Kinetics and Mechnism of Oxidation of Benzhydrol by 4-Methyl Pyridinium Di Chromate in Acetic Acid Water Medium

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ABSTRACT

Kinetics of oxidation of benzhydrol using 4-methyl pyridinium di chromate(4-MPDC) in acetic acid water medium has been studied. There is no effect of sunlight on rate of reaction, so reaction was carried out in diffused sunlight. The rate of the reaction is first order in [4-MPDC], [Substrate]and [H^+]. The effect of the dielectric constant of the medium and the the ionic strength of the medium indicate the reaction to be ion-dipole type. Activation parameters for the reaction have been evaluated from Arrhenius plot by studying the reaction at different temperature and the mechanism is predicted. The addition of ionic salts Na_2So_4 and $NaClO_4$ do not affect the rate constant. Effect of Mn(II) and Ce(III) also observed and free radical absence was proved. Effect of substituent on the oxidation of Benzhydrol by 4-MPDC was also determined. A mechanism involving the participation of water molecule in rate determining step.

KEY WORDS Kinetics, 4-Methyl pyridinium di chromate, Benzhydrol, Benzophenone

INTRODUCTION

Inorganic chromium (VI) in the form of chromic acid and metal dichromate, is a versatile oxidant for oxidation of Primary and secondary alcohols to carbonyl compounds. But immiscibility is one of the limiting factors in working with inorganic chromium (VI) compounds. In view of these difficulties, a number of complexed chromium derivatives have been prepared and used in synthetic

organic chemistry [1-6].

Benzhydrols are industrially important compounds. On oxidation Benzhydrols yields Benzophenone, which are useful synthones for fullerenes, bioactive oxygen heterocycles, dyes and medicines. Various Cr (VI) and other oxidizing agents are used for oxidizing benzhydrol [7-15].

In the presents work derivative of PDC i. e. 4MPDC (4-Methyl pyridinium di chromate) is used as oxidizing agent to oxidize benzhydrol. PDC[16] is a mild and selective oxidizing agent and is soluble in water and many organic solvents. Therefore, advantage over inorganic dichromate.

MATERIAL AND METHOD

Analar grade 4-methyl pyridine (distilled before used) and chromium trioxide were used for synthesis of oxidant. The benzhydrol was obtained from Aldrich chemical company and their purity of was checked by melting point measurement. Acetic acid was purified by literature procedure. Other chemicals used were of high purity.

EXPERIMENTAL
PREPARATION OF OXIDANT [4-MPDC]

To prepare 4-MPDC 10 gms of CrO_3 was taken and dissolved in little quantity of water and cooled at 0^0 C. Then to this cooled solution 4-methyl pyridine was added drop by drop. After 15-20 minutes brown crystals of 4-MPDC were formed. These crystals were filtered and dried. These dried crystals were recrystallised by 98% Acetone ± 2% water mixture and characterized by FT- IR spectra. Standard solution of 4-MPDC was prepared by dissolving known amount of 4-MPDC in distilled and purified acetic acid. The solution, so prepared was standardized by titrating it with standard solution of sodium thio sulphate iodometrically

FT- IR spectra (cm^{-1}): 1350, 1500, 1650, 950, 875, 785 and λ_{max}= 352 nm. , M. P. = 382K.

KINETIC MEASUREMENT

The reactions have arranged to be under pseudo first older conditions by keeping an excess (x 10 or greater) of the substrate over the oxidant. The reactions were carried out in glass-stoppered flask at constant temperature ± 0. 1^0C and started by adding a solution of the oxidant. The solution of 4-MPDC in acetic acid obeys Beer-Lamberts Law i. e. optical density at λ_{max} = 352 v/s [4-MPDC] is a straight line upto 4 x 10^{-3} M. Therefore reactions were followed by monitoring the decreasing in [4-MPDC] at 352 nm for at least half lives. No other reactant or product had any significant absorption at these wave lengths.

STOICHIOMETRIC ANALYSIS

Stoichiometric study when [oxidant] >> [substrate] shows that in benzhydrol, 3 moles of substrate are consumed by each mole of oxidant (4 methyl pyridinium di chromate). In three experiments ratio was found to be (1:2. 8, 1:3. 1, and 1:2. 9) i. e. each mole of oxidant oxidizes three moles of benzhydrol. This corresponds to the reaction:

4-MPDC + 3RR'CHOH → 3RR'CO + 2Cr (III)
(1 mole)   (3 mole)
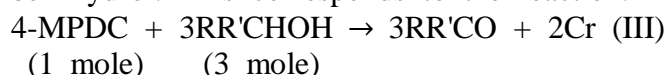
PRODUCT STUDY

The product study has been done under Kinetic conditions. After completion of the reaction, the resultant solution was neutralized by aqueous sodium bi carbonate and then extracted with ether. The ether layer extracted was treated with 2, 4-dinitrophenyl hydrazine solution. Ether was evaporated. Benzhydrol gives Benzophenone and confirmed by its Melting Point.

RESULT AND DISCUSSION

Benzhydrol was oxidized by 4-MePDC in acetic acid medium in presence of perchloric acid at 303K maintain pseudo first order conditions.

On the basis of Product analysis and Stoichiometric study the overall reaction is suggested as

4-MePDC + 3RR' CHOH + 3H2O → 3R CO R' + 2 Cr (III) + 6H$^+$

Effect of varying oxidant concentration

The reaction is First order with respect to oxidant concentration **[Table-1]** and independent of initial concentration of oxidant. The rate law can be express as:

$$-\frac{d\ [4MPDC]}{dt} = k_1\ [4MPDC]$$

Effect of varying substrate concentration

The concentration of the substrate benzhydrols was varied in the range 8×10^{-3} to 28×10^{-3} M at 308 k keeping all other reactant concentration as constant and the rates were measured. **[Table-1]**

Effect of perchloric acid

Perchloric acid was used as a source of H$^+$ in reaction medium. Increase in Perchloric acid concentration in reaction medium increases the rate of oxidation indicating that oxidation of benzhydrols is catalyzed by acid **[Table 1]**. The plot of log k_1 and log [H$^+$] is quite linear and the slope is nearly one. To find out role of H$^+$ in reaction various hypothesis like Zucker-Hammet (log K_1 v/s H_0), Bannett[17] and Bunnett-Olsen[18] were fitted. The sign and magnitude of ω>3 [slope of plot of log k_1 + H_o vs log a_{H2O}. and Φ >0. 58

[slope of plot of log k_1+H_o against log [acid] $+H_o$] indicate the nature of participation of water molecule in the rate determining step of the reaction **[Table 2]**. Here water acts as a proton transfer agent in the rate determining step.

Effect of temperature
Rate of reaction increases with increase in temperature **[Table-1]**. The Energy of activation favors C-H bond, fission in this oxidation the negative value of entropy pointed that reaction is slow [19]. The negative entropy of activation is large and positive, the reaction will be normal and fast but if it is negative, the reaction is slow. In this case, the values of entropy of activation come under a category of slow reactions. The negative entropy of activation and energy of activation suggests formation of a chromic ester, which decomposes in rate-determining step to give products. Negative values of entropy also suggest bimolecular reaction in the rate-determining step in the presence of water as a solvent and the involvement of a proton transfer during the rate-determining step.

Effect of ionic strength
The rate of reaction does not depend on ionic strength of the medium. By the addition of ionic salts such as Na_2SO_4 and $NaCIO_4$ do not affect the rate constants ruling out the possibility of ion-ion type interaction in rate-determining step.
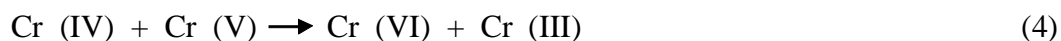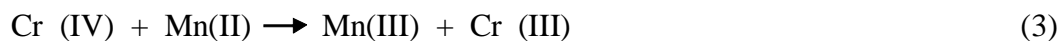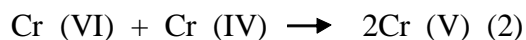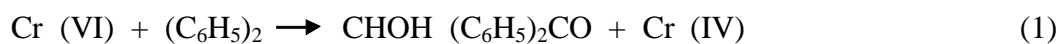
Effect of solvent composition
Increasing the AcOH% (V/V) in the solvent mixture increases the rate of oxidation **[Table-1]**. The plot of reciprocal of dielectric constant of the medium versus log K, is a straight line with slope $> + 20$ this suggests that the reaction involves the interaction of a cation and a polar molecule. Increase in the reaction rate with increase in the proportion of acid may be traced due to solute solvent interaction. In presence of acetic acid the oxidant 4-MPDC may form acetyl 4-Methyl PDC.

Effect of MnSO₄ concentration
The addition of low concentration of Mn (II) ions retards the rate of oxidation **[Table-4]**. The retardation of the reaction by addition of Mn(II) ion can be explained by the disproportion of Cr(VI) and Cr(V). Mn (III) formed in step (3) being an unstable species is likely to used by the substrate and converted to Mn(II).   In the absence of any addition of Mn(II), partial regeneration of Cr(VI) occurs (Step4) from the reduced Cr(IV) species. But addition of Mn(II) fixes the Cr(IV) species as Cr(III) and thus the total concentration of Cr(VI) available in a given time is lowered by the addition of Mn(II) and hence observed deceleration with increasing addition of Mn(II) ion. This may be taken as evidence for formation of Cr (IV) species and hence 4MPDC is acting as two-electron transfer oxidant.

Slow

$$Cr\ (VI) + (C_6H_5)_2 \longrightarrow CHOH\ (C_6H_5)_2CO + Cr\ (IV) \tag{1}$$

$$Cr\ (VI) + Cr\ (IV) \longrightarrow 2Cr\ (V) \tag{2}$$

$$Cr\ (IV) + Mn(II) \longrightarrow Mn(III) + Cr\ (III) \tag{3}$$

$$Cr\ (IV) + Cr\ (V) \longrightarrow Cr\ (VI) + Cr\ (III) \tag{4}$$

Effect of substituent

The comparative rates of oxidation of benzhydrols in constant kinetic conditions are summarized in **[Table 5].**

A linear correlation is observed when log k_1 is plotted against **σ.** This indicates that there is electron deficiency at the carbinol carbon in the transition state i. e. $(C_6H_5)_2CHOH$ tend to become $(C_6H_5)_2C^+HOH$ i. e. a change from sp^3 hybridization to sp^2 type, the extent to which this can be attained is measured by ρ value. The large kinetic hydrogen isotope (k_H/k_D ~ 6. 7) affect observed suggest C-H bond stretching to be affected in the TS, the extent of stretching is towards the reactant state and not advance so much as create carbon-cation in TS.

MECHNISM AND RATE LAW

On the basis of above observation the probable mechanism of the oxidation is given in Figure-1.

Rate law

Rate=-d [4-MePDC]/dt =k'[C]

  =k'K_2 [BH] [H$^+$4-MePDC]

  =k'K_2 K_1 [BH] [H$^+$4-MePDC]

  = K_{obs} [4-MePDC]

  = K_1 [4-MePDC]

Here $K_{obs=}$ k'K_2 K_1 [BH] [H$^+$] = K_1

 [BH]= Benzhydrol

Benzhydrol

K_2

$+ H_2O$

[C]

$$Cr(IV) - O - Cr(VI) \xrightarrow{fast} Cr(V) - O - Cr(V)$$

$$Cr(V) - O - Cr(V) + 2RR'CHOH \xrightarrow{Fast} 2RCOR' + 2Cr(III) + 4H^+$$

Overall reaction is

$$\begin{array}{l} 4\text{-MPDC} + 3RR'CHOH + 3H_2O \longrightarrow 3RCOR' + 2Cr(III) + 6H^+ \\ \text{(1 mole)} \quad\quad \text{(3 mole)} \end{array}$$

Figure 1

CONCLUSION

Oxidation of benzhydrol by 4-methyl pyridinium di chromate (4-MPDC) in acetic acid water medium proceed via formation of a chromic ester, which

decomposes in rate-determining step to give products. Stoichiometric study shows that 3 moles of substrate are consumed by each mole of oxidant The rate of the reaction is first order in [4-MPDC], [Substrate] and [H^+]. The sign and magnitude of ω and Φ indicate participation of water molecule in the rate determining step. 4MPDC is acting as two-electron transfer oxidant.

Table1: Effect on Rate by variation of [4-MePDC], [Benzhydrol], [HClO₄], [CH₃COOH] and Temperature on oxidation

[4-MePDC] $x10^4$M	[Benzhydrol] $x10^3$M	[HClO₄] x 10^2 M	[CH₃COOH] % v/v	Temperature K	k_1 $x10^5$ sec^{-1}
5. 0	20. 0	6. 0	60	308	76. 38
7. 5	20. 0	6. 0	60	308	76. 41
10. 0	20. 0	6. 0	60	308	76. 50
15. 0	20. 0	6. 0	60	308	76. 62
18. 0	20. 0	6. 0	60	308	76. 82
20. 0	20. 0	6. 0	60	308	76. 58
20. 0	8. 0	6. 0	60	308	29. 17
20. 0	12. 0	6. 0	60	308	46. 98
20. 0	20. 0	6. 0	60	308	76. 08
20. 0	24. 0	6. 0	60	308	87. 51
20. 0	28. 0	6. 0	60	308	102. 80
20. 0	30. 0	6. 0	60	308	110. 54
20. 0	20. 0	6. 0	50	308	53. 74
20. 0	20. 0	6. 0	55	308	61. 89
20. 0	20. 0	6. 0	60	308	75. 88
20. 0	20. 0	6. 0	65	308	92. 12
20. 0	20. 0	6. 0	70	308	120. 26
20. 0	20. 0	6. 0	80	308	278. 50
20. 0	20. 0	1. 0	60	308	10. 79
20. 0	20. 0	3. 0	60	308	38. 38
20. 0	20. 0	6. 0	60	308	76. 28
20. 0	20. 0	12. 0	60	308	148. 15
20. 0	20. 0	18. 0	60	308	224. 33
20. 0	20. 0	24. 0	60	308	291. 42
20. 0	20. 0	6. 0	60	298	41. 46
20. 0	20. 0	6. 0	60	303	54. 80
20. 0	20. 0	6. 0	60	308	76. 63
20. 0	20. 0	6. 0	60	310	81. 68
20. 0	20. 0	6. 0	60	313	100. 56
20. 0	20. 0	6. 0	60	315	120. 15
20. 0	20. 0	6. 0	60	318	146. 08

Table 2: CORRELATION OF RATE WITH ACID CONCENTRATION

Correlation	Slope
$\log k_1$ v/s $\log [H^+]$	0. 99
$\log k_1$ v/s H_0 Zucker-Hammet plot	0. 82
$\log k_1 + H_0$ v/s $\log a_{H2O}$ Bunnett plot slope (ω)	12. 3
$\log k_1 + H_0$ v/s $H_0 + \log [H^+]$ Bunnett Olsen plot slope (Φ)	0. 96

Table 3: THERMODYNAMIC PARAMETERS FOR BENZHYDROL

THERMODYNAMIC PARAMETERS	Values
Energy of activation ΔEa kJ mol^{-1}	46. 27
Entropy of Activation ΔS JK^{-1}	-102. 38
Free energy ΔF kJ mol^{-1}	77. 78

TABLE 4: EFFECT OF Mn(II) ON RATE OF REACTION

[Mn(II)] x 10^3 M	$\log k_1$ x 10^5 sec^{-1}
0. 0	76. 13
1. 0	56. 12
2. 0	46. 16
3. 0	38. 32
4. 0	26. 28
5. 0	17. 29

TABLE 5: EFFECT OF SUBSTITUENT

Compound	$\log k_1$ x 10^5 sec^{-1}	σ	ρ
Benzhydrol	1. 88	0. 00	
2-methyl benzhydrol	1. 93	-0. 13	
4-methyl benzhydrol	2. 08	-0. 17	-0. 87
4-chloro benzhydrol	1. 63	+0. 23	
4, 4'dichloro benzhydrol	1. 49	+0. 46	

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