Oxidation of phenyl thioacetic acid by pyridinium chlorochromate:

A kinetic and mechanistic study

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ABSTRACT

The kinetics and mechanism of the oxidation of phenyl thioacetic acid (PTAA) by pyridinium chloro chromate (PCC) has been studied by spectrophotometric method in 50% acetic acid – 50% water (v/v) medium in a temperature range of 308 K – 313 K. Under the conditions of the pseudo-first order, the reaction follows first order with respect to [PTAA], [H^+] and [PCC]. The reaction is catalyzed by perchloric acid. There is no salt effect. The rate increases with increase in the percentage of acetic acid. Activation parameters have been evaluated. Based on the experimental results, a probable reaction mechanism of oxidation was proposed.

Keywords: Kinetics, Oxidation, phenyl thioacetic acid, pyridinium chlorochromate.

INTRODUCTION

Chromium (VI) is a versatile oxidant and it is extensively used in the oxidation of organic substrates. Different forms of chromium (VI) such as chromium trioxide, chromylchloride, chromyl acetate and dipyridine chromium (VI) Oxide (Collin's reagent) acts as oxidant in Kinetic studies. However restriction arise in the selection of solvent since chromium (VI) is a powerful oxidant and the usual choice is acetic acid.

Symons[1] pointed out that the dichromate ion exists only as an acetyl chromate ion ($CH_3COCrO_2O^-$) in aqueous acetic acid. The oxidation by this species is fast as the acetyl group increases the electron accepting power of chromium (VI)[2]. Even the oxidation of diphenyl sulphides[3] in acetic anhydride is very fast as chromium (VI) exists as diacetyl chromium in this solvent.

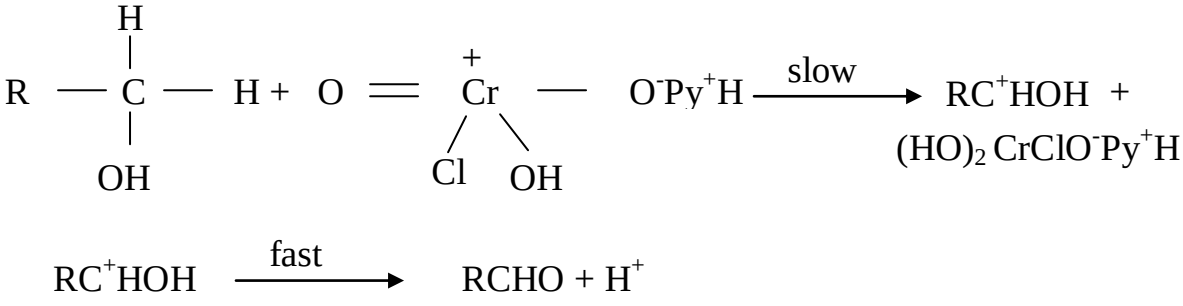
Corey and Suggs[4] reported a new oxidant pyridinum chlorochromate (PCC). PCC is a complex of chromium trioxide, pyridine and hydrochloric acid. This is called as Corey's reagent. It is a versatile oxidant for the oxidation of alcohols to carbonyl compounds with the yield of 80% in dipolar aprotic solvent. The PCC oxidation in the preparatory scale is usually carried out in dichloromethane. Use of acetonitrile or acetone leads to inconveniently long reaction time. The report of PCC as a new oxidant prompted many workers to

carryout studies on the kinetics of oxidation of several organic substrates by this oxidant.

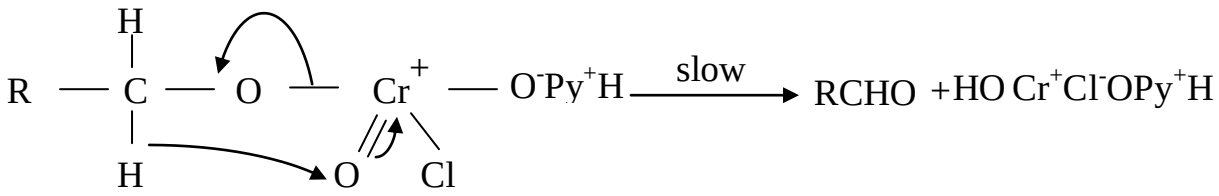
There are reports on the kinetic studies on the PCC oxidation of wide variety of organic substrates such as primary alcohols[5,6], benzhydrol[7], mandelic acid[8], hydroxy acid[9], cyclanols[10] and diols[11].

The kinetics and mechanism of oxidation of primary alcohols[5] by PCC have been studied in 1:1 (v/v) dichloro-methane – nitrobenzene solution. The reaction is found to be first – order each in alcohol and PCC. The enhancement of rate with increase in acidity of the medium suggests the involvement of a protonated chromium (VI) species in the rate – determining step. A hydrogen abstraction mechanism has been proposed. Hydride ion transfer takes place either directly (scheme 1) or by the prior formation of a chromate ester (scheme 2).

Scheme 1

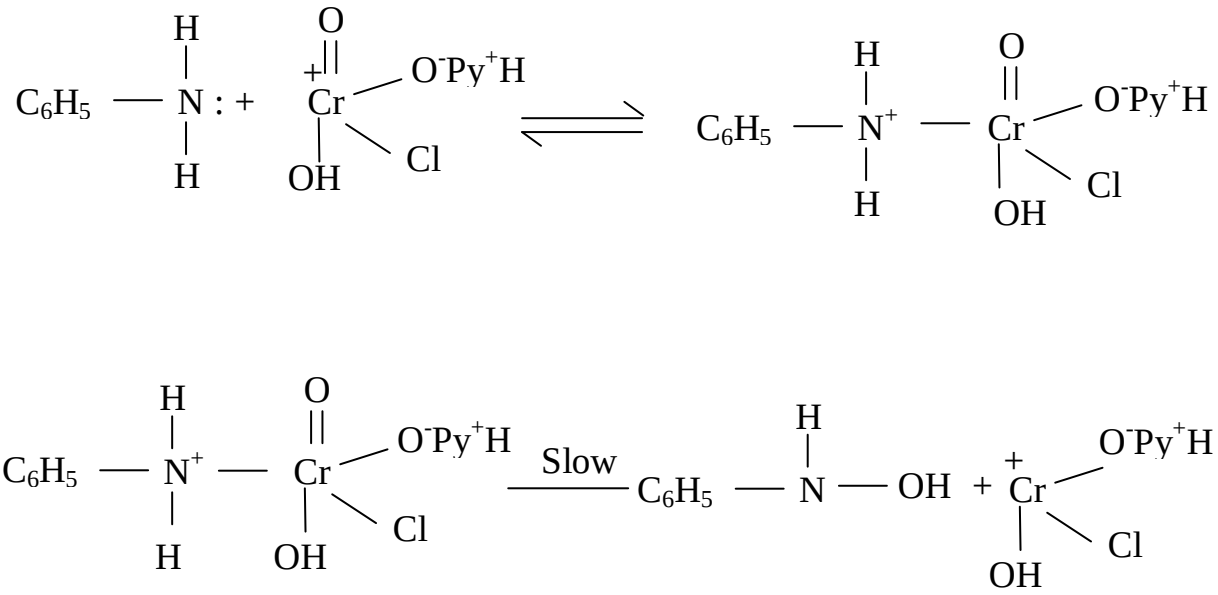


Scheme 2:

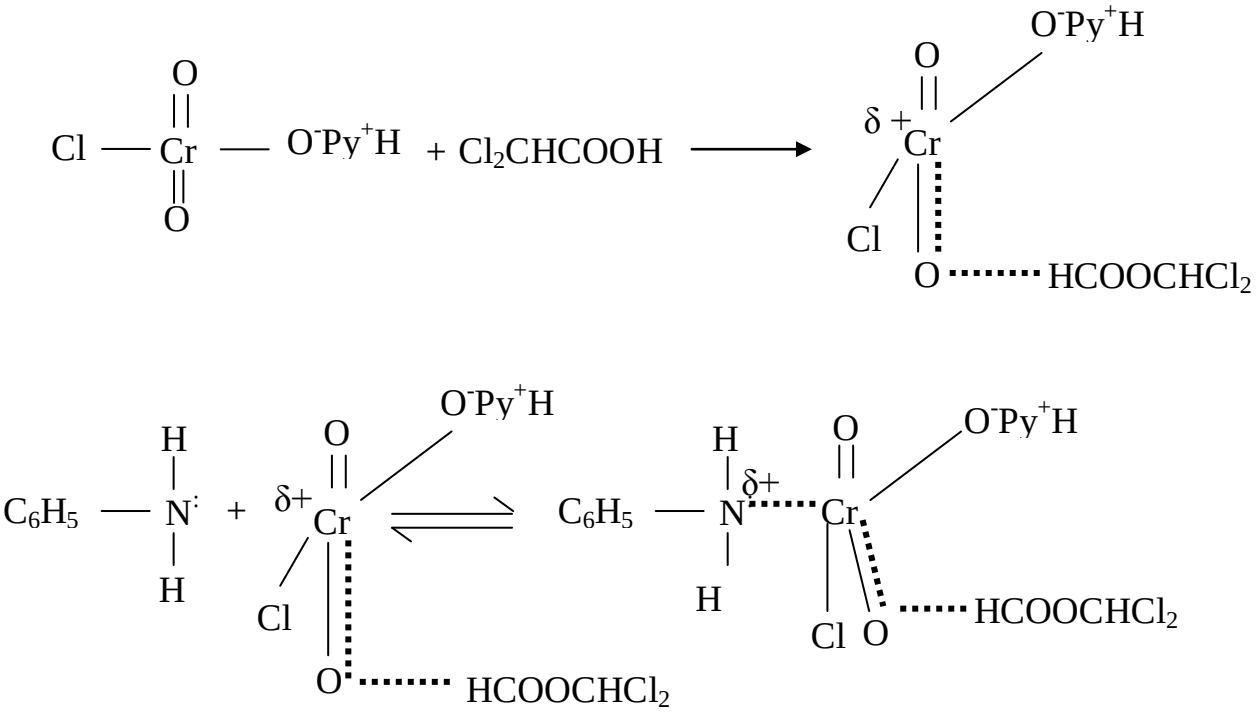


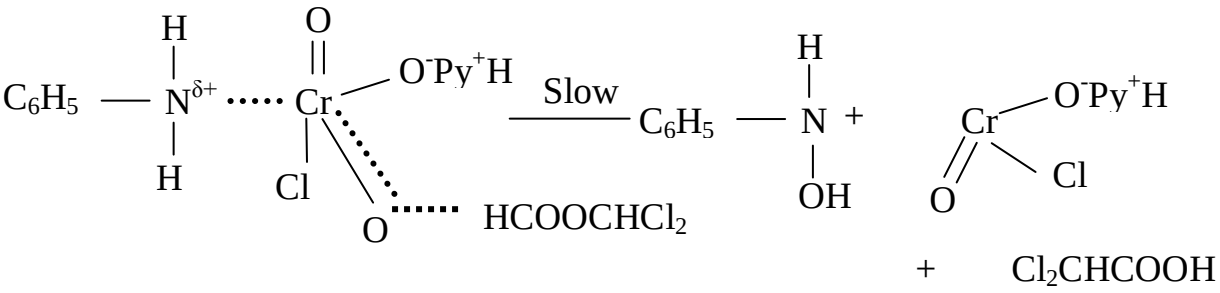
The kinetics and mechanism of oxidation of substituted benzyl alcohols [12] by PCC have been studied in 1:1 (v/v) methylenechloride – nitrobenzene. The reaction follows first – order kinetics with respect to both the oxidant and the alcohol. Mechanisms involving a hydride ion transfer in the rate – determining step have been proposed.

Panigrahi and Mahapatro[13] have studied the oxidation of aniline and substituted anilines with PCC in nonaqueous medium in presence of dichloroacetic acid. The reaction is found to be first – order each in aniline, PCC and dichloroacetic acid. Azobenzene and P – benzoquinone have been obtained as products. Electron – releasing substituents accelerate the reaction whereas electron – attracting substituents produce the opposite effect. A Hammett ρ value of – 3.75 has been obtained. A mechanism involving the formation of an intermediate complex between protonated PCC and aniline which decomposes in a slow step has been proposed.

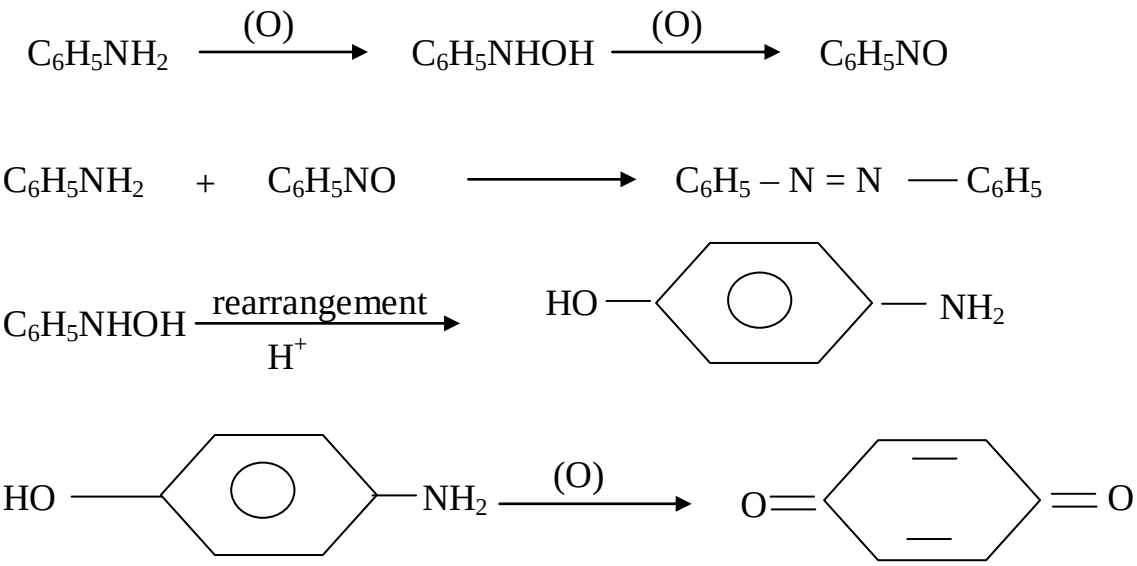


The dissociation of dichloroacetic acid in aprotic solvent is questionable, and so PCC may be involved in hydrogen bonding with a molecule of dichloroacetic acid rather than undergoing protonation. Hence an alternative mechanism has been suggested.



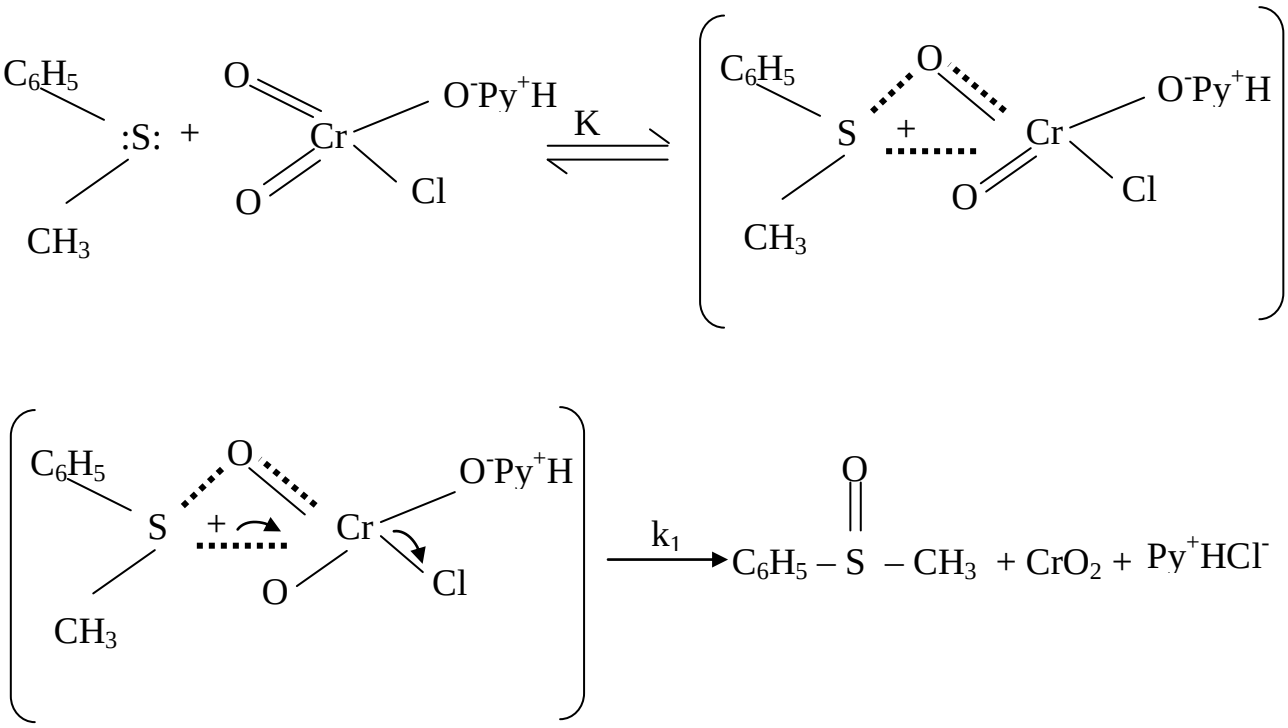


The formation of azobenzene and P – benzoquinone from phenylhydroxylamine has been given as,



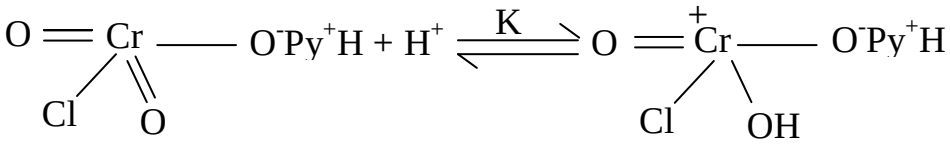
The oxidation of some phenyl methyl sulphides[14] by PCC has been studied in binary solvent mixtures of 60% (v/v) aqueous acetic acid and 50% (v/v) chlorobenzene – nitrobenzene. The reaction follows second – order kinetics in aqueous acetic acid and Michaelis – Menten type kinetics in

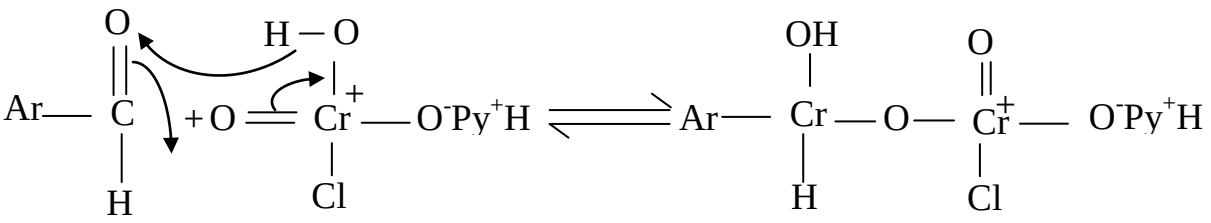
chlorobenzene – nitrobenzene mixture. The following mechanism has been proposed for the oxidation of methyl phenyl sulphide by PCC.

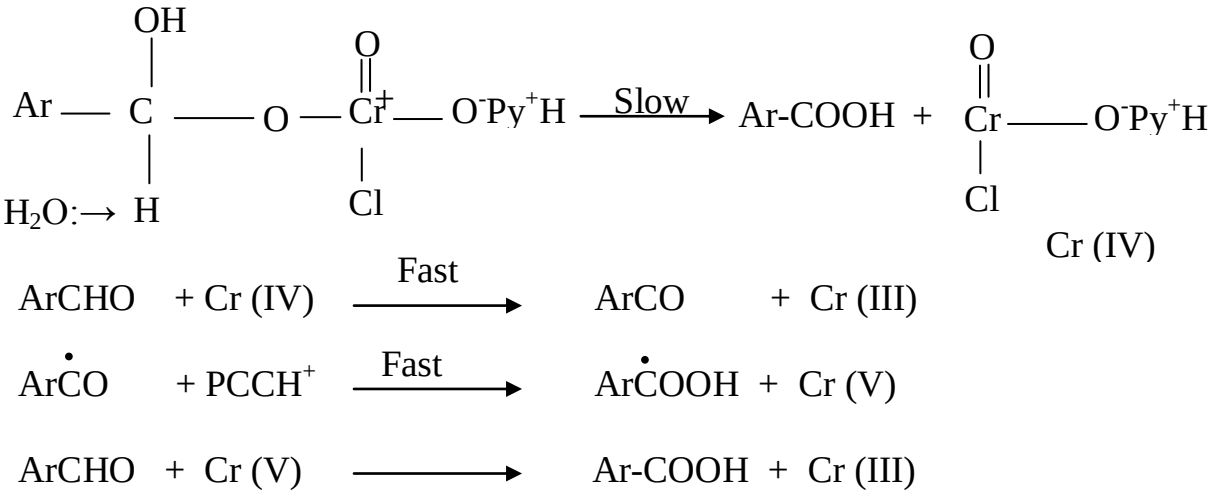


In aprotic solvent the decomposition of the complex is the rate – limiting step. In protic solvent the formation of the complex is the rate – limiting step. A study of ortho – effect in the oxidation of ortho – substituted phenyl methyl sulphides by PCC has been reported[15].

The kinetics of oxidation of para and meta – substituted benzaldhydes[16] by PCC have been studied in aqueous acetic acid (1:1, v/v)







The reaction is first order each in [substrate], [PCC] and H^+] . Electron – releasing substituents retard and electron withdrawing groups enhance the rate. Addition of monomer to the reaction mixture gives a polymer. A mechanism involving the formation of a PCC – ester as the intermediate has been proposed.

General survey of phenylthio acetic acid

The crystal study[17] of phenylthio acetic acid (PTAA) reveals that it belongs to monoclinic space group. The molecules are planar and exist as centro symmetrically hydrogen bonded cyclic dimers. The thioacetic side chain

has syn planar – syn planar conformation. The crystal structures of barium and potassium phenylthio acetates have also been studied [18].

The ionization constants and degree of dissociation of several substituted phenyl thioacetic acids have been measured at various experimental condition and solvent systems [19-22]. From the comparison of Hammett ρ value of phenyl thioacetic acids (0.30) with β –phenylpropionic acid (0.24) and phenylacetic acid (0.23) it is clear that thio group transmits inductive effect more effectively than methylene or oxo group and the order of dissociation constant[23] is phenoxyaceticacid < PTAA < β-phenyl propionic acid.

Analysis of stability constants of the silver complexes of substituted phenylthioacetic acids gave good Hammett correlation with σ constants [24]. In a series of $PhXCH_2COOH$. Where X = O, S or Se, the stability order of silver complexes has been shown to be Se>S>>O. The seability constant of the bis complex of silver and PTA has been recorded by Larsson[24].

The existence of interaction between the lone pair electrons of the sulphur atom with the π electrons of the benzene ring in PTAA was inferred from the UV absorption spectrum[25]. The substituent effects on the ^1H NMR spectra of substituted phenylthioacetic acids have been reported by Srinivasan and Pitchumani[26].

PTAA eliminates PhSH by hydrogen rearrangement during fragementation[27] to yield CH_2COO^-. The pyrolysis of PTAA [28] over the temperature range 760-835°C gave benzenemercaptol, acetic acid methyl phenyl sulphide, carbondioxide and dibenzyl as major products.

$$C_6H_5SCH_2COOH \rightarrow C_6H_5S^{\bullet} + {}^{\bullet}CH_2COOH$$

$$C_6H_5SCH_2COOH \rightarrow C_6H_5SCH_3 + CO_2$$

PTAA undergoes a one electron reduction to give Phs^- and acetic acid, polarographically[29]. The half-wave potential for the reduction is 2.425v.

Light induced decarboxylation in PTAA gave methyl phenyl sulphide as the product. This reaction is photosensitized by benzophenone [30,31], aromatic ketones [32], aromatic nitrocompounds [33] and heterocyclic compounds [34]. The reaction proceeds by electron transfer from the acid to an excited state of the sensitizer.

$$R_2CO \rightarrow R_2CO^*$$

$$R_2CO^* + PhSCH_2COOH \rightarrow R_2C^{\bullet}OH + PhS\ {}^{\bullet}CH_2 + CO_2$$

$$R_2C^{\bullet}OH + PhS\ {}^{\bullet}CH_2 \rightarrow R_2CO + PhSCH_3$$

PTAA and substituted phenylthioacetic acids were found to posses many biological activities as revealed by their tendency to act as herbicides [35,36],

systemic fungicides [37], pesticides [38] and used to activate the growth of certain plants[39-41]. Halogen substituted phenylthioacetic acids exhibit phytohormal activities [42] and the reactivity decreases in the order Cl > Br > 1.

Phenylthioacetic acids are effective in the treatment of poultry enterohepatitis [43] and industrially used in the manufacture of plasticizers for vinyl chloride resins [44,45]. Certain phenylthioacetic acids were found to be of great use as precursors in the production of some new antibiotics [46] and in the biosynthesis of a new penicillin [47].

Depending upon the experimental conditions, different products are formed during bromination of PTAA. Bromination in aceticacid gave p-$BrC_6H_4SCH_2COOH$ but in the presence of water $(p\text{-}BrC_6H_4S)_2$ is produced [48]. Refluxing with bromine in carbon tetra chloride in UV light [49] gave phSCHBrCOOH while in the absence of radiation the main product is p-$BrC_6H_4SCHBrCOOH$. These brominated products give $(PhS)_2CHCOOH$ and $(p\text{-}BrC_6H_4S)_2CHCOOH$ with hydrochloric acid.

Phenylthioacetic acid react with aromatic aldehydes to yield α-substitued cinnamic acids [50.51].

SCOPE OF THE PRESENT INVESTIGATION

The reactions of PCC ions with various organic and inorganic compounds have been extensively studied. Studies of electron transfer (ET) reactions in organized assemblies are of recent interest owing to the possible application for mimicking of many biochemical processes. Chemical reactions have been extensively carried out to understand the processes, however only limited reports are available on the oxidation of sulphur compounds by PCC.

A survey of literature points out that the kinetics of oxidation of phenylthioacetic acid (PTAA) by PCC has received little attention.

In order to fill the void and understand the mechanistic path way followed it has been proposed to conduct experiments on the oxidation of PTAA by PCC. Such a study will throw light on the interactions that are to influence the rate of oxidation.

EXPERIMENTAL

Preparation of phenylthioacetic acid

The acid was prepared by the method adopted by Pasto et.al.[52]. To a cold solution of sodium hydroxide (10ml, 20%) was added a solution of chloroaceticacid (4.7g) in water (10ml) without allowing the temperature to rise. The thiophenol (5.5 g) dissolved in sodium hydroxide (10ml, 20%) was added to the above solution with cooling and constant shaking. The mixture was heated in an oil bath at 120-130°C for five hours. The solution was cooled and extracted with a small amount of ether and the ether layer was rejected. The sodium salt of the acid was obtained as a solid. It was dissolved in 50% hydrochloric acid, and extracted with ether. The ether layer was evaporated and it gave a solid phenylthioacetic acid.

The phenylthioacetic acid used in the present study was purified by recrystallisation in hot water to a constant melting point. The purity of the acid was checked by melting point. The melting point observed for the phenylthioacetic acid is 63°C. The literature [52] value is 63.5 to 64°C.

REAGENTS

Water

Deionised water was distilled twice in all – glass 'Corning' assembly, the second distillation being from potassium permanaganate. All the solution were prepared using double distilled water.

Pyridinium chlorochromate (PCC)

PCC was prepared by the method of Corey and Suggs[4]. 12g of chromium trioxide was dissolved in 22ml of 6NHcl and 9.5g of pyridine was added under stirring at 40°C during a 10 minutes period. Then the mixture was cooled to 0°C and the crystalline yellow – orange PCC was collected on a sintered glass funnel and dried for one hour in vacuo. The compounds was not hygroscopic and stable at room temperature. The purity was detected by estimating Cr (VI) iodometrically

Acetic Acid

Glacial acetic acid (BDH, Analar) was purified by the method of Orton and Bradfield[53]. It was refluxed with chromium trioxide (CrO_3, 2g/100ml) for two hours and then distilled. The middle fraction was collected and used for kinetic studies.

Sodium Acetate

Sodium acetate (BDH, AnalaR) was used as such to maintain the ionic strength of the medium in PCC oxidation studies.

Perchloric acid

Perchloric acid (60% solution, GR, E.Merck) was used as such to maintain the H^+ ion concentration of the medium.

Other reagents

All the other reagents used in the kinetic investigation viz., sodium thiosulphate, starch, potassium iodide and sulphuric acid were of AnalaR grade.

Glassware

Glasswares used for handling the solution were cleaned with a warm solution of chromic acid, rinsed profusely with double distilled water and dried.

Thermostat

The thermostat supplied by Toshiniwal and Co. with an accuracy of ± 0.1°C was used for all the kinetic experiments.

Kinetic Measurement

The kinetic studies were carried out in 50% acetic acid – 50% water (v/v) mixture at constant ionic strength (maintained by the addition of sodium acetate) under pseudo first – order condition with a large excess of substrate concentration in vessels coated on the outside with black paint. The reaction mixture containing the required amounts of substrate, perchloric acid and sodium acetate was thermostated. The requisite amount of standard PCC solution, separately thermostated, was then pipetted out carefully into the reaction mixture at zero time and shaken well. Aliquots (5ml) were withdrawn at definite time intervals and transfered to an iodine flask containing 10ml of 10% potassium iodide solution. Then 10ml of 1M sulphuric acid was added. The liberated iodine was titrated with a standard sodium thio-sulphate solution using starch as the indicator.

According to the first – order rate equation,

$$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{a - x}$$

$$t = \frac{2.303}{k_1} \log_{10} \frac{a}{a - x}$$

k_1 = 2.303 x slope expressed in sec^{-1}

where k_1 is the pseudo first – order rate constant and 't' is time in seconds, a and (a – x) denote the initial concentration and concentration at time 't' respectively of the oxidant. The second – order rate constant was evaluated using the expression.

$$k_2 = k_1 / [\text{substrate}]$$

It is expressed in $M^{-1}s^{-1}$. The precision of k values in all the kinetic runs is given in terms of 95% confidence limit (CL) of the 'student t' [54].

Evaluation of activation parameters

According to Eyring the rate coefficient of a reaction in given by

$$k = \frac{k_B T}{h} e^{-\Delta H^{\neq}/RT} e^{\Delta S^{\neq}/R}$$

where K_B is the Boltzmann constant , h is the plancks constant and T is temperature in Kelvin. The parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ are the enthalpy of activation and entropy of activation respectively. These parameters were calculated from a linear plot of log(k/T) vs 1/T based on the logarithmic form of Eyrings equation

$$\log (k/T) = 10.319 + (\Delta S^{\neq} / 4.576) – (\Delta H^{\neq} /4.576T)$$

$\Delta H^{\neq}$ and $\Delta S^{\neq}$ were calculated from the slope and intercept of the plot respectively.

Thus,

$$\Delta H^{\neq} = \frac{4.576 \times \text{slope} \times 4.186}{1000} \quad kJmol^{-1}$$

$$\Delta S^{\neq} = 4.576\ (\text{Intercept} - 10.319) \times 4.186 \quad JK^{-1}mol^{-1}$$

Stoichiometry of product

Stoichiometry of the reaction was studied by estimating the unrreacted PCC in the reaction mixture, where [PCC] > [substrate] after the completion of the reaction. It shows that three moles of PTAA are oxidised for two moles of PCC.

$$3ArSCH_2COOH + 2PCC + 2H^{+} \rightarrow 3ArS\overset{\overset{O}{||}}{CH_2}COOH + 2Cr\ (IV)$$

Product Analysis

Thin layer chromatogsaphy (TLC) were used for product analysis. The reaction mixture from an actual kinetic run was extracted with ether and dried over anhydrous sodium sulphate. The solvent was removed under reduced pressure. A solvent system of benzene – chloroform (50 – 50%) was chosen and the TLC studies confirmed the formation of the product of $ArSCH_2COOH$.

RESULTS AND DISCUSSION

In the present investigation the results obtained by the detailed kinetic studies of the oxidation of pheylthioacetic acid (PTAA) by pyridinium chlorochromate (PCC) in acetic acid – water mixture are discussed. The results are analysed with a view to obtain the mechanism of the reaction.

Kinetic runs were carried out in 50% acetic acid – 50% water (v/v) mixture ionic strength (maintained by the addition of sodium acetate) and at constant $[H^+]$ under pseudo first – order conditions. The reaction was followed by estimating the unreacted PCC by iodometric procedure.

Dependence of reaction rate on the concentration of reactants

The rate constants for various initial concentrations of phenylthioacetic acid and pyridinium chlorochromate at constant ionic strength and constant temperature are presented in Table I. The reaction is found to be first order in PCC as shown by the linearity of the Plots of log [PCC] versus time. (Fig.1). This is further confirmed by the constancy of the pseudo first order rate constants (k_1) calculated from the slopes of these linear plots by the least square method, at different initial concentrations of PCC. The dependence of the rate of oxidation on varying initial concentration of PTAA in given in fig.2. The concordant values obtained for the second order rate constants (Table II) evaluated from the equation.

$$k_2 = \frac{k_1}{[PTAA]}$$

establishes a first order dependence in PTAA. The fact that the reaction is first – order with respect to PTAA is further substantiated by the unit slope obtained for the logarithmic plot (fig.3) of the rate constants (k_1) and [PTAA]. (Slope = 1.05 , r = 0.994)

A plot of k_1 versus [PTAA] passes through the origin (fig.4, r = 0.98) indicating the absence of any substrate independent path under the experimental conditions employed.

Table I : Psuedo first – order and second – order rate constant for the reaction of PTAA with PCC at 40°C

$[HClO_4]$ = 3.0×10^{-2} M I = 1.0×10^{-1} M
Solvent = 50% acetic acid – 50% water (v/v) mixture

[PCC] M x 10^{-3}	[PTAA] M x 10^{-2}	$k_1 \times 10^4$ s^{-1}	$K_2 \times 10^2$ $M^{-1} s^{-1}$
1.0	1.0	2.26 ± 0.24	2.26 ± 0.24
1.4	1.0	2.28 ± 0.07	2.28 ± 0.07
1.6	1.0	2.13 ± 0.09	2.13 ± 0.09
1.8	1.0	2.11 ± 0.11	2.11 ± 0.1
1.0	1.5	3.58 ± 0.28	2.38 ± 0.19
1.0	2.0	4.63 ± 0.09	2.31 ± 0.04
1.0	2.5	6.71 ± 0.56	2.68 ± 0.22
1.0	4.0	9.50 ± 0.56	3.16 ± 0.18

Dependence of rate on $[H^+]$

The rate of the reaction increases significantly with increasing $[H^+]$ (Table II).

Table II Effect of $[H^+]$ on the rate of the reaction

[PTAA] = 1.0×10^{-2} M I = 1.0×10^{-1} M

[PCC] = 1.0×10^{-3} M t = 40°C

Solvent = 50% aceticacid – 50% water (v/v) mixture

$[HClO_4]$ M x 10^{-2}	$k_1 \times 10^4$ s^{-1}	$k_2 \times 10^2$ $M^{-1}s^{-1}$
2.0	0.62 ± 0.05	0.62 ± 0.05
3.0	2.30 ± 0.24	2.30 ± 0.24
4.0	6.15 ± 1.12	6.15 ± 1.12
5.0	12.3 ± 3.55	12.3 ± 3.55
6.0	12.5 ± 1.77	12.5 ± 1.77

Effect of varying Ionic strength

The rate of oxidation is affected by change in ionic strength brought out by the addition of sodium acetate (Table III).

Table III : Influence of ionic strength on the rate of oxidation

[PTAA] = 1.0×10^{-2} M [$HClO_4$] = 3.0×10^{-2} M

[PCC] = 1.0×10^{-3}M t = 40°C

Solvent = 50% acetic acid – 50% water (v/v) mixture

I $\mathbf{M \times 10^{-1}}$	$\mathbf{k_1 \times 10^4}$ $\mathbf{s^{-1}}$	$\mathbf{k_2 \times 10^2}$ $\mathbf{M^{-1} s^{-1}}$
0.5	2.43 ± 0.33	2.43 ± 0.33
1.0	2.30 ± 0.24	2.30 ± 0.24
1.5	1.45 ± 0.51	1.45 ± 0.51
2.0	0.55 ± 0.09	0.55 ± 0.09
2.5	0.37 ± 0.11	0.37 ± 0.11

As the ionic strength of the medium increases, the rate of the reaction decreases.

Effect of Solvent composition

The influence of solvent on the rate of oxidation of PTAA has been studied by using binary mixtures of acetic acid and water. The data in table IV indicate that the rate of the reaction increases with increase in the acetic acid content in the reaction mixture. This may be due to the increased acidity of the medium.

Table IV : Effect of solvent composition on the rate of oxidation

[PTAA] = 1.0×10^{-2} M

[PCC] = 1.0×10^{-3} M I = 1.0×10^{-1} M

[$HClO_4$] = 3.0×10^{-2} M t = 40°C

Acetic acid % (v/v)	$k_1 \times 10^4$ s^{-1}	$k_2 \times 10^2$ $M^{-1} s^{-1}$
35	1.67 ± 0.12	1.67 ± 0.12
45	1.77 ± 0.28	1.77 ± 0.28
50	2.30 ± 0.24	2.30 ± 0.24
60	2.72 ± 0.29	2.72 ± 0.29
65	3.73 ± 0.23	3.73 ± 0.23

Temperature dependence and activation parameter

The temperature dependence of the oxidation of PTAA by PCC is studied at three different temperatures and the values of rate constants are given in table V.

Activation parameters ($\Delta H^{\neq}$ and $\Delta S^{\neq}$) are evaluated from the linear Eyring's plot of log k_2/T vs 1/T (fig 6, r = 0.999). The activation parameters are presented in Table V. The negative value of the entropy of activation (-169 $Jk^{-1}mol^{-1}$) implies that the activated complex should have an exacting specificity of orientation.

Table V: Effect of temperature on the reaction rate

[PTAA] = 1.0×10^{-2} M [$HClO_4$] = 3.0×10^{-2} M

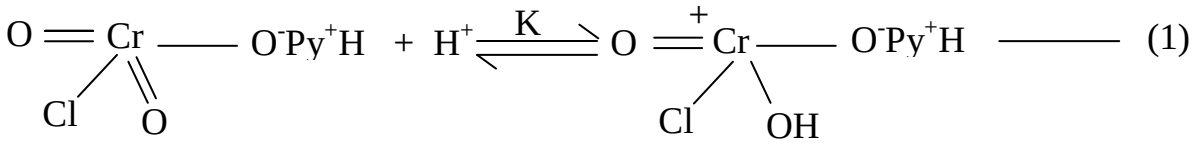
[PCC] = 1.0×10^{-3} M I = 1×10^{-1} M

Solvent : 50 % acetic acid – 50% water (v/v mixture)

TEMP °C	$k_1 \times 10^4$ s-1	$k_2 \times 10^2$ $M^{-1}s^{-1}$	$\Delta H^{\neq}$ $kJmol^{-1}$	$-\Delta S^{\neq}$ $JK^{-1}mol^{-1}$
35	2.06 ± 0.32	2.06 ± 0.32		
40	2.30 ± 0.24	2.30 ± 0.24	15.9	169
45	2.58 ± 0.35	2.58 ± 0.35		

Mechanism and rate law

On the basis of the foregoing arguments based on kinetic data the following two electron transfer mechanism may be postulated for the oxidation of PTAA by PCC.



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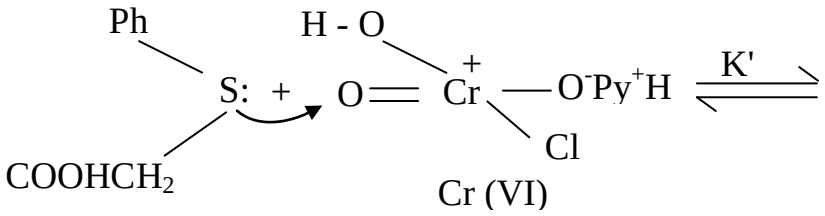
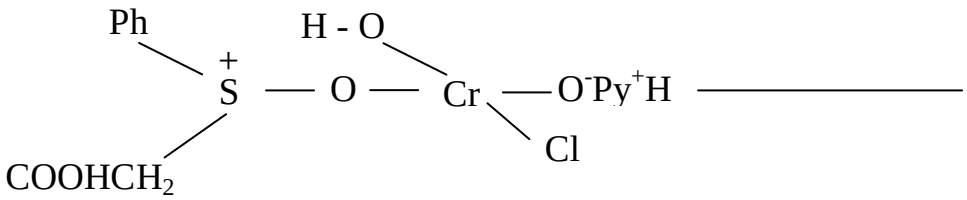
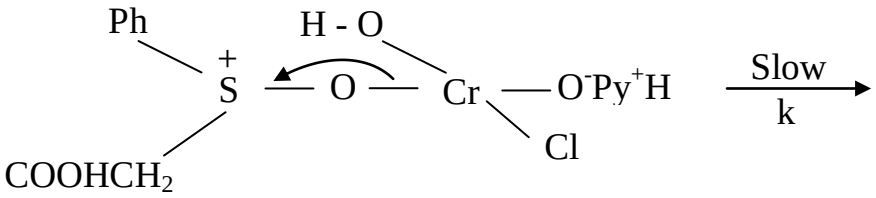
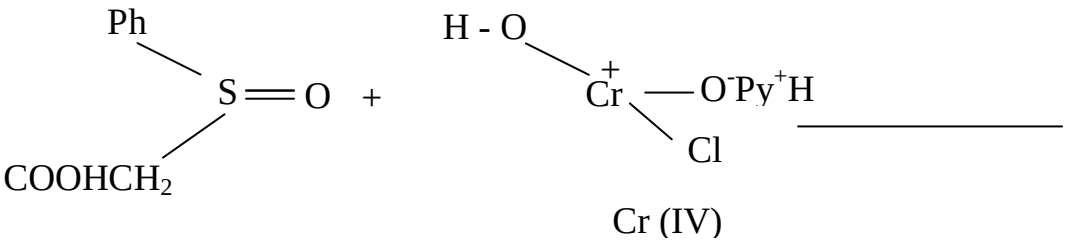




(2)





(3)

The mechanism envisages the formation of intermediate complex between PTAA and protonated PCC which decomposes in a slow step to give the products. Similar type of mechanism has been postulated for the oxidation of alcohols, [5,12] aniline [13] and benzaldehyde [16] by PCC.

Based on the proposed mechanism, the rate law for the PCC oxidation of PTAA may be written as,

$$\frac{-d[PCC]}{dt} = k\,[\text{intermediate complex}]$$

From equation (2),

$$K' = \frac{[\text{intermediate complex}]}{[PTAA]\,[PCCH^+]} \qquad (4)$$

Hence,

$$[\text{intermediate complex}] = K'\,[PTAA]\,[PCCH^+]$$

From equation (1),

$$K = \frac{[PCCH^+]}{[PCC]\,[H^+]} \qquad (5)$$

Hence,

$$[PCCH^+] = K\,[PCC]\,[H^+]$$

Using equations (4) and (5), the rate law can be written as,

$$\frac{-d[PCC]}{dt} = k K K' [PTAA] [PCC] [H^+]$$

The proposed mechanism and rate law are in conformity with the following observed experimental features:

(i) The reaction is first – order each in [PCC] and [PTAA]

(ii) The rate of the reaction increases with increase in $[H^+]$

(iii) As the ionic strength increases on the rate of oxidation decreases.

(iv) Increase in acetic acid content in the solvent mixture increases the reaction rate.

(v) $ArSCH_2COOH$ (with O) is the sole product and the stoichiometry of the reaction is 3 : 2.

SUMMARY

Organic sulphur compounds form a system of growing interest in the field of chemistry, biology and technology and their oxidation kinetic studies have been carried out extensively. However detailed kinetic study of the oxidation of PTAA has not been carried out so far. The availability of selective oxidants for organic compounds for use in selective synthesis is important and PCC ion, an easily handled oxidant fulfills this requirement and the author has decided to investigate the kinetics of PCC oxidation of PTAA.

The kinetics and mechanism of oxidation of PTAA by PCC have been studied in 50% acetic acid – 50% water (v/v) mixture at 40°C. The rate of the reaction was followed by estimating the unreacted PCC by iodometric procedure. The reaction is first order each in [PTAA] and [PCC]. As the Ionic strength decreases the rate of the reaction increases. The reaction rate increases with increase in the acetic acid content in the reaction medium. On the basis of the observed experimental features, a suitable mechanism in proposed. The mechanism envisages the formation of an intermediate between PTAA and protonated PCC which decomposes in a slow step to give the product.

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