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OXIDATION OF BENZALDEHYDE BY QUINOXALINIUM DICHROMATE

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ABSTRACT

The kinetics and mechanism of oxidation of benzaldehyde by quinoxalinium dichromate has been studied in the presence of perchloric acid in 70 % acetic acid - water medium. The reaction follows first order with respect to benzaldehyde, quinoxalinium dichromate and fractional order with respect to perchloric acid. There is no effect on the reaction rate with increase in ionic strength of the medium by adding sodium perchlorate. The rate of reaction increases with increase in the percentage of acetic acid. The reaction does not induce the polymerization with acrylonitrile. The rate of reaction decreases with increase in the concentration of manganoussulphate. The thermodynamic and activation parameters have been calculated and a probable mechanism has been proposed.

Keywords

Oxidation, Kinetics, Mechanism, Benzaldehyde, Quinoxalinium dichromate

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

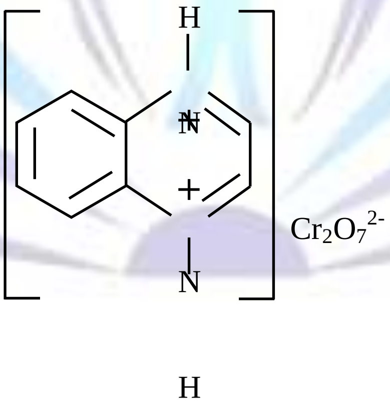
Physical Organic Chemistry

TYPE (METHOD/APPROACH)

Oxidation Kinetics

INTRODUCTION

Quinoxalinium dichromate $(C_8H_6N_2H_2)Cr_2O_7$ (QxDC) has been used in the oxidation of many organic substrates. QxDC[1] is reported to be neutral and mild oxidant for selective oxidation reactions and readily separable from the desired products. The probable structure of quinoxalinium dichromate is given below,



Quinoxalinium dichromate

Kinetics of oxidation of some organic substrates[2-5] by quinoxalinium dichromate has also been reported. The kinetics and mechanism of oxidation of oxidation of benzaldehyde by various oxidants have been reported[6-19]. In this paper, we report the mechanistic aspects of the oxidation of benzaldehydes by quinoxalinium dichromate.

EXPERIMENTAL

Preparation of Quinoxalinium dichromate

A solution of 26.4 g of quinoxaline (0.2 mol) in 60 cc of water was slowly added to a cooled solution of 21.0 g of chromic acid (0.2 mol) in 20 cc of water. After 30 min, the reaction mixture was diluted with 40 cc of acetone, cooled to -15 ^{o}C, and the orange solid was filtered, washed with acetone and dried in vaccuo. The compound melted at 115 °C (literature m.p. 115 – 116 °C) and further analyzed through spectral data. Its purity was checked by estimating Cr(VI) iodometrically.

Benzaldehyde (AnalaR) was purchased from Aldrich and used as such. Acetic acid was refluxed over chromium trioxide containing acetic anhydride for 6 h and then fractionated. Other chemicals were of AnalaR grade. Double distilled water was used throughout the kinetic study.

Kinetic measurements

The pseudo-first order conditions were attained by keeping a large excess (10 fold excess or greater) of the benzaldehyde with respect to quinoxalinium dichromate. The reactions were carried out at constant temperature (±0.3 K) using thermostat and were followed up to 75 % conversion by monitoring the decrease in [QxDC] at 470 nm on a spectrophotometer. The pseudo-first order rate constant k_1 was evaluated from the linear plots of log absorbance versus time. Duplicate kinetic runs showed that the rates were reproducible within ±3%.

Product analysis

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 constants (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.

RESULTS AND DISCUSSION

The reaction was studied under different experimental conditions in the presence of acetic acid–water (70% *v/v*) as solvent medium. At a constant temperature, the rate increased steadily on increasing the concentration of the substrate as shown in Table 1. The linear plot of log k against log [substrate] with a slope (1.07) of unity clearly indicates that the reaction has unit order dependence on the concentration of the substrate. At fixed [H^+] with [substrate] in excess, the plot of log absorbance against time was linear indicating first order with respect to QxDC.

Table 1. Rate Constants for the Oxidation of Benzaldehyde by QxDC at 313 K

[Benzaldehyde] 10^2 *mol dm^{-3}*	[QxDC] 10^3 *mol dm^{-3}*	[H^+] 10 *mol dm^{-3}*	k_1 10^4 *s^{-1}*
4.0	2.0	3.0	7.69
5.0	2.0	3.0	9.36
6.0	2.0	3.0	11.19
7.0	2.0	3.0	13.68
8.0	2.0	3.0	16.11
5.0	1.0	3.0	9.42
5.0	2.0	3.0	9.36
5.0	3.0	3.0	9.44
5.0	4.0	3.0	9.34
5.0	2.0	1.5	7.00
5.0	2.0	3.0	9.36
5.0	2.0	4.5	12.85
5.0	2.0	6.0	14.35

% AcOH:Water = 70:30

The effect of added H^+ ion on the pseudo-first order rate constant was studied by adding $HClO_4$ in the region of 0.15 - 0.60 M. The rate of reaction increased with increase the concentration of $HClO_4$. The plot of log k against log [H^+] gave a straight line with slope 0.54 (Fig. 1) indicating that fractional order with respect to hydrogen ion concentration. The rate of reaction increased with the increase in the percentage of acetic acid (Table 2), the plot of log k_1 against 1/D was found to be linear with a positive slope (Fig. 2), which was confirmed the ion-dipole interaction [20-22] in the rate determining step.

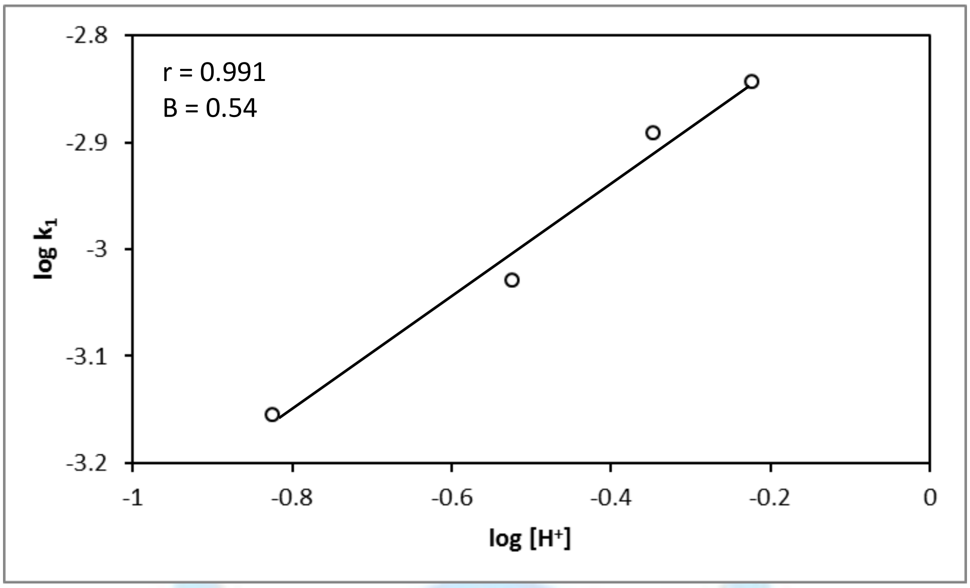


Figure 1 Plot of log k_1 against log $[H^+]$

Table 2. Rate Constants for the Oxidation of Benzaldehyde by QxDC at 313 K

% AcOH:Water (*v/v*)	$[NaClO_4]$ 10^3 *mol dm^{-3}*	$[MnSO_4]$ 10^3 *mol dm^{-3}*	k_1 10^4 *s^{-1}*
70:30	-	-	9.36
72:28	-	-	12.42
74:26	-	-	17.22
76:24	-	-	31.91
78:22	-	-	56.49
80:20	-	-	86.29
70:30	0.00	-	9.36
70:30	5.05	-	9.42
70:30	10.10	-	9.31
70:30	15.15	-	9.51
70:30	20.20	-	9.44
70:30	-	0.00	9.36
70:30	-	1.02	7.98
70:30	-	2.04	7.12
70:30	-	3.06	6.55
70:30	-	4.08	6.14

[QxDC] = 2.0×10^{-3} *mol dm^{-3}* [Benzaldehye] = 5.0×10^{-2} *mol dm^{-3}*

$[H^+] = 3.0 \times 10^{-1}$ *mol dm^{-3}*

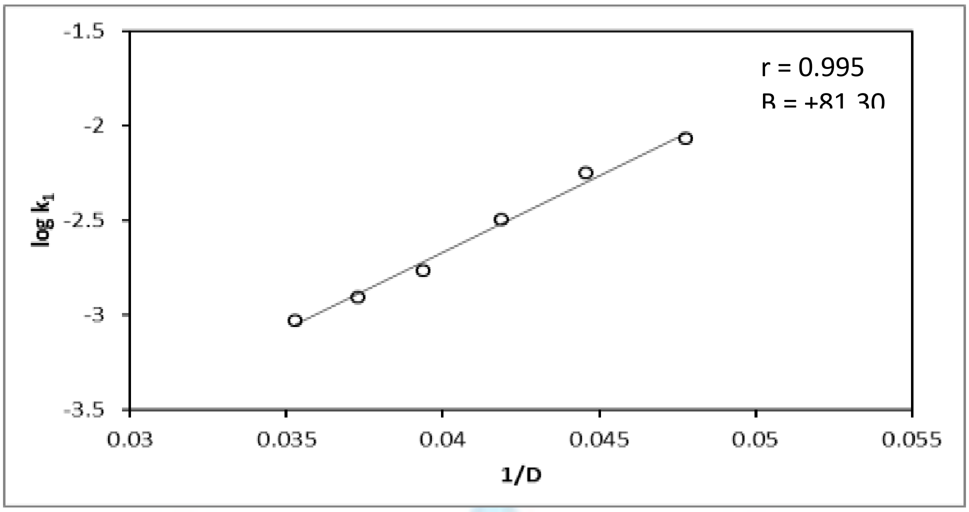


Figure 2 Plot of log k_1 against 1/D

Increase in ionic strength of the medium by adding sodium perchlorate has no effect on the reaction rate indicating the involvement of charged species in the rate-determining step. The reaction mixture showing the absence of any free radical in the reaction has ruled out the possibility of a one electron transfer during the addition of acrylonitrile. But a noticeable catalytic effect on the reaction rate on the addition of $MnSO_4$. The rate of oxidation reaction was considerably showing that the rate-determining step involves a two electron transfer in the mechanism.

The rate constants were measured at four different temperatures *viz*., 303, 313, 323, 333 K, thermodynamic and activation parameters have been calculated from the plot of log k_2/T against 1/T (Fig. 3) using the Eyring's equation (Table 3).

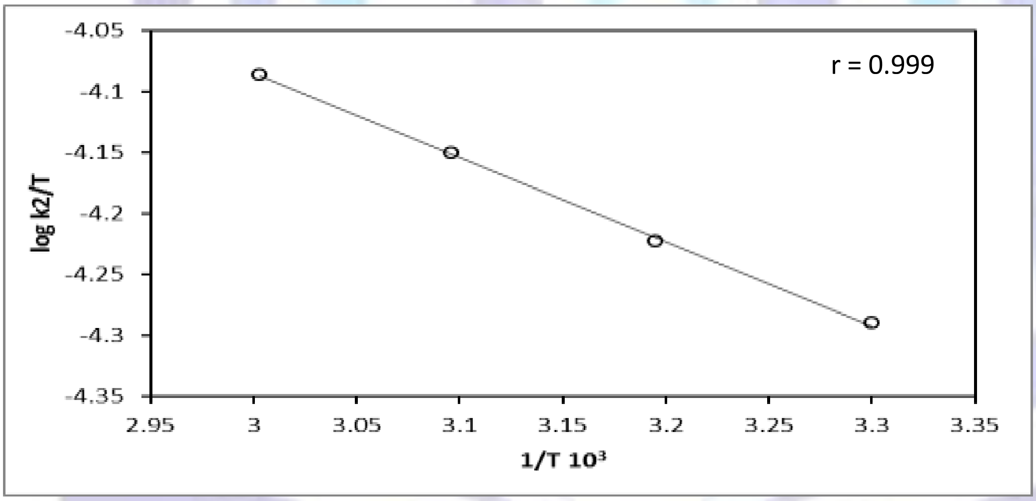


Figure 3 Plot of log k_2/T against 1/T

Table 3. Effect of Temperature for the Oxidation of Benzaldehyde by QxDC

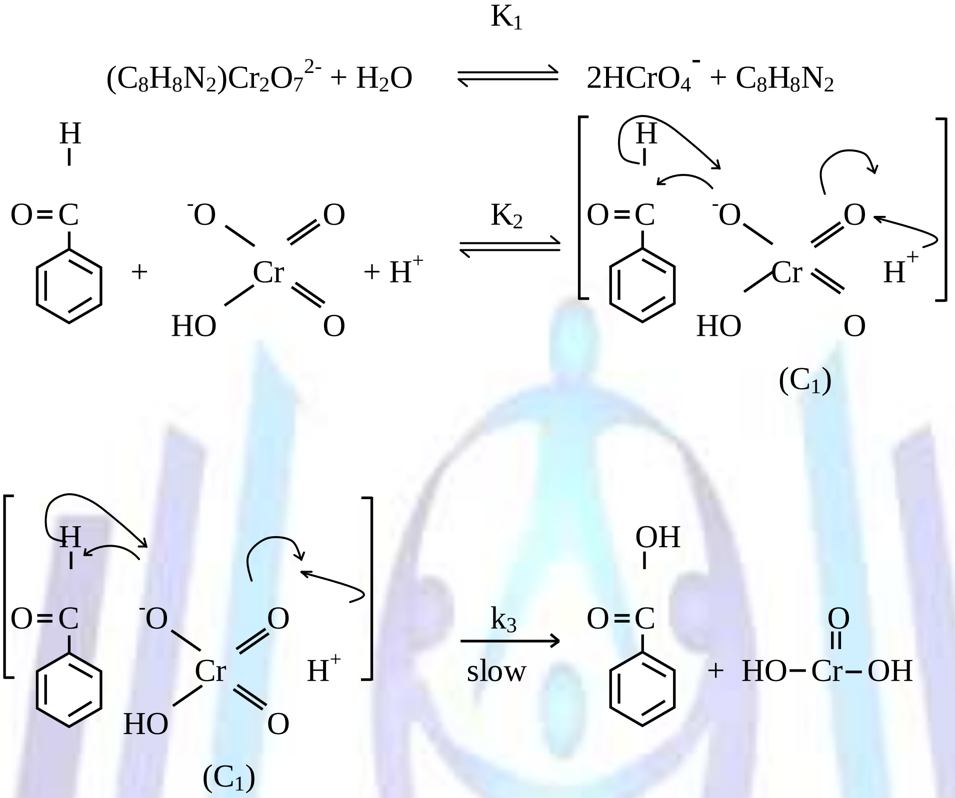
Temperature K	k_1 10^4 s^{-1}	Thermodynamic & Activation Parameters
303	7.77	$\Delta H^{\#}$ = 5.75 *kJ mol⁻¹*
313	9.36	$\Delta S^{\#}$ = -214.25 JK^{-1} mol^{-1}
323	11.44	$\Delta G^{\#}$ = 72.81 $kJ\ mol^{-1}$
333	13.67	Ea = 8.35 $kJ\ mol^{-1}$

[QxDC] = 2.0 x 10^{-3} $mol\ dm^{-3}$ [Benzaldehye] = 5.0 x 10^{-2} $mol\ dm^{-3}$

[H^+] = 3.0 x 10^{-1} $mol\ dm^{-3}$ % AcOH:Water = 70:30

The reaction shows first order with respect to QxDC, benzaldehyde and fractional order with respect to H^+ ion. The rate increases with increase acetic acid medium and increase in ionic strength has perceptibly changed the rate. The retardation of the rate by the addition of Mn^{2+} ions confirms that a two electron transfer process is involved in the reaction. Based on the above facts, the following mechanism (scheme 1) was proposed.

Mechanism



Scheme 1

The above mechanism leads to the following rate law.

Rate law

Rate $= k_3C_1$

$= k_3K_2\,[QxDC]\,[H^+]\,[S] / 1 + K_2[H^+]$

$= k_3K_2K_1\,[QxDC]\,[H^+]\,[S] / 1 + K_2[H^+]$

The rate law explains all the observed experimental facts.

CONCLUSION

The oxidation of benzaldehyde by quinoxalinium dichromate 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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Research Project

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