OXIDATION KINETICS OF PHENOL, ITS DERIVATIVES AND SOME PARA-SUBSTITUTED PHENOL BY PYRAZINIUM CHLOROCHROMATE IN ACIDIC MEDIUM: A NON-LINEAR HAMMETT PLOTS

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ABSTRACT
In the presence of perchloric acid, the kinetics and oxidation of phenol, phenoxy acetic acid, and a few para-substituted phenols and phenoxyacetic acids by pyrazinium chlorochromate (PzCC) were investigated in acetic acid and water medium. The reaction was fractional-order for both the substrates and unit order for oxidant and acid. The products of oxidation are quinone. Comparing the reaction rate for phenols and their derivatives revealed a similar behavior. The oxidation and kinetics of phenol and its derivatives are established using the non-linear Hammett plots plot which reveal that para-methyl groups slow down the reaction rate and para-nitro and para-chloro groups speed up the reaction rate. Based on the kinetic data and product analyses, an appropriate mechanism has been provided.

Keywords: Kinetics, Phenols, Para-Substituted Phenols, Phenoxy Acetic Acids, Pyrazinium Chlorochromate, Perchloric Acid, Hammett Plots.

INTRODUCTION
Hexavalent chromium compounds are employed in aqueous and non-aqueous conditions as a multifunctional oxidizing agent for a variety of substrates. The heterocyclic compounds include isoquinolinium chlorochromate (IQC)¹, Quinaldinium chlorochromate (QnCC), morpholinium chlorochromate², quinolinium fluorochromate³, quinolinium bromochromate, tripropyl ammonium fluorochromate, Imidazolium Chlorochromate⁴, benzyl trimethyl ammonium chlorochromate⁵ pyridinium dichromate⁶, and many more. The Cr (VI) hexavalent chromium is converted to Cr (III) trivalent chromium salt when bonded inside the heterocyclic ring. Phenol is manufactured synthetically and used in the development of abundant products for several industrial, agricultural, and commercial applications like resins, pesticides, paper, and pulp, oil shale processing, paint, agriculture, etc.⁷⁻⁸ Even at low concentrations, it is detrimental and lethal⁹⁻¹¹ pollutant. The widespread presence of phenol causes a variety of environmental problems, such as rising temperature, pH, water hardness, dissolved oxygen levels, salinity, and so on. In antibiotic fermentations, phenoxy acetic acid (glycolic acid phenyl ether) is the precursor of penicillin V. Plant regulators, pesticides, herbicides, flavoring agents, and antibacterial agents all use this molecule. PAA has a lower hygroscopicity and is soluble in organic solvents such as glacial acetic acid, ether, methanol, and carbon disulphide. The current research examines and compares the oxidation kinetics of phenols and phenoxy acetic acids¹² in the presence of pyrazinium chlorochromate oxidant. The important tools in determining the mechanism of the reaction are substituent effects, isokinetic relations, and thermodynamic parameters. To establish the reactivity and ascertain the nature of the mechanism, a methodical approach was used.

EXPERIMENTAL
Materials and Methods
The Analytical grade phenol and substituted phenols were utilized. The standard procedure involves the distillation of acetic acid at 118⁰C and doubly distilled water was utilized for all the purposes.

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Preparation of Pyrazinium Chlorochromate
The weighed Pyrazine was dissolved in 0.6 mL hydrochloric acid and purified water. The 0.3g of chromium trioxide was dissolved in 3mL distilled water with 0.4 mL of 12 M hydrochloric acid added to this reaction mixture which was then allowed to cool. Then it was poured together and stirred at degrees Celsius for 1 hour which yields an orange-colored solid which was filtered and dried. The melting point (148°C to 150°C) was used to establish the crystal's purity.

\[ C_4N_2H_4 + HCl + CrO_3 \rightarrow C_4N_2H_5CrO_3 + Cl^- \]

Preparation of Phenoxy Aceticacid
The phenoxy acetic acid was obtained by adding chloroacetic acid to phenol in the presence of sodium hydroxide and stirring it continuously at a temperature, not more than 70°C from which a white crystalline product is obtained which was filtered and purified. The melting point of 97.5°C to 99°C was used to assess the solid's purity and the same method was utilized to prepare the substituted phenoxy acetic acid.

\[ C_6H_5OH + CH_2ClCO_2H + NaOH \rightarrow C_6H_5OCH_2CO_2H \]

Stoichiometry and Product Analysis
Experiments with increasing amounts of PzCC over phenol show that one mole of PzCC interacts with one mole of the substrate and TLC was used to examine the oxidative products, yielding 1,4-benzoquinone melting point 112°C (Literature 114°C) and ultraviolet absorbance at 250 nm.

RESULTS AND DISCUSSION
The oxidation of phenols and phenoxy acetic acids by PzCC was studied in AcOH: H_2O medium in the ratio of 60:40 under pseudo-first-order conditions. The rate constants of both the substrates were studied and the compared rate values are shown graphically.

Order of the Reaction
The rate values (k_1) obtained at various concentrations of PzCC reveal that the rates are independent of the starting concentration of PzCC, and hence the order with regard to [PzCC] is unity (r = 0.994). The plot of 1/k_1 versus 1/[PzCC] indicates the presence of hexavalent chromium ions in the reaction medium is less in the case of phenol and its derivative (Fig.-1). The rate of reaction (k_1) was found to be fractional order with respect to substrate (Phenol and Phenoxy acetic acid), table-1 as evidenced from the Fig.-2, with slope value (phenol: r = 0.997, slope = 0.553 ± 0.02, PAA: r = 0.998, slope = 0.443 ± 0.02).

![Fig.-1: For the Oxidation of Phenol and PAA, plot 1/k_1 vs 1/[PzCC]](image)

<table>
<thead>
<tr>
<th>10^3[C_4N_2H_5CrO_3Cl] (mol dm^-3)</th>
<th>10^3[C_6H_5OH] (mol dm^-3)</th>
<th>10^3[H^+] (mol dm^-3)</th>
<th>k_1 10^3 s^-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>H(Phenol)</td>
<td>p-methyl phenol</td>
<td>p-chloro phenol</td>
<td>p-nitro phenol</td>
</tr>
<tr>
<td>0.5</td>
<td>1.5</td>
<td>1.0</td>
<td>5.93</td>
</tr>
<tr>
<td>0.5</td>
<td>2.25</td>
<td>1.0</td>
<td>6.63</td>
</tr>
<tr>
<td>0.5</td>
<td>3.0</td>
<td>1.0</td>
<td>9.7</td>
</tr>
<tr>
<td>0.5</td>
<td>3.75</td>
<td>1.0</td>
<td>10.27</td>
</tr>
</tbody>
</table>
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For phenol (C₆H₅OH), the rate constant rose as the [acid] increased from 1.05 x 10⁻¹ to 2.10 x 10⁻¹ mol dm⁻³, and for PAA, the rate constant increased from 1.6 x 10⁻¹ to 3.2 x 10⁻¹ mol dm⁻³. As shown in Fig.-3, the plot of log k₁ vs log [acid] yielded a linear graph with strong correlation coefficients, r = 0.993 (Phenol) and r = 0.998 (PAA).

Effect of Sodium Perchlorate and MnSO₄ Concentrations

The reaction kinetics were studied using different concentrations of NaClO₄ while keeping the substrate concentration (phenol and phenoxy acetic acid), [acid], and [O] constant. The rate constant of the reaction had no effect on increasing the ionic strength of the reaction medium. This is attributed to the ionic species in the rate-determining step (slow step). The effect of MnSO₄ decreased the rate of the reaction due to the transfer of two electrons (Mn²⁺) as indicated in Fig.-4.

Effect of Varying the Solvent Composition

The concentration of acetic acid and water varied from 60 % to 40 % and the effect of solvent on the reaction rate was determined. For the substrate phenol, the plot of log k₁ versus 1/D (dielectric constant) shown in the Fig.-5 gave a straight line with a positive slope value, r = 0.998, B = +11.94, and for PAA, r = 0.998, B = +44.06. The increase in the rate of the reaction with an increase in the composition of CH₃COOH and

<table>
<thead>
<tr>
<th>0.5</th>
<th>4.5</th>
<th>1.0</th>
<th>12.19</th>
<th>78.38</th>
<th>29.88</th>
<th>28.49</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁷[C₄N₃H₂CrO₃Cl] (mol dm⁻³)</td>
<td>10⁷[C₃H₆O₃] (mol dm⁻³)</td>
<td>10¹[^H⁺] (mol dm⁻³)</td>
<td>H(PAA)</td>
<td>p-methyl PAA</td>
<td>p-chloro PAA</td>
<td>p-nitro PAA</td>
</tr>
<tr>
<td>2.0</td>
<td>1.95</td>
<td>2.0</td>
<td>7.49</td>
<td>15.88</td>
<td>17.43</td>
<td>21.58</td>
</tr>
<tr>
<td>2.0</td>
<td>2.25</td>
<td>2.0</td>
<td>8.03</td>
<td>17.22</td>
<td>19.32</td>
<td>22.81</td>
</tr>
<tr>
<td>2.0</td>
<td>2.55</td>
<td>2.0</td>
<td>8.49</td>
<td>20.24</td>
<td>22.49</td>
<td>24.89</td>
</tr>
<tr>
<td>2.0</td>
<td>2.85</td>
<td>2.0</td>
<td>8.87</td>
<td>23.43</td>
<td>23.95</td>
<td>26.72</td>
</tr>
<tr>
<td>2.0</td>
<td>3.15</td>
<td>2.0</td>
<td>9.22</td>
<td>24.84</td>
<td>24.84</td>
<td>30.67</td>
</tr>
</tbody>
</table>

Fig.-2: Plot of 1/k₁ vs 1/[PzCC] for Phenol and PAA Oxidation

Fig.-3: For the Oxidation of Phenol and PAA, plot log k₁ vs log [H⁺].
H$_2$O indicates that the interaction is between neutral molecule and ion. This is due to the involvement of chromium (VI) species in the slow step.

![Graph](image1)

Fig.–4: Log $k_1$ vs log [MnSO$_4$] Plot (Oxidation of Phenol and PAA)

![Graph](image2)

Fig.–5: For the Oxidation of Phenol and PAA, plot log $k_1$ vs 1/D.

**Correlation and Structural Effect**

PzCC oxidized para-substituted phenols and phenoxy acetic acids in 60-40 percent (v/v) CH$_3$COOH-H$_2$O medium in the acidic medium at 293 K, 303 K, 313 K, and 323 K. All the para compounds of the substrates (phenol and phenoxy acetic acid) exhibited fractional order. The activation parameters and thermodynamic parameters were evaluated using Eyring's (least square) method.$^{15-17}$ The rate constant value grew as the temperature increased, as seen by the linear plot of log $k_2$/$T$ vs 1/$T$ in Fig.-6. The negative value of change in entropy of activation ($\Delta S^\#$) implies solvation of intermediate state over the reactants as indicated in the table-2. The free energy of activation values was low, indicating that PzCC oxidized all of the substrates in a concerted mechanism.

![Graph](image3)

Fig.–6: Plot of log $k_2$/$T$ versus 1/$T$ x 10$^{-3}$ for the Oxidation of Phenol and PAA

**Isokinetic Relation**

The applicability of the Hammett equation at different temperatures is linearly related to enthalpies (isokinetic relation) using:$^{18}$

$$\Delta H^\# = \Delta H_o^\# + \beta \Delta S^\#$$
The variation of substituents at isokinetic temperature does not affect the free energy of activation. The plot of $\Delta H^\circ$ versus $-\Delta S^\circ$ gives a good correlation for the substrates ($r = 0.950$ for phenol, $r = 0.983$ for PAA) as shown in Fig.-7 and 8. The isokinetic temperature ($\beta$) obtained from the slope is 351.6 K for phenol and 309.9 K for PAA. The change in enthalpy of activation and the low values of activation energy confirms the concerted mechanism for all the substituted compounds.

The decrease in the entropy of activation ($\Delta S^\circ$) produced negative values which implies the transition state is extensively solvated due to the increased polarity of the reactants. The linear association between $\Delta H^\circ$ and $\Delta S^\circ$, according to Exner, is:

$$\log (k_1)_{T_1} = a + b \log (k_1)_{T_2}$$

Where $T_2 > T_1$

The plot of $\log k_1(323K)$ versus $\log k_1(313K)$ gave a straight line (Fig.-7 and 8) with $r = 0.989$ (phenol) and $r = 0.995$ (PAA) such a good correlation indicates that all the substituents follow a common mechanism.

### Table-2: PzCC Oxidation of Substrates: Thermodynamic and Activation Parameters

<table>
<thead>
<tr>
<th>S. No</th>
<th>Substrates</th>
<th>Order w.r.to [S]</th>
<th>$k_1 \times 10^4$ (s^{-1})</th>
<th>$\Delta H^\circ$ (kJ mol^{-1})</th>
<th>$\Delta S^\circ$ (JK mol^{-1})$</th>
<th>$\Delta G^\circ$ at 303 K (kJ mol^{-1})</th>
<th>E, at 303 K (kJ mol^{-1})</th>
<th>r</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Phenol (-H)</td>
<td>0.552</td>
<td>3.73</td>
<td>5.93</td>
<td>8.17</td>
<td>10.81</td>
<td>13.44 ± 1.51</td>
<td>0.995</td>
</tr>
<tr>
<td>2</td>
<td>p-Chlorophenol</td>
<td>0.534</td>
<td>11.07</td>
<td>15.41</td>
<td>22.11</td>
<td>30.18</td>
<td>12.92 ± 1.53</td>
<td>0.999</td>
</tr>
<tr>
<td>3</td>
<td>p-Methyl phenol</td>
<td>0.624</td>
<td>31.87</td>
<td>39.21</td>
<td>49.11</td>
<td>61.67</td>
<td>8.93 ± 1.53</td>
<td>0.998</td>
</tr>
<tr>
<td>4</td>
<td>p-Nitro phenol</td>
<td>0.592</td>
<td>137.0 1</td>
<td>147.5 4</td>
<td>160.1 2</td>
<td>173.7 4</td>
<td>4.12 ± 1.49</td>
<td>0.997</td>
</tr>
<tr>
<td>5</td>
<td>Phenoxy acetic acid (-H)</td>
<td>0.433</td>
<td>6.88</td>
<td>8.03</td>
<td>10.21</td>
<td>13.08</td>
<td>9.08 ± 1.5</td>
<td>0.998</td>
</tr>
<tr>
<td>6</td>
<td>p-Chlorophenoxy acetic acid</td>
<td>0.662</td>
<td>15.04</td>
<td>18.92</td>
<td>24.11</td>
<td>30.24</td>
<td>9.39 ± 1.5</td>
<td>0.997</td>
</tr>
<tr>
<td>7</td>
<td>p-Methylphenoxy acetic acid</td>
<td>0.807</td>
<td>12.3</td>
<td>18.02</td>
<td>25.95</td>
<td>34.75</td>
<td>13.32 ± 1.5</td>
<td>0.992</td>
</tr>
<tr>
<td>8</td>
<td>p-Nitro phenoxy acetic acid</td>
<td>0.628</td>
<td>18.92</td>
<td>23.01</td>
<td>27.97</td>
<td>34.62</td>
<td>8.26 ± 1.5</td>
<td>0.995</td>
</tr>
</tbody>
</table>

**Mechanism of Reactions**

The oxidation of the substrate phenols ($C_6H_5OH$) by the oxidant pyrazinium chlorochromate in an acidic medium ($HClO_4$) is specified in scheme-1. The reaction is slow though catalyzed by acid and the protonated form of the hexavalent chromium is evident. The addition of manganous sulphate retarded the reaction rate...
and the free radical mechanism is absent. This confirms the presence of hexavalent chromium as an intermediate in the oxidation reaction and also reduces Cr$^{6+}$ to Cr$^{3+}$ states.

**Fig.-8: Plot of $\Delta H^\circ$ (KJmol$^{-1}$) versus $-\Delta S^\circ$ (JK$^{-1}$mol$^{-1}$) for the Oxidation of PAAs**

Non-linear Hammett Plot

The Hammett constant ($\sigma$) and rate constant data ($k_1$) for the para-substituted phenols and phenoxy acetic acids proved to be non-linear given in Fig.-9 and 10. The electron-donating groups were aligned on one side and the electron-accepting groups on the other side of the curve.
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CONCLUSION

The oxidation of phenol, phenoxy acetic acid, substituted phenols, and their derivatives was studied in this work. The behavior of phenoxy acetic acid and the p-substituted phenoxy acetic acids were similar to that of the oxidation kinetics of phenols. The rate of the reaction for all substrates was fractional-order and unit order for [O] and [acid]. The oxidation of para-substituted phenols and their derivatives resulted in the formation of 1, 4-benzoquinone. The risky character of both substrates is lowered by oxidizing them with heterocyclic chromium compounds, which converted chromium (VI) to chromium (III) during oxidation (III). The non-linear Hammett plot reveals that the p-CH₃ group retard the reaction rate and the p-NO₂, and the p-Cl group accelerates the reaction rate in both the substrates. The formation of an activated complex in the rate-determining step is supported by the negative value of change in entropy. From the above results, we conclude that all the substrates follow the same mechanism pathway.

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