

Kinetics of Oxidation of Aldehyde by Piperidinium Chlorochromate

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Abstract: Oxidation of aliphatic aldehydes (acetaldehyde and propanaldehyde) by piperidinium chlorochromate (Pipcc.) in aqueous acetic acid medium proceeds a mechanism involving transfer of hydride ion from aldehyde to pipcc. (oxidant) through an intermediate complex. The reaction is sensitized by hydrogen ions. The oxidation of aldehydes indicated an α -C-H bond cleavage in the rate-determining step leads to formation of corresponding carboxylic acids. The reaction is first-order in Pipcc. The structure-reactivity correlation with thermodynamic parameters and non-kinetic parameters was suggested.

Key words: acetaldehyde, propanaldehyde, Piperidinium chlorochromate, kinetics, oxidation.

1. INTRODUCTION

Several halo chromates have been employed as a moderate, effective, and selective oxidants in synthetic organic chemistry.^[1-4] Piperidinium chlorochromate (pipcc.) is also one of such heterocyclic base used for the quantitative oxidation of α -hydroxy acid,^[5] *s*-phenyl mercapto acetic acid,^[6] benzaldehyde^[7] and alcohols.^[8] Aliphatic aldehydes are a family of carbonyl compounds discharged from anthropogenic and pyrogenic sources, and have extensive industrial usage in perfumery, solvents, resins and pharmacy.

Earlier authors observed that the oxidation of aldehydes except HCHO proceed via enol form, formed by the interaction between aldehydes and hydrogen ion.^[9] Since acetaldehyde propanaldehyde etc. are enolizable, it would be interesting to investigate whether enol form of aldehydes will also involve in the kinetics as reported.^[10,11] Aldehydes exist both in the gem-diol (hydrated form) as well as free carbonyl form ($>C=O$) in aqueous solution.^[12] In this article, as per plans of the present works are to quantifying the kinetics and understanding the mechanism and rate law are being discussed here.

2. EXPERIMENTAL

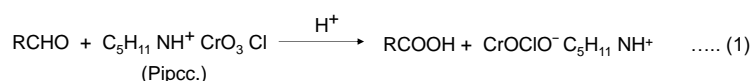
Materials : The commercial samples of acetaldehyde (B.D.H.) and propanaldehyde (Reidel) were used and purified by fractional distillation.^[13] The solution of weighed amount of synthesized pipcc.,^[14] was prepared in deionized water and little mineral acid and its standardization was carried out analytically. All other chemicals used were of analytical grade.

Kinetic measurements

Reactions were carried out under pseudo-order conditions by keeping an excess of aldehyde (10-fold or higher) over Pipcc. in a thermostat ($\pm 0.1^\circ\text{K}$) and maintained at experimental temperature (313 K) of the reaction. The reactions were followed up to 75% to 80% conversion by monitoring the decrease in [Pipcc.] iodometrically. The pseudo first-order rate constant k_{obs} was computed from the linear plot of $\log [\text{Pipcc.}]$ vs. time.

3. RESULTS AND DISCUSSION

The overall stoichiometric ratio [aldehyde] : [Pipcc.] (1:1) for all the compounds studied depicted by equation (1). The products are the corresponding acetic acid and propionic acid, which have been identified by the usual, spot test, physical and chemical methods.



where, R = $-\text{CH}_3$ and $-\text{CH}_2\text{CH}_2$ for acetaldehyde, and propanaldehyde respectively.

The addition of monomer acrolonitrile / acryloamide / butylated hydroxy toluene had no effect on the rate of oxidation. It was observed that BHT was recovered unchanged almost quantitatively. This, rules out the initiation of free radicals based mechanism. The reactions were observed to be of first-order with respect to [Pipcc.]. In individual runs, the plots of $\log [\text{Pipcc.}]$ versus time were linear. The computed slopes were found nearly unity. The values of k_{obs} were found independent of the initial concentration of Pipcc.

The rate constants for various substrates studied are reported in Table 1. The results presented indicate that the k_o values initially increases and then begins to decrease at higher concentration of substrate following Michaelis-Menten type kinetics. This is confirmed by double reciprocal plot of $1/k_{\text{obs}}$ vs. $1/[\text{aldehyde}]$ (Fig. 1) that yielded non-zero intercept on ordinate axis, showing fractional-order kinetics with respect to substrate.

Table 1: Effect of varying [substrate] on the rate of aliphatic aldehydes by Piperidinium chlorochromate

$10^3 \times [\text{Pipcc.}]$ (mol dm⁻³) = 3.33 (1, 2) ; $[\text{H}^+]$ (mol dm⁻³) = 0.15 (2), 0.20 (1) ;

CH₃COOH-H₂O %, (v/v) = 60 : 40 (1, 2) ; Temperature K = 313 (1, 2)

10 ² [substrate] (mol dm ⁻³)	10 ⁴ k (s ⁻¹)	
	CH ₃ CHO (1)	CH ₃ CH ₂ CHO (2)
1.25	-	1.73
1.50	1.27	-
2.00	1.68	2.52
2.50	2.01	3.11
3.33	2.73	2.90
4.00	3.08	4.24
5.00	3.21	4.75
6.25	3.43	4.70

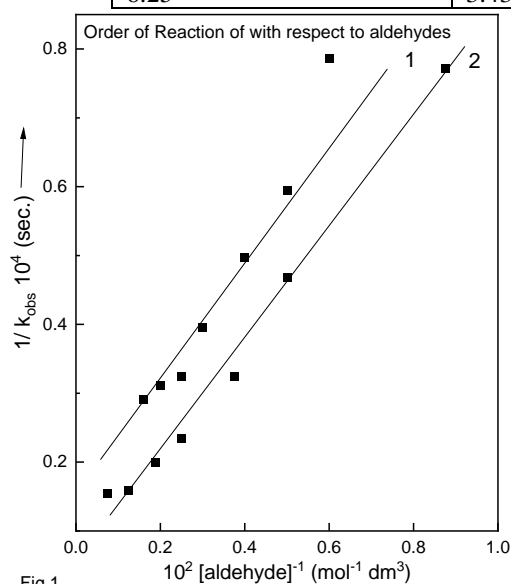


Fig.1

Graphic plot of k_{obs}^{-1} vs. $[\text{aldehyde}]^{-1}$

10³ × [Pipcc.] (mol dm⁻³) = 3.33 (1, 2) ;
 [H⁺] (mol dm⁻³) = 0.15 (2), 0.20 (1) ;
 CH₃COOH-H₂O %, (v/v) = 60 : 40 (1, 2) ;
 Temperature K = 313 (1, 2)

The reaction is catalysed by the hydrogen ions (Table 2). The hydrogen ion dependence has the following form $k_{\text{obs}} = a + b [\text{H}^+]$. The plots of $\log k$ against $\log [\text{H}^+]$ (Fig. 2) shows derived slope values are less than one.

Table 2: Effect of varying [H₂SO₄] on the rate of oxidation of aliphatic aldehydes by Piperidinium chlorochromate

10³ × [Pipcc.] (mol dm⁻³) = 3.33 (1, 2) ; 10² × [substrate] (mol dm⁻³) = 3.33 (2), 4.0 (1) ;

CH₃COOH-H₂O %, (v/v) = 60 : 40 (1, 2) ; Temperature K = 313 (1, 2)

[H ⁺] (mol dm ⁻³)	10 ⁴ k (s ⁻¹)	
	CH ₃ CHO (1)	CH ₃ CH ₂ CHO (2)
0.05	-	1.49
0.08	1.29	-
0.10	1.66	2.69
0.15	2.30	3.90
0.20	3.07	5.24
0.25	3.76	6.34
0.333	5.13	-

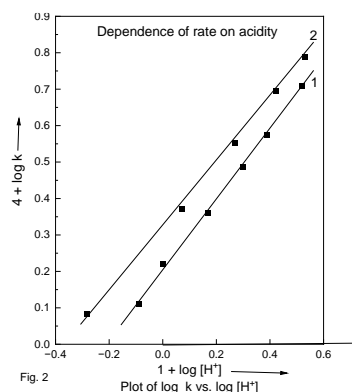


Fig. 2

Plot of log k vs. log [H⁺]
 $10^3 \times [\text{aldehyde}] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (1, 2) ;}$
 $10^2 \times [\text{Pipcc.}] \text{ (mol dm}^{-3}\text{)} = 3.33 \text{ (2), 4.0 \text{ (1) ;}$
 $\text{CH}_3\text{COOH-H}_2\text{O \% (v/v)} = 60 : 40 \text{ (1, 2) ;}$
 Temperature K = 313 (1, 2)

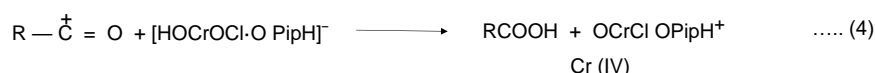
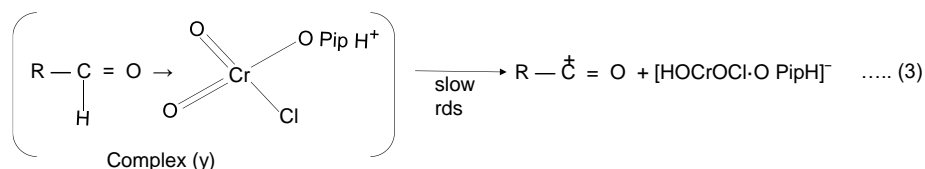
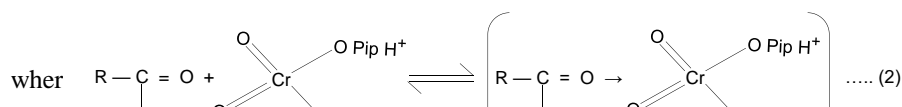
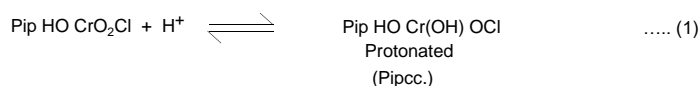
The pseudo first-order rate constants were estimated for the oxidation of aldehydes with pipcc., by varying the proportion of acetic acid 50% to 80% (v/v) in the solvent medium. The enhancement of the reaction rate with increasing amount of acetic acid may be attributed as the acidity increases at constant [H⁺], and the decreases in the dielectric constant of the medium with increase in the acetic acid content. The plot of log k vs. 1/D (dielectric constant) or (D-1) / (2D+1). The positive slope indicates that the reaction involves a cation dipole type of interaction in the rate-determining step.

The effect of addition of neutral salt, sodium chloride on the oxidation rate is found to be negligible and there is no influence of ionic strength on the reaction rate and pointing thereby the ion-dipole nature of the reaction. The acid dependence is in fraction-order depending upon the nature of the substrates. This may be attributed to the equilibrium between the hydrated form (gem-diol) and the free aldehyde molecule. By many reasons it is only the carbonyl form of aldehyde reactive entity that participates in reaction. Exactly in the similar manner, the protonated species was assigned as a strong species electrophile of oxidant Pipcc.

Mechanism

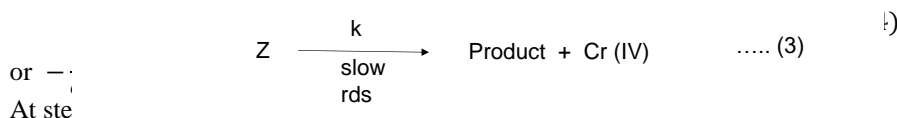
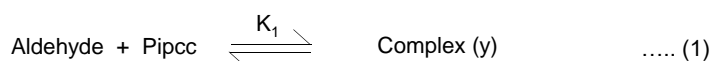
The following possible mechanism involving an hydrogen atom abstraction from the aldehydic group, after the formation of a pre-reaction complex with protonated species of piperidinium chlorochromate is suggested (Scheme-1)

Acid protonated Path



Integrated Rate law

The above postulated mechanism leads to the following rate law
(Acid dependent path)



$$-\frac{d}{dt} [\text{Cr(VI)}] = k K_2 K_1 [\text{H}^+] [\text{ald}] [\text{Cr(VI)}] \quad \dots (6)$$

$$\text{or } R = -\frac{d}{dt} [\text{Cr(VI)}] = \frac{k K_1 K_2 [\text{H}^+] [\text{ald}] [\text{Cr(VI)}]_t}{1 + K_1 K_2 [\text{H}^+] [\text{ald}]} \quad \dots (7)$$

$$\text{Since, } k_{\text{obs}} = \frac{\text{Rate}}{[\text{Pipcc}]_t} \quad \dots (8)$$

$$\text{Moreover, } [\text{Cr(VI)}]_t = [\text{Cr(VI)}] + [\text{Z}] \quad \dots (9)$$

we assume as K_2 is low and produced by [y]
therefore, equation (8) becomes

$$k_{\text{obs}} = -\frac{d}{dt} \frac{[\text{Cr(VI)}]}{[\text{Cr(VI)}]_t} \quad \dots (10)$$

From equation (10) and equation (9)

The final rate is given by

$$k_{\text{obs}} = \frac{k K_1 K_2 [\text{H}^+] [\text{ald}]}{1 + K_1 K_2 [\text{H}^+] [\text{ald}]} \quad \dots (11)$$

writing the equation (11) for double reciprocal plot as :

$$\frac{1}{k_{\text{obs}}} = \frac{1}{k K_1 K_2 [\text{H}^+] [\text{ald}]} + \frac{1}{k} \quad \dots (12)$$

The above rate law explains all the orders observed with respect to aldehyde and H^+ and Michaelis-Menten kind of kinetics. The existence of complex was validated by plot of $1/k_{\text{obs}}$ vs. $1/[\text{aldehyde}]$ with non-zero intercept.

The effect of change of structure on the reaction kinetics has been investigated. The results indicate that order of reactivity is propanaldehyde > acetaldehyde. This shows that electron withdrawing groups accelerate the oxidation process while electron releasing groups retard it. The propanaldehyde exhibit fastest rate rather than acetaldehyde. An ideally designed molecule $\text{CH}_3\text{CH}_2\text{CHO}$ in terms of its structure towards oxidation. Under the influence of positive Inductive effect, due to ionisation of $>\text{C}=\text{O}$ and weak hyperconjugative effect, it favours the faster formation of complex which ultimately loses a hydride ion making the carbonyl carbon strong electrophilic centre. An electron deficient intermediate carbo-cationic centre produced and support hydride ion transfer. It was suggested that oxidation was facilitated by a high electron density at the C-H bond.

Reaction rate slow down in CH_3CHO because $-\text{CH}_3$ group is replaced by H, thus reducing the electron donating potential and retarding the rate of reaction less than propanaldehyde, besides this other reason of reactivity might be electronegativities of alkyl groups and having same dipole moment.

Similar views have also been reported in the oxidation of aldehydes by V(V) [15] and chromic acid, [16] suggesting that the rate of reaction retarded by rupturing $\alpha\text{-CH}$ bond.

The evaluated thermodynamic parameters data of the effect of temperature on the reaction rate are collected in Table 3. It is crystal clear that energy of activation (E_a) is highest for slowest reaction and vice-versa. The values of entropy of activation (ΔS^\ddagger) and (ΔH^\ddagger) are in the reverse of reactivity specifically indicating the reaction is enthalpy controlled. The two ends become highly solvated consequently an immobilization of a large number of solvent molecules reflected in loss of ΔS^\ddagger . The values of Gibb's free energy lies in close vicinity shows that similar mechanism is operative in each case of aldehyde studied.

Table 3: Activation parameters for the reaction between aldehydes and Piperidinium chlorochromate

Aldose	E_a (kJ/ mol)	ΔH^\ddagger (kJ/ mol)	ΔG^\ddagger (kJ/ mol)	$-\Delta S^\ddagger$ ($\text{JK}^{-1} \text{mol}^{-1}$)
CH_3CHO (acetaldehyde)	61.96	60.34	90.08	86.10
$\text{CH}_3\text{CH}_2\text{CHO}$ (Propanaldehyde)	57.99	51.46	88.64	98.81

Conclusions

The reaction is proposed to proceed through a hydride ion transfer from aldehyde to the oxidant (pipcc.), and is supported by major role of cation solvating power of the solvent. The protonated form of pipcc. is the reactive oxidising species and keto form of

substrate participate in reaction. An aldehydic C-H bond is cleaved in the rate-determining step. The order of reactivity was discussed based on + inductive and hyperconjugative effects. The presence of free radicals rules out in the mechanism with stoichiometric ratio (1:1) of the reaction. The derived order was found unity with respect to oxidant and fractional-order to substrate.

Acknowledgement

One of the author is grateful to the Professor and Head, Department of Chemistry, A.P.S. University, Rewa (M.P.) for encouraging and providing facilities for work.

Conflict of Interest

The authors declare conflict of no interest whatsoever.

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