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Research Article

MECHANISTIC ASPECTS FOR THE OXIDATION OF BENZALDEHYDE BY PIPERIDINIUM CHLOROCHROMATE

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ABSTRACT

The kinetics of oxidation of benzaldehyde by piperidinium chlorochromate has been studied in the presence of perchloric acid in aqueous acetic acid medium. The main product of the oxidation is benzoic acid. The reaction order is one with respect to benzaldehyde, piperidinium chlorochromate and fractional order with respect to perchloric acid. The rate of reaction rises with increase in the percentage of acetic acid. The reaction does not track the polymerization with acrylonitrile. The rate of reaction decreases with variation in the concentration of manganous sulphate. The thermodynamic and activation parameters have been calculated using Eyring's plot. From the obtained kinetic results, a plausible mechanism has been proposed and suitable rate law is derived.

Keywords: Oxidation, Kinetics, Mechanism, Benzaldehyde, Piperidinium chlorochromate.

1. INTRODUCTION

The aldehydes on oxidation give carboxylic acids based on the nature of the oxidant. Benzaldehyde is a clear colorless to yellow liquid with a bitter almond odour. Its flash point is near 145 °F. It is denser than water and insoluble in water. The vapors are heavier than air. It is used in flavoring and perfume making. In synthetic organic chemistry, the oxidation of aldehyde or alcohol to carbonyl group is of greater importance [1-2]. The metal based oxidants like $KMnO_4$, Cr (VI), RuO_4, produce large amounts of toxic end-products [3-4]. Chromium (VI) (Cr^{+6}) are powerful oxidizing agent for the oxidation of varieties of organic compounds [5]. In order to avoid the flexibility of these oxidants, mild Cr^{+6} derivatives are synthesized from heterocyclic halochromate or dichromates. Kinetics of oxidation of benzaldehydes have been studied using several mild chromium (VI) compounds [6-20].

Piperidinium chlorochromate is found to be a mild selective reagent for the oxidation of alcohols to the corresponding carbonyl compounds [21].Kinetics of oxidation of some organic substrates [22-25] by piperidinium chlorochromate has also been reported. The present work involves the kinetic study of oxidation of benzaldehyde with piperidinium chlorochromate in the presence of perchloric acid.

2. EXPERIMENTAL

2.1. Material

Piperidinium chlorochromate (PipCC) was prepared by a known procedure [21] and its purity was checked by determining Cr(VI) concentration iodometrically. The benzaldehyde (Sigma Aldrich) was of the highest purity available and used as such in the reaction kinetic study. Acetic acid was refluxed over chromium trioxide for 6 h and then fractionated [26]. All other chemicals used were of AnalaR grade. Only double distilled water used throughout the experiment. The reaction mixture was homogeneous throughout the course of the reaction.

2.2. Kinetic Measurements

The concentration of benzaldehyde was maintained in large excess concentration than the oxidant to attain pseudo-first order conditions. The reactions were carried out at constant temperature using thermostat (RAAGAA). The absorbance was recorded using colorimeter at 470nm, Elico CL-63 Photometer. The pseudo-first order rate constants k_{obs} were determined up to 80% completion of the reaction from the linear plots, r = 0.990 to 0.999 for log [absorbance] *versus* time.

2.3. Correlation Analysis

Linear regression(r) analysis was carried using computer software, Micro cal origin. The reproducibility of the rate constants was approximately ± 2%.

2.4. Stoichiometry and Product Analysis

The stoichiometry of the reaction [PipCC]: [benzaldehyde] was determined by taking excess of [PipCC] over [benzaldehyde] and allowing the reaction to go for completion. After sufficient length of time, all the benzaldehyde had completely reacted with piperidinium chlorochromate leaving behind the unreacted piperidinium chlorochromate which was estimated iodometrically. The estimation of unreacted piperidinium chlorochromate showed that 1 mole of benzaldehyde consumes 1 mole of piperidinium chlorochromate.

The reaction mixture with excess of oxidant over the substrate was added. Then, it was slightly warmed and kept at room temperature for 24 h. It was extracted with ether and the product was obtained and dried with anhydrous sodium sulphate. The product was identified by checking its physical constant (m.p. 120°C). It was dissolved with ethanol and tlc analysis was done with benzoic acid and standard sample of benzoic acid as a reference. It was further confirmed by spectral studies.

3. RESULTS AND DISCUSSION

The kinetics of oxidation of benzaldehyde was studied in 50% aqueous acetic acid medium in presence of perchloric acid at constant temperature.

3.1. Effect of Varying Substrate

The rate of reaction was increased linearly with increase in the concentration of benzaldehyde in Table 1. The order with respect to substrate was found to be one as evidenced by the liner plot of log k *versus* log[s].

3.2. Effect of Varying Oxidant

At fixed concentration of substrate and perchloric acid for varying the concentration of PipCC, the plot of log absorbance *versus* time (Figure 1) was linear indicating first order in PipCC.

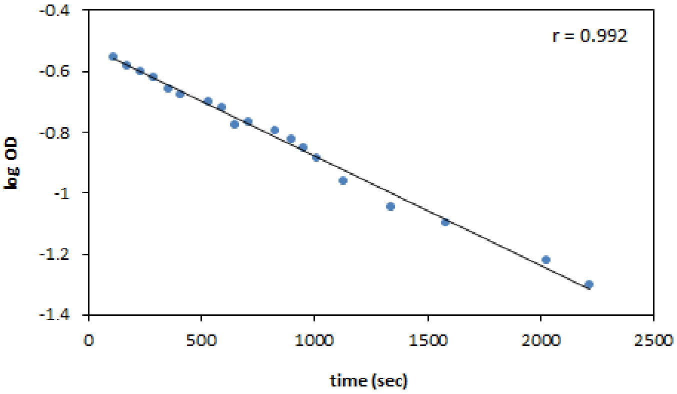


Fig. 1: Plot of log absorbance *versus* time

But, the rate of the reaction decreased with increase in the concentration of oxidant [27-28] in Table 1. It is attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium.

3.3. Effect of Perchloric Acid

The effect of added H^+ ion on the pseudo-first order rate constant was studied by adding perchloric acid in the region of 0.2-0.6 M. The rate of reaction increased with increase the concentration of perchloric acid (Table 1). The plot of log k against log $[H^+]$ gave a straight line (Figure 2) with slope 0.34 (r = 0.998) indicating that the protonated species of the oxidant in the effective nature. It can be concluded that the reaction is simply an acid catalyzed one [29].

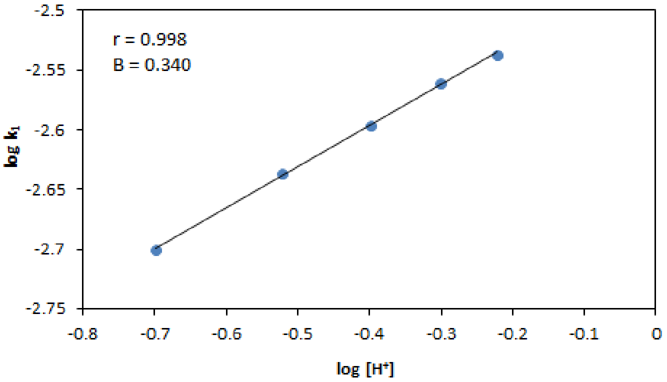


Fig. 2: Plot of log k_1 *versus* log $[H^+]$

Table 1: Effect of Substrate, Oxidant and Hydrogen Ion Concentration on the Oxidation of Benzaldehyde by Piperidinium Chlorochromate in 50% Acetic acid Medium at 303 K

[Benzaldehyde] 10^2 (*mol dm^{-3}*)	[PipCC] 10^3 (*mol dm^{-3}*)	$[H^+]$ (*mol dm^{-3}*)	k_1 10^4 (*s^{-1}*)
4.5	3.0	0.2	14.322
6.0	3.0	0.2	19.924
7.5	3.0	0.2	25.822
9.0	3.0	0.2	31.550
10.5	3.0	0.2	39.445
6.0	2.0	0.2	21.770
6.0	3.0	0.2	19.924
6.0	4.0	0.2	17.821
6.0	5.0	0.2	15.513
6.0	6.0	0.2	13.305
6.0	3.0	0.2	19.924
6.0	3.0	0.3	23.067
6.0	3.0	0.4	25.351
6.0	3.0	0.5	27.475
6.0	3.0	0.6	29.444

AcOH:Water (v/v) = 50:50

3.4. Effect of Ionic Strength and Solvent Composition

The reaction was carried out at various concentrations of sodium perchlorate while the other variables were kept constant. Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate (Table 2) indicating the involvement of charged species in the rate-determining step. The reaction was carried out at five different percentages of acetic acid-water mixtures while all other factors were constant. The rate of reaction increased with the increase in the percentage of acetic acid (Table 2).

Table 2: Effect of Ionic Strength, Solvent and $MnSO_4$ Concentration on the Oxidation of Benzaldehyde by Piperidinium Chlorochromate at 303 K

$[NaClO_4]\ 10^3$ (*mol dm^{-3}*)	AcOH:Water (*v/v*)	$[MnSO_4]\ 10^3$ (*mol dm^{-3}*)	$k_1\ 10^4$ (*s^{-1}*)
-	40:60	-	15.345
-	45:55	-	17.274
-	50:50	-	19.924
-	55:45	-	23.211
-	60:40	-	26.994
0.0	50:50	-	19.924
2.0	50:50	-	19.677
4.0	50:50	-	19.88
6.0	50:50	-	20.032
8.0	50:50	-	19.905
-	50:50	0.0	19.924
-	50:50	2.0	15.219
-	50:50	4.0	15.044
-	50:50	6.0	14.728
-	50:50	8.0	14.555

[Benzaldehyde] = 6.0 x 10^{-2}mol dm^{-3} [PipCC] = 3.0 x 10^{-3}mol dm^{-3} [H$^+$] = 0.2 mol dm^{-3}

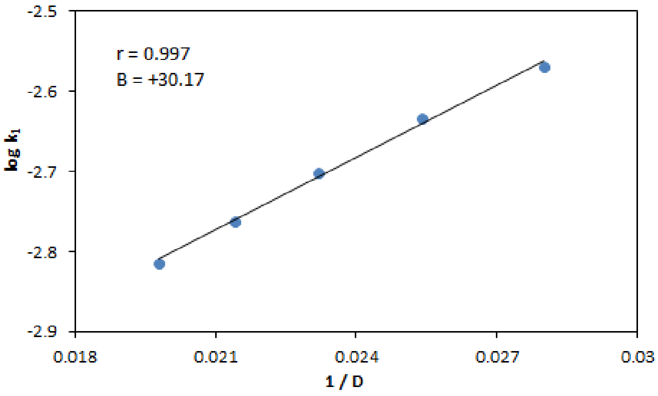


Fig. 3: Plot of log k_1 *versus* 1/D

The plot of log k_1 *versus* 1/D (Figure 3) was found to be linear (r= 0.997) with positive slope (+ 30.17). This might be probably due to ion-dipole interaction [30] in the rate determining step.

3.5. Test for Free Radical Reaction

The reaction does not induce polymerization by the addition of acrylonitrile. It has no effect on the reaction mixture indicating the absence of free radical mechanism.

3.6. Effect of varying $MnSO_4$

The reaction was carried out with the varying concentrations of $MnSO_4$ ions keeping all the other factors constant. There was a noticeable negative catalytic effect on the reaction rate for the addition of manganous sulphate (Table 2). Thus, it is possible that the reaction involves a two electron process.

3.7. Effect of Temperature

The rate constants were measured at four different temperatures viz., 303, 308, 313 and 318 K. thermodynamic and activation parameters have been calculated from the plot of log k_2/T *versus* 1/T using the Eyring's equation (Table 3).

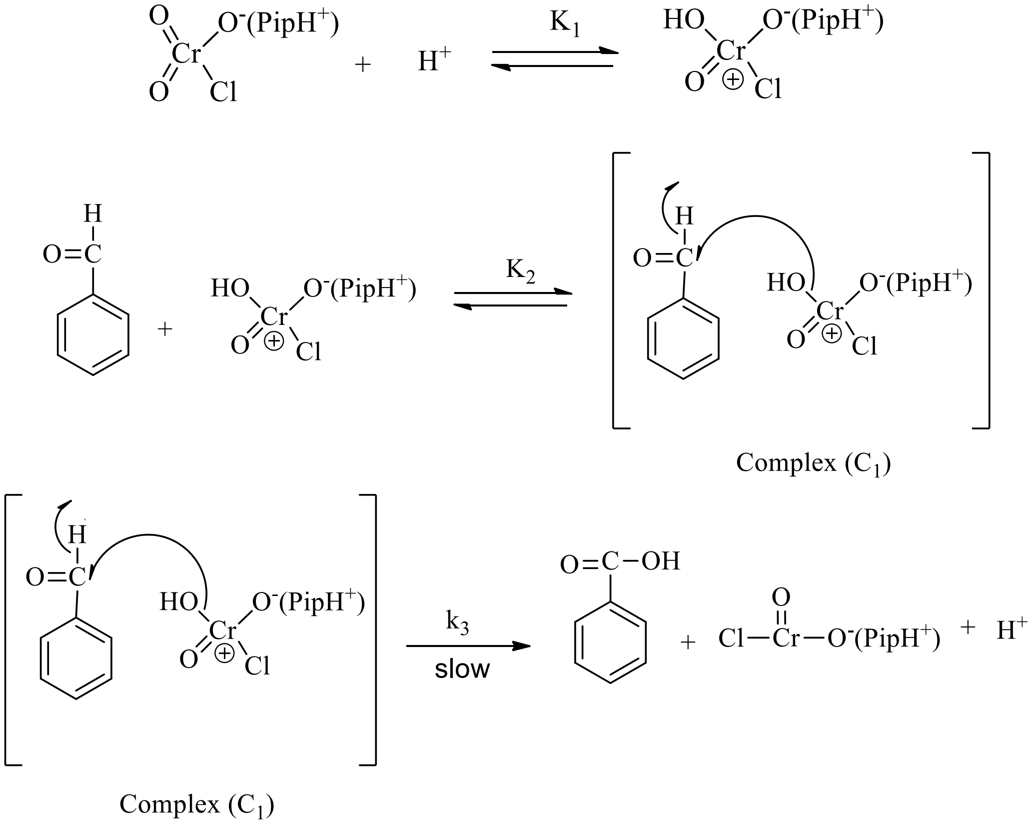
Table 3: Effect of Temperature for the Oxidation of Benzaldehyde by Piperidinium Chlorochromate in 50% Aqueous Acetic acid Medium

Temperature (*K*)	**$k_1\ 10^4$ (s^{-1})**	**Thermodynamic and Activation Parameters**
303	19.924	$\Delta H^{\#}$ = 5.36 *kJ mol^{-1}*
308	21.615	$\Delta S^{\#}$ = - 212.78 *kJ mol^{-1}*
313	23.827	$\Delta G^{\#}$ = 69.83 *kJ mol^{-1}* at 303 K
318	26.318	Ea = 7.88 *kJ mol^{-1}* at 303 K

[Benzaldehyde] = 6.0 x 10^{-2}mol dm^{-3} [PipCC] = 3.0 x 10^{-3}mol dm^{-3} [H$^+$] = 0.2 mol dm^{-3}

3.8. Mechanism

The benzaldehyde was oxidized by piperidinium chlorochromate to give benzoic acid in presence of perchloric acid. The reaction shows first order with respect to oxidant, substrate and fractional order with respect to hydrogen ion concentration. But, it was simply acid catalyzed one. In this case, the concentration of oxidant is attributed to the decrease in effective concentration of Cr (VI) species in the reaction medium. From these observations, the following mechanism (Scheme 1) was proposed and suitable rate law was derived.



Scheme 1: Mechanism for the Oxidation of Benzaldehyde by PipCC

3.9. Rate Law

Rate $= k_3$ [Complex]

$= k_3K_2$ [PipCCH$^+$][S]

$= k_3K_2K_1$ [PipCC][S][H$^+$]/1+K$_1$[H$^+$]-d [PipcC]/dt

$= k_{obs}$[PipCC][S][H$^+$]/1 + K$_1$[H$^+$]

The proposed mechanism and the suitable rate law support all the observations made including the effect of solvent polarity and the negative entropy of activation.

4. CONCLUSION

The oxidation of benzaldehyde by piperidinium chlorochromate in aqueous acetic acid medium leads to the formation of a complex giving benzoic acid as the final product. The reactions were followed under pseudo-first order kinetics. The mechanism proposed for this oxidation kinetics in accordance with the observed kinetic data and suitable rate law was derived.

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