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A Kinetics and Mechanistic Study of The Oxidation of Pentanol by Chromium(VI) in Dioxan-Water Medium

Abstract

The oxidation of pentanol by Pyridinium dichromate has been studied by spectrophotometrically in the presence of perchloric acid in dioxan-H₂O (70:30%) mixture in presence of perchloric acid leads to the formation of corresponding aldehyde. The reaction is first order with respect to PDC, [H⁺] and pentanol. Michaelis-Menten type kinetics was observed with pentanol. The reaction rates were studied at different temperatures [25, 30, 35, 40, 45, 50 °C] and the activation parameters were computed. The reaction rate increased with increasing volume percentage of dioxan in reaction mixture, suggesting the involvement of an ion and neutral molecule in the rate-determining step. The main reaction product were identified as chromium (III) and acetaldehyde. A suitable mechanism for the reaction was postulated.

Keywords: Pyridinium Dichromate (PDC), Pyridinium Chloro Chromate (PCC), Pyridinium Bromochromate (PBC), Quinolinium Dichromate (QDC), Quinolinium Bromochromate (QBC)

Introduction

Corey and Schmidt¹ 1979 found PDC is a mild and selective oxidizing agent and is soluble in water and many organic solvent. Its solubility is for advantage over inorganic dichromate. A lot of literature are available on oxidation of several substrate by pyridinium dichromate like, cycloalkanols², α -hydroxy acid³. Palanippan et al⁴ oxidation of oxime in 60% acetic acid. Meenakshisundram et al⁵ oxidation of organic sulphide in acetonitrile medium and its substituted oxidant 4-methyl pyridium dichromate developed in 1999 by B. L. Hiral et or⁶ studied oxidation some substituted benzylhydrol.

Our literature survey reveals that the oxidation of pentanol by different oxidants the oxidation of alcohols by PBC,⁷⁻⁸ BPCC,⁹ QFC,¹⁰ QCC,¹¹ and QDC,¹² has received limited attention; we are particularly interested to see the mechanism of the oxidation of pentanol by PDC in Dioxan-Water media.

Materials and Methods

Prepare of pyridinium dichromate by the method describe in the literature¹, and its purity was checked by melting point and iodometrically titration, and pentanol, dioxin, HClO₄ (analar BDH) was used as supplied and purity was cheked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. Double distilled water was used throughout in the investigation. Measurements of rate at 40 ± 0.1 °C in 0.3 mole dm⁻³ HClO₄ under the experimental condition [pentanol] >> [PDC], in the solvent system of 70-30 % (v/v) Dioxan-H₂O. The reaction was initiated by mixing a calculated amount of thermostatted pyridinium dichromate in to the reaction mixture. Reaction progress was followed by measuring the decreasing absorbance of PDC at 350 nm in one cm cell placed in the thermostatted compartment of JASCO model 7800 UV/VIS spectrophotometer.

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The kinetics run were followed for more than 60-70% completion of the reaction and first order kinetics were observed. First order rate constant kobs were obtained from the slope of the plot of log (absorbance) v/s time.

Results and Discussion

Stoichiometry and product analysis by treating the excess concentration of PDC with substrate (PDC and substrate concentration was always kept in 10:1 ratio) in presence of perchloric acid (0.5mol) stoichiometry was ascertained. The residual concentration of PDC determine by iodometrically after complete of reaction. In the case of

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primary alcohol the results revealed that 3 mole of primary alcohol 2 mole of PDC and given by reaction $3\text{CH}_3(\text{CH}_2)3\text{CH}_2\text{OH} + 2\text{Cr(VI)} \rightarrow 3\text{CH}_3(\text{CH}_2)3\text{CHO} + 2\text{Cr(III)} + 6\text{H}^+$

To take 100 to 250 ml. of reaction mixture (10:1 ratio of PDC and pentanol) for product analysis. It was treated with 2, 4-DNP solution heat on water bath and allow to stay for 6 to 8 hours, the yellow precipitate was obtained. The precipitate was filtered, washed with cold water and dried. Then it was

weighed and than moles of 2, 4-DNP calculated, hence moles of aldehyde forms of reaction.

Effect of PDC

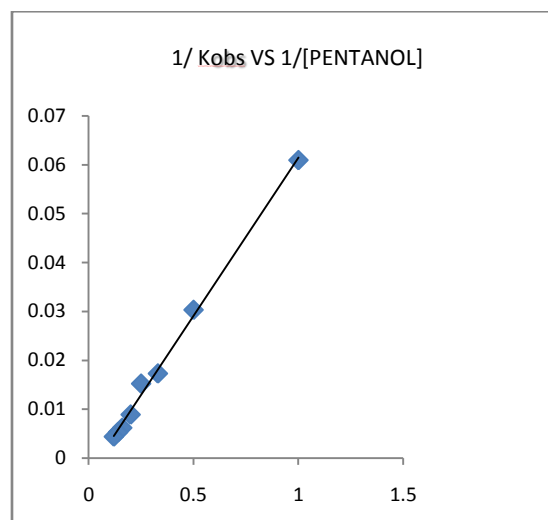
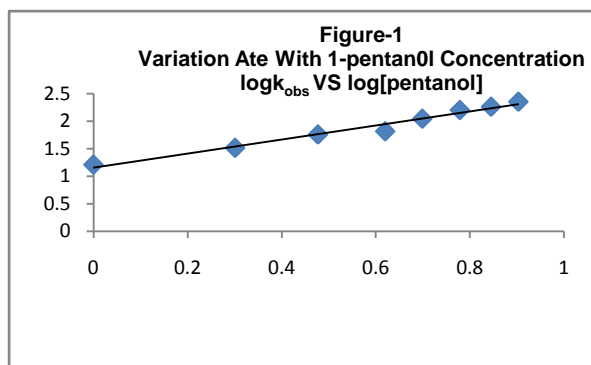
At constant [pentanol], $[\text{HClO}_4]$, Dioxan % and temperature, the rate constant did not change with change in concentration of pyridinium dichromate [Table 1]. Plots of $\log [\text{PDC}]$ v/s time was linear indicating first order reaction and rate of reaction is depend on [PDC].

Table 1. Variation of Rate with PDC, Pentanol, Perchloric Acid Concentrations and Temp.

[PDC]×10M	10M ×[pentanol] mol dm	10× [H] dm mol	Temp. k	Kobs×10
0.2	4.0	5.0	308	62.10
0.3	4.0	5.0	308	62.10
0.4	4.0	5.0	308	62.10
0.5	4.0	5.0	308	62.10
0.6	4.0	5.0	308	62.10
1.0	4.0	5.0	308	62.10
2.0	4.0	5.0	308	62.10
3.0	4.0	5.0	308	62.10
4.0	1.0	5.0	308	16.40
4.0	2.0	5.0	308	33.01
4.0	3.0	5.0	308	57.60
4.0	4.0	5.0	308	65.67
4.0	5.0	5.0	308	111.20
4.0	6.0	5.0	308	160.27
4.0	7.0	5.0	308	185.60
4.0	8.0	5.0	308	225.68
4.0	4.0	2.0	308	1.87
4.0	4.0	4.0	308	4.87
4.0	4.0	6.0	308	7.07
4.0	4.0	8.0	308	9.77
4.0	4.0	10	308	10.17
4.0	4.0	20	308	27.44
4.0	4.0	5.0	303	58.96
4.0	4.0	5.0	308	99.06
4.0	4.0	5.0	313	103.36
4.0	4.0	5.0	318	117.85
4.0	4.0	5.0	323	129.36
4.0	4.0	5.0	328	149.28

Effect of Substrate

At constant [PDC], $[\text{HClO}_4]$, temperature and Dioxan % [table 1] the reaction rate is increased with increasing of pentanol concentrations. When the logarithms of kobs values were plotted against the logarithms of the [pentanol], (Figure 1) a linear plot with a slop of .99 was obtained. Its indicating the order with respect to pentanol first order The plot of 1/kobs versus 1/[pentanol], (Figure 2) linear with passing through origin. Indicates that Michaelis-Menten type kinetics that no intermediate complex. A similar observation have been found in the oxidation of alcohol by Cr (VI)¹³⁻¹⁵



Effect of Ionic Strength and Dielectric Constant

The effect of ionic strength in range of Debye-Huckel limiting law (below 0.01 M) studied and find out the interacting species in rate-determining step. It was observed that addition of salt such as sodium nitrate, sodium sulphate and sodium

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perchlorate in reaction mixture. The rate constant do not affected. It proves that the reaction does not proceed via ion-ion type interaction in rate determining step. The results are summarized in table [2]. The influence of variation of dielectric constant of the medium was carried out by the changing Dioxan (% v/v) in the reaction medium, keeping other conditions remaining constants and the reaction rate was affected considerably. The rate of reaction increased with an increasing volume percentage of Dioxan [Table 3]. A lot of theories have been given to quantitative explanation^{16,17} for the effect of dielectric constant (D) of the reaction medium on the kinetics of liquid phase reaction. For the limiting case of a zero angle of approach between two dipoles or ion-dipole system, Amis¹⁶ had shown that in a linear plot of logk_{obs} vs. 1/D. The positive slope indicates a positive ion-dipole reaction, while a negative slope indicates the involvement of two dipoles or a negative ion-dipole reaction. In the present investigation a plot of logk_{obs} vs. 1/D [Figure 3] shows a straight line with a positive slope, clearly supporting that there is involvement of positive ion-dipole in the rate determining step. Amis¹⁸ had shown in a linear of logk_{obs} vs. 1/D. The positive slope indicate a positive ion-dipole reaction, while a negative slope indicates the involvement of two dipoles or a negative ion-dipole reaction. In the present investigation a plot of logk_{obs} vs. 1/D [Figure 3] shows a straight line with a positive slope, clearly supporting that there is

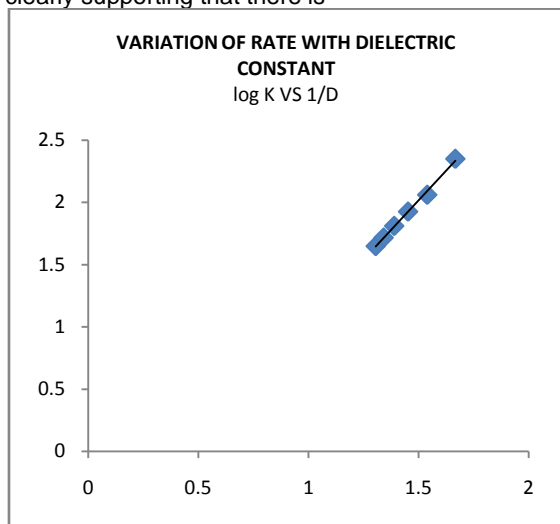


Table 2 Variation of rate with sodium nitrate concentration of pentanol at 313 K

[pentanol]=4.0 x10⁻² mol dm⁻³ [HClO₄] = 0.5 mol dm⁻³ [Temp.]=308K

[PDC] = 4.0 x10⁻³ mol dm⁻³ Dioxan = 30 % (v/v)

[Na ₂ NO ₃]x10 mol dm	0.3	0.4	0.5	0.6	1.0
10 Kobs (s-1)	62.19	62.80	62.15	61.07	62.09

Table 3 variation of rate with solvent composition at 313 K

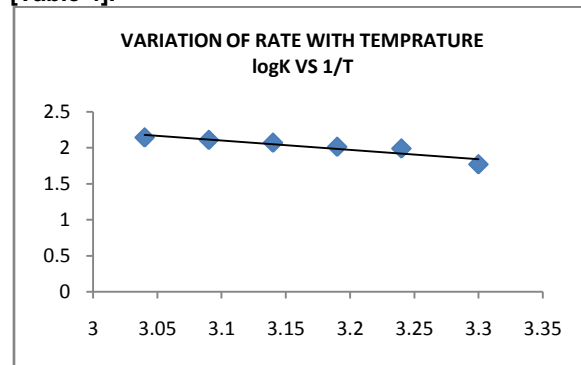
[pentanol]=4.0 x10⁻² mol dm⁻³ [HClO₄] = 0.5 mol dm⁻³

[PDC] = 4.0 x10⁻³ mol dm⁻³ Dioxan = 30 % (v/v)

Dioxan % v/v	10	20	30	40	50
Kobsx10 ⁻⁵	25.87	31.47	47.89	60.69	79.58

Effect of Temperature

At different temperatures limiting range (298-323 K), keeping other experimental conditions constant. The rate constant is increase with increase of temperature [Table 1]. From the Arrhenius plot of logk_{obs} versus 1/T [Figure 4], activation energy and other thermodynamic parameters were calculated [Table 4].



Parameters	Average log pZ s-1 mol-1 dm-3	Energy of Activation Ea kj mol-1	Energy of Entropy S j mol-1 k-1	Free Energy of Activation F kj mol-1
Values	5.26	52.38	-148.03	84.43

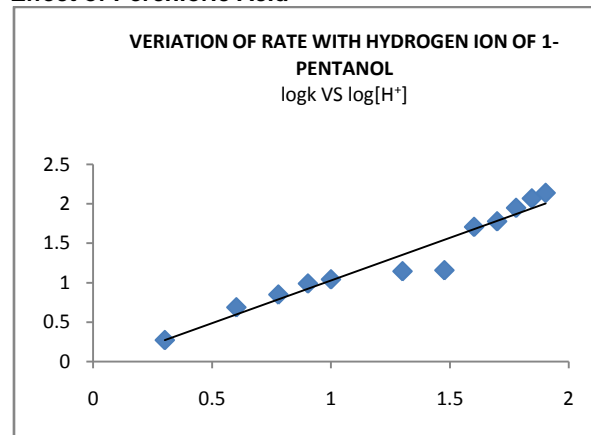
Test for Free Radicals

To test for free radicals, the reaction mixture containing stabilizer free acrylonitrile was kept for 24 hours in an inert atmosphere. On diluting the reaction mixture by methanol and no precipitate was observed. Its indicating that there is no intervention of free radicals in the reaction.

Effect of Pyridine

It has been observed that there no effect of addition of pyridine on rate of reaction, indicating that PDC is not hydrolyzed in the reaction. Further this shows stability of PDC in the conditions understudy.

Effect of Perchloric Acid



The rate of oxidation of alcohols with increasing initial concentration of hydrogen ions. Perchloric acid was used as a source of hydrogen ions. A plot of log K1 against log [H⁺] gives a straight line with slope =1. A first order dependence of rate can be explained, assuming the following equilibrium.

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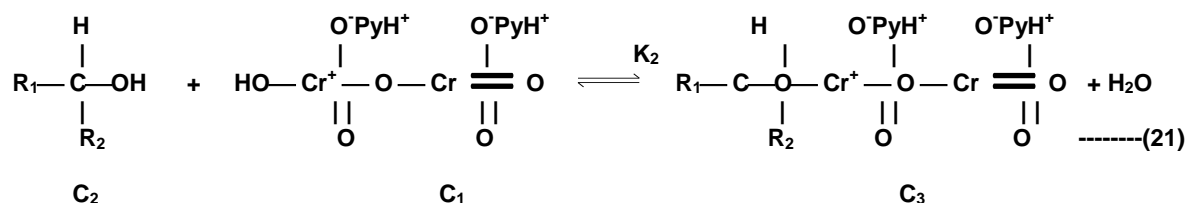
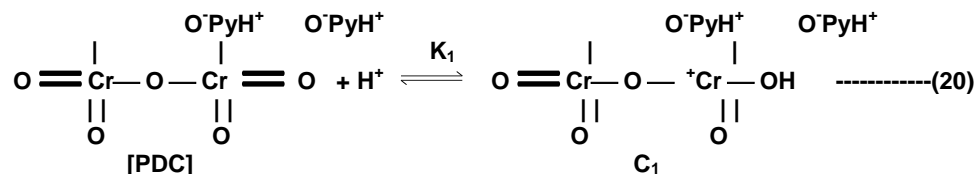
[H⁺] is used for protonation of PDC. An attempt to correlated the rate of oxidation. It well known that reaction in moderately concentrated mineral acids log Kobs is first order and linearly related to -log [H⁺] and other time to log [H⁺]. This forms the basis of Zucker-Hammett hypothesis [17]. Aplot of log kobs against -log [H⁺] is straight line range 0.7 to 1.0 M with slope =1.

Ideally the slope should be 1.0 However zucker-Hammett hypothesis has been sharply critised^{18,20}.

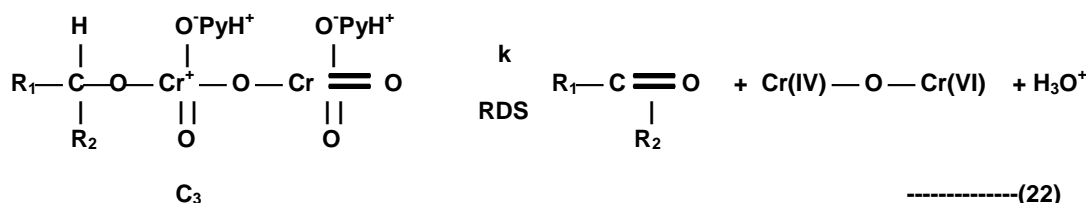
Mechanism

On the basis of above experimental results, a suitable mechanism is given below:

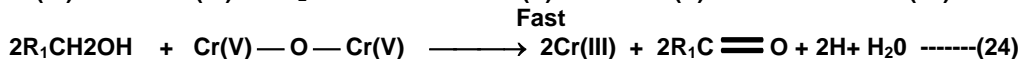
In Case of Both Type of Alcohol, A Tentative Mechanism may be Given as



H₂O:



Fast



(If R₁ = CH₃(CH₂)₃, product R₁HC=O = aldehyde group product)

Conclusion

At room temperature the reaction between pentanol and PDC is very slow in the low perchloric acid concentration in Dioxan-water medium. The oxidation of pentanol by PDC is first order with respect to [PDC], [pentanol] and [HClO₄].

The reaction was studied at different temperatures. In the temperature range of 298-323 K, Arrhenius equation is valid. The negative value of entropy indicates that the complex C is more ordered than reactant. The description of the mechanism is consistent with all experimental evidence.

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