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Study on Catalysed Oxidation of 1,5-þentane diol by Piperidinium Chlorochromate in Aqueous Acetic Acid Medium

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Abstract : This article describes the micellar (cationic cetyltrimethylammonium bromide) catalysed oxidation of 1,5-pentane diol by piperidinium chlorochromate in aqueous acetic acid medium. The reaction proceeds via a mechanism involving fission of α-C-H bond at transition state of complex (1:1) to afford hydroxycarbonyl compound. The degree of dissociation of micellar (CTAB) complex formed with diol, þipcc and [H^+] of the order of 1 to 0 was reported. The proton abstraction based mechanism in the oxidation process was verified by rate law and other kinetic parameters.

Key words - Micellar, 1,5-pentane diol, þiperidinium chlorochromate, catalysis, oxidation.

I. INTRODUCTION

Recently halochromate[1], a heterocyclic base of piperidine has been developed as a new Cr(VI) reagent [2,3] for the effective and selective oxidation of several organic compounds[4-7]. One such oxidant of Cr(VI) series is piperidinium chlorochromate (þipcc) which has been widely employed in synthetic chemistry, requires short reaction times and provides high yields.

1,5-pentane diol is used as a solvent, preservatives, and in pharmaceuticals, kinetic method involving this diol is applied to quality change in food industry[8] in bio-chemical processes especially in cell membrane[9] shows a variety of reactions owing to presence of -CH_2OH alcoholic group. The quantitative transformation of 1,5-pentane diol to hydroxy carbonyl compound (aldehyde) has been available in literature [10-13] by different oxidants.

Micellar are basically used as enzyme catalysts[14-22] in various industries and biological processes in colloidal form. The aggregation of these surfactants are responsible for altering the rate of redox reactions[23], being temperature functionary as entropy driven process. By virtue of this trait, they can achieve segregation of their hydrophobic portion from solvent by self aggregation, hence, cationic cetyltrimethylammonium bromide (CTAB) has been chosen as catalyst in this text of study. The role of this micellar can be explained based on Baren’s model.

The available information reveals that, no kinetic work on the micellar catalysed oxidation of 1,5-pentane diol by þipcc was documented. Hence, in this perspective our prime aim is to investigate the dynamics and to elucidate the reaction mechanism for above task of the reaction.

II. EXPERIMENTAL

Materials : The commercial sample of substrate 1,5-pentane diol (B.D.H.) and micellar CTAB (Sigma) analytical grade were distilled over and employed in standard form. The piperidinium chlorochromate (pipcc) was synthesized and its standard solution was prepared as per mentioned process in literature.[24,25] All other necessary solutions of participating reagents (A.G.) used in reaction were of appropriate concentration.

KINETICS : The entire study was made in a thermostat well equipped with thermally regulated thermometer (precision, ± 0.1^{0}C) and electrically operated magnetic stirrer. The pseudo first-order reaction conditions was maintained ten-fold as [1,5-pentane diol] >> [þipcc].

The solution of oxidant (þipcc] and diol alongwith other reagents in appropriate amount were allowed to equilibrate in the water bath at 30^{0}C for 30 min. The kinetics of reaction was monitored by mixing of two contents at regular intervals of time and measuring the unreacted [þipcc] iodometrically. The rate constants (k) were computed graphically and also by using integration method. The repeated rate measurements showed that k_{obs} were replicable within ±3%.

STOICHIOMETRY

The stoichiometry of the 1,5-pentane diol-þipcc reaction was determined under prevailing conditions and unconsumed þipcc (oxidant) was estimated by iodometric process. The outcome assigned Δ[þipcc] / Δ[substrate] ratio as 1:1 formulated by equation

(1)

$$R\,CH_2OH + \text{þ}ip.HCrO_3Cl \;\rightarrow RCHO + H_2O + \text{þ}ip.HCrOClO$$

where, $R = \;-(CH_2)_4OH\ and\ pipcc = C_5H_{11}N$

The hydroxycarbonyl compound was detected by spot test, TLC method and characterized by m.pt. determination of its 2,4-DNP derivative.

The free radicals presence in the reaction mixture did not induce polymerization when tested with acrylonitrile (monomer) using trapping method. Thus, participation of one-electron mechanism is completely dealing not taken into account in light of this fact.

III. RESULTS AND DISCUSSION

(a) The effect of variation of [þipcc] on rate of oxidation was studied, the unit slope of the plot of ln [þipcc] vs. time resultedfrom slanting paralleled afford order with respect to oxidant unity i.e. independent of [þipcc].

(b) The reaction dynamics of initiated oxidation undertaken diol for study increases at low content of substrate but shows deviation in its higher range of concentration (Table 1) and curve (plots of k vs. [substrate]) obtained tends to go towards X-axis. Thus, order tumbles from one to zero with respect to [diol]. However, the ratio of second-order kinetics k_2 / [diol] is not fairly constant. The study provides an ample of evidence for the existence of activated complex at the top of the barrier i.e. transition state by two-fold corresponding plot k_{obs}^{-1} vs. $[diol]^{-1}$ (Fig. 1), which is linear with non-zero intercept made on ordinate axis.

The complex behaviour of the reaction is due to reaction between protonated species of þipcc and diol. The complex formed is presumed to transient not so rigid and can't be isolated.

Table 1 : Effect of varying concentration of diol on the rate of oxidation by þiperidinium chlorochromate
[þipcc.] = 4.0×10^{-3} (mol dm^{-3}) ; $[H^+]$ = 0.10 (mol dm^{-3}) ;
[CTAB] = 1.0×10^{-3} (mol dm^{-3}) ; AcOH-H_2O = 25 %, (v/v); Temp. = 303 K

10^2 ×[1,5-pentane diol] (mol dm^{-3})	10^4 k (s^{-1})
0.80	1.52
1.05	1.80
1.66	2.88
2.00	3.16
2.50	3.19
3.33	4.49
4.00	5.13
5.00	5.51

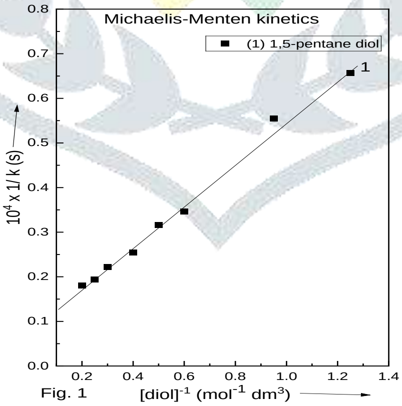


Fig. 1
Michaelis-Menten plot (1/ k_{obs} vs. 1/[1/diol]

(c) An increase in concentration of H^+ ions significantly not only reduce the induction period but also increases the rate of dynamics (Table 2). This concept of acid catalysed reaction leads the protonation of oxidant which is main reaction profile of reacting species participating in the reaction. However, the plot of log k versus log $[H^+]$ (Fig. 2) indicating the appearance of less than unit slope value exhibiting fractional-order kinetics for $[H^+]$ ions at its higher level range of concentration.

Table 2 : Effect of acidity on rate

[1,5-pentane diol] =1.66 ×10^{-2} (mol dm^{-3}); [þipcc.] = 4.0 ×10^{-3} (mol dm^{-3}) ;
[CTAB] = 1.0 ×10^{-3} (mol dm^{-3}) ; AcOH-H_2O = 25 %, (v/v) ; Temp. = 303 K

$[H^+]$ (mol dm^{-3})	10^4 k (s^{-1})
0.05	1.48
0.08	2.17
0.10	2.88
0.15	2.56
0.20	4.05
0.25	4.47
0.333	4.70
0.40	4.83

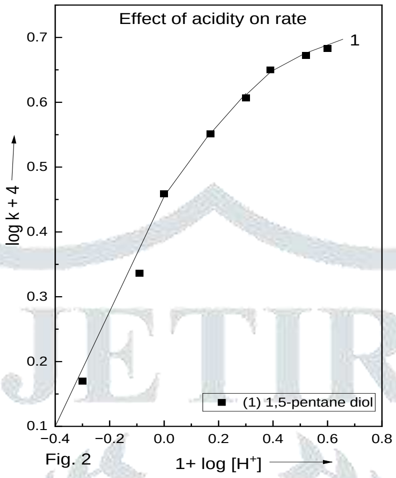


Fig. 2

Plot of ln k vs. ln $[H^+]$

(d) The rate of dynamics almost steadily shows enhancement with rising percentage composition of acetic acid (20% to 50%, v/v) i.e. with decline of values of dielectric constant of the medium (D). The linear Amis plot (ln k vs. 1/D) yielded a positive slope indicates the nature of reaction as positive ion-dipole type.

(e) Initially the oxidation rate of dynamics increases due to aggregation of the cationic surfactant CTAB below CMC, forming catalytically an intermediate complex, and order falls from one to zero at its optimum concentration. The reason behind this fact was that the inhibition in rate assessed by several operative entities such as Beregin's model, hydrophobicity, intramolecular rearrangement, repulsive force between surfactant, head groups**[26]** that may outcome as of counter ion inhibition. The addition of multi-fold concentration of neutral salt (NaCl) did not show any substantial effect on rate. The ionic strength of the medium in different range of concentrations have no appreciable effect on rate.

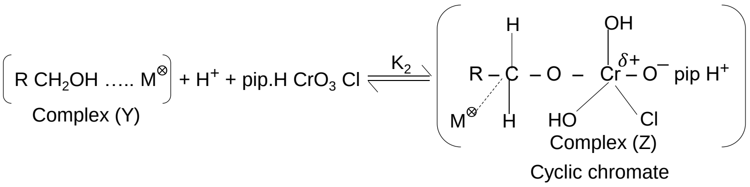
MECHANISM

Involving solvent, micellar (CTAB) catalysed oxidation of 1,5-pentane diol by protonated species of piperidinium chlorochromate, a possible mechanism may be illustrated. The mechanism accounts for the rate-determining loss of hydride ion owing to α-C-H bond fission.

Acid dependent path

$$R\,CH_2OH + \underset{\text{Micellar}}{M^{\otimes}} \overset{K_1}{\rightleftharpoons} \underset{\text{Complex (Y)}}{\left[R\,CH_2OH \ldots\ldots M^{\otimes} \right]} \ldots\ldots\ldots\ldots\ldots(1)$$

where, $R = -(CH_2)_4\,OH$ & $þip = C_5H_{11}N$



........(2)

$$\text{Complex (Z)} \xrightarrow[\text{rds slow}]{k} M^{\otimes} + Cr(IV) + R\,CHO + H_2O + HOCrClO.\ Þip.H^+ \ldots\ldots\ldots\ (3)$$

Considering the above seps involved in the proposed mechanism and applying the condition of steady-state approximation, the rate law may be enumerated as:

$$\frac{-d}{dt}[Cr(VI) = k\ (Z) \ldots \ldots (4)$$

Since, $[Cr(VI)]_t = [Cr(VI)] + [Y] \ldots \ldots (5)$

Here, $[Y] = \frac{K_2\,[Z]\,[Cr(VI)]_t\,[H^+]}{1+K_2[Cr(VI)]} \ldots..(6)$

and, $[Z] = \frac{K_1[M^{\otimes}][Substrate]}{1+K_1[Substrate]} \ldots.(7)$

using equations (4, 6, and 7), we get, rate law expression as:

$$\frac{-d}{dt}[Cr(VI)] = \frac{k\ K_1 K_2 [Cr(VI)]_t \times [H^+] \times [M^{\otimes}] \times [S]}{1 + K_1 K_2 [H^+][S]} \ldots \ldots (8)$$

where, [S] = conc. of substrate (diol) …… (9)

Since, $rate = k_{obs} \times [Cr(VI)]_t\ \ldots..(10)$

Thus, from equation (8) and equation (9). The rate law was obtained as :

$$k_{obs} = \frac{k\ K_1 K_2 [H^+][S][M^{\otimes}]}{1 + K_1 K_2 [H^+][S]} \ \ldots (11)$$

Equation (10) can be re-written as equation (12)

$$k_{obs}^{-1} \times M^{\otimes} = \frac{1}{[S]} \times \frac{1}{k'[H^+]} + \frac{1}{k} \ldots..(13)$$

where, k' = (k K_1 K_2)

Equation (11) shows the expected linear relationship and explains the Michaelis-Menten type double reciprocal plot (k_{obs}^{-1} vs. $[S]^{-1}$) with positive intercept on ordinate axis showing the association of diol and þipcc with micellar ($M^{\otimes}$) in pre-equilibrium step.

The hydride ion transfer from substrate to, oxidant occur by cyclic chromate ester complex in transition state, followed by decomposes to give product.

The α-C-H bond cleaved is most probably supported by several reasons:

(i) +I effect exhibited by alkyl group attached to hydroxyl group.
(ii) Immobilization of a large number of molecules CTAB (Micellar) acts here both as solvent and catalyst.
(iii) Reduction translational and rotational degree of freedom to low value of entropy of activation ($-\Delta S^{\#}$),

The activation parameters (Table 3) in text of reaction was measured at four different temperatures and two concentrations of 1,5-pentane diol. The proposed mechanism is accompanied by the deduced rate law and other kinetic parameters.

Table 3 : Activation parameters for the reaction between diol and þipcc

Diol	$\Delta H^{\#}$ kJ mol^{-1}	$\Delta G^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}
1,5-pentane diol	48.23	84.78	119.62

CONCLUSION

The micellar cationic cetyltrimethylammonium bromide (CTAB) catalysed oxidation of 1,5-pentane diol by þiperidinium chlorochromate (þipcc) was found to proceed through rupture of α-C-H bond in rate-controlling step at T.S. to yield product aldehyde (a hydroxy carboxyl compound). The stoichiometry (1:1) was measured and CTAB-þipcc H^+ complex formed follows Michaelis Menten mode of kinetics w.r.t. micellar and H^+ at their optimum concentrations. The reaction order is unity for [þipcc] and rules out completely the induced polymerization by acrylonitrile polymer. A hydrogen abstraction based mechanism is accompanied by loss of entropy of activation ($-\Delta S^{\#}$) and other kinetic parameters with favourable rate expression.

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CONFLICT OF INTEREST : None.

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