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Mechanistic Investigation of Copper (II) Catalysed Oxidation of Benzyl Alcohol by Bispyridinesilver(I)Dichromate

Vanitha.V[1], Krishnasamy.K[2], and Ravichandran.C[1]

Department of Chemistry, Easwari Engineering College, Ramapuram, Chennai, India[1]

Department of Chemistry, Annamalai University, Annamalai Nagar, India[2]

ABSTRACT: The problems to be solved in any kinetic investigation are (i) the establishment of the relationship between the rate of the reaction and various factors such as concentrations of the reactants, temperature, reaction medium, solvent composition etc., and (ii) interpretations of the empirical rate law proposed interms of the reaction mechanisms, incorporating the possible intermediate and the product (or) products formed in the reaction. In the present investigation the kinetics of benzyl alcohol by Cr(VI) oxidant viz., Bispyridinesilver(I) dichromate in aqueous acetic acid medium has been investigated with a view to propose suitable mechanism.

KEYWORDS: Oxidation kinetics, Benzyl alcohol, Bispyridinesilver(I)dichromate, aqueous acetic acid medium, reaction rate, suitable mechanism.

I. INTRODUCTION

A series of chemical reactions are the deciding factors of life cycle as we know that our life is depending upon chemicals in different forms of our fundamental need. A chemical reaction may have several aspects one of which being oxidation. Oxidation processes are commonly met within everyday life. Oxidation reactions are no less common in general chemistry and their importance has resulted in the accumulation of a large number of empirical observations and conclusions. The study of such oxidation reactions through elucidation of their mechanisms and hence the investigation of reaction kinetics in chemical reactions are important aspects in chemistry. The kinetics deals with the study of change in concentration of the components of the reaction system in the gas phase as well as liquid phase with the passage of time and the results are summarised in the form of rate expressions. Among oxo derivatives of valence metals, chromium compounds play a major role as oxidants. A number of chromium reagents are readily available.

Chromium compounds have been widely used in aqueous and non-aqueous media for the oxidation of variety of organic compounds. Chromium compounds especially Cr(VI) reagents have been proved to be versatile reagents capable of oxidising almost all the oxidisable organic functional groups. Kinetics and mechanism of oxidation of benzyl alcohols by many oxidising agents have been studied. Literature survey reveals that very less number of kinetic work has been substantially done so far using BPSDC as an oxidant. This prompted us to undertake the present investigation.

II. EXPERIMENTAL

2.1 Preparation of bispyridinesilver(I) dichromate (BPSDC)[78]
A warm solution of potassium dichromate (3.68g, 0.025mol) in water (25ml) was added to the magnetically stirred pyridine (10ml) in a round bottomed flask (100ml). The orange yellow precipitate was filtered with suction and the resulting solid was washed with dry benzene and was left in a desiccator over night. Yield (95-100%); m.p. 123-127°C.
2.2 Kinetic measurements for the oxidation of benzyl alcohol by BPSDC

The reactions were carried out under pseudo-first order conditions keepting [benzylalcohol' >> [BPSDC] in a solvent system of 60% (v/v) acetic acie-water medium at 308 K unless otherwise mentioned. The course of the reaction was followed iodometrically in the presence of $HClO_4$ in the reaction mixture. The reactions were carried out at constant temperatures and were followed upto 75% completion. Duplicate kinetic runs showed that the rate constants were reproductive to within 3%.

Known volume of substrate, water, perchloric acid and acetic acid were mixed to bring the percentage of acetic acid to the desired value and thermostated.   The reaction was started by adding the oxidant to the mixture. A stop watch was started by adding the oxidant to the mixture. A stop watch was started when half of the oxidant solution had been delivered. Aliquots (2ml) were withdrawn at definite intervals of time and the unreacted BPSDC was estimated iodometrically draining 10ml of 3N sulphuric acid and 10ml of 5% potassium iodide solution and liberated iodine awas titrated against standard sodium thiosulphate solution using starch as an indicator. The pseudo-first order rate constants (k_1) were calculated from the slope of linear plots of log (titre) versus time by the method of least squares.

III. RESULTS AND DISCUSSION

3.1 Stoichiometry and Product Analysis: Reaction mixture containing an excess of the oxidant over benzyl alcohol were kept at room temperature for sufficient length of time under the conditions employed for the kinetic runs. Estimation of unchanged oxidant showed that one mole of benzyl alcohol consumed one mole of BPSDC. Then the reaction mixture from actual kinetic run, after about 70% completion of the reaction, was neutralised with sodium bicarbonate and extracted with chloroform and dried well. The residue was confirmed as benzaldehyde by T.L.C. and from I.R spectral analysis.

3.2 Kinetics and Mechanism of oxidation of benzyl alcohol by bispyridinesilver(I) dichromate.
In order to obtain the clear picture on the mechanism of oxidation of benzyl alcohol with BPSDC in protic solvent system, the reaction was carried out under pseudo-first order conditions using acetic acie-water (60% v/v) as a solvent at 308K.

3.3 Effect of varying [BPSDC]
The oxidation of benzyl alcohol by BPSDC was investigated at several initial concentrations of the oxidant and keeping the concentrations of the other reactants as constant. A plot of log [BPSDC] versus time is linear indicating a first order dependence of rate on [BPSDC]. The pseudo first order rate constants k_1, were evaluated from the plots, according to the first order equation by the method of least square's

3.4 Effect varying [benzyl alcohol]
The reactions were carried out with varying concentrations of benzyl alcohol while keeping all the other reactants concentrations as constant at 308K. The reaction rate was increased with increased in the substrate concentration. The plot of log k_{obs} versus log [substrate] gave the slope 0.63 (r = 0.995, S.D = 0.020) shows that this oxidation reaction was fractional order with respect to [substrate]. The plot of $1/k_{obs}$ versus $1/[substrate]$ is linear with good correlation coefficient (r = 0.990, S.D. = 0.001). The positive intercept value obtained in this plot indicated that the reaction mechanism is a Michaelis – Menten type.

3.5 Effect of Perchloric acid on reaction rate
Reations were conducted in the presence of different concentrations of perchloric acid while keeping the concentrations of other reactant concentrations as constant and the rates were measured. The rate of oxidation decreases with increase in perchloric acid concentration. The plot of log k_1 versus log $[H^+]$ is linear (r = 0.990, S.D = 0.037) with a slope of 0.85. This shows that this oxidation reation is fractional order with respect to $[H^+]$. It was noticed that the added hydrogen ions had very significant effect on the rate of reaction showing that the hydrogen ions provided by the solvent molecules were adequate for the protonation of the oxidant.

3.6 Effect of varying the solvent composition

The reactions were conducted at different solvent compositions by varying the percentage of acetic acid in the reaction mixture. The rate of the reaction has been found to increases with the decrease in the dielectric constant of the medium suggesting the involvement of an ion and a neutral molecule in the rate determining step.[79]

3.7 Effect of added sodium perchlorate

In order to know the effect of ionic strength on the reaction rate, the reactions were carried out with varying concentrations of added sodium perchlorate and keeping all other reactant concentrations as constant. The rate constant deceases with increasing concentration of sodium perchlorate. Hence, the reaction may be between an ions or ion and dipole molecule.[79]

3.8 Effect of Acrylonitirile

The reaction was studied by adding different concentrations of acrylonitrile solutions to the reaction mixture, while keeping the concentrations of all other reactants constant. Addition of acrylonitrile has no effect on the reaction rate showing the absence of free radical pathway mechanism.[80]

3.9 Effect of Mn^{2+} on the reaction rate

The effect of added Mn^{2+} ion has been studied to know the transformation of Cr(VI) to Cr(IV) in the rate – determining step. The results how that there is an appreciable decrease in the rate along with the increasing concentration of Mn^{2+}, suggesting an involvement of two electron change in the rate determining step.[80]

3.10 Effect of Temperature

This oxidation reaction was conducted at four different temperature viz., 298, 303, 308 and 313K. The reaction rates and activation parameters were calculated using Eyring's equation. A plot of ln k_2/T versus 1/T were linear and activation parameters $\Delta H^{\#}$ and $\Delta S^{\#}$ were obtained from the slope and intercept of the above plot. The values of $\Delta H^{\#}$ and $\Delta S^{\#}$ were given below.

$\Delta H^{\#}$ = 51.61 KJ mol^{-1}
$\Delta S^{\#}$ = -113.69 JK^{-1} mol^{-1}

3.11 Effect of added Zn^{2+}, Cu^{2+} and Al^{3+}

To know the caratlytic effect of added Zn^{2+}, Cu^{2+} and Al^{3+} the oxidation reaction were carried out with fixed concentration of Zn^{2+}, Cu^{2+} and Al^{3+} and the reaction rates were measured and given in Table-I. The reaction rate shows that the added Al^{3+}
has larger catalytic effect than Zn^{2+} but the added Cu^{2+} shows no catalytic effect. The order of catalytic behaviour were arranged as follows: $Al^{3} > Zn^{2+} > Cu^{2+}$

Table 1: Effect of added Zn^{2+}, Cu^{2+} and Al^{3+}

| Added ion	10^4 [concentration] mol dm^{-3}	10^4 k$_{obs}$ s^{-1}
Zn^{2+}	5.00	19.13
Cu^{2+}	5.00	2.35
Al^{3+}	5.00	23.00

3.12 Oxidation reaction of Ethanol, 1-Propanol and 1-Butanol with BPSDC

To know the structure reactivity relationship, the oxidation reaction were carried out with ethanol, 1-propanol and 1-butanol and the corresponding reaction rates were given in table – 2. The reaction rate shows that the reactivity of Cr(VI) with benzyl alcohol is faster than with ethanol, 1-propanol and 1-butanol. The high reactivity of benzyl alcohol is accounted may be due to the resonance interaction inbetween benzene ring and the reaction site.

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Table 1: **Reaction rates on Ethanol, 1-Propanol and 1-Butanol with Cr(VI)**

Compound Name	10^2 [concentration] mol dm^{-3}	10^4 k_{obs} s^{-1}
Benzyl Alcohol	2.00	2.76
Ethanol	2.00	0.31
1-Propanol	2.00	0.44
1-Butanol	2.00	0.47

Based on the above discussion, the detailed mechanism of the uncatalyzed reaction pathway is given in Scheme 1.
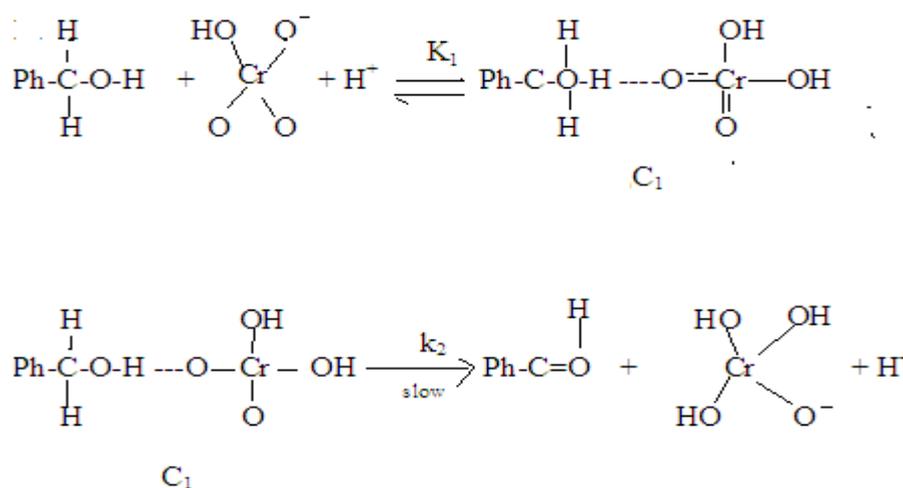
Rate was derived as

$$\text{Rate} = \frac{K_1 k_2\,[HCrO_4^-]\,[H^+]\,[S]}{1 + K_1\,[S]\,[H^+]}$$

IV. CONCLUSION

The kinetics of oxidation of benzyl alcohol by BPSDC has been studied in 60% (v/v) acetic acid – water medium in the presence of perchloric acid. The reaction has been carried out under pseudo first order conditions and the results are given below.

4.1) The order of the reaction is found to be one with respect to the [oxidant] and fractional with respect to the [substrate]. The order of the reaction is found to be fractional with respect to the [H$^+$]. The rate of the reaction has been found to decreases with increasing concentration of sodium perchlorate shows that the reaction may be between an ions oor ion and dipole molecule. Increase in the percentage composition of acetic acid in the binary solvent-mixture increase the rate of the reaction. This k J mol^{-1} and -113.69 J K^{-1} mol^{-1} respectively. Oxidation of benzyl alcohol with BPSDC shows catalytic effect due to the addition of Al^{3+} and Zn^{2+} ion but the addition of Cu^{2+} ion shows no catalytic effect. To know the structure reactivity relationship, the oxidation reaction were carried out with ethanol,

1 - propanol and 1 - butanol. The reaction rate shows that the reactivity of Cr(VI) with benzyl alcohol is faster than with ethanol, 1 – propanol and 1 – butanol. This high reactivity of benzyl alcohol with Cr(VI) is due to the resonance interaction inbetween benzene ring and the reaction site. Benzaldehyde was identified as product of the reaction. The stoichiomedtry was found to be 1 mol of benzyl alcohol consumed by 1 mol of BPSDC. Based on the experimental evidences, a suitable was proposed.

might probably be due to the reation in between two molecules formoing a polar product or two ions of same sign/opposite sign and neutral molecule. The reaction has been studied at four different temperatures. The enthalpy of activations and entropy of activation have been computed as 51.61

Kinetics of the oxidation of histidine by peroxomonosulphate in acetic acid-sodium acetate buffered medium (pH 3.6-5.2) in presence and absence of copper(II) ions was investigated. Catalytic constant k_c has been calculated as 0.15 mol^{-1}dm^{3}s^{-1}, when the [Cu (II)] catalyst was 2.5 x10^{-3} mol dm^{-3}.The effect of ionic strength on the rate revealed that PMS attack the amino group of histidine rather than the carboxylate group of histidine. ESR spectra taken for the reaction mixture at various time intervals, confirmed the reaction proceeding through molecular intermediate. Cyclic voltammetric studies and UV-Visible absorption studies established the formation of copper(II) – histidine – PMS complex. A suitable reaction mechanism was proposed to explain the experimental observation.

ACKNOWLEDGEMENTS

REFERENCES

[1]T.A Turney, "Oxidation Mechanisms", Butterworths, London, P.6, 1965.
[2]K.B. Wiberg, " Oxidation in Organic Chemistry", Part-A, 69, Academic Press, New York, 1965, 71, 98-105.
[3]H.O. House, "Modern Synthetic Reactions", Ed. Benja,min, Londcon, 1972.
[4]G. Cainelli and G. Cardilla¸Chromium Oxidations in Organic Chemistry", Springer – Verlog, Berlin, 1984.
[5]A.K. Das, Inorg. React. Mech., 1999, 1 (2), 161-168.
[6]V. Bora, M.K. ChaudhKalita, Tetrahedron., 2001, 57 (12), 2445-2448.
[7]Sun Do 'Choi and Cho Young Park, Kongop, Hwahak, 2002, 13 (3), 291-296.
[8]F.S. Guziec and F. Luzzio, Synthesis, 1980, 691.
[9]E. Santaniello, F. Milani and R. Casati, Synthesis, 1983, 749.
[10]S.K. Bae, S.B. Lee, D.C. Park and K. Lee, Taehan Hwahakoe Chi., 1989, 33, 106, Chem. Abst., 1989, 111, 77606 V.
[11]H.B. Davis, R.M. Sheets, J.?M. Brannfors and W.W. Paudler, Heterocycles, 1983, 20, 2029.
[12]Santaniello and P. Ferraboshi, Synth. Commun., `1980, 10, 75.
[13]P. Kannan, Ph.D., Thesis, Annamalai University, 2003.
[14]N.S. Srinivasan, V. Thiagarajan, N. Venkatasubramanian, Curr. Sci., 1969, 38, 138.
[15]N.S. Srinivasan, N. Venkatasubramanian, Indian J. Chem., 1972, 10, 1014.
[16]A. Agarwal, S. Mathus, K.K. Banerji, J. Chem. Res (S), 1987, 176.
[17]S.C. Negi, I. Bhatia, K.K. Banerji, J. Chem. Res. (S), 1981, 360 (H) 3936.
[18]J. Cunningham, S.J. Srijananae, Photochem. Photobiol Chem., 1991, 58, 361.
[19]E.J. Corey, E.P. Barrette, P.A. Magriotis Tetrahedron Lett., 1985, 26, 5855.
[20]S. Kanemoto, S. Matsubarra, K. Takai, K. Oshima, K. Utimo, H. Nozaki, Bull. Chemi. Soc. Jan., 1988. ^1, 3607.
[21]J.E. Sarneski, Michos, H.H. Tholp, M. Diduk, T. Poon, J. Blavitt, G.W. Brudvig, R.H. Carbtree, Tetrahedron Lett., 1991, 32, 1153.
[22]J.T. Grooves, W.J. Kruper, J. Am., Chem., Soc., 1979, 101,7613.
[23]P. Arumugam, M. Velayutham, Oxid. Commun., 1997, 20 (1). 93.
[24]H. Ozguin, /h. Beytiyl, Degirmenbasi, Nebahat, J. Chem. Res. (S) 1997, 32.
[25]A. Parek, S. Kothari, K.K. Banerji, ?Indian J. Chem. Sec. B., 1995, 34, 968.
[26]S.M. Lin, T.C. Wen, J. Applied Electrochem., 1995, 25,73.
[27]T.C Wen, S.M. Lin, J.NM. Tsai, J Applied Electrochem.,1994, 24, 449.
[28]D. Susi, K.K. Banerji, S. Kothari, J. Chem. Res. (S), 1995, 274.
[29]P.J. Carisen, K.B. Jorgensen, Abstracts of Papers of the American Chemical Society., 1995, 209, I April, Part 2, P.400 – Orgn.
[30]Sonu Saraswat, Vinita Sharrma and K.K. Banerji, Proc. Indian. Acad. Sci, 2003, 115, 75 – 82.
[31]H. Firouzabadi, A. Sardarian and H. Gharibi, Synth. Commun., 1984, 14(I), 89 – 94.
[32]K. Ganapathy and S. Kabilan, Int.J.Chem. Kinets., 1989, 21, 423.
[33]S. Kabilan, K. Pandiarajan, K. Krishnasamy and P. Sankar, Int. J. Chem. Kinets., 1995, 443 – 451.