic Parameters**

| Substrate | Ea KJ mol-$^1$ | log A | ΔS J mol-1K-$^1$ | ΔH KJ mol-$^1$ | ΔG KJ mol-$^1$ |
|---|---|---|---|---|---|
| Butan-1-ol | 50.36 | 8.58 | -84.63 | 47.8 | 73.87 |
| Butan-2-ol | 48.56 | 8.3 | -89.99 | 46.01 | 73.72 |

## Reference:-

1. Corey E J and Suggs W J, Tetrahedron Lett., (1975) , 26,47.
2. Kwart H and Nickle J H, J Am Chem Soc., (1973), 95,3394.
3. Banerji K K, Bull Chem, Soc Jpn., (1978),51,2732.
4. Venkatarman K S, Sundaram S and Subramanian V, Indian J Chem, (1978),16(B),84.
5. Karim E and Mahanti M K, Oxid Commun,. (1992), 15,211.
6. Karim E and Mahanti M K, Oxid Commun., (1998), 21,559.
7. Pillay M K and Jameel AA, Indian J Chem., (1992), 31(A),46.
8. Agrawal S, Choudhary K and Banerji K K, J Org Chem., (1991),56,5111.
9. Kumbhat V, Sharma P K and Banerji K K, Indian J Chem., (2000), 39 (A), 1169.
10. Khurana M, Sharma P K and Banerji K K, React Kinet Catal Lett (1999), 67,341.
11. Adari K K, Nowduri A and Vani P, Trans Metal Chem (2006),31(6),745.
12. Jain Sapana ,E-Journal of Chemistry (2009) 6(1), 237-246
13. Rathor Shilpa, Dangarh B. K.,IJSR 2277-9655 (2017)
14. Rathor Shilpa, Dangarh B. K.,International Journal of Science and Research (IJSR) (2015): 78.96
15. Rathor Shilpa, Dangarh B. K.,IOSR Journal of Applied Chemistry (IOSR-JAC) (2017), 2278-5736. 10
16. Thakur Sagar Singh , Dangarh B. K. IJSR,June( 2016) • 2277 - 8179
17. Zucker L and Hammett L P, J Am Chem Soc., (1961),83,4960
18. Bunnett, J F, J Am Chem Soc., (1961), 83, 4968.30.
19. Bunnett J F and Olsen E P, Canad J Chem., (1966),44,1927.