Catalytic Oxidation of Diols by Piperidinium Chlorochromate: Reaction Kinetics

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Abstract—**This paper contains the results of oxidation of diols (1,3-propane diol and 1,4-butane diol) with piperidinium chlorochromate catalysed by micellar in aqueous acetic acid. The rate-determining step involves the α-C-H bond fission of complex 1:1 at transition state, affording corresponding hydroxy carbonyl compounds. The reaction was sensitized by duo micellar (CTAB) and H^+ ions (k_{obs} = a+b $[H^+]$) at their low concentration. In an isoentropic reaction, the enthalpy of activation determines the reactivity. The dynamics and reaction mechanism suggested for the hydride ion transfer in the oxidation process.**

***Index Terms*—piperidinium chlorochromate, cetyltrimethylammoniumbromide, 1,3-propane diol, 1,4-butane diol, oxidation.**

I. INTRODUCTION

The cationic cetyltrimethylammoniumbromide (CTAB) micellar is employed in several industrial processes inclusive of pharmacy and bio-chemical research.[1] It is believed that such a micellar possesses, midway activity between homogeneous and heterogeneous catalysis. It gives an excellent catalyst results when used below CMC in various reactions. [2-5] in colloidal form for organic compounds with different oxidants.[6-9] The micelles CTAB catalysed study is basically owing to its rate base on the facts that, its rate is proportional to the concentration of micellar.[10] This specificity of the cationic CTAB leads to enunciate Lock-and-key type mechanism that justifies Michaelis-Menen law at line weaver-Burk condition. The CTAB micelles practically associated with salvo- phobic interactions with aqueous acetic acid [11]. The hydrocarbon chains are in interior, having the polar COO^- groups in the outer surface in contact with water which stabilised it.

The most recently synthesized reagent is piperidinium chlorochromate a heterocyclic base of Cr(VI) [12-15] which is sensitive to high acidity employed as oxidant in the synthesis and kinetic study of various compounds viz. aldehydes,[16] α-hydroxy acid,[17] and alcohols[18] etc.

Diols are dihydric alcohols in which the functional group (–OH) is directly attached to the carbon atom. The lengthening of the $-CH_2$ chains and their structural variations will bring about a definite change in rate and mechanism. Diols are industrially important compounds, widely used as preservatives, medicine, food, biological processes and analytical chemistry.

The literature contains a few examples of diols for comprehensive oxidation reactions catalysed and non-catalysed by different oxidants by Cr(IV),[19] PBC,[20] QBC,[21] QDC,[22] QFC,[23] and IQCC [24] etc. There is, however, no reported information on the possible reaction mechanism nor its selectivity. The task of kinetic study was undertaken to formulate a possible reaction mechanism which would permit confirmation of the proposed hypothesis.

II. EXPERIMENTAL

All chemicals were of reagent grade (Sigma, aldrich & C.D.H.) and were used after purification. In accordance with the literature [25] we obtained a solution of piperidinium chlorochromate (þipcc) [26] and diluted with distilled water and sulphuric acid. The solution did not decompose even after keeping long periods at 100^0 C. Other solutions at the required concentrations were prepared by dilution, and testing the stability was carried out under the same operating conditions.

KINETICS

The kinetic study of the catalytic reaction was approached by the integration method of initial rates, varying the [Diol] >> [þipcc.] at a time. All the necessary reagent's solutions were kept in thermostat at the reaction temperature before the substrate was added. We followed the reduction reaction by adding the diol directly into the thermoregulated cell containing þipcc. solution. The entire kinetics was followed physically control the reaction rate, using iodometric process.

III. RESULTS AND DISCUSSION

The dependence of the initial velocity expressed as þipcc. consumption at reaction temperature was studied. By plotting the decrease in [þipcc.] of the reaction as a function of time (Fig. 1) on examining the data (Table 1) and slope calculation showed that the reaction rate is found to be of first-order for the oxidant (þipcc.) and independent of the [þipcc].

The rate increases non-linearly with raising the concentration of duo diols. Their order tumbles from 1 to 0 favouring that the order includes complex development between oxidant's species and diols i.e. the reactions follow Michaelis-Menten type kinetics. Hydrogen ions are employed to catalyse the reaction. The hydrogen ion dependency of rate can be of the form as : $k_{obs} = a + b\,[H^+]$.

Table 1 : Effect of varying [þipcc.] on the rate of Micellar catalysed oxidation of diols

$10^2 \times$ [Diol] = 2.50 (1), 2.00 (2) M.; $[H^+]$ = 0.166 (2), 0.188 (1) M. ;

$10^3 \times$ [þipcc.] = 4.00 (1, 2) M. ; $10^3 \times$ [CTAB] = 1.0 (2), 1.25 (1) M. ;

AcOH-H_2O % (v/v) = 25 (1, 2) ; Temp. K = 303 (1,2)

t (sec.)	0	900	1800	2700	3600	4500	5400	6300
1,3-propane diol 10^4 k_{obs} (s^{-1})	-	2.16	2.08	2.06	2.10	2.11	2.15	2.13
log (a-x)	0.681	0.596	0.518	0.439	0.352	0.267	0.176	0.069
1,4-butane diol 10^4 k_{obs} (s^{-1})	-	2.45	2.34	2.34	2.29	2.30	2.34	2.33
log (a-x)	0.681	0.585	0.498	0.406	0.322	0.230	0.130	0.041

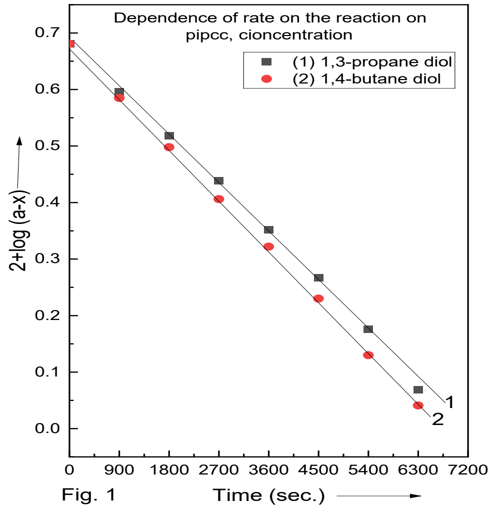


Fig. 1

Plot of log (a-x) vs. time

$10^2 \times$ [Diol] = 2.50 (1), 2.00 (2) M.; $[H^+]$ = 0.166 (2), 0.188 (1) M. ;
$10^3 \times$ [þipcc.] = 4.00 (1, 2) M. ; $10^3 \times$ [CTAB] = 1.0 (2), 1.25 (1) M. ;
AcOH-H_2O % (v/v) = 25 (1, 2) ; Temp. K = 303 (1,2)

The micellar cationic cetyltrimethylammonium bromide (CTAB) interacts physically with the diol to form catalytically active entities. The acceleration in rate with increasing [CTAB] (Table 2) may be due to increasing association/ solubilization of substrate species with rise in its concentration. Owing to exhibition of hydrophobicity, intramolecular rearrangement and significantly charged surfactant (CTAB) could be result of counter ion in inhibition of rate, by these reasons, it bears fractional-order kinetics, supported by graphic plots of k_{obs} vs. [CTAB]. (Fig 2).

Table 2 : Effect of varying concentration of Micellar (CTAB) on the rate of oxidation of Diols by þiperidinium chlorochromate

[$10^3 \times$ [þipcc] = 4.00 (1, 2) M. ; [H^+] = 0.166 (2), 0.188 (1) M. ;
Ac-OH:H_2O, % (v/v) = 25 (1, 2) ; Temp. K = 303 (1, 2)

S. No.	[Diols]	$10^3 \times$[CTAB] × M.	10^4 k M. s^{-1}
1	1,3-propane diol (0.025 M.)	1.00	1.80
		1.25	2.11
		2.00	2.87
		3.33	3.48
		4.00	3.69
		5.00	4.01
		6.25	4.17
2	1,4-butane diol (0.020 M.)	0.80	1.97
		1.00	2.34
		1.50	3.08
		2.00	3.90
		.50	4.31
		3.33	4.65
		4.00	4.88
		5.00	4.54

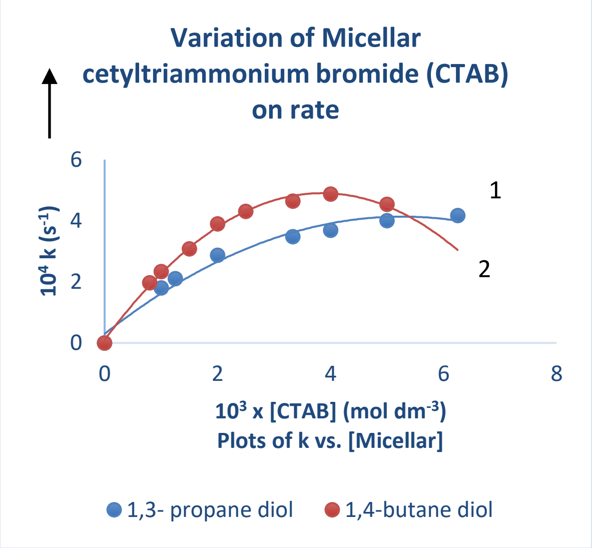


Fig. 2 [$10^2 \times$ [diol] = 2.00 (2), 2.50 (1) M. ;
[$10^3 \times$ [þipcc] = 4.00 (1, 2) M. ;
[H^+] = 0.166 (2), 0.188 (1) M. ;
Ac-OH:H_2O, % (v/v) = 25 (1, 2) ;
Temp. K = 303 (1, 2)

The various composition of acetic acid influence the permittivity of the medium that increases eventually the rate. The effect of addition of sodium chloride and ionic strength, the oxidation rate are found to be negligible pointing thereby the ion-dipole nature of the reaction.

The observed H^+ ion catalysed rate may be attributed to a protonation of þipcc. to yield þipcc. H^+ i.e. Cr(VI) species which is stronger oxidizing agent and electrophile

$$O_2CrClO^-C_5H_{11}NH^+ + H^+ \rightleftharpoons HOCrOClO^-C_5H_{11}NH^+ \quad \dots(1)$$

STOICHIOMETRY

The stoichiometric ratio [þipcc] : [diol] was measured under dynamic prevailing conditions i.e. a large excess of the [diol] over [pipcc]. The results suggested that one mole of diol is disappeared equally by one mole of þipcc for all the compounds studied þipcc. The overall stoichiometry of reaction may be depicted by equation (1).

$$RCH_2OH + C_5H_{11}NHCrO_3Cl \rightarrow R\,CHO + H_2O + C_5H_{11}NH^+\,CrO\,Cl$$

Þipcc. [Cr(VI)]

Here, R= -$(CH_2)_2$ OH, and -$(CH_2)_3$ OH for 1,3-pentane diol and 1,4-butane diol respectively. The products are hydroxy carbonyl compounds (RCHO) which have been analysed (yield was around 89%) by quantitively and identified by forming their 2:4-DNP derivatives and employing spot tests.

The free radical test

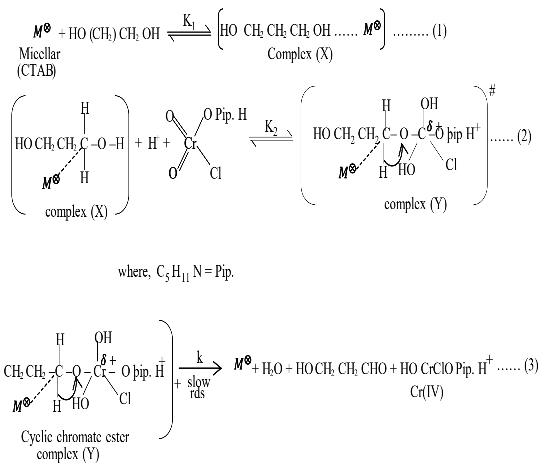
The addition of acrylonitrile to reaction mixture containing diol and þipcc. in slow stream of nitrogen failed to induce polymerization of polymer had no effect on oxidation rate. Thus, one electron mechanism in the present reaction is ruled out.

MECHANISM

As a first approach we suppose that a redox type mechanism is operating for the solvent micellar (CTAB) catalysed oxidation of diols by þipcc. The cleavage of α-C-H bond in the rate-controlling step might occur due to the transfer of hydride ion from diol to the oxidant i.e. through cyclic process via chromate ester formation in a cyclic transition state. The real symmetric processes involving liner H transfer are inherently sigma tropic rearrangements which are characterised by the transfer of hydrogen to the cyclic transition state

Acid-dependent path

Scheme-1



where, $C_5H_{11}N$ = Pip.

The proposed mechanism leads to the following expression

$$-\frac{d}{dt}\,[Cr(VI)] = k\,[Y]\ \ldots..(4)$$

rate = k K_2 [Cr(VI)] [H^+] [X] = k K_2 K_1 [H^+] $[Cr(VI)]_t$ [diol] $[M^{\otimes}]$ ..(5)

Since, $[Cr(VI)]_t = [Cr(VI)] + [Y]$ …. (6)

and $[Cr(VI)_t = [Cr(VI)] + [X] \ldots..(7)$

The [X] and [Y] are obtained as :

$$[X] = \frac{K_2[Y][Cr(VI)_t[H^+]}{1+K_2[Cr(VI)]} \ldots..(8)$$

and $[Y] = \frac{K_1[M^{\otimes}][diol]}{1+K_1[diol]} \ldots..(9)$

Using equations (4, 7 & 8) and on simplification, we get, the rate

$$\frac{-d}{dt}[Cr(VI)] = \frac{k\,K_1K_2[Cr(VI)]\,[H^+][M^{\otimes}][diol]}{1+K_1K_2\,[H^+][diol]} \ldots (10)$$

Applying the condition of steady state approximation

Since, $k_{obs} = \frac{Rate}{[Cr(VI)]_t} \ldots.(11)$

i.e. $k_{obs} = \frac{d}{dt}\,\frac{[Cr(VI)}{[Cr(VI)]_t} \ldots..(12)$

k_{obs} = from equation (10) and equation (12)

we get, final rate law

$$k_{obs} = \frac{k\,K_1K_2[H^+][M^+][diol]}{1+K_1K_2[H^+]\,[diol]} \ \ldots (13)$$

The inverse of k_{obs} takes the form as :

$$M^{\otimes} \times \frac{1}{k_{obs}} = \frac{1}{[diol]k'\,[H^+]} + \frac{1}{k} \ldots.(12)$$

where, k' = (k K_1K_2)

The above rate expression justifies all the orders observed w.r.t. to micellar, acid and diol.

IV. ORDER OF REACTIVITY

The effect of variation of structure on the reaction kinetics has been probed and the rate constants (k_{obs}) for various diols studied, indicate the order of reactivity as : 1,4-butane diol > 1,3-propane diol. It shows that the electron withdrawing groups enhance the oxidation process while electron releasing groups retard it. The negative polarity of the reaction constant actually measures the presence of an electron deficient center in the rds. consequently in an increase in the rate of reaction with an increase in the electron donating power of alkyl group.

A near constancy of the free energy of activation ($\Delta G^{\#}$) implies that the duo diols are oxidized by the same mechanism. The involvement of protonated specie Cr(VI) seems to be a stronger oxidant and electrophile. A hydrogen abstraction may be discounted in a view to the failure of induce polymerization of acrylonitrile and magnitude of reaction constant.

The large negative reaction constant together with the lengthening of carbon chain and long alkyl groups to which hydroxyl group is attached, producing more +I effect may cause the hydride ion transfer from diol to oxidant in rds. Is suggested. The rupture of α-C-H bond in the proposed mechanism is also gained cogent solvating power of the solvent. The hydride ion transfer may take place either by cyclic process or chromate ester complex formation in a cyclic transition state concerted sigma tropic reactions. The chromate ester disproportionation of the ester in a subsequent slow step via a cyclic concerted symmetrical T.S. yield to the product.

The similar phenomena have also been observed earlier in the oxidation of diols by BPCC **[27]** and that of alcohols by PFC **[28]** and BTEACC**[26,29]**. The lower value of (E_a = 55.76 kJ / mol) of 1,4-butane diol than 1,3-propane diol (E_a = 58.99 kJ/mol) (Table 3, (Fig. 3) justifies the reactivity among the diols studied. Overall the $\Delta H^{\#}$ determines the reactivity and assessed for enthalpy controlled.

Table 3 : Rate constant and the activation parameters for the catalysed oxidation of diols by þipcc.

[$10^3\times$ [þiperidinium chlorochromate] = 4.00 (1, 2) M. ; [H^+] = 0.166 (2), 0.188 (1) M. ;

10^3 × [CTAB] = 1.00 (2), 1.25 (1) M.; Ac-OH:H_2O, % (v/v) = 25 (1, 2)

S. No.	[Diols]	$10^4 \times$ k M. (s^{-1})			
		298	303	308	313
1.	1,3-propane diol (0.040 M.)	2.19	3.20	4.69	6.81
2.	1,4-butane diol (0.020 M.)	1.63	2.34	3.32	4.73
			$\Delta H^{\#}$ (kJ mol^{-1})	$\Delta G^{\#}$ kJ mol^{-1}	$-\Delta S^{\#}$ JK^{-1} mol^{-1}
1.	1,3-propane diol (0.025 M.)		57.23	86.56	95.99
2.	1,4-butane diol (0.020 M.)		52.65	85.76	108.37

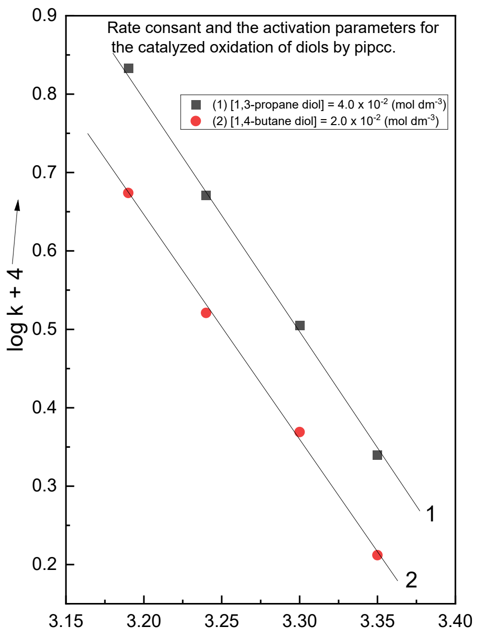


Fig. 3

Arrhenius plot of log k against 1/T

[10^3× [þiperidinium chlorochromate] = 4.00 (1, 2) M. ;
[H^+] = 0.166 (2), 0.188 (1) M. ;
103 × [CTAB] = 1.00 (2), 1.25 (1) M.;
Ac-OH:H2O, % (v/v) = 25 (1, 2)

V. CONCLUSION

The micellar (CTAB) catalysed oxidation of diols by þipcc. have been studied in aqueous acetic acid. The cleavage of α-C-H bond in rate-determining step yields corresponding hydroxy carbonyl compounds (aldehydes) as the main product of oxidation. The reactivity order follow the sequence 1,4-butane diol > 1,3-propane diol. The hydride ion transfer based mechanism from diol to oxidant is suggested, which is supported by the vital role of cation solvating power of solvent.

The reaction does not induce polymerization of acrylonitrile. The reaction is catalysed by micelles (CTAB) as well as acid the catalysed reaction being nearly of fist-order with kinetic form k_{obs} = a+b [H^+]. The protonated species of oxidant proposed to involve in mechanism of the formation of a cyclic chromate ester complex in a fast pre-equilibrium step, has been suggested.

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