# A Kinetic Study of Oxidation of New $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ Complex by N-bromosuccinimide (NBS) 

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#### Abstract

The kinetics of the oxidation of the $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ complex by $N$-bromosuccinimide (NBS) in aqueous media ( $L=$ bidentate ligand mono deprotonated anion derived from methyl salicylaldehyde and sulfacetamide) were investigated over a pH range of 4.2-5.4, temperatures ranging from $25^{\circ} \mathrm{C}$ to $40^{\circ} \mathrm{C}$, and an ionic strength of $0.1 \mathrm{~mol} / \mathrm{l}-0.4 \mathrm{~mol} / \mathrm{l}$ for both NBS and complex concentrations. The reaction rate over the studied pH ranges was predicted to be first order NBS and complex dependent and to rise with decreasing $\left[\mathrm{H}^{+}\right]$. It was compatible with the experimental rate law to say that a process in which the complex's dehydrogenated form is greater reactivity compared to its conjugate acid. Acrylonitrile polymerisation was tested for its abundance of free radicals in the reaction admixture. It was supposed that transfer of electrons and formation of initial cobalt(III) products, which were eventually were tardily transformed into the final cobalt(III) products, occurred by an inner-sphere mechanism.


Keyword: kinetics, oxidation, rate equation, n-bromosuccinimide, cobalt(ii)- complex

## 1. INTRODUCTION

N -bromosuccinimide (NBS) is an organic reagent that has been utilised to oxidise various organic compounds. ${ }^{1-3}$ In a polar media, this oxidation can take place using the bromonium ion $\left(\mathrm{Br}^{+}\right)^{4,5}$ or by pathway of the free radical, which includes hemolytic dissociation of NBS. ${ }^{6,7} \mathrm{Cr}(\mathrm{IV})$ and $\mathrm{Cr}(\mathrm{V})$ are produced as a result of
the biphasic oxidation of cis-diaquabis ( 1,10 phenanthroline) Cr (III) by NBS. The kinetics of Cr (III) oxidation by NBS was investigated in aqueous solutions and $\mathrm{H}_{2} \mathrm{O}-\mathrm{MeOH}$ solvent mixtures. ${ }^{8,9}$ The reaction was characterised by a first order dependence on all reactants and an increase in pH between 7.0 to 8.0. A suggested mechanism of an inner-sphere identified the deprotonated precursor complex of Cr (III) as the primary reactive species, relative to its conjugate acid. Additionally, it has been studied how NBS impacts the mechanism and the kinetics of the ternary complex's oxidation made up of dipicolinato-Cr (III) ${ }^{10}$ and DL-aspartic acid. ${ }^{11,12}$ The form of deprotonated, $\left[\mathrm{Cr}(\mathrm{III})(\mathrm{Dpc})(\mathrm{Asp})\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]$, was believed to be the species that was more reactive in comparison to its conjugate acid, according to the mechanism supported by its experimental rate law. The theory held that transfer of electron was accomplished through a mechanism of an inner-sphere. Spectrophotometric research was also done on the oxidation of ternary and binary Cr (III) complexes involving inosine and glycine, $\left[\mathrm{Cr}(\mathrm{Ino})\left(\mathrm{H}_{2} \mathrm{O}\right)_{5}\right]^{3+}$ and $[\mathrm{Cr}(\mathrm{Gly})$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{3}\right]^{2+}$, to $\mathrm{Cr}(\mathrm{VI})$ in aqueous solutions by NBS, over the temperature range of $25^{\circ} \mathrm{C}$ to $45^{\circ} \mathrm{C} .{ }^{3}$ About [NBS] and [ $\mathrm{Cr}(\mathrm{III})$ ], in both instances, the reaction was first order. The Cr (III) hydroxo-complexes $\left[\mathrm{Cr}(\mathrm{Ino})\left(\mathrm{H}_{2} \mathrm{O}\right)_{4}(\mathrm{OH})\right]^{2+}$ and $[\mathrm{Cr}(\mathrm{Ino})(\mathrm{Gly})$ $\left.\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}(\mathrm{OH})\right]$ were substantially greater reactive compared to their conjugate acid. Additionally, the kinetics of ferrocyanide oxidation by NBS was investigated spectrophotometrically measured in an aqueous acidic medium at temperatures between $20^{\circ} \mathrm{C}$ and $35^{\circ} \mathrm{C}, \mathrm{pH}$ values between 2.8 and 4.3 , and ionic strength values between $0.1 \mathrm{~mol} \mathrm{dm}^{3}$ and $0.50 \mathrm{~mol} \mathrm{dm}^{3}$. The reaction showed first order dependence on both reactants and intensified with rising pH , NBS concentration and $\mathrm{Fe}^{2+}$ concentration. The oxidation rate followed the rate law: $\mathrm{d}\left[\mathrm{Fe}^{3+}\right] / \mathrm{dt}=\left[\mathrm{Fe}(\mathrm{CN})_{6}\right]^{4}$ $\left[\mathrm{HNBS}^{+}\right] /\left(\mathrm{k}_{2}+\mathrm{k}_{3} /\left[\mathrm{H}^{+}\right]\right)$. It has been suggested that pathway of the oxidation of both deprotonated and protonated ferrocyanide species is caused by an outersphere process. ${ }^{13}$ By utilising spectrophotometry, the oxidation of kinetics of the (ethylenediamine diacetate)-Cr (III), $\left[\mathrm{Cr}(\mathrm{EDDA})\left(\mathrm{OH}_{2}\right)^{2}\right]^{+}$by NBS in aqueous solution to produce $\mathrm{Cr}(\mathrm{VI})$, was investigated throughout the temperature range of $20^{\circ} \mathrm{C}-40^{\circ} \mathrm{C}$. With regard to [NBS] and [CrIII], First order reaction was observed, and it grew faster with pH over the range of $(4.8-5.8) .{ }^{14}$ It proposed a mechanism in which the major reactive species was deprotonated $\left[\mathrm{Cr}(\mathrm{III})(\mathrm{EDDA})\left(\mathrm{OH}_{2}\right)\right.$ $(\mathrm{OH})]$. Through the hydroxo-ligand bridging of the two reactants, the electron transfer may occur through mechanism in an inner-sphere. In an aqueous solution, over a range of pH values and temperatures between $25^{\circ} \mathrm{C}$ and $45^{\circ} \mathrm{C}$, kinetics of the inner-sphere oxidation of the ternary iminodiacetatochromium (III) complex, which includes succinate, $\left[\mathrm{Cr}(\mathrm{III})(\mathrm{IDA})(\mathrm{Su})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]$ and $[$ IDA $=$ iminodiacetate, $\mathrm{Su}=$ succinate], by NBS has been studied. The oxidation rate followed using the formula: $\mathrm{d}[\mathrm{Cr}(\mathrm{IV})] / \mathrm{dt}=\left\{[\mathrm{Fe}(\mathrm{II})]\left(\mathrm{k}_{5}+\mathrm{k}_{6} \mathrm{~K}_{1} /\left[\mathrm{H}^{+}\right]\right)+[\mathrm{NBS}]\left(\mathrm{k}_{7} \mathrm{~K}_{2}+\mathrm{k}_{8} \mathrm{~K}_{1} \mathrm{~K}_{3} /\left[\mathrm{H}^{+}\right]\right)\right\}$ $\left[\mathrm{Cr}(\mathrm{III})(\mathrm{IDA})(\mathrm{Su})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{-}$. The oxidising agent, iron (II), which served as the catalyst for the reaction, is thought to have catalysed the reaction by converting
iron (II) to iron (III). Likewise, in an aqueous solution, the oxidation kinetics of $\left[\mathrm{Co}(\mathrm{II}) \mathrm{NM}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{3-}(\mathrm{N}=$ nitrilotriacetate, $\mathrm{M}=$ malonate $)$ by NBS has proven to follow the formula:

$$
\mathrm{d}[\mathrm{Co}(\mathrm{III})] / \mathrm{dt}=\mathrm{k}_{1} \mathrm{~K}_{2}[\mathrm{NBS}][\mathrm{Co}(\mathrm{II})]_{\mathrm{T}} /\left\{1+\mathrm{K}_{2}[\mathrm{NBS}]+\left(\mathrm{H}^{+} / \mathrm{K}_{1}\right)\right\}
$$

where $\mathrm{k}_{1}$ is the rate constant for the transfer of electron process, $\mathrm{K}_{1}$ the constant of equilibrium for dissociation of $\left[\mathrm{Co}(\mathrm{II}) \mathrm{NM}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{3-}$ to $[\mathrm{Co}(\mathrm{II}) \mathrm{NM}(\mathrm{OH})]^{4-}+\mathrm{H}^{+}$and $\mathrm{K}_{2}$, the constant of pre-equilibrium formation. ${ }^{15,16}$ In the $20^{\circ} \mathrm{C}$ to $40^{\circ} \mathrm{C}$ range, the spectrophotometric oxidation kinetics of $\left[\mathrm{Co}(\mathrm{II}) \mathrm{NS}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]_{3},(\mathrm{~N}=$ nitrilotriacetate, $\mathrm{S}=$ succinate) by NBS have been investigated. ${ }^{17}$ First order reactions occurred in both [NBS] and $\left[\mathrm{Co}(\mathrm{II}) \mathrm{NS}\left(\mathrm{H}_{2} \mathrm{O}\right) 2\right]^{3-}$ and the reaction's rate was greater as the pH rose between 6.6 and 7.7. In comparison to its conjugate acid, the form of deprotonated $\left[\mathrm{Co}(\mathrm{II}) \mathrm{NS}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{4}$ is thought to be the most reactive of all species, additionally rate law of the experimental method supports this theory. It is believed that an inner-sphere mechanism was used to transport electrons. We present our results for the kinetic oxidation of $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ complex by NBS in this study, being that the complex may be unstable and coordinated water substitution before the electron transfer is likely.

## 2. EXPERIMENTAL

### 2.1 Materials and Solutions

All substances utilised in the present research were of the reagent grade and were not further purified before usage. All tests and solution formulations used double distilled water. Solutions for buffers were developed by combining the appropriate concentrations of $0.2 \mathrm{~mol} / 1 \mathrm{Na}_{2} \mathrm{HPO}_{4}$ and $0.1 \mathrm{~mol} / 1$ citric acid for the required pHs . Different buffers used were modified for ionic strength using a known-molarity solution NaCl . By carefully weighing, freshly created solutions of the NBS and complex were created. The Schiff base was made using a hot methyl salicylaldehyde solution in ethanol ( 0.02 mole ) and a hot sulfacetamide solution in ethanol ( 0.02 mole) were mixed in a 1:1 molar ratio, stirred vigorously until a precipitation of yellow produced, repeatedly rinsed, recrystallised and dried under vacuum over anhydrous calcium chloride. The Schiff base metal complex $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ was prepared by adding a hot water solution of $\mathrm{Co}\left(\mathrm{NO}_{3}\right)_{2}(0.02$ mole) with vigorous stirring to a hot (E)-N-(4-(2-hydroxy-3-methyl benzylideneamino) phenylsulfonyl) acetamide solution in ethanol ( 0.02 mole ) in $1 \mathrm{M}: 2 \mathrm{~L}$ molar ratio, the reaction was refluxed for a long period until a white powder formed.

Variables in this experiment are as follows:
Melting point was $\left(>300^{\circ} \mathrm{C}\right)$, yield $82.3 \%$, molecular weight (743.64) $\mathrm{g} / \mathrm{mol}$ $\mathrm{C}_{31} \mathrm{H}_{32} \mathrm{CoN}_{4} \mathrm{O}_{10} \mathrm{~S}_{2}$

Elemental analysis: Calculation. Found: C 50.02 (50.03), H 4.30 (4.18). N 7.53 (7.51), S 8.60 (8.62), Co 7.92 (7.90)

IR bands (Figure 1): $\mathrm{vH}_{2} \mathrm{O}$ br 3451, v N-H 3376, v $\mathrm{C}=\mathrm{O} 1653$, v $\mathrm{C}=\mathrm{N} 1572, \mathrm{vCH}_{3}$ $1433, \mathrm{vSO}_{2}$ as $1327, \mathrm{vSO}_{2}$ sym $1152, \mathrm{vM}-\mathrm{N} 566, \mathrm{vM}-\mathrm{O} 444 \mathrm{~cm}^{-1}$

UV spectra: $\lambda_{\max } \mathrm{nm} 620,553,488,457,369,316,277,261,227,211$
$\mu \mathrm{eff} .=11.61$ (B.M.)
$\Lambda \mathrm{m}=4.46 \Omega^{-1} \mathrm{~mol}^{-1} \mathrm{~cm}^{2}$
Geometry: Octahedral


Figure 1: IR Spectra of $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ complex.

### 2.2 Kinetic Procedure

The reaction of oxidation of Co(II)-complex by NBS was studied using a Shimadzu 1700 UV (Shimadzu, Japan) Vis spectrophotometer. The oxidation products' absorbance between 520 nm and 545 nm was monitored, where the pH utilised had the highest absorbance of $\mathrm{Co}(\mathrm{III})$ products $\mathrm{Co}(\mathrm{II})$-complex and NBS solutions were combined in the appropriate buffers to start the reaction. A particular period of time was used to measure the oxidation products' absorbance. A measurement of pH was made of the reaction mixture through the use of a Jenway pH meter 3505 (Jenway, UK). By employing a significant (10 times) excess of [NBS] in
comparison to [complex] in all kinetics tests, pseudo-first order conditions were implemented. The oxidation's kinetics of $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ by NBS was investigated for a range of the concentrations of all reactants at $(4.2-5.4) \mathrm{pH},(0.10-0.40) \mathrm{mol} / 1$ ionic strength, and $25^{\circ} \mathrm{C}-40^{\circ} \mathrm{C}$ temperature. The reaction media will be examined for the presence of free radicals. Acrylonitrile was added to the reaction mixture and let stand for a day. Acrylonitrile polymerisation was noticed, which indicated the presence of free radicals. To confirm the reality of free radicals, to the reaction mixture, a solution of silver nitrate was added. The precipitate of silver bromide $(\mathrm{AgBr})$ exhibited a light-yellow colour, which is a characteristic of the presence of free radicals. This study's findings indicate that the oxidation reaction of $\mathrm{Co}(\mathrm{II})$ complex by NBS is a free radical-mediated process.

## 3. RESULT AND DISCUSSION

Once the each of reactants were combined, the oxidation products' absorbance was calculated, and it curled over time. $\ln \left(\mathrm{A}_{\infty}-\mathrm{A}_{t}\right)$ plots against time was linear approximately $\geq 85 \%$ of the reaction, where $A_{t}$ is the oxidation products' absorbance at time $t$ and $\mathrm{A}_{\infty}$ at infinity, respectively. The slopes of the first order plots were used to calculate the pseudo-first order rate constants or, $\mathrm{K}_{\text {obs }}$. Values' constancy over the range of complex concentration $\left(1.0 \times 10^{-4}-3.0 \times 10^{-4}\right) \mathrm{mol} / \mathrm{l}$, according to Table 1, it corresponds with Equation 1.

$$
\begin{equation*}
\mathrm{d}[\mathrm{Co}(\mathrm{III})] / \mathrm{dt}=\mathrm{K}_{\mathrm{obs}} \cdot[\mathrm{Co}(\mathrm{II})]_{\mathrm{T}} \tag{1}
\end{equation*}
$$

The overall concentration of the $\mathrm{Co}(\mathrm{II})$-complex is represented by $[\mathrm{Co}(\mathrm{II})]_{\mathrm{T} .}$. Over $\left(0.1 \times 10^{-2}-4.0 \times 10^{-2}\right) \mathrm{mol} / \mathrm{l}$ range, the relationship between $\mathrm{k}_{\text {obs }}$ and [NBS] was studied. According to the kinetic data presented in Table 1, it is predicted that while [NBS] grew, the reaction rate rose. Figure 2 shows the relationship between $1 / \mathrm{K}_{\mathrm{obs}}$ and $1 /[\mathrm{NBS}]$ at constant temperatures. This relationship is consistent with Equation 3 and is predicted by the equation $\mathrm{y}=\mathrm{mx}+\mathrm{c}$.

$$
\begin{align*}
& \mathrm{K}_{\mathrm{obs}}=\mathrm{a}[\mathrm{NBS}] /(1+\mathrm{b}[\mathrm{NBS}])  \tag{2}\\
& 1 / \mathrm{K}_{\mathrm{obs}}=1 / \mathrm{a}[\mathrm{NBS}]+\mathrm{b} / \mathrm{a} \tag{3}
\end{align*}
$$



Figure 2: Plots of $[\mathrm{NBS}]^{-1}$ versus $\mathrm{K}_{\mathrm{obs}}{ }^{-1}$ at different temperature.

Table 1: The reaction rate depend on $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right],[\mathrm{NBS}]$ and temperatures at $\mathrm{pH}=4.2$ and $\mathrm{I}=0.10 \mathrm{~mol} / \mathrm{l}$.

| Temperature $\left({ }^{\circ} \mathrm{C}\right)$ | $10^{2}[\mathrm{NBS}](\mathrm{mol} / \mathrm{l})$ | $10^{4} \mathrm{~K}_{\text {obs }}\left(\mathrm{s}^{-1}\right)$ |
| :---: | :---: | :---: |
| 25 | 1.0 | 6.11 |
| 25 | 2.0 | 7.71 |
| 25 | 3.0 | 8.78 |
| 25 | 4.0 | 9.25 |
| 25 | $2.0^{\mathrm{a}}$ | 7.68 |
| 25 | $2.0^{\mathrm{b}}$ | 7.74 |
| 25 | $2.0^{\mathrm{c}}$ | 7.73 |
| 25 | $2.0^{\mathrm{d}}$ | 7.70 |
| 30 | 1.0 | 7.45 |
| 30 | 2.0 | 8.99 |
| 30 | 3.0 | 9.65 |
| 30 | 4.0 | 10.14 |
| 35 | 1.0 | 9.88 |
| 35 | 2.0 | 10.79 |
| 35 | 3.0 | 11.40 |
| 35 | 4.0 | 11.70 |
| 40 | 1.0 | 11.78 |
| 40 | 2.0 | 12.51 |
| 40 | 3.0 | 13.14 |
| 40 | 4.0 | 13.91 |

Notes: Unless otherwise stated, $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]=1.0 \times 10^{-4} \mathrm{~mol} / \mathrm{l}$; ${ }^{\mathrm{a}-\mathrm{d}}$ $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ was $1.5 \times 10^{-4} \mathrm{~mol} / 1,2.0 \times 10^{-4} \mathrm{~mol} / 1,2.5 \times 10^{-4}$ $\mathrm{mol} / \mathrm{l}$ and $3.0 \times 10^{-4} \mathrm{~mol} / \mathrm{l}$, respectively.

For calculating the values of $a$ and $b$, the intercepts and slopes of the plots at many different temperatures were employed (Table 2). By altering the pH values within the range of $(4.2-5.4)$ and holding the other parameter constant, the impact of pH on the measured rate constant was investigated. Table 3's values for $\mathrm{K}_{\text {obs }}$ at various pH level showed that over the range under study, the oxidation rate accelerated with decreasing $\left[\mathrm{H}^{+}\right]$. This behaviour is consistent with the deprotonated Co (II)-complex's participation in the rate-determining step. In conformity with the formula $\mathrm{y}=\mathrm{mx}+\mathrm{c}, 1 / \mathrm{K}_{\text {obs. }}$ plots against $1 /[\mathrm{NBS}]$ at various pH level (Figure 3) had an obvious intercept as well as were linear. The reaction rate is not impacted by ionic strength, according to Table 4. Given that the reactant's product of charges was zero, this behaviour is predictable. NBS are present as $\mathrm{HNBS}^{+}$, a protonated form in strongly acidic conditions, but in the study we have just shown, NBS is the dominant species. ${ }^{9,16}$ The subsequent reaction scheme, that contains three quick pre-equilibria states, is able to explain the reported kinetics of $\mathrm{Co}(\mathrm{II})$-complex with NBS's oxidation in a setting for experiments.

Table 2: Values of $a$ and $b$ at different temperature.

| $\mathrm{T}\left({ }^{\circ} \mathrm{C}\right)$ | $\mathrm{a}\left(\mathrm{mol} / \mathrm{l}, \mathrm{s}^{-1}\right)$ | $\mathrm{b}(\mathrm{mol} / \mathrm{l})$ |
| :--- | :--- | :---: |
| 25 | 0.73680 | 90.56827 |
| 30 | 0.46841 | 87.53468 |
| 35 | 0.20215 | 81.42352 |
| 40 | 0.15614 | 70.08224 |

Table 3: Effect of pH on $\mathrm{K}_{\mathrm{obs}}\left(\mathrm{s}^{-1}\right)$ at $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]=1.0 \times 10^{-4} \mathrm{~mol} / \mathrm{l}$, $\mathrm{I}=0.20 \mathrm{~mol} / \mathrm{l}$ and $\mathrm{T}=25^{\circ} \mathrm{C}$.

| $10^{4}[\mathrm{NBS}] \mathrm{mol} / 1$ | $\mathrm{pH}=4.2$ | $\mathrm{pH}=4.6$ | $\mathrm{pH}=5.0$ | $\mathrm{pH}=5.4$ |
| :---: | :---: | :---: | :---: | :---: |
|  | 6.11 | 7.35 | 8.32 | 9.21 |
| 1.0 | 7.71 | 9.33 | 10.42 | 11.33 |
| 2.0 | 8.78 | 10.29 | 11.54 | 12.42 |
| 3.0 | 9.25 | 10.86 | 12.04 | 13.26 |

Table 4: Ionic strength's effect on the rate of the reaction at $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ $=1.0 \times 10^{-4} \mathrm{~mol} / 1, \mathrm{pH}=4.2,[\mathrm{NBS}]=0.02 \mathrm{~mol} / 1$ and $\mathrm{T}=25^{\circ} \mathrm{C}$.

| $\mathrm{I}(\mathrm{mol} / \mathrm{l})$ | $10^{4} \mathrm{~K}_{\text {obs }}\left(\mathrm{s}^{-1}\right)$ |
| :--- | :---: |
| 0.10 | 7.69 |
| 0.2 | 7.70 |
| 0.30 | 7.75 |
| 0.40 | 7.73 |



Figure 3: Plots of $[\mathrm{NBS}]^{-1}$ versus $\mathrm{k}_{\text {obs }}{ }^{-1}$ at different pH 's

$$
\begin{align*}
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right] \rightleftharpoons\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{-}+\left[\mathrm{H}^{+}\right]}  \tag{4}\\
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]+\mathrm{NBS} \rightleftharpoons\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]+\mathrm{H}_{2} \mathrm{O}}  \tag{5}\\
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{-}+\mathrm{NBS} \rightleftharpoons\left[\mathrm{Co}(\mathrm{~L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]^{-}}  \tag{6}\\
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right] \longrightarrow\left[\mathrm{R}-\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{+}+\mathrm{Br}^{-}}  \tag{7}\\
& {\left[\mathrm{R}^{\cdot}-\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]+\mathrm{Br}^{-} \longrightarrow\left[\mathrm{Co}(\mathrm{~L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]^{-}} \tag{8}
\end{align*}
$$

where $\mathrm{R}^{\cdot}$ denotes the radical succinimide. The rate law is depicted by the following mechanism from the above:

$$
\begin{align*}
\text { Rate } & =\mathrm{K}_{4}\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]+\mathrm{K}_{5}\left[\mathrm{Co}(\mathrm{~L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]^{-} \\
& =[\mathrm{NBS}]\left[\mathrm{Co}(\mathrm{~L})(\mathrm{Ac})\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]\left\{\mathrm{K}_{2} \mathrm{~K}_{4}+\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5} /\left[\mathrm{H}^{+}\right]\right\} \tag{9}
\end{align*}
$$

If all $\mathrm{Co}(\mathrm{II})$ species' various forms are represented by $[\mathrm{Co}]_{\mathrm{T}}$, then:

$$
\begin{align*}
& {[\mathrm{Co}(\mathrm{II})]_{\mathrm{T}}=\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]+\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{-}+\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{NBS})\right]} \\
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})(\mathrm{NBS})\right]^{-}} \\
& {\left[\mathrm{Co}(\mathrm{~L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]=[\mathrm{Co}(\mathrm{II})]_{\mathrm{T}} / 1+\mathrm{K}_{1} /\left[\mathrm{H}^{+}\right]+[\mathrm{NBS}]\left\{\mathrm{K}_{2}+\mathrm{K}_{1} \mathrm{~K}_{3} /\left[\mathrm{H}^{+}\right]\right\}} \tag{10}
\end{align*}
$$

Equation 8 is substituted for Equation 9 next.

$$
\begin{align*}
& \text { Rate }=[\mathrm{NBS}][\mathrm{Co}(\mathrm{II})]_{\mathrm{T}}\left\{\mathrm{~K}_{2} \mathrm{~K}_{4}+\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5} /\left[\mathrm{H}^{+}\right]\right\} / 1+\mathrm{K}_{1} /\left[\mathrm{H}^{+}\right]+[\mathrm{NBS}] \\
& \left\{\mathrm{K}_{2}+\mathrm{K}_{1} \mathrm{~K}_{3} /\left[\mathrm{H}^{+}\right]\right\}  \tag{11}\\
& \mathrm{K}_{\text {obs }}=[\mathrm{NBS}]\left\{\mathrm{K}_{2} \mathrm{k}_{4}+\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5} /\left[\mathrm{H}^{+}\right]\right\} /\left\{1+\mathrm{K}_{1} /\left[\mathrm{H}^{+}\right]+\right. \\
& {[\mathrm{NBS}]\left(\mathrm{K}_{2}+\mathrm{K}_{1} \mathrm{~K}_{3} /\left[\mathrm{H}^{+}\right]\right)} \tag{12}
\end{align*}
$$

The complex's conjugate base, $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{-}$, is regarded as the more reactive species due to the existence of the $\mathrm{OH}^{-}$group which acted as bridge through which the electron transfer took place, hence Equation 11 converts into Equation 12.

$$
\begin{equation*}
\mathrm{K}_{\mathrm{obs}}=[\mathrm{NBS}]\left(\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5} /\left[\mathrm{H}^{+}\right]\right) /\left\{1+\mathrm{K}_{1} /\left[\mathrm{H}^{+}\right]+[\mathrm{NBS}]\left(\mathrm{K}_{2}+\mathrm{K}_{1} \mathrm{~K}_{3} /\left[\mathrm{H}^{+}\right]\right)\right\} \tag{13}
\end{equation*}
$$

On rearrangement:

$$
\begin{equation*}
1 / \mathrm{K}_{\text {obs }}=\left(\left[\mathrm{H}^{+}\right]+\mathrm{K}_{1}\right) /[\mathrm{NBS}]\left(\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5}\right)+\left(\mathrm{K}_{2}\left[\mathrm{H}^{+}\right]+\mathrm{K}_{1} \mathrm{~K}_{3}\right) / \mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5} \tag{14}
\end{equation*}
$$

Equation 13 is consistent with Equation 2 at constant $\left[\mathrm{H}^{+}\right], 1 / \mathrm{a}=\left(\left[\mathrm{H}^{+}\right]+\mathrm{K}_{1}\right) /$ $\left.\mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5}\right)$ and $\mathrm{b} / \mathrm{a}=\left(\mathrm{K}_{2}\left[\mathrm{H}^{+}\right]+\mathrm{K}_{1} \mathrm{~K}_{3}\right) / \mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5}$.

The relationship between $1 / \mathrm{a}$ and $\left[\mathrm{H}^{+}\right]$was linear, with a correlation value of 0.99023 , a slope of $1 / \mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5}$, and an intercept of $1 / \mathrm{K}_{3} \mathrm{~K}_{5}$. The intercept is divided by the slope of the plot, $\mathrm{K}_{1}$ was computed. The $\mathrm{b} / \mathrm{a}$ against $[\mathrm{H}+$ ] plot similarly had a linear relationship, with a correlation coefficient of 0.99156 ; the $\mathrm{b} / \mathrm{a}$ 's slope against $\left[\mathrm{H}^{+}\right]$plot corresponded to $\mathrm{K}_{2} / \mathrm{K}_{1} \mathrm{~K}_{3} \mathrm{~K}_{5}$, and the intercept to $1 / \mathrm{K}_{5} . \mathrm{K}_{3}$ was determined by taking the reciprocal of the $\mathrm{a} / \mathrm{b}$ versus $\left[\mathrm{H}^{+}\right]$plot's intercept. The $\mathrm{a} / \mathrm{b}$ 's slope against $\left[\mathrm{H}^{+}\right]$plots was then divided by the $1 / \mathrm{a}$ 's slope against $\left[\mathrm{H}^{+}\right]$ plots to calculate $\mathrm{K}_{2}$. The intercept of $1 /$ a against the $\left[\mathrm{H}^{+}\right]$plot can be used to substitute the value $\mathrm{K}_{5}$ and obtain the value of $\mathrm{K}_{3}$. The transition state theory equation was fitted using least squares to get the parameters $\Delta \mathrm{S}^{*}$ and $\Delta \mathrm{H}^{*}$ for the thermodynamic activation, $\Delta \mathrm{S}^{*}$ and $\Delta \mathrm{H}^{*}$, connected to the constant a in Equation 2 Thermodynamic activation parameters including $\Delta H^{*}$ and $\Delta S^{*}$ associated with the constant were calculated using a least square fit (Figure 4) to the transition state theory equation as $96.63 \mathrm{~K} \mathrm{~J} \mathrm{~mol}^{-1}$ and $-2.3 \mathrm{JK}^{-1} \mathrm{~mol}^{-1}$, respectively. The value of $\Delta \mathrm{H}^{*}$ is a composite enthalpy that accounts for both the activation enthalpy of the step of intramolecular transfer of electrons and the formation enthalpy associated with the precursor complex $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]^{-}$. According to the $\Delta \mathrm{H}^{*}$ value that is positive, the transfer of electron step is endothermic. It was asserted that the step of intramolecular transfer of electrons step and equilibrium reactions both significantly ordered the
solvated water molecules, which is substantially responsible for the composite $\Delta S^{*}$ 's negative value. ${ }^{14,18}$ An inner-sphere process for the $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ oxidised by NBS through the production of a initial cobalt(III) products was proposed based on the discussion above. This is because:

1. NBS has the ability to coordinate a metal ion via the carbonyl group to create the intermediate precursor. ${ }^{16,18}$
2. Acrylonitrile polymerisation shows that initial Co(III) products are slowly transformed into a final Co(III).


Figure 4: Plot of $\mathrm{Ln} \mathrm{K} / \mathrm{T}$ versus 1/T.
The complex's conjugate base, $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)(\mathrm{OH})\right]$-, was thought to be more reactive than its conjugate acid, where the hydroxo-group serves as a bridge for the transfer of electrons. Additionally, the coordinated $\mathrm{H}_{2} \mathrm{O}$ in the complex $\left[\mathrm{Co}(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)_{2}\right]$ appears to be labile, and NBS is likely to replace it before the electron transfer. It is feasible to convert the products of initial cobalt(III) into a final form of cobalt (III), and as a result:

$$
\begin{aligned}
& {\left[\mathrm{R}^{-}-\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{+} } \rightleftharpoons \\
& {\left[\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}\left(\mathrm{H}_{2} \mathrm{O}\right)\right]^{+}+\mathrm{R}^{\cdot} } \\
& {\left[-\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)\right] } \rightleftharpoons \\
& {\left[\mathrm{Co}(\mathrm{III})(\mathrm{L})_{2}(\mathrm{OH})\left(\mathrm{H}_{2} \mathrm{O}\right)\right]+\mathrm{R}^{\cdot} }
\end{aligned}
$$

The polymerisation of acrylonitrile demonstrated the existence of succinimide radical (R'), which was created by the transformation of a initial cobalt (III) into a final cobalt(III) products. In order to make succinimide. The succinimide radical might choose to take a hydrogen atom from the solution instead of dimerising and produce bisuccinimide. ${ }^{14,18}$

## 4. CONCLUSION

The kinetic oxidation of a complex in aqueous solution by NBS has been investigated using spectrophotometry. Both reactants' first-order reaction rates rose with pH and complex concentration, the concentration of NBS, and temperature. This indicates that the reaction is bimolecular, meaning that it involves the collision of two molecules. The increase in reaction rate with increasing temperature is consistent with the Arrhenius equation. The complex's deprotonated form was more reactive than the conjugate acid. An inner-sphere mechanism was proposed, which involved the production of initial $\mathrm{Co}($ III ) products. The acrylonitrile polymerisation confirmed this mechanism. Thermodynamic activation parameters were also calculated.

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