



(RESEARCH ARTICLE)



Kinetic and mechanistic study of oxidation of phenyl thiourea by pyridinium chlorochromate in aqueous DMF medium

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Abstract

Oxidation of Phenyl Thiourea by pyridinium chlorochromate in aqueous DMF medium, containing perchloric acid has been studied. The rate of reaction was found to be of first order with respect to [PCC], [PTU] and [H⁺]. The increase in the rate of oxidation with increase in acidity indicates the involvement of a protonated chromium(VI) species in the rate-determining step. The rate of reaction increased with increase in dielectric constant of the reaction medium, which indicates that there is involvement of an ion-dipole type of interaction in the rate-determining step. The activation parameters have been evaluated. On the basis of the experimental findings, a suitable mechanism and rate law has been proposed.

Keywords: Kinetics, oxidation; DMF (N, N-dimethylformamide); PTU (Phenyl Thiourea); PCC (pyridinium chlorochromate)

1. Introduction

Pyridinium chlorochromate being one of the most versatile available oxidizing agent[1]. A number of reports on the oxidation of several substrates by pyridinium chlorochromate (PCC) are available in the literature like methionine[2], oximes[3], unsaturated acids[4], cysteine[5], alcohols[6]. There seems to be no report on the oxidation of Tyrosine by pyridinium chlorochromate.

Phenyl Thiourea is an organosulfur compound with the formula H₂NSCNHPh (also called Thiocarbamide or Sulfoarea). It is structurally similar to urea, except that the oxygen atom is replaced by a sulfur atom, but the properties of urea and Phenyl Thiourea differ significantly. Phenyl Thiourea is a reagent in organic synthesis. "Phenyl Thioureas" refers to a broad class of compounds with the general structure (R¹R²N)(R³R⁴N)C=S. Phenyl Thioureas are related to thioamides,

2. Material and methods

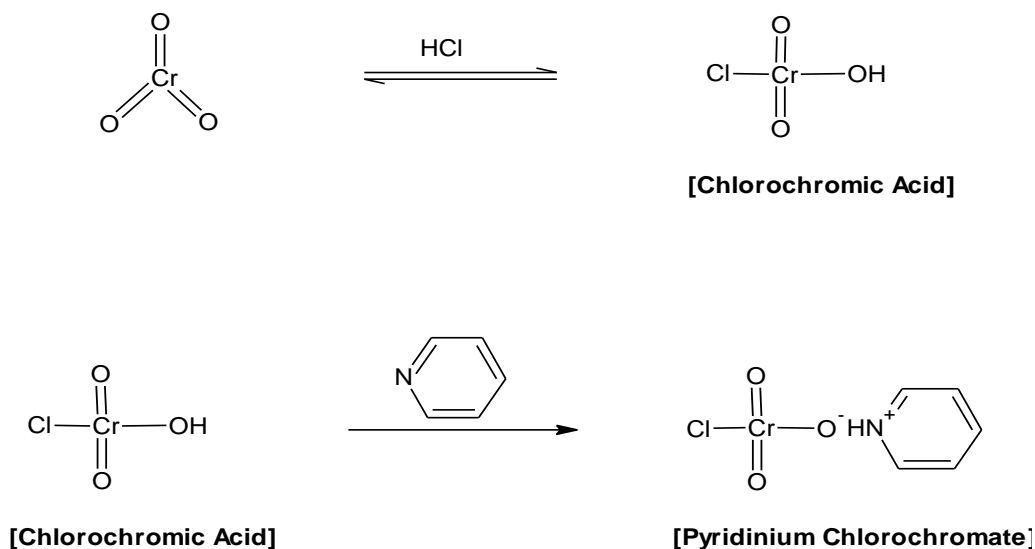
2.1. Materials

In this investigation Phenyl Thiourea Analar grade (SRL) were used as supplied and purity was checked by its melting point. All other chemicals used in this investigation were of analytical reagent grade. Solution of HClO₄ was prepared by diluting known volume of acid in water. The prepared solution was standardized by titration with previously standardized NaOH using phenolphthalein as an indicator. Doubly distilled analytical grade DMF (SRL) was used. And all other Chemicals used were of analytical grade with 99.9% purity.

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2.2. Synthesis of Pyridinium Chlorochromate

Pyridinium chlorochromate was synthesized by the method of Corey and Suggs[7] and Agrawal[8]. To 184 ml of 6 M hydrochloric acid (1.1 mol.) was added 100 g (1.0 mol) of CrO_3 rapidly with stirring. After 5 min. the homogeneous solution was cooled to 0°C and 79.1 g (1.0 mol) of pyridine was carefully added over 10 min. recooling to 0°C gave a yellow orange solid which was collected on a sintered glass funnel and dried for 1 hr in vacuum; yield 172.9 g (80 %). The solid is not appreciably hygroscopic and can be stored for extended periods at room temperature without change. Purity was checked by iodometrically, melting point, elemental analysis and by the IR and UV-VIS spectral analysis [U. V. - $\lambda_{\text{max}}=354 \text{ nm}$; I. R. - ν_{max} (KBr) = 3066, 2033, 1898, 1599, 1533, 1485, 1033, 949, 750 cm^{-1}]



2.3. Method

The measurements of rate were carried out at $27 \pm 0.1^\circ\text{C}$ in $0.3 \text{ mole dm}^{-3} \text{ HClO}_4$ under the condition $[\text{PTU}] \gg [\text{PCC}]$, in the solvent system of 50-50 % (v/v) DMF- H_2O . The reaction was initiated by mixing a calculated amount of thermostatted pyridinium chlorochromate in to the reaction mixture. The progress of the reaction was followed by measuring the absorbance of PCC at 354 nm in 1 cm cell placed in the thermostatted compartment of JASCO model 7800 UV/VIS spectrophotometer.

The kinetics runs were followed for more than 60-70% completion of the reaction and good first order kinetics were observed. Pseudo-first order rate constant k_{obs} were obtained from the slope of the plots of $\log(\text{absorbance})$ versus time.

2.4. Stoichiometry and Product analysis:

To determine the stoichiometry of reaction, a known slight excess of pyridinium chlorochromate was added to a known amount of Phenyl Thiourea, by keeping constant all other condition of reaction, and after 12 hours the residual pyridinium chlorochromate was determined spectrophotometrically at 354 nm. The results indicated that one mol of PCC consumed three mol of Phenyl Thiourea for complete oxidation. The stoichiometry of the reactions was found correspond to the equation.

At the completion of the reaction between concentrated solutions of Phenyl Thiourea and PCC, 200 ml of ethanol and 60 ml of concentrated HCl were added to the reaction mixture. It resulted in the formation of white crystals that were filtered, washed and dried in a vacuum desiccator. These crystals decomposed at 168°C indicating that the crystals are those of formimidine dihydrochloride[9]. The oxidation product of Phenyl Thiourea is formamidine disulfide¹⁰ and the dihydrochloride salt is formed in presence of concentrated hydrochloric acid[10]. The other oxidation product was characterized to be Cr(III) by comparing the spectra.

The observed Stoichiometry may be represented as



2.5. Test for Free Radicals:

The reaction mixture was treated with required amount of acrylonitrile (pre-washed with aqueous NaOH followed by washing with distilled water) under nitrogen atmosphere. Milky appearance in the solution was not observed but rate of reaction decrease drastically which indicated the presence of free radicals in the reaction.

3. Results and discussion

3.1. Effect of Oxidant Concentration on Rate of Reaction

The reaction has been investigated by varying pyridinium chlorochromate concentration to see the effect on rate of oxidation by keeping the other conditions constant. The rate constant did not change with increase in concentration of pyridinium chlorochromate. Table-1. The logarithm of concentration of pyridinium chlorochromate decreases linearly with time, thereby showing that the rate law of the reaction is first order with respect to [PCC].

3.2. Effect of Substrate Concentration on Rate of Reaction

The effect of Phenyl Thiourea concentration was studied at constant pyridinium chlorochromate concentration, $[H^+]$ and temperature, the rate of reaction increased with an increase in the concentration of Phenyl Thiourea from 2.0×10^{-2} to 3.0×10^{-2} mole/dm³ (Table-1). The plot of $\log k_{obs}$ versus $\log [PTU]$ [Figure-1] was linear with positive slope value =0.848, indicating fractional order with [Phenyl PTU]. The plot of $1/k_{obs}$ versus $1/[PTU]$, [Figure-2] gives straight line with positive intercept, which indicates that Michaelis–Menten type kinetics is followed with respect to Phenyl Thiourea. Complex formation between Phenyl Thiourea and pyridinium chlorochromate is also indicated by shifting of λ_{max} from 354 to 340nm. Although intercept is very small it may be due to highly reactive complex.

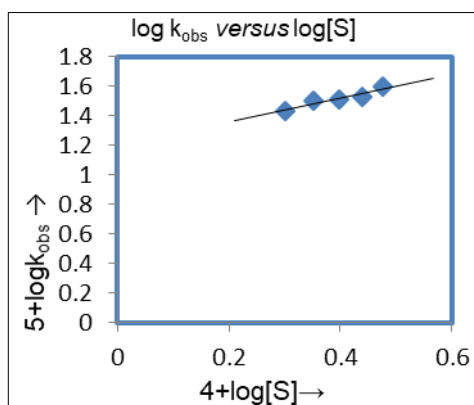
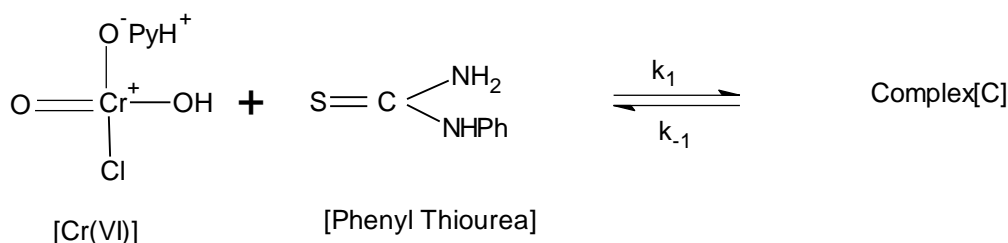


Figure 1 Variation of rate with substrate concentration

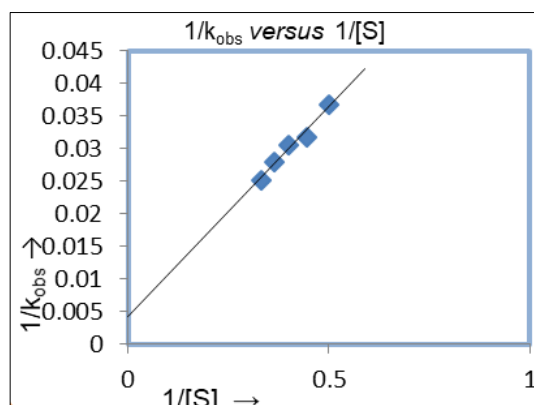
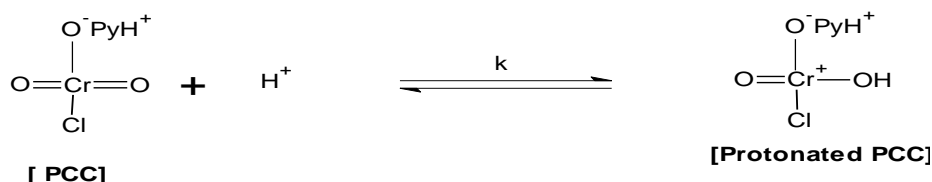


Figure 2 Variation of rate with substrate concentration

3.3. Effect of Hydrogen Ion Concentration on Rate of Reaction

The reaction was carried out in the concentration of 1.0×10^{-2} to 10×10^{-2} mole/dm³ by keeping remaining other conditions constant of the reaction, to find out the effect of hydrogen ion concentration on rate of reaction. The results of the effect of perchloric acid concentration on rate of reaction are summarized in Table-1. In general, rate constant increases with increase in hydrogen ion concentration. A plots of $\log k_{obs}$ versus $\log [HClO_4]$ [Figure-3] are a straight line

with a positive slope ≈ 1 . This shows that reaction is of first order with respect to the hydrogen ion concentration. The results are similar to the chromium(VI)[11], 12-tungstocobaltate(III) ion[12], methylene blue[13] and octacyanomolybdate(V) ion[14] oxidation of Phenyl Thiourea. M. Mehrotra and R. N. Mehrotra¹ suggested protonated Phenyl Thiourea as reactive species in oxidation of Phenyl Thiourea by 12-tungstocobaltate(III) ion. The formation of a protonated species of PCC has been also reported[15-18]. Under the present experimental conditions, the possible protonated species may be either PCC or Phenyl Thiourea. If both PCC and Phenyl Thiourea are the protonated species, the rate law predicts a second-order dependence of the rate on $[H^+]$, which is contrary to experimental results. So that the PCC is only the protonated species in this reaction and we also considered protonated pyridinium chlorochromate in the oxidation of amino acids.



In the absence of perchloric acid the reaction is very slow, it shows that the hydrogen ion act as catalyst in the reaction. Protonated Phenyl Thiourea does not take part in reaction as it will decrease complex formation & hence will decrease rate which was not observed, with there are large no of reports which have reported participation of protonated Phenyl Thiourea.

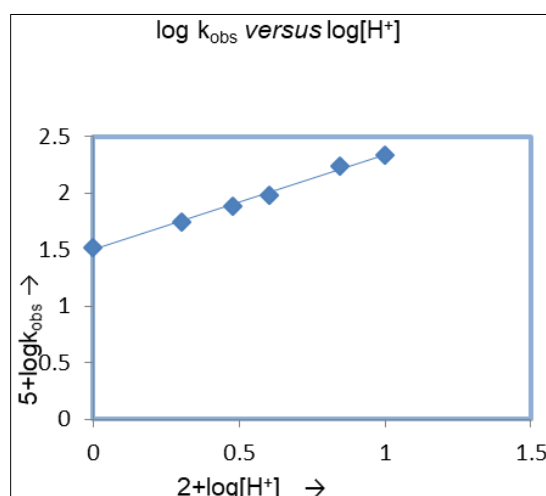


Figure 3 Variation of rate with perchloric acid concentration

3.4. Effect of Temperature on Rate of Reaction

To find out the effect of temperature on oxidation reaction, the reaction was carried out at different temperatures. The rate constant of the reaction was found to increase with an increase in temperature. The results are given in table-1. The plots of $\log k_{\text{obs}}$ versus $1/T$ are linear (figure -4), this shows that Arrhenius equation is valid for these oxidation reactions.

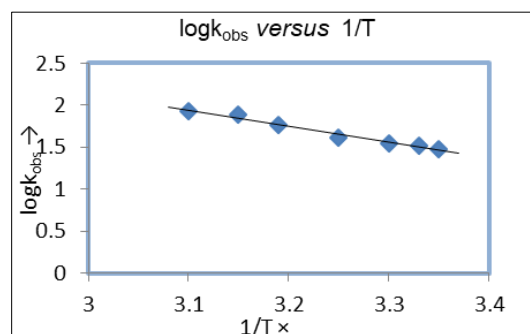


Figure 4 Variation of rate with temperature

Table 1 Variation of rate with PCC, Phenyl Thiourea, perchloric acid concentrations, DMF % and temperature

10³ x [PCC] mol dm⁻³	10² x [PTU] mol dm⁻³	10² x [H⁺] mol dm⁻³	Temp. (k)	DMF: H₂O % (V/V)	k_{obs} X 10⁵ s⁻¹
2.0	2.5	1.0	300	50:50	35.57
2.25	2.5	1.0	300	50:50	35.96
2.50	2.5	1.0	300	50:50	35.62
3.0	2.5	1.0	300	50:50	35.77
2.5	3.0	1.0	300	50:50	42.56
2.5	2.75	1.0	300	50:50	37.30
2.5	2.50	1.0	300	50:50	35.61
2.5	2.25	1.0	300	50:50	33.45
2.5	2.0	1.0	300	50:50	30.78
2.5	2.5	0.0	300	50:50	03.50
2.5	2.5	1.0	300	50:50	35.61
2.5	2.5	2.0	300	50:50	59.64
2.5	2.5	3.0	300	50:50	81.75
2.5	2.5	4.0	300	50:50	99.94
2.5	2.5	7.0	300	50:50	171.51
2.5	2.5	10.0	300	50:50	250.49
2.5	2.5	1.0	298	50:50	31.37
2.5	2.5	1.0	300	50:50	35.61
2.5	2.5	1.0	303	50:50	38.62
2.5	2.5	1.0	308	50:50	45.56
2.5	2.5	1.0	313	50:50	64.77
2.5	2.5	1.0	318	50:50	84.75
2.5	2.5	1.0	323	50:50	91.36
2.5	2.5	1.0	300	70 :30	65.38
2.5	2.5	1.0	300	60:40	69.13
2.5	2.5	1.0	300	50:50	35.62
2.5	2.5	1.0	300	40:60	72.92
2.5	2.5	1.0	300	30:70	75.12
2.5	2.5	1.0	300	20:80	77.89
2.5	2.5	1.0	300	0.0:100	80.54
Activation Parameters $E_a = 36.23 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 31.73 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -129.98 \text{ kJ mol}^{-1}$, $\Delta F^\ddagger = 70.43 \text{ Jk}^{-1} \text{ mol}^{-1}$					

3.5. Effect of Ionic Strength on Rate of Reaction

To determine the effect of ionic strength, the reaction was studied in range of Debye-Huckel Limiting Law (below 0.01 M) by varying the sodium sulfate concentration. It has been observed that there was no significant effect of ionic strength on the rate. This indicates that the reaction may be between an ion and a neutral molecule or between neutral molecules[19].

Table 2 Variation of rate with ionic strength

$[\text{Na}_2\text{SO}_4] \times 10^3 \text{ mole/dm}^3$	5.0	6.0	7.0	8.0	9.0	10.0
$k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$	35.15	35.70	34.80	33.35	35.24	35.90

- $[\text{PCC}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$
- Temperature = 300 K
- $[\text{HClO}_4] = 0.01 \text{ mol dm}^{-3}$
- DMF = 50 % (v/v)
- $[\text{PTU}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$
- Water = 50 % (v/v)

3.6. Effect of Dielectric Constant on Rate of Reaction

The effect of variation in dielectric constant on rate of reaction has been studied by varying DMF% in the reacting solution by keeping other conditions constant (table-1). The result shows the rate of reaction increased with increase in dielectric constant of the reaction medium. The plots of $\log k_{\text{obs}}$ versus $1/D$ are straight lines with negative slope (figure- 5). Amis[20] had shown that in a linear plot of $\log k_{\text{obs}}$ versus $1/D$ indicates two dipoles or an ion-dipole reaction. In the present investigation a plot of $\log k_{\text{obs}}$ versus $1/D$ gives a straight, clearly supporting that there is an involvement of two dipoles or an ion-dipole in the rate determining step.

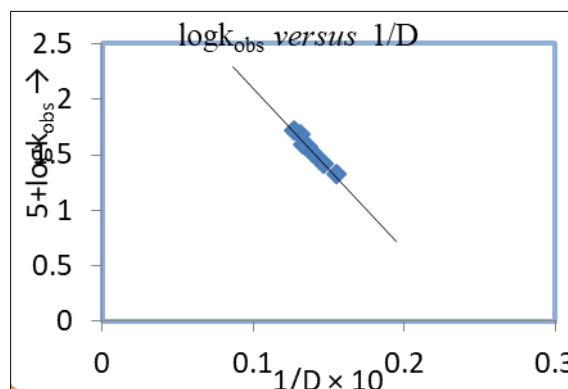


Figure 5 Variation of rate with solvent composition

3.7. Effect of MnSO_4 on Rate of Reaction

It was observed that an addition of Mn(II) ions retard the rate of reaction with increase in concentration of Mn(II) ions (Table-3). The result is similar with the observation of Zaheer Khan et al¹¹ in the oxidation of Phenyl Thiourea by chromium (VI). Cr(IV) combines with Mn(II) to give Mn(III) & Cr(III). Mn(III) is slow oxidant than Cr(IV) in this low acidic conditions. Therefore decrease in rate by addition of Mn(II) supports formation of Cr(IV) in the reaction course.

Table 3 Variation of Rate with MnSO_4 Concentration

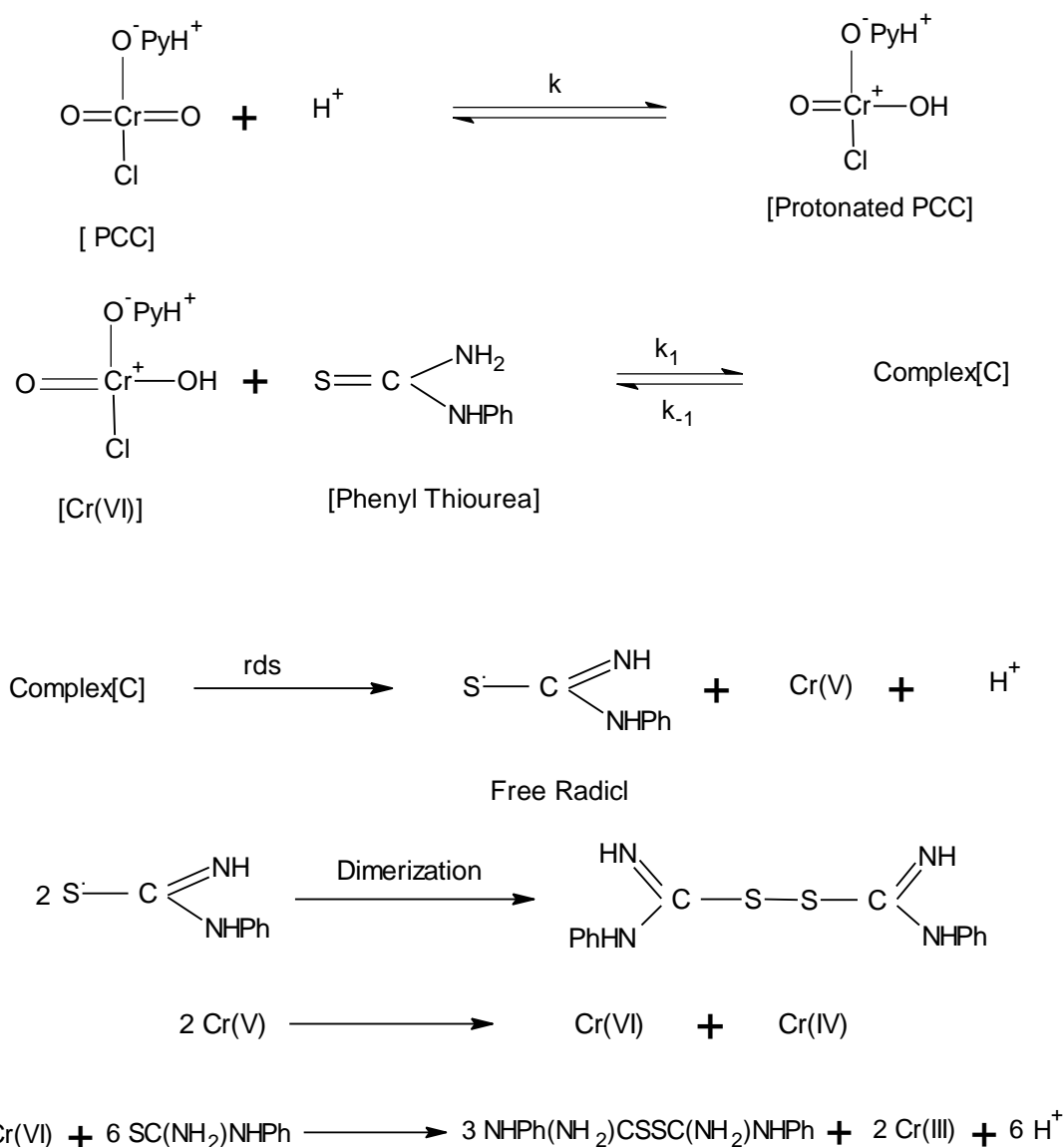
$[\text{MnSO}_4] \times 10^3 \text{ mole/dm}^3$	0.0	2.0	4.0	5.0	7.0	9.0	10.0
$k_{\text{obs}} \times 10^5 \text{ sec}^{-1}$	35.60	33.80	31.50	29.15	27.27	24.20	22.90

- $[\text{PCC}] = 2.5 \times 10^{-3} \text{ mol dm}^{-3}$

- $[\text{HClO}_4] = 0.01 \text{ mol dm}^{-3}$
- $[\text{PTU}] = 2.5 \times 10^{-2} \text{ mol dm}^{-3}$
- Temperature = 300 K
- DMF: Water = 50:50 % (v/v)

3.8. Mechanism

On the basis of above experimental results the following reaction mechanism has been proposed for the oxidation of Phenyl Thiourea.



3.9. Rate Law

On the basis of above mechanism, the rate law can be expressed as:

$$\begin{aligned}
 \text{Rate of reaction} &= -\frac{d[\text{C}]}{dt} \propto [\text{C}] \\
 &= k [\text{C}] \dots\dots\dots 1
 \end{aligned}$$

Concentration of complex, [C] can be calculated by applying steady state concept.

Rate of formation of complex = Rate of disappearance of complex

$$k_1 [\text{PTU}] [\text{PCC}]_{\text{prot.}} = k_{-1} [\text{C}] + k' [\text{C}] \dots\dots\dots 2$$

Since

$$[\text{PCC}]_{\text{total}} = [\text{PCC}]_{\text{prot.}} + [\text{C}]$$

Therefore

$$[\text{PCC}]_{\text{prot.}} = [\text{PCC}]_{\text{total}} - [\text{C}] \dots\dots\dots 3$$

Hence

$$k_1 [\text{PTU}] \{[\text{PCC}]_{\text{total}} - [\text{C}]\} = (k_{-1} + k') [\text{C}]$$

$$k_1 [\text{PTU}] [\text{PCC}]_{\text{total}} - k_1 [\text{PTU}] [\text{C}] = (k_{-1} + k') [\text{C}]$$

$$k_1 [\text{PTU}] [\text{PCC}]_{\text{total}} = k_1 [\text{PTU}] [\text{C}] + (k_{-1} + k') [\text{C}]$$

$$k_1 [\text{PTU}] [\text{PCC}]_{\text{total}} = \{k_{-1} + k' + k_1 [\text{PTU}]\} [\text{C}]$$

$$[\text{C}] = \frac{k_1 [\text{PTU}] [\text{PCC}]_{\text{total}}}{k_{-1} + k' + k_1 [\text{PTU}]}$$

$$= \frac{[\text{PTU}] [\text{PCC}]_{\text{total}}}{\frac{k_{-1} + k'}{k_1} + [\text{PTU}]}$$

$$= \frac{[\text{PTU}] [\text{PCC}]_{\text{total}}}{k_m + [\text{PTU}]}$$

Hence

$$\text{Rate} = k' [\text{C}]$$

$$= k' \frac{[\text{PTU}] [\text{PCC}]_{\text{total}}}{k_m + [\text{PTU}]}$$

$$= k [\text{PCC}]_{\text{total}} = k_{\text{obs}} [\text{PCC}]_{\text{total}} \text{ (when } [\text{PTU}] = \text{constant)}$$

Where

$$k_{\text{obs}} = k' \frac{[\text{PTU}]}{k_m + [\text{PTU}]}$$

$$\frac{1}{k_{\text{obs}}} = \frac{k_m}{k'} \frac{1}{[\text{PTU}]} + \frac{1}{k'}$$

There for k_m can be calculated by intercept of plot $1/k_{\text{obs}}$ versus $1/[\text{PTU}]$.

4. Conclusion

The study on the oxidation of Phenyl thiourea by pyridinium chlorochromate in DMF-water media in the presence of perchloric acid reveals that the neutral phenyl thiourea take part in the reaction, protonated Phenyl Thiourea is not involved in the reaction as it will decrease complex formation & hence will decrease rate which was not observed. The reaction was carried out at different temperatures. In the temperature range of 298-323 K, Arrhenius equation is valid.

The overall mechanistic sequence described here is consistent with the product analysis and by kinetic and mechanistic studies.

Compliance with ethical standards

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Disclosure of conflict of interest

There is no conflict of interest in this manuscript.

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