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An Analytical Studies of Pyridinium Chlorochromate Oxidation Species

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Abstract - A study has been analyzed the "Pyridinium Chlorochromate Oxidation Species." The method was analysed on reaction initial reaction of pyridinium chlorochromate. Further, This reaction has a mostly [cysteine] dependent effect. So, the plot study has been taken from 1/k` VS 1/[cysteine] It is a straight line with a positive slope and intersected at the valence axis, providing kinetic evidence for the complexation of cysteine with reactive species. And the Chromium (III), It was determined that one of the products had no effect on the vaccine. As $[H^+]$ increases, the reaction increases and the $[H^+]$ degree is found to be less than One. The results were shows that Stoichiometry of the (Reaction) on product analysis and carried out chromatography and the stoichiometry of the reaction were pyridinium cysteine.

Keywords: Pyridinium chlorochromate, Product Analysis, Stoichiometry, and Oxidation Species etc.

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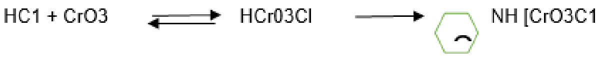
INTRODUCTION

Pyridinium chlorochromate (PCC) is a midline, A selective and stable reagent for the efficient oxidation of various alcohols to carbonyl compounds.[1] he first reports of the chlorochromate anion date back to 1833, when Peligot and Sisler described the preparation of potassium chlorochromate.[2] Pyridinium chlorochromate was first synthesized in 1899. Following preliminary research, the analysis of the crystal structure of potassium chlorochromate was studied. Confirmation that the chlorochromate anion exhibits C3v symmetry using X-ray diffraction and IR Raman spectroscopy.[3]

Oxidation of organic compounds is an important transformation in organic synthetic chemistry. Chromium (III), is the form of inorganic dichromate's, it has largest been used on organic-chemistry as an oxidising agent. However, Because of its harsh nature and need for strong acids, attempts were made to produce small, selective and effective chromium (III) derivatives; Collin's and Corey's reagents were the first reported. Their discovery has led to interest in the field of organic derivatives of chromium (III) as oxidizing agents. Study the mechanism of complex chromium (III) reactions.[4] Some other organic chromium(III) compounds include pyridinium bromochromate (PBC), pyridinium fluochromate (PFC), quinoline dichromate (QDC), quinoline fluochromate (QFC), and others etc.

The first advantage of pyridinium chlorochromate is that it is easy to prepare and safe. Add chromium trioxide to 6N hydrochloric acid to obtain unstable chlorochromic acid. Then add pyridine at °C and immediately obtain pyridinium chlorochromate as a yellow-orange product with no obvious hygroscopicity.[5]



The second advantage is its high efficiency in converting primary alcohol into aldehydes. Pyridinium chlorochromate is slightly acidic and does not normally react with simple olefinic C-C double bonds, but can cause cis-trans isomerization as seen in the oxidation of cis-1-hydroxy-4-tetrahydropyranyloxy-2-butene. Chlorochromate anions are also used as oxidizing agents on polymer matrices.[6] Poly-Vinyl Pyridinium Chlorochromate, (PVPCC) can be easily prepared by adding stoichiometric amounts of chromic acid and concentrated hydrochloric acid to a suspension of cross-linked polyvinylpyridine in water. This oxidant is useful because less than one molar equivalent of the reactant is consumed in the reaction.

Cheng et al., Pyridinium chlorochromate adsorbed on alumina has been reported to be a suitable reagent for the oxidation of alcohols to aldehydes and ketones. The reagent has a small yield, good selectivity and significant potency; the use of pyridinium chlorochromate as an oxidizing agent in carbohydrate chemistry is quite interesting and risky. Recently, Herscovici and Antonakis8 used the oxidation of pyridinium chlorochromate supported on molecular sieves and found that the reaction rate was very fast, leading to good yields of ketonucleosides and ketoses in dichloromethane solution at room temperature. The many uses of pyridinium chlorochromate in organic synthesis include the oxidation of alcohols, the oxidation of organometallic compounds, deoxidation reactions, the synthesis of unsaturated carbonyl compounds, oxidative cation cyclization reactions and the oxidation of activated carbon-carbon double bonds.[7]

Mechanistic model of pyridinium chlorochromate oxidation - The oxidation occurring with pyridinium chlorochromate can be divided into two groups.[8]

1. Reaction of complex formation of pyridinium chlorochromate and substrate.

2. The reaction occurs directly without creating any difficulties.

1. The reaction involves the formation of a complex between pyridinium chlorochromate and the substrate. In this type of reaction, a complex is formed between pyridinium chlorochromate and the substrate which decomposes directly into products;

substrate + PCC -> "~ [complex]

[complex] —j—> products

which leads to the rate equation

$$\text{Rate}=\frac{kK[sub][PCC]}{1+K[sub]}.$$

The oxidation of thioglycolic acid, thiolactic acid, thiomalic acid 9 and methionine 10 by pyridinium chlorochromate (PCC) in 19 different organic solvents was investigated. This reaction is first order for pyridinium chlorochromate and fractional for the substrate.

The oxidation of tellurium(III) with pyridinium chlorochromate was studied in aqueous hydrochloric acid at 30 ° C. The authors presented the following procedure:

PyHC102Cr = O + H+ ^ PyHCl 02 Cr- OH

PyHCl 02Cr-OH + OH-TeOOH ^ ^ PyHCl 02Cr-0-TeOOH + H20

The kinetics of the oxidation of diethyl sulfide (Et2S) by pyridinium chlorochromate in 50 vol% aqueous solution of acetic acid (AcOh) was investigated. The reactions in Et2S, PCC and [H+] are all first order. The reaction product was found to be Et2SO. They reported a mechanism involving the slow formation of an intermediate between protonated PCC and Et2S.

Oxidation of phosphite is carried out. They found that as the reaction progresses, a complex is formed which gradually decomposes into chromium (IV) and then disproportionates. The pricing policy is determined accordingly:

$$\text{Rate}=\frac{K1Ke[H+][H3PO3][Pub][PCC]}{1+Ke[H3PO3]([H+]Kd)}.$$

So, the Ramakrishnan reported the EDTA-catalyzed oxidation of some cycloalkanones with pyridinium chlorochromate. This observation was that whether the Cr (III)-EDTA- The cycloalkanone ternary complex decomposes to α-ketool by slow oxidation, which is then rapidly oxidized to the mature ketone.[9]

Kinetics and oxidation mechanism of L-cysteine

The oxidation mechanism of cysteine, a sulfur-containing non-essential amino acid, has been demonstrated with hexacyanoferrate (III) (uncatalyzed and catalyzed), chromium (III), cerium (III) and vanadium (IV), etc. work, 12-tungstocobaltate (III), trioxalatocobaltate, α,-osapiaquabis (2,2'-bipyridyl) ruthenium (III), chloramine-T and bromazine. Cystine (disulfide of cysteine) has been reported to be the main oxidation product in most oxidation reactions. However, sulfoalanine and acetaldehyde have also been reported to be oxidation products in some oxidation reactions. Therefore, to better understand the oxidation mechanism of cysteine, the authors conducted a kinetic study on the oxidation of an organic dichromate, namely pyridinium chlorochromate (PCC), and the results are presented in this section.

EXPERIMENTAL RESEARCH

Cysteine solution: A solution containing approximately 0.05 mol $dm^3$of cysteine in 0.1 mol dm^3 of perchloric acid was prepared from 99.9% pure L-cysteine (Hi Media). The strength of the solution is determined by the iodometric method. Consider the amount of perchloric acid present in the cysteine solution when preparing the reaction mixture for kinetic study.

Pyridinium Chlorochromate solution: A 0.01 molar dm3 pyridinium chlorochromate (PCC) solution was prepared by rapidly adding 100 g of chromium trioxide to 184 ml of 6.0 molar dm^3 hydrochloric acid while continuing to stir the solution. After 5 min, the homogeneous solution was cooled to 79°C.

Backwashing to °C gave a yellow-orange product, which was collected on a sintered glass and dried in vacuo for 1 h. The product has no significant hygroscopicity and can be stored for long periods at room temperature. A 0.01 mol dm^3 solution of Prepared by dissolving pyridinium chlorochromate in double distilled water and performing standard spectrophotometry at 356 nm. [(e) = 1296 dm3 mol-1 cm-1.]

Chromium (III) solution: Prepare 0.01 mol dm^3 chromium (III) double distilled solution by dissolving chromium (III) potassium sulfate (E.Merck) in water.

Perchloric acid solution: Prepare and use approximately 6.0 mol^{-1} dm^3 perchloric acid solution (E.Merck 'ProAnalysi' 70%) (Chapter III, Section II).

Sodium perchlorate solution: Prepare and use approximately 8.0 mol dm3 of sodium perchlorate solution as described in Chapter II, Section II.

Acrylonitrile solution: Commercial acrylonitrile is washed three to four times with aqueous sodium hydroxide solution to remove phenolics used as stabilizers. It is then distilled under reduced pressure and stored in tightly stoppered amber bottles.

All other chemicals used in this study were of analytical reagent grade. Doubly distilled water was used throughout the study.

RESULTS

To determine the stoichiometry of the reaction, a known excess of pyridinium chlorochromate was added to a known amount of cysteine in a 0.1 mol^{-1} dm^3 perchloric acid medium at 30 °C. After 12 h, 393 [PCC] remaining in all cases was determined spectrophotometrically at nm. The stoichiometry of the reaction was found to obey the following equation:

HSCH2CH(NH3)COOH + 2Cr(VI)(PC C) H 2 ° > H03SCH2CH(NH2)COOH + 2Cr(III)

Product analysis was done by chromatography. The reaction products were found on a chromatography plate, saturated with phenol vapor and then run in phenol saturated with water. After the chromatogram was produced, the plate was removed from the container and dried. A 1% solution of ninhydrin in n-butanol was then sprayed on and heated in an oven at 100°C for five minutes. The value is 0.15, confirming the presence of sulfoalanine. Effect of ionic strength - Study the effect of ionic strength on reactions, perform kinetic studies to hold the concentrations of all other reactants constant and vary the ionic strength in the range of 0.15-0.50 mol dm"3 using sodium perchlorate as the calculation. The pseudo first value determined continuously from the slope of the logarithm (absorbance) versus the run time is listed in Table 1:

Table-1

EFFECT OF IONIC STRENGTH, V , ON THE PSEUDO FIRST ORDER RATE CONSTANT, k' ,

[cysteine] - 4.0x10^{-3} mol dm^{-3}; [PCC] = 4.0x10^{-4} mol dm^{-3} [H$^+$] = 0.1 mol dm^{-3} ; t = 30 ± 0.1°C

μ (mol dm^{-3})	K`x10^4 (sec^{-1})
0.15	6.09
0.20	6.19
0.30	6.14
0.35	6.28
0.40	6.14
0.50	6.19

From the data in Table 1, it is seen that the effect of ionic strength on the reaction rate is negligible.

To study the effect of chromium(III) on the reaction rate, kinetic studies were carried out by keeping the concentrations of all other reactants constant but varying the concentration of chromium(III). The resulting pseudo-first-order constant values are listed in Table 2.

Table-2

EFFECT OF [CHROMIUM(III)] ON THE PSEUDO FIRST ORDER RATE CONSTANT, k'

[cysteine] = 4.0x10^{-3} mol dm^3; [PCC] = 4.0x10^4 mol dm^3 [H+] = 0.1 mol dm^3 ; t = 30 ± 0.1°C

[Cr^{III}]x10^4 (mol dm^{-3})	K`x10^4 (sec^{-1})
1.0	6.14
2.0	6.28
3.0	6.71
4.0	6.58
6.0	6.14
8.0	6.71

From the data in Table 2, it is seen that the effect of Chromium (III) on the reaction rate is negligible.

In order with respect to pyridinium chlorochromate- To determine the effect of PCC, kinetic study was done at 30 °C; the difference of PCC was 1.0-8.0X10-4 mol dm^3 and the concentration of all other ions was kept unchanged with delay. Therefore, the pseudo prime payment constants are listed in Table-3.

Table-3

EFFECT OF [CHROMIUM(III)] ON THE PSEUDO FIRST ORDER RATE CONSTANT, k'

[cysteine] = 4.0x10^3 mol dm^3 ; [PCC] = 4.0x10^4 mol dm^3 [H+] = 0.1 mol dm^3 ; t = 30 ± 0.1°C

[PCC]x10^4 (mol dm^{-3})	K`x10^4 (sec^{-1})
1.0	6.28
2.0	6.71
3.0	6.58
4.0	6.14
6.0	6.71
8.0	6.28

A careful reading of the data in the table above shows that the pseudo-first-order value constant k, obtained from the data of logarithmic (absorbance) versus time (Table 1), is the constant indicating its action with respect to pyridinium chlorochromate.

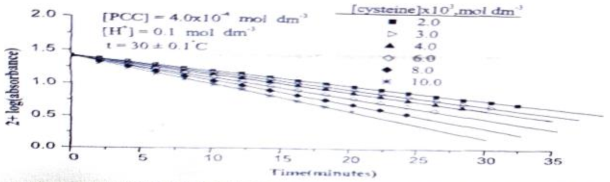
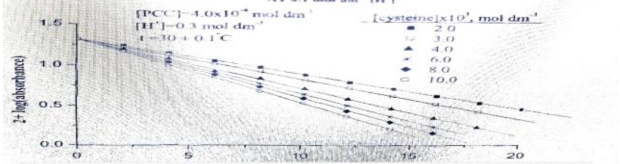


Fig.5.2a: EFFECT OF [CYSTEINE] ON THE PSEUDO FIRST ORDER RATE CONSTANT, k' AT 0.1 mol dm^-3 [H^+]



Time (min): Effect of [Cysteine] on the PSEUDO first order rate constant, k' at 0.3mol dm^-3 [H^+]

CONCLUSION

This study reviews a critical analysis of the oxidation state of pyridinium chlorochromate. The oxidative effect of pyridinium chlorochromate on cysteine was investigated. This reaction is the first reaction in pyridinium chlorochromate. This reaction has a mostly [cysteine] dependent effect. In addition, the plot of 1/k' and 1/[cysteine] is a straight line with a positive slope and the valence axis intersects, providing kinetic evidence for many reactive species of cysteine. One of the elements, chromium (III), was found to have no effect on the reaction.

In most of the reactions where pyridinium chlorochromate (PCC) was used as the oxidant, studies were carried out in aqueous acidic medium and the kinetics were shown to be similar to PCC and K2Cr2O7. In light of this, the authors had previously found that most complexed hexavalent chromium compounds would eventually hydrolyze to chromic acid in aqueous medium. According to the present experiment (0.1-0.3 mol^{-1} dm^{3} [H^{+}]), protonated chromium(III) is considered to be a reactive species, the value of which increases with [H^{+}].

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