Kinetics and Mechanism of the Reduction of Tetraoxochromate(VI) by Thiophenol

P. O. Ukoaha, S. O. Okonkwo, N. N. Ukwueze and O. T. Ujam*

Department of Pure & Industrial Chemistry, University of Nigeria, Nsukka 410001, Enugu State, Nigeria
*Corresponding Author: e-mail: oguejiofo.ujam@unn.edu.ng

Received 04 May 2018; accepted 07 June 2018, published online 23 June 2018

Abstract

The kinetics and mechanism of the reduction of tetraoxochromate(VI), to chromium(III) by thiophenol, was studied in aqueous perchloric acid at 27±0.5°C, I = 0.05 mol dm⁻³ (NaClO₄), [H⁺] = 0.5 mol dm⁻³ and λ_max = 350 nm. Spectrophotometric titration following the Yoe-Jones method gave a point of inflexion at the mole ratio of 1:1 inferring that one mole of the oxidant was consumed as one mole of the reductant was oxidized. Kinetic decays indicated first order dependence of the reaction on both oxidant and reductant and gave the reaction as second order overall. Pseudo-first order rate constants increased with increase in concentration of the reductant and k₂ values were constant within 0.114±0.006 dm³mol⁻¹s⁻¹. The reaction rate increased with [H⁺] and ionic strength. Catalytic effects by CH₃COO⁻ and Cl⁻ was not very significant. The reaction was rationalized on the basis of two parallel routes: an outer-sphere path that is non-acid dependent and an inner-sphere route that is acid dependent.

Keywords: kinetics, mechanism, tetraoxochromate(VI), reduction, thiophenol, chromium(III)

Introduction

The dynamics of the redox reactions of chromium(VI) has generated a lot of interest because it is highly soluble, oxidizing and toxic to living organisms causing mutagenic and carcinogenic effects. Chromium(VI) compounds are respiratory tract irritants and cause pulmonary sensitization¹⁴. On inhalation, it has been found to induce lung, nasal and sinus cancer and could lead to severe dermatitis on contact with the skin⁵⁻⁶.

Environmental contamination with chromium(VI) is mainly through industrial effluents and mining activities. The lethal dose L₅₀ of Cr(VI) has been pegged at 50 to 150 mg/kg⁴⁻⁷. The basis is on the fact that when ingested into the body, Cr(VI) could be reduced to chromium(III) by several pathways before it reaches the cells. Cr(III) could be excreted but Cr(VI) is transported via same transport route as SO₄²⁻ and PO₄³⁻ and could thus cause oxidative damage of the blood cells which may result into serious physiological implications including hemolysis, kidney and liver damage could result⁸.

Chromium(III) is less soluble and considered less toxic. Therefore, the reduction of Cr(VI) to Cr(III) is a potential detoxification process that may be achieved chemically in the environment or through several biological pathways. It has also been suggested that the reduction of Cr(VI) to Cr(III) by biologically friendly reductants should be a major biological pathway in mediating the toxicity of chromium compounds⁹.

In the biological systems conversion of Cr(VI) to Cr(III) takes place outside the cells thereby reducing Cr(III) toxicity and forming a major protection scheme for the cells. Cr(III) formed plays a major role in glucose, fat and protein metabolism by protecting insulin functions in the body¹⁰. In line with these findings, various workers have sought to find explicit sequences for the role of biological molecules in mitigating Cr(VI) toxicity and carcinogenicity especially its redox reactions in vivo and in vitro.¹¹
Reduction of Cr(VI) by ascorbate, diols and thiol containing molecules have been studied\(^1\). Results implicated hydroxyl free radicals as major culprits in cellular damage, DNA strand breakage and hydroxylation of 2'-deoxyguanosine. Previous reports demonstrated that in vitro activation of Cr(VI) by the thiols; glutathione, cysteine, p-aracrythmol and dithrothretol, leads to formation of Cr(V), bonding of Cr(V) to DNA and could alter DNA conformation\(^2\). This is a confirmation that Cr-thiol interactions may be very vital in Cr(VI) genotoxicity.

X-ray absorption near-edge structure spectroscopic studies of the reduction of Cr(VI) by thiols revealed the involvement of thiol/disulfide couple and the formation of Cr(III)\(^3\). The type of species formed in such reactions are also pH dependent\(^4\). Another similar investigation, reduction of Cr(VI) by L-cysteine, gave variable reduction rates and resulted in formation of Cr(III)-DNA adducts. The report inferred that cysteine is the predominant Cr(VI) reductant in lymphocytes\(^5\).

Redox kinetics of Cr(VI) reduction with glutathione and other thiols showed three rate constants and formation of Cr(IV) and Cr(III) as reduced forms of Cr(VI)\(^6\). However, oxidation of 3-sulfanyl-D-valine and γ-glutamylystelylglyane (glutathione) by CrO\(_4^{2-}\) at pH ≥ 7 was biphasic for glutathione and monophasic for 3-sulfanyl-D-valine. Glutathione Cr(VI) adduct was first formed which later decayed to yield disulphide and Cr(III). The final products were bis(chelates) of the thiols\(^7\). Oxidation of methylphenylsulphide by Cr(VI) in aqueous HClO\(_4\) produce a precursor complex which decayed at the rate determining step to yield only Cr(III) and the sulfoxide, \(\text{H}_2\text{C-S-C}_6\text{H}_5\)\(^8\). The rate law for the reaction was given as;

\[
K_1 K_2 k_3[\text{Cr(VI)}][\text{H}^+][\text{S}]/1 + K_2[\text{S}].
\]

Sulphydryl compound (thiols) play very significant biological roles. Their redox couple, RSH/RSSR play major role in mediating cell potentials at biological sites. Their actions help in mitigating the toxicity of Cr(VI)\(^9,10\). Biological and biomimetic iron-sulfur cluster like ferrodoxin and rubredoxins are complexes of cysteine where various thiol fragments are ligated to metal centers. These iron-sulfur clusters play very important physiological roles in electron transfer, enzymatic transformation, storage and regulation of gene expression\(^20,22\). Cysteine-supported Fe-S clusters tend to give more negative redox potentials (-300 to -460 mV) when compared to histidine supported Fe-S clusters which give +490 to +100 mV versus normal hydrogen electrode\(^23\). The implication is that ligation of RS\(_2\) to the metal centre encourages more facile electron transfer and other redox reactions in the cellular network\(^24\).

A clear understanding of Cr(VI) interaction with thiols at cellular sites has not been proffered. This has prompted a frenzy of investigations into the dynamics of the reduction of Cr(VI) by thiols\(^11\). Many thiols have been tried in these biomimetic processes but thiophenol has seldom been used, not just for Cr(VI) reduction but also for other metals. This might not be unconnected with the very foul odour of thiophenol and relative toxicity\(^25\). Our group has so far investigated the reduction of Ce(IV) and V(V) by thiophenol\(^26\). The reaction followed the inner-sphere path Ce(IV) was reduced to Ce(III) whereas V(V) was reduced to V(IV).

The present report is an effort to investigate the redox kinetics of Cr(VI) using thiophenol, a hitherto relatively uninvestigated thiol. It is our hope that the kinetic data generated will give clearer meaning to the interaction of Cr(VI) with thiols at cellular sites.

**Experimental**

All reagents used are of analytical grade and were used as supplied without further purification unless otherwise stated. Thiophenol (99.5% C\(_6\)H\(_5\)SH, Fluka) herein after denoted as PhSH was used as the reductant. Its solutions were prepared in degassed 1:1 ethanol/water mixture. Potassium tetraoxochromate(VI) (99.5% K\(_2\)CrO\(_4\), Sigma-Aldrich) was used as the oxidant, Cr(VI). Its solutions were prepared fresh for each run using doubly distilled deionized water. Ionic strength was maintained constant using NaClO\(_4\). Absorbances of solutions were obtained on a B. Bran 722-2000
Spectronic 20D and Jenway 6405 UV-vis spectrophotometer.

**Kinetic Measurements**

The kinetic data for the oxidation of thiophenol by Cr(VI) were recorded as the decrease in absorbance of the reacting mixture at 350 nm. Only CrO$_4^{2-}$ absorbed at this wavelength Cr(III) and the organic product did not absorb at this wavelength and therefore did not interfere with the measurement.

The stoichiometry of the reaction was determined by spectrophotometric titration on the basis of the mole ratio method$^{27}$. The concentration of CrO$_4^{2-}$ was kept constant at 5.0 x 10$^{-5}$ mol dm$^{-3}$ and [PhSH] varied between 1 x 10$^{-5}$ to 5 x 10$^{-4}$ mol dm$^{-3}$. At the end of the reactions final absorbances, $A_\infty$ of the reaction mixtures were obtained at 350 nm and plotted against the mole ratios, [PhSH]/[CrO$_4^{2-}$] and the stoichiometry of the reaction derived from the point of inflexion on the curve.

The reactions were performed under pseudo-first-order conditions of a large excess of the reductant, at least 20-fold, over the concentration of the oxidant. At these conditions, obtained kinetic curves were exponential and pseudo-first-order rate constants, $k_{obs}$, were obtained from least square fits of the logarithmic plot of the absorbance difference ($ln(A_t - A_\infty)$) against time. $k_{obs}$ was determined from the slope of the plots based on the relationship$^{27,28}$

$$ln(A_t - A_\infty) = k_{obs}t + ln(A_0 - A_\infty) \quad (1)$$

Where $A_\infty = \text{final absorbance, } A_t = \text{absorbance at time } t, A_0 = \text{initial absorbance} \text{ and } k_{obs} = \text{pseudo-first-order rate constant. Plot of kinetic decays were linear for at least 80 }\% \text{ extent of reaction and specific rates for replicate runs were reproduced within } \pm 5 \%. \text{ Second order rate constant, } k_2, \text{ were calculated as the ratio of } k_{obs}/[\text{PhSH}].$

The effect of acidity on the rate of reaction of Cr(VI) by PSH was studied using HClO$_4$. The acid concentration was varied between 0.01 ≤ [H$^+$] ≤ 0.5 mol dm$^{-3}$, at constant concentration of PhSH, CrO$_4^{2-}$ and ionic strength of the medium. The temperature was maintained at 27 ± 0.5 °C and $\lambda_{max}$ of 350 nm. In the ionic strength range of 0.01-0.05 mol dm$^{-3}$ (NaClO$_4$), the effect of ionic strength on the rate of reaction was investigated. Concentration of PhSH Cr(VI) and acid were kept constant at T = 27 ± 0.5 °C and [H$^+$] = 0.01 mol dm$^{-3}$.

Variable amounts of CH$_3$COO$^-$ and Cl$^-$ within the range 10$^{-4}$ - 10$^{-1}$ mol dm$^{-3}$ were added to check the effect of added ions on the rate of reaction with other parameters kept constant.

Propan-2-one was used to alter the dielectric constant of reacting media between 43.70 to 72.70 and other parameters kept constant. The rate of reaction was monitored to evaluate the influence of medium dielectric constant on the rate of reaction.

**Results and Discussion**

Spectrophotometric titration showed that one mole of PhSH was oxidized per mole of Cr(III) reduced eqn. (2)

$$\text{CrO}_4^{2-} + 5\text{H}^+ \rightarrow \text{Cr(III)} + \text{PhS} = \text{O} + 3\text{H}_2\text{O} \quad (2)$$

Similar stoichiometry has been reported for other reactions of Cr(VI) with thiols$^{14-18}$. Formation of Cr(III) is also a major feature of the reduction of Cr(VI) by thiols$^{15-18}$. However, most researchers have reported the formation of disulfides in reactions of Cr(VI) with thiols. In some other reactions, formation of sulphoxide was reported$^{18}$, as the organic product at [H$^+$] = 0.22 mol dm$^{-3}$

The solution of the product absorbed at 590 nm which is typical of Cr(III). Also a green precipitate which is presumably Cr(OH)$_3$ was formed on reacting NHCl/NH$_2$OH with the products of the reaction. As a further confirmation, the solution of the products was acidified with CH$_3$COOH and some quantity of lead ethanoate added. A yellow precipitate was formed which was soluble in aqueous NaOH indicating Cr(III).

The organic product was extracted with diethylether and analyzed by FTIR. A strong band centred at 1055 cm$^{-1}$ indicated $\nu$(S = O) of a sulphoxide. Absence of peaks at 2590 – 2250 cm$^{-1}$ showed absence of S-H group in the
product and confirmed oxidation of S-H to \(-\)S\(=\)O.\textsuperscript{25}

**Reaction Order**

Pseudo-first-order plots of \(\ln(A_{oc})\) versus time were linear up to 80% extent of reaction, indicating first order dependence of reaction rate on concentration of the Cr(VI). Pseudo-first-order and second order rate constants are shown in Table 1. \(k_{obs}\) increased with [PhSH] and \(k_2\) values were invariant with values within 0.114±0.006 mol dm\(^{-3}\) s\(^{-1}\). Least square fits (\(r = 0.930\)) of the plot of \(\log k_{obs}\) against \(\log[PhSH]\) (Figure 1) was linear with a slope of 1.2 indicating first order dependence of rate on[PhSH]. Therefore the rate of reaction at constant pH can be given as equ. (3).

\[
\frac{-d[Cr(VI)]}{dt} = k_2[PhSH][Cr(VI)]
\]

Most reactions of Cr(VI) with thiols also showed first order dependence on each of the redox partners and were second order overall\textsuperscript{14-18}.

![Figure 1: Plot of \(\log k_{obs}\) Vs \(\log[PhSH]\)](image)

**Table 1** Pseudo-first order and second order rate constant for the reduction of Cr(VI) by PhSH at \([CrO_4^{2-}] = 5 \times 10^{-5} \text{ mol dm}^{-3}\), \(T = 27 \pm 0.5 \text{ }\text{C}\) and \(\lambda_{max} = 350 \text{ nm}\).

<table>
<thead>
<tr>
<th>(10^3[\text{[PhSH]}] \text{ (mol dm}^{-3})</th>
<th>([\text{H}^+] \text{ (mol dm}^{-3})</th>
<th>(I \text{ (mol dm}^{-3})</th>
<th>(10^3 k_{obs} \text{ (s}^{-1})</th>
<th>(k_2 \text{ (dm}^3\text{mol}^{-2}\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.00</td>
<td>0.50</td>
<td>0.50</td>
<td>2.50</td>
<td>0.13</td>
</tr>
<tr>
<td>2.50</td>
<td>0.50</td>
<td>0.50</td>
<td>2.75</td>
<td>0.11</td>
</tr>
<tr>
<td>3.00</td>
<td>0.50</td>
<td>0.50</td>
<td>3.10</td>
<td>0.10</td>
</tr>
<tr>
<td>3.50</td>
<td>0.50</td>
<td>0.50</td>
<td>3.50</td>
<td>0.10</td>
</tr>
</tbody>
</table>

**Acid Dependence**

The effect of [\(\text{H}^+\)] on rate of reaction was investigated at 0.01≤[\(\text{H}^+\)]≤0.5 mol dm\(^{-3}\) with concentration of oxidant, reductant and ionic strength maintained constant. At the operating condition increase in [\(\text{H}^+\)] resulted in increase in rate of reaction as shown in Table 1. Least square fits (\(r = 0.985\)) of the plot, \(k_2\) versus [\(\text{H}^+\)]\(^2\) (Figure 2) was linear without \(\approx\) zero intercept in conformity with equ. (4).

\[
k_{H^+} = a[\text{H}^+]^2
\]

(\(\text{where } a = 5.245 \text{ dm}^9\text{mol}^{-3}\text{s}^{-1}\)).

![Figure 2: \(k_2\) Vs [\(\text{H}^+\)]\(^2\)](image)

Direct hydrogen ion dependence of rate of reaction is a pointer to protonation of reactants before electron transfer. In accord with this, at the pH 0.30 of this reaction thiophenol (pKa = 9.93) will be predominantly in the protonated state. Its dissociation will be diminished and existence of PhS\(^+\) will be minimal in the reaction media. However, many electron transfer reactions of thiols have been reported to operate by inverse acid dependence\textsuperscript{25,30,31}. This has been attributed to ease of deprotonation of thiols at high pH.
Direct acid dependence is also likely due to the various equilibrium established by CrO₄²⁻ in aqueous acid media leading to formation of HCrO₄⁻ and H₂CrO₄, with equilibrium constants of 10⁻⁵⁹ and 4.1 respectively. H₂CrO₄ predominates at pH < 1⁴². HCrO₄⁻ has been implicated as the active species in most Cr(VI) oxidation reactions ³³. It is therefore very realistic that the reaction between Cr(VI) and PhSH involves H₂CrO₄, HCrO₄ and PhSH₂⁺ as the reactive species.

Effects of Ionic Strength, Dielectric Constant and Added Ions

Variation of ionic strength of the reaction media between 0.015 – 0.05 mol dm⁻³ was achieved using NaClO₄. Table 2 shows the variation of pseudo-first-order rate and second rate constants with ionic strength at [H⁺] = 0.01 mol dm⁻³, [PhSH] = 5 x 10⁻³, [Cr(VI)] = 2.5 x 10⁻⁴ and T = 27.0 °C at λ max = 350 nm.

Table 2: Effect of ionic strength on Cr(VI)-PhSH reaction at [CrO₄²⁻] = 2.5 x 10⁻⁴ mol dm⁻³, [PhSH] = 5 x 10⁻³ mol dm⁻³, [H⁺] = 0.01 mol dm⁻³, λ max = 350 nm and T = 27±0.50 °C.

<table>
<thead>
<tr>
<th>I/(mol dm⁻³)</th>
<th>10⁶ k obs/s⁻¹</th>
<th>k₂/dm³mol⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.015</td>
<td>17.2</td>
<td>0.69</td>
</tr>
<tr>
<td>0.020</td>
<td>15.5</td>
<td>0.62</td>
</tr>
<tr>
<td>0.030</td>
<td>14.7</td>
<td>0.58</td>
</tr>
<tr>
<td>0.040</td>
<td>12.0</td>
<td>0.48</td>
</tr>
<tr>
<td>0.050</td>
<td>11.15</td>
<td>0.45</td>
</tr>
</tbody>
</table>

The data in Table 2 indicate that as the ionic strength of the medium is increased the rate constant increased. This is indicative of positive primary kinetic salt effect. This result is in accord with a reaction where the redox partners interact with positive charges or negative charges at the rate determining step ³⁴. The mostly likely redox partners will be HCrO₄⁻ and PhS⁻.

Figure 3: Plot of logk₂ vs √I

A plot of logk₂ versus √I (Figure 3) was linear with a slope of -1.88 indicating product of charges at the rate determining step to be ≈ -2.0. This infers interaction of opposite charged ions at the rate determining step ³⁴. For chemically controlled ionic reactions in solution, operation of the primary kinetic salt effect requires the rate of reaction be affected by the medium ionic strength according to eqn. (5)

\[
\log_{10}k_2 = \log_{10}k_2^\infty + 1.02Z_AZ_C\left(\frac{I^{1/2}}{1+I^{1/2}}\right) - 0.301
\]

Where k₂ = second order rate constant, k∞ = rate constant at infinite dilution. I = ionic strength, Zₐ = charge on reactant A and Zₐ = charge on reactant C.

A plot of logk₂ versus 1⁴/ₚ/(1x1⁴/ₚ)-0.301 should be linear with slope of 1.02 ZₐZₐ at low ionic strengths ³⁵. Expectedly PhSH⁺ and HCrO₄⁻ or CrO₄²⁻ should be the redox partners in the title reaction.

Dielectric constant (D) was varied from 72.70 to 43.70 by mixing with aliquots of propan-2-one and other parameters kept constant. The results displayed in Table 3 indicate slight increase in rate constant with D. This observation infers interaction of anions and cations at the rate determining step.

Table 3: Effect of dielectric constant on Cr(VI)-PhSH reaction system at [PhSH] = 2 x 10⁻³ mol dm⁻³, [CrO₄²⁻] = 5 x 10⁻⁵, mol dm⁻³, [H⁺] = 0.5 mol dm⁻³, T = 27 °C, λ max = 350 nm

<table>
<thead>
<tr>
<th>Dielectric const (D)</th>
<th>10⁶ k obs/s⁻¹</th>
<th>k₂/dm³mol⁻¹s⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>43.70</td>
<td>3.7</td>
<td>0.19</td>
</tr>
</tbody>
</table>
The catalytic effect of added ions was investigated by adding various amounts of CH₃COO⁻ and Cl⁻ in the concentration range of 1 x 10⁻⁴ - 1 x 10⁻¹ mol dm⁻³ with other parameters kept constant. The results in Table 4 indicate that rate of reaction was retarded by the presence of CH₃COO⁻ and Cl⁻ ions. This observation supports operation of two negatively charge ions at rate determining step where presence of negatively charged ions will increase the degree of repulsion and leading to retardation of rate of reaction. However, the degree of retardation is very insignificant which is attributable no catalytic effect. This a pointer to an inner-sphere process.

Table 4: Effect of added ions on Cr(VI) – PhSH reaction at [PhSH] = 2 x 10⁻³ mol dm⁻³, [CrO₄²⁻] = 2.5 x 10⁻⁵ mol dm⁻³, [H⁺] = 0.5 I = 0.61, T= 27 °C, λmax = 350 nm

<table>
<thead>
<tr>
<th>[Cl⁻]</th>
<th>mol dm⁻³</th>
<th>10⁴k obs/S⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻²</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻¹</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10⁻²</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Other worker have reported involvement of RS⁻, RSH₃⁺, HCrO₄⁻ and H₂CrO₄ in the rate determining steps of Cr(VI) reactions with thiols. The active redox partners are dependent on medium pH. In some of the reactions H⁺ dependence did not feature at pH ≥ 7 but biphasic reactions occurred involving formation of chromate-thiol adducts. It is also interesting to note that reactions involving bacterial cells and Cr(VI) operated without intervening hydrogen atoms.

### Reaction Mechanism

On the basis of the stoichiometry, acid dependence, effect of ionic strength and catalysis, the following mechanism is proposed for the reaction:

1. \[ \text{CrO}_4^{2-} + \text{H}^+ \underset{k_1}{\overset{}{\rightarrow}} \text{CrO}_3\text{OH}^- \] (6)
2. \[ \text{PhSH} + \text{H}^+ \underset{k_2}{\overset{}{\rightarrow}} \text{PhSH}_2^+ \] (7)
3. \[ \text{CrO}_4^{2-} + \text{PhSH}_2^+ \underset{k_3}{\overset{}{\rightarrow}} [\text{HCrO}_3\text{PhSH}] \] (8)
4. \[ [\text{HCrO}_3\text{O-PhSH}_2] \underset{k_4}{\overset{}{\rightarrow}} \text{HCrO}_2 + \text{H}_2\text{O} + \text{PhS} = 0 \] (9)
5. \[ \text{HCrO}_2 + 3\text{H}^+ \underset{k_5}{\overset{}{\rightarrow}} \text{Cr}^{3+} + 2\text{H}_2\text{O} \] (10)

The rate is given by:

\[ \text{Rate} = k_d[\text{HCrO}_3\text{O-PhSH}_2] \] (11)

But \[ [\text{HCrO}_3\text{O-PhSH}_2] = k_d[\text{CrO}_3\text{OH}^-] [\text{PhSH}_2^+] - k_d[\text{HCrO}_3\text{PhSH}_2] = 0 \] (12a)

\[ k_d[\text{CrO}_4^{2-}][\text{PhSH}_2^+] = k_d[\text{HCrO}_3\text{PhSH}_2] \] (12b)

That is \[ [\text{HCrO}_3\text{PhSH}_2] = k_d[\text{CrO}_3\text{OH}^-][\text{PhSH}_2^+] \] (13)

Also \[ [\text{CrO}_3\text{OH}^-] = K_a[H^+][\text{CrO}_4^-] \] (14)

and \[ [\text{PhSH}_2] = K_a[H^+][\text{PhSH}] \] (15)

substituting eqns. (14) and (15) into (11) gives

\[ [\text{HCrO}_3\text{O-PhSH}_2] = k_d[\text{CrO}_3\text{OH}^-][\text{PhSH}_2^+] \] (16)

substituting (16) into (11) gives

\[ \text{Rate} = k_d[\text{HCrO}_3\text{O-PhSH}_2] \] (17)

Equations (6) and (7) imply an electron transfer process mediated by protons. It gives insight to the fact that the acid –independent path may not play any significant role. Such non-acid catalyzed reaction will to a large extent be extremely slow. Plot of \( k_2 \) versus \( [\text{H}^+] \) was linear with insignificant intercept and has slope of 5.024 dm⁻³ mol⁻¹ s⁻¹.

Equ. (8) suggests interaction of redox partners with opposite charge at the rate determining step. This is buttressed by the fact that primary kinetic salt effect showed decrease in rate with ionic strength and least square fits of log\( k_2 \) versus \( I^{1/2} \) was linear with a slope of -1.88
implying interaction of HCrO$_4^-$ and PhSH$_2^+$ at the rate determining step.

Equation (17) is similar to equation(4)
Where $a = k_3K_2K_1$

The rate determining step (equation 9) show the formation of a chromate ester intermediate as a precursor prior to electron transfer. Such reaction is substitution controlled and decomposition of the precursor complex coupled with electron transfer marks determines the rate of reaction.

The precursor complex is readily formed and the rate of transformation to the precursor complex is relatively slow. Intermolecular electron transfer and decomposition of the precursor complex indicates an inner-sphere electron transfer pathway.

References


