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Reduction of 3-Methyl Pyridinium Bromochromate by C_3 Alcohols : A Kinetic and Mechanistic Study

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Kinetics of oxidation of alcohols containing three carbons, *i.e.*, allyl alcohol (prop-2-en-1-ol), 1-propanol and 2-propanol by 3-methyl pyridinium bromochromate in $HClO_4$-water medium revealed first order each in 3-methyl pyridinium, alcohol and H^+. Bunnett-Olsen plots suggest that water acts as proton abstracting agent in slow step. Rate increases by decrease in dielectric constant of solvent and remains unchanged by ionic strength. Products of oxidation are acraldehyde, propanal and propanone from allyl alcohol, 1-propanol and 2-propanol respectively. Activation parameters for rate-determining step have been computed. Keeping awareness of all the experimental observations, mechanism-involving ion-dipole interaction and rate law has been suggested. Order of reactivity of alcohols was observed: Allyl alcohol > 1-Propanol > 2-Propanol.

Key Words: Kinetics, Oxidation, 3C Alcohols, 3-Methyl pyridinium bromochromate.

INTRODUCTION

More work has been initiated in the area of development of new Cr(VI) reagents[1–9] for the effective and selective oxidation of organic substrates. Mahanti and Banerji[10] have reviewed the work on Cr(VI) reagents. Cr(VI) in the form of organic halo chromates has now become a familiar oxidizing agent due to the promising nature of these species. These are mild and possess considerable selectivity. To this series some new reagents like 3- and 4-methyl pyridinium dichromate, 3- and 4-methyl pyridinium bromochromate were prepared in our laboratory. The present study is aimed at comparing the reactivity pattern and electron transfer between three-carbon alcohols (allyl, *n*-propyl and *iso*-propyl alcohols) and 3-methyl pyridinium bromo chromate.

EXPERIMENTAL

All chemicals, 2-propen-1-ol (allyl alcohol), 1-propanol and 2-propanol used were either of AnalaR grade or purified by the method described in literature and further purity was checked by boiling point. Acetic acid (E. Merck, India) was purified by 6 h refluxing with chromium trioxide and followed by distillation. Perchloric acid (BDH, AnalaR) was used after standardization. All other solutions were prepared in doubly distilled water.

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Preparation of 3-methyl pyridinium bromochromate: For preparing the oxidant 10 g of CrO_3 (BDH AnalaR) was dissolved in minimum water at –10°C and then 47% hydrobromic acid was added slowly with vigorous stirring. To this, 19.5 mL solution of 3-methyl pyridine was added dropwise to afford a brown solid. The reaction mixture was cooled for 4 h. Then dark brown crystals of β-methyl pyridinium bromochromate were filtered and crystallization was carried out from water solution. 3-MePBC is soluble in water, DMF, DMSO, acetic acid, acetonitrile and dichloromethane but partially soluble in benzene, carbon tetrachloride and chloroform.

m.p. 117°C; m.f. $C_6H_8NO_3BrCr$; m.w.273.91; Elemental analysis (%), EFound (Calcd.): C 26.23 (26.28), H 2.89 (2.92), N 5.09 (5.11).

The IR spectrum is similar to that of pyridinium bromochromate. ν_{max} (KBr, cm^{-1}): 3035, 2370–2037, 1628–1473, 1323–1156, 1044, 875, 739 and 667.

The reagent solution was prepared by dissolving a known amount of 3-Me PBC in purified acetic acid. The reagent solution was standardized iodometrically. It gave a characteristic band at 356 nm and obeys Beer-Lambert's law in dilute solution and kinetic study range.

Rate measurement: The reactions were carried out at constant temperature (± 0.1 K) and in pseudo first order conditions (large excess of the substrate over 3-MePBC). The reactions were followed by monitoring the decrease in 3-MePBC at 356 nm spectrophotometrically (Jasco, model 7800) for at least half-lives. Rate constants were calculated by plotting log OD *vs.* time, *i.e.*, first order rate constant. Reproducibility was observed ± 5%.

Product analysis: For qualitative product analysis, substrate and oxidant were taken in 10 : 1 ratio in the reaction mixture (250 mL) and kept for 24 h. The reaction mixture was then treated with saturated solution of 2,4-dinitrophenyl hydrazine prepared in 2 M HCl to get corresponding hydrazones. The products (acraldehyde from allyl alcohol, propanal from 1-propanol and propanone from 2-propanol) were obtained whose melting points were in agreement with literature values. The final product from the oxidant is Cr(III), which has been identified by spot test with diphenyl carbazide[11]. The exact composition of Cr(III) compound could not be ascertained.

Stoichiometry: An excess of 3-MePBC was treated with aliphatic alcohols in presence of perchloric acid. Before and after completion of the reaction, the remaining 3-MePBC was determined by measuring optical density. In case of primary alcohols the reactions indicated 3 : 4 stoichiometry.

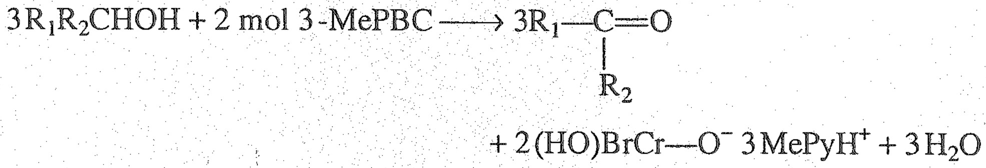
$$3RCH_2OH + 2\text{ mol } 3MePBC \longrightarrow 3RCHO + 2Cr(III) + 3H_2O$$

$$3RCHO + 2\text{ mol } 3\text{-}MePBC + 3H_2O \longrightarrow 3RCOOH + 2Cr(III) + 3H_2O$$

Overall reaction is

$$3RCH_2OH + 4Cr(3\text{-}MePBC) + 3H_2O \longrightarrow 3RCOOH + 4(HO)BrCr\text{-}O^- \, 3MePyH^+ + 6H_2O$$

while in case of secondary alcohol, the reaction indicated 3 : 2 stoichiometry.



$$3R_1R_2CHOH + 2\text{ mol } 3\text{-}MePBC \longrightarrow 3R_1\text{—}\underset{\displaystyle R_2}{\underset{|}{C}}\text{=O} + 2(HO)BrCr\text{—}O^- \, 3MePyH^+ + 3H_2O$$

RESULTS AND DISCUSSION

At constant $[H^+]$, temperature and excess of substrate (alcohol), the log of optical density, *i.e.*, log [3-MePBC] against time is linear indicating that the reaction is first order with respect to 3-MePBC concentrations.

In all the alcohols, rate of reaction is not affected by addition of $NaNO_3$ and Na_2SO_4; therefore ionic strength was not kept constant in all the experiments.

The rate of reaction increased with increase in concentration of substrates (Table-1). A plot of $1/k_{obs}$ *vs.* 1/[substrate] is a straight line with slope *ca.* 1 passing through the origin in all the cases. This indicates that the reaction is first order with respect to concentration of alcohols (Table-1).

TABLE-1
VARIATION OF RATE WITH SUBSTRATE, OXIDANT AND PERCHLORIC ACID CONCENTRATION AT 308 K

[Substrate] $\times 10^2$ M	[3-MePBC] $\times 10^3$ M	$[HClO_4]$ $\times 10^1$ M	$k_{obs} \times 10^{-5}$ (s^{-1})		
			Allyl alcohol	1-Propanol	2-propanol
2.50	2.5	5.0	99.8	13.3	11.2
2.86	2.5	5.0	111.1	15.2	12.9
3.33	2.5	5.0	136.6	17.5	14.9
5.00	2.5	5.0	204.0	26.3	22.2
6.67	2.5	5.0	286.0	36.4	30.8
10.00	2.5	5.0	345.0	48.0	40.0
2.50	0.5	5.0	99.8	13.2	11.2
2.50	0.7	5.0	99.8	13.0	11.3
2.50	0.9	5.0	99.7	13.4	11.2
2.50	1.1	5.0	99.5	13.5	11.1
2.50	1.3	5.0	98.9	13.4	11.1
2.50	1.5	5.0	99.4	13.3	11.2
2.50	2.0	5.0	99.8	13.1	11.3
2.50	2.5	5.0	99.8	13.3	11.2
2.50	2.5	1.0	24.0	2.5	2.3
2.50	2.5	2.0	45.7	4.8	5.5
2.50	2.5	3.0	66.1	7.6	7.2
2.50	2.5	4.0	79.5	10.1	9.5
2.50	2.5	5.0	99.8	13.3	11.2
2.50	2.5	6.0	126.0	17.4	14.4
2.50	2.5	7.0	138.0	27.5	15.9

The rate of reaction increases with increasing hydrogen ion concentration. The effect of $[H^+]$ was observed in 0.1 to 0.7 mol dm^{-3} of $HClO_4$ in all the alcohols. Plot of log k_{obs} against log $[H^+]$ is linear with positive slope *ca.* 1.

The effect of polarity of solvent was studied by increasing the acetic acid percentage in reaction mixture. In all the alcohols taken for study, the reaction rate increased with increase in acetic acid in solvent mixture (acetic acid-water mixture) (Table-2). Plot of log k_{obs} *vs.* (1/D) of the medium gave a straight line with positive slopes.

It has been investigated that the addition of low concentration (0.001–0.01 mol dm^{-3}) of Mn(II) and Ce(III) ions retards the rate of reaction (Table-3). The retardation of the reaction can be explained by the disproportion of Cr(VI).

In the proposed mechanism a direct chromium to carbon bond does not account for the insensitivity to steric effects very often observed in the addition of olefins by Cr(VI).

TABLE-2

SOLVENT EFFECT ON OXIDATION OF ALCOHOLS BY 3-MePBC AT 308 K

[Substrate] = 2.5×10^{-2} M, [3-MePBC] = 2.5×10^{-3}M, [$HClO_4$] = 5.0×10^{-1} M

Acetic acid % (v/v)	Dielectric constant	$k_{obs} \times 10^5$ (s^{-1})		
		Allyl alcohol	1- Propanol	2-Propanol
0	74.19	99.8	33.3	11.2
30	55.56	131.3	44.7	42.6
40	48.54	136.9	50.2	48.1
50	41.49	146.9	60.3	58.2
60	34.48	162.6	76.0	73.9
70	27.39	182.2	95.5	93.4
80	20.32	244.7	158.0	155.9

TABLE-3

VARIATION OF RATE WITH Mn(II) AND Ce(III) ION CONCENTRATION.

[Substrate] = 2.5×10^{-2} M, [3-MePBC] = 2.5×10^{-3}M, [$HClO_4$] = 5.0×10^{-3}, Temp. = 313 K

Salt	[Salt] × 10^3 M	$k_{obs} \times 10^5$ (s^{-1})		
		Allyl alcohol	1- Propanol	2-Propanol
Mn(II)	0.0	141.0	18.8	14.6
	1.0	131.0	17.1	12.9
	5.0	115.0	11.1	10.1
	10.0	106.0	9.9	8.8
Ce(III)	0.0	141.0	18.8	14.6
	1.0	110.4	16.2	13.3
	5.0	99.8	10.9	10.6
	10.0	87.9	9.0	8.8

It was observed in all the alcohols that addition of 3-methylpyridine does not affect the rate of reaction.

Rate of reaction increassd with increase in temperature (298–323 K). Plot of log k_{obs} against 1/T is linear. This shows that Arrhenius equation is valid for these oxidations. The energy of activation $E_a^{\#}$ ranges between 42–50 kJ mol^{-1}. The values of $\Delta S^{\#}$ and $\Delta E_a^{\#}$ are given in Table-4.

TABLE-4
THERMODYNAMIC PARAMETERS FOR ALIPHATIC ALCOHOLS
[Substrate] = 2.5×10^{-2} M, [3-MePBC] = 2.5×10^{-3}M, [$HClO_4$] = 5.0×10^{-1} M

Temperature (±0.1 K)	$k_{obs} \times 10^5$ (s^{-1})		
	Allyl alcohol	1-Propanol	2-Propanol
298	59.0	7.0	5.2
303	77.5	10.8	8.1
308	107.9	13.7	10.2
313	138.0	18.7	14.6
318	165.5	24.4	19.8
323	219.0	34.7	25.7
$\Delta E_a^{\#}$ (kJ mol^{-1})	42.8 ± 2.1	49.9 ± 2.5	50.9 ± 2.5
$\Delta S^{\#}$ (J mol^{-1} K^{-1})	–130.9 ± 6.2	–124.4 ± 6.2	–123.8 ± 6.2
$\Delta F^{\#}$ (kJ mol^{-1})	83.1 ± 4.2	88.3 ± 4.3	89.0 ± 4.5

RESULTS AND DISCUSSION

The reaction was first order each in alcohol and oxidant and independent of initial concentration of 3-Me PBC.

$$\frac{-d[\text{3-MePBC}]}{dt} = k_1[\text{3-MePBC}]$$

At constant temperature addition of H^+ (0.1 to 1.0 M), 3-methyl pyridine and warming the oxidant up to 60°C, there was no change in optical density and spectra proved the stability of 3-MePBC during the course of reaction and did not get hydrolyzed in bromochromic acid and 3-methyl pyridine. In all the alcohols addition of ionic salts had no effect on the reaction rate indicating non-involvement of ion-ion type interaction in rate determining step[12, 13]. The rate was directly proportional to the concentration of different alcohols. The plot of $1/k_{obs}$ *vs.* 1/[substrate] was a straight line passing through origin in all the cases. The rate of reaction increases with increase in acetic acid percentage suggesting that low dielectric constant medium favours oxidation process in all the three alcohols. The plot of log k_{obs} *vs.* $(D - 1)/(2D + 1)$ gives curvature indicating absence of dipole-dipole interaction in rate determining step. Further the plot of log k_{obs} *vs.* [1/D] gives a linear line (r *ca.* 0.99) with positive slopes suggesting the presence of either ion-ion or ion-dipole type interaction between oxidant and substrate. Ion-ion interaction was ruled out by absence of effect of ionic strength on rate while plot of log k_{obs} *vs.* mole fraction of water gave negative slops indicating cation-dipole type interaction[14, 15] in rate determining step. Transition state is stabilized due to water (polar solvent), as water molecule surrounds the transition state and hence less disproportion.

Rate increased with increasing [H^+] concentration indicating the involvement of protonated 3-MePBC and alcohols to form chromic ester followed by decomposition in rate determining step. The protonated forms of the oxidant are found to be more effective in acid medium similar to pyridinium chlorochromate (PCC) and quinolinium fluorochromate (QFC) oxidation[10]. The oxidation of primary alcohol by QDC in acid medium gave the corresponding aldehydes[16]. The reaction was first order in each substrate, oxidant and acid. The oxidation α,α'-dideuterioethanol gave a value of $k_H/k_D = 6.03$ and [alcohol]. The linear increase in the oxidation rate of alcohol with acidity suggests the involvement of protonated Cr(VI) species in the rate determining step. Bunnet[17] and Bunnet-Olsen[18] hypotheses were tested. Plots of $\log k_{obs} + H_0$ *vs.* $\log a_{H_2O}$ and $\log k_{obs} - \log [H^+]$ *vs.* $\log a_{H2O}$ were linear with slope > 3.3 and > 0.20 respectively. Further plot of $\log k_{obs} - \log [H^+]$ *vs.* $\log [H^+]$ was linear with slope > +0.58 suggesting that the water molecule acts as proton transfer agent in the rate determining step.

Retardation of reaction by addition of Mn^{2+} and Ce^{3+} ions suggests that 3-MePBC acts as a two-electron transfer oxidant. Jain *et al.*[19] observed similar results in oxidation of aliphatic aldehydes by quinolinium dichromate. Brown and coworkers[20] also established that PCC is a 2-electron oxidant and is reduced to a Cr(IV) species.

Thangara and Gopalan[21] also observed similar effect of Mn^{2+} and Ce^{3+} ions in oxidation of 2-propanol by chromic acid in acetic acid-water medium. Also the observed kinetic results for the oxidation of various alcohols have an analogy with previously reported oxidation studies with Ni(III)[22], Fe(VI)[23], N-chloromethyl carbamate[24] and BAT[25] at lower acid strength for aliphatic alcohols. Westheimer's mechanism for the reaction of 2-propanol with Cr(VI)[26–30] involved the formation of a chromate ester. An alternative mechanism proposed by Rocek involves a cyclic hydride ion abstraction by $HCrO_3^+$. Wiberg and Schafed[26, 27] followed the oxidation of isopropyl alcohol in 97% aqueous acetic acid. On the basis of kinetic isotope effect these authors feel that the secondary hydrogen is cleaved in the rate-limiting step: (i) whether it is lost as a proton or a hydride ion and (ii) whether the formation of the chromate-ester is a pre-requisite for the reaction, are subject of controversy. Srinivasan and Venkatsubramanian[30] while investigating the kinetics of the oxidation of a series of substituted isopropyl alcohols in acetic acid-water mixtures, obtained a ρ value of -1.6, which is in accordance with the hydride ion loss[30]. In the present study acid catalysis suggests that hydrogen is removed from chromate ester as proton in the rate determining step.

Nandibewoor and Raju[31] proposed a mechanism for the oxidation of allyl alcohol by chromium(VI) in 90% acetone solution, which was very similar to the oxidation of 2-propanol by Cr (VI).

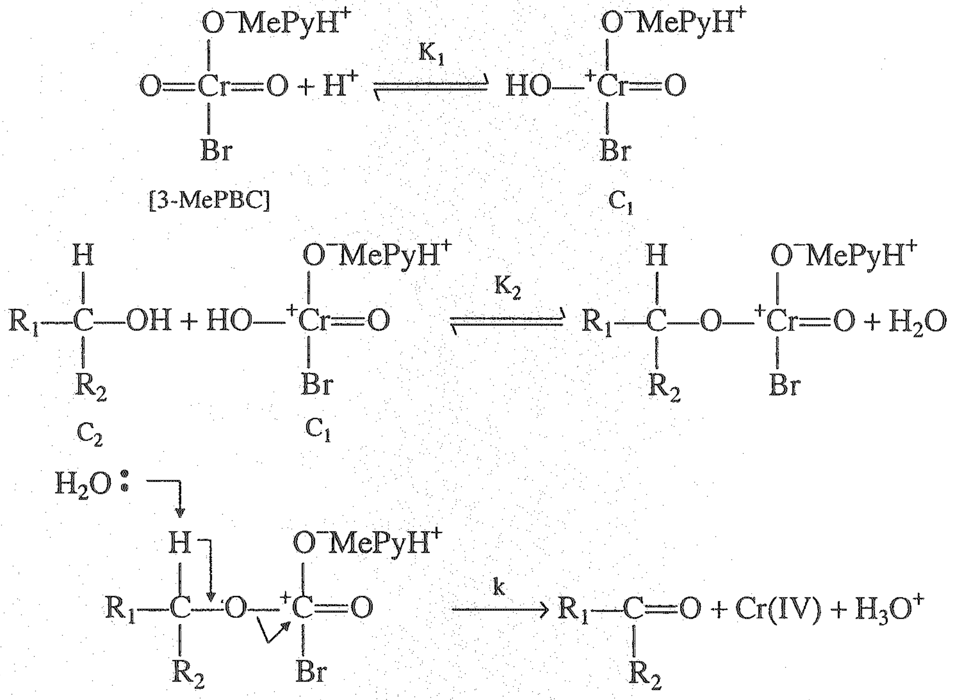
Rate of reaction increased by increasing the temperature. Energy of activation did not correspond to carbon-carbon fission in the decomposition of organic substrates by Cr(VI). Activation parameters indicate that these reactions are not enthalpy controlled. Large negative value of $\Delta S^{\#}$ suggest that the reactions were slow[32] and bimolecular in the rate determining step in the presence of water as a solvent in rate determining step. The plot of $E_a^{\#}$ versus $\Delta S^{\#}$ was linear showing that all the alcohols studied follow a similar mechanism.

Order of reactivity of alcohols

Allyl alcohol > 1-Propanol > 2-Propanol

The highest rate of oxidation of allyl alcohol can be explained due to stabilization of incipient carbonyl group by conjugation of the double bond.

The proposed mechanism is shown as:



$$\underset{[3\text{-MePBC}]}{O{=}\overset{O^-MePyH^+}{\underset{Br}{Cr}}{=}O} + H^+ \overset{K_1}{\rightleftharpoons} \underset{C_1}{HO{-}{}^{+}\overset{O^-MePyH^+}{\underset{Br}{Cr}}{=}O} \tag{1}$$

$$\underset{C_2}{R_1{-}\overset{H}{\underset{R_2}{C}}{-}OH} + \underset{C_1}{HO{-}{}^{+}\overset{O^-MePyH^+}{\underset{Br}{Cr}}{=}O} \overset{K_2}{\rightleftharpoons} R_1{-}\overset{H}{\underset{R_2}{C}}{-}O{-}{}^{+}\overset{O^-MePyH^+}{\underset{Br}{Cr}}{=}O + H_2O \tag{2}$$

$$H_2O:$$

$$R_1{-}\overset{H}{\underset{R_2}{C}}{-}O{-}{}^{+}\overset{O^-MePyH^+}{\underset{Br}{C}}{=}O \xrightarrow{k} R_1{-}\underset{R_2}{C}{=}O + Cr(IV) + H_3O^+ \tag{3}$$

Rate determining step

$$Cr(IV) + \underset{[3\text{-MePBC}]}{Cr(VI)} \xrightarrow{\text{Fast}} 2Cr(V) \tag{4}$$

$$2Cr(V) + 2R_1R_2CHOH \xrightarrow{\text{Fast}} 2R_1R_2C{=}O + 2Cr(III) + 2H_2O \tag{5}$$

Overall:

$$3R_1R_2CHOH + 2[3\text{-MePBC}] \longrightarrow 3R_1R_2C{=}O + 2Cr(III) + 3H_2O \tag{6}$$

Here Cr(III) is probably (OH) $BrCr(O^-3MePyH^+)$

Based on above mechanism, the rate law can derive (under kinetic conditions) as follows:

$$\begin{aligned} \text{Rate} &= \frac{-d[3\text{-MePBC}]}{dt} \propto [C_3] \\ &= k[C_3] \\ &= kK_2[C_1][C_2] \\ &= kK_2[RCH_2OH]K_1[3 + MePBC][H^+] \\ &= kK_1K_2[RCH_2OH][3\text{-MePBC}][H^+] \\ &= k_{obs}[3\text{-MePBC}] \end{aligned}$$

where

$$\begin{aligned} k_{obs} &= kK_1K_2[RCH_2OH][H^+] = k_1 \\ &= k_s[RCH_2OH][H^+] \end{aligned}$$

and specific rate constant, k_s, as

$$k_s = \frac{k_{obs}}{[RCH_2OH][H^+]}$$

This rate law is consistent with experimental results.

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