Research Article

Kinetics Investigation in to the Reaction between Hexamethyl Pararosanaline Chloride and Cobaltinitrite Ions in Acidic Medium

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Abstract The kinetics of crystal violet (CV^+) fading by $Co(NO_2)_6^{3-}$ were carried out in aqueous acidic medium, The investigation was done in excess cobaltinitrite concentration and at T = 25.0 ± 1°C and λ_{max} = 580 nm. The stoichiometric studies showed that one mole of the crystal violet was found to be consumed by one mole cobaltinitrite ion. The reaction rates increased with increase in [H^+], added cations and decrease in dielectric constant (D). The kinetic data data shows that the reaction rate was independent of [CV^+] and hence, the reaction obeys the rate law:

$$-d[CV^+]/ dt = (a + b[H^+])[CV^+].$$

Where [H^+] = 1.0×10^{-3} mol dm^{-3} μ = 1.0 mol dm^{-3} λ_{max} = 580 nm

The second order rate constant for the crystal violet – $Co(NO_2)_6^{3-}$ reaction was found to be fairly constant. The reaction showed zero salt effect. Spectroscopic test indicate a shift in λ_{max} and Michaelis- Menten plot indicate a significant intercept, these is an evidence for intermediate complex formation. Innersphere mechanism has been proposed for the reaction.

Keywords Kinetics, crystal violet, spectroscopy

Introduction
Crystal violet (CV^+) is a carbonium ion that is stabilized by the presence of aromatic rings, with which it forms highly resonant structures that result in a deep blue–violet colour with an absorption maximum in the visible region λmax = 588 nm [1]. The reactivity of this cation is of a high physico–chemical interest and was studied simultaneously with that of related cations with a view to establishing Ritchie's N^+ nucleophilic index. Its chemistry has been examined under a variety of conditions in homogeneous and micro-heterogeneous media [2].

Dye Colour
The crystal violet color is due to the extensive system of alternating single and double bonds which extends over all three benzene rings and the central carbon atom. This alternation of double and single bonding is termed conjugation, and molecules which have extensive conjugation are usually highly coloured. Trace the conjugation in the crystal violet structure and note that in the reaction product, the three rings are no longer in conjugation with one another, and hence, the material is colorless [3].

Sodium Cobaltinitrite
Sodium cobaltinitrite is a coordination compound with the formula $Na_3Co(NO_2)_6$. The anion of this yellow-coloured salt consist of a cobalt (III) center N-bonded to six nitro ligands. It is a reagent for the quantitative test for potassium

and ammonium ions [4]. It is a nitrosation reagent of conversion of aromatic amine 1, 2-diaryltriazenes with excellent yield.

Kinetic Study of Cobaltinitrite

Literature survey reveals that no work has been done on oxidation and kinetics of cobaltinitrite with any dye.

This paper would give an idea on the oxidation and reduction of crystal violet with cobaltinitrite ions and the mechanism involve in the reaction. The idea derived would be very useful to industrial and medicinal chemist in improving it's uses.

Experimental

All chemical reagents and solvents used were analytical grade, and were used without further purification. Single distilled water was used throughout for all solution preparation. HCl was used to study the effect $[H^+]$ on the reaction rate, NaCl was used to maintain the ionic strength. Binary solvent of water and acetone was used to investigate the effect dielectric constant. The oxidation and reduction crystal violet by cobaltinitrite ion was investigated using 721 Visible spectrophotometer.

Stoichiometry

Spectrophotometric titration following the mole ratio method was employed in determining the stoichiometry of the reaction. The $[CV^+]$ was kept constant while the $[Co(NO_2)_6^{3-}]$ were varied. The absorbance of the reaction mixtures were measured at 580nm until the completion of the reaction which was indicated by a constant absorbance value. A plot of absorbance $(A_t - A_\infty)$ versus mole ratio were made, from which the stoichiometry of the reaction was evaluated.

Kinetic Measurement

All kinetic measurements was carried out under pseudo- first order conditions with respective to [reductant] at temperature $T = 25 \pm 1°C$, ionic strength as well as the hydrogen ion concentrations of the media was maintained constant for the reaction. The rate of reaction was study by monitoring the decrease in the absorbances of crystal violet at 580 nm.

Acid, Ionic Strength and Effect of Added Ions Dependence

Spectrophometric techniques was used to determine the acid, ionic strength, and effect of added ions dependence on reaction rate. The $[CV^+]$ was kept constant while $[H^+]$ was varied in acid dependence, $[NaCl]$ was varied in ionic strength dependence, while selected cations and anions was varied in determining the effect of added ions.

Results and Discussion

Stoichiometry

The result of the stoichiometric studies, from the Plot of absorbance against mole ratio clearly presented in (figure 1) shows that, the mole ratio of the reaction was found to be 1:1 this indicates that for every one mole of CV^+, one moles of $Co(NO_2)_6^{3-}$ is being oxidized. This is in line with the equation

$$+ Co(NO_2)_6^{3-} \rightarrow CV^+ + Co^{2+} + \text{Other product} \qquad\qquad ......1$$
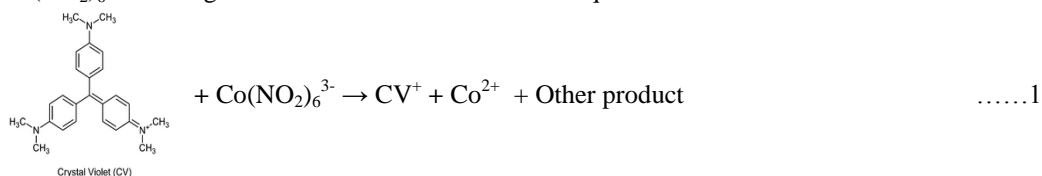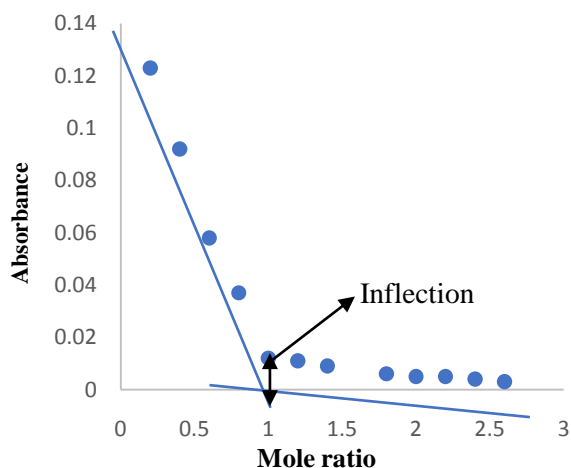
Figure 1: Plot of absorbance versus mole ratio for determination of stoichiometry for the reaction of CV^+ with $Co(NO_2)_6^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6^{3-}] = (0.16 - 1.92) \times 10^{-2}$) mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $T= 26.0 \pm 1.0$ °C and $\lambda_{max} = 580$ nm

Literature survey reveals that no work has been done on kinetics oxidation of cobaltinitrite with any dye.

Order of reaction

The plot of $(A_t - A_\infty)$ versus time t, for the reactions was linear to about 80-90% of the reaction (Figure 2), at constant $[H^+]$ and $[\mu]$. But the rate of the reaction was found to vary with increase in $[H^+]$ and $[\mu]$. The plot of log k_1 versus log $(Co(NO_2)_6^{3-})$ was linear with a slop of 0.01, indicate that the reaction was zero order in $[Co(NO_2)_6^{3-}]$. The k_2 for the reactions was found to be fairly constant (Table 1) and was obtained from $k_2 = k_1/[Co(NO_2)_6^{3}]$, while the rate equation for the reaction can be written as:
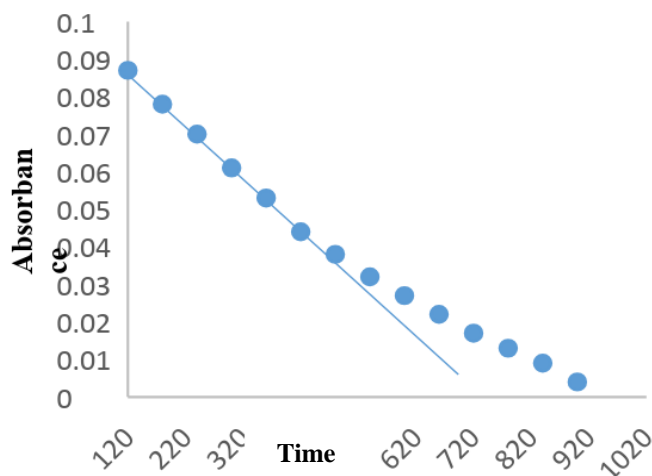
$$-d[CV^+]/dt = K_2[CV^+][Co(NO_2)_6^{2-}] \qquad \ldots\ldots\ldots 2$$

Where $k_2 = 4.01 \pm 0.16$ mol dm^{-3} s^{-2}

Figure 2: Typical pseudo-first order plot for the redox reaction of CV^+ with $[Co(NO_2)_6^{3}]$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6^{3-}]=0.8 \times 10^{-3}$ mol dm^{-3}, $[H^+]=1.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $T = 24.0 \pm 1.0$ °C and $\lambda_{max} = 580$ nm

Effect of $[H^+]$ on Reaction Rates

The acid dependence rate of reaction was found to increase with increase in concentration of hydrogen ion as reported in (Table 1). The plot of k_{H+} versus $[H^+]$ was also linear (Figure 3), hence the acid dependent rate constant k_H is expressed by the equation:
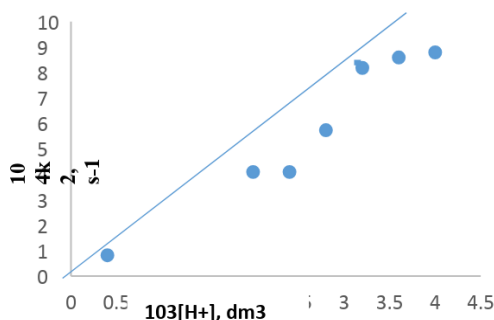
$$-d[CV^+]/dt = k_H[CV^+] \qquad \ldots\ldots 3$$

Figure 3: Plot of k_{H+} versus $[H^+]$ for the redox reaction of CV^+ and $Co(NO_2)_6)^{3-}$ at $[CV^+]=1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}]= 4.0 \times 10^{-4}$, $[H^+] = (0.40 – 4.8) \times 10^{-3}$ mol dm^{-3}, $\mu = 1.92 \times 10^{-1}$ mol dm^{-3} (NaCl), T = 25 ± 1.0°C and $\lambda_{max} = 580$ nm

Effect of ionic strength on the reaction rates

The effect of ionic strength on the reaction rates was investigated within the range studied $(1.12 – 2.92) \times 10^{-1}$ mol dm^{-3}. The rate of reaction was unaffected with Increase in ionic strength concentration as reported in (Table 1).

Table 1: Pseudo first order and second order rate constants for the reaction of CV^+ with $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $\lambda_{max} = 580$ nm and T = 27.0 ± 1.0°C

$10^3[Co(NO_2)_6)^{3}]$ (mol dm)	$10^3[H^+]$ (mold)	$10^1\mu$ (moldm^3)	10^4k_1 (s^{-1})	10^4k_2 (dm^3)
0.8	4.0	1.92	2.30	4.70
1.6	4.0	1.92	2.30	4.30
2.4	4.0	1.92	2.30	4.21
3.2	4.0	1.92	2.30	4.10
4.0	4.0	1.92	2.30	4.01
5.6	4.0	1.92	2.30	4.00
6.4	4.0	1.92	2.30	4.00
8.0	4.0	1.92	2.30	4.00
4.0	0.8	1.92	2.30	3.99
4.0	1.2	1.92	2.30	3.99
4.0	1.6	1.92	2.30	4.00
4.0	2.0	1.92	2.30	4.00
4.0	2.4	1.92	2.76	4.79
4.0	2.8	1.92	3.22	5.59
4.0	3.2	1.92	4.60	7.99
4.0	3.6	1.92	4.84	8.39
4.0	4.0	1.92	5.07	8.79
4.0	4.0	1.12	2.30	4.00
4.0	4.0	1.32	2.30	4.00
4.0	4.0	1.52	2.30	4.00
4.0	4.0	1.72	2.30	4.00
4.0	4.0	1.92	2.30	4.00
4.0	4.0	2.12	2.30	4.00
4.0	4.0	2.32	2.30	4.00
4.0	4.0	2.52	2.30	4.00
4.0	4.0	2.72	2.30	4.00
4.0	4.0	2.92	2.30	4.00

Effect of Anions

The effect of added anion was studied within the range for $[X] = (2.0 – 10.0) \times 10^{-2}$ mol dm^{-3} for (X = CH_3COO^- and NO_3^-). Increase in concentration of the anions decreases the rate of the reaction. The results are presented (Table 2),

and the least square plot of dependence of k_2 on [X] is presented in Figure 4 – 7. The plot was linear and fitted to the equation 4.10.

$$K_2 = p + q[X^{n-}]$$

Where n = 1 or 2

p = slope

q = intercept

$CV^+ / Co(NO_2)_6)^{3-}$

    $p(NO_3^-) = 1.24$ mol dm^{-3} s^{-1} and $q(NO_3^-) = 4.0$ x 10^{-4} mol dm^{-3} s^{-1}

    $p(CH_3COO^-) = 1.34$ mol dm^{-3} s^{-1} and $q(CH_3COO^-) = 4.0$ x 10^{-4} mol dm^{-3} s^{-1}

$CV^+ / Co(NO_2)_6)^{3-}$

    $p(K^+) = 7.95$ mol dm^{-3} s^{-1} and $q(K^+) = 4.0$ x 10^{-4} mol dm^{-3} s^{-1}

    $p(Li^+) = 14.9$ mol dm^{-3} s^{-1} and $q(Li^+) = 4.0$ x 10^{-4} mol dm^{-3} s^{-1}

Table 2: The effect of cations and anions on the first and second order rate constant for CV^+ and $Co(NO_2)_6)^{3-}$ reaction at $[CV^+] = 1.6x10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 4.0$ x 10^{-3} mol dm^{-3}, $[H^+] = 2.0$ x 10^{-3} mol dm^{-3}, $\mu = 1.0$ mol dm^{-3}, $T = 25 \pm 1^oC$, and $\lambda_{max} = 580$ nm

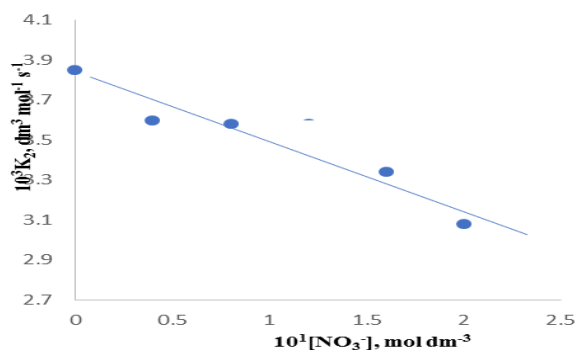| X	$10^2[X]$, mol dm^{-3}	$10^4k_1(s^{-1})$	$10^4k_2(dm^3\ mol^{-1}\ s^{-1})$
Li^+	0	2.30	4.00
	0.4	6.91	12.0
	0.8	9.21	15.9
	1.2	9.21	15.9
	1.6	18.4	32.0
	2.0	6.91	12.0
K^+	0.	2.30	4.00
	0.4	4.61	7.99
	0.8	6.91	12.0
	1.2	9.21	15.9
	1.6	9.21	16.0
CH_3COO^-	0	2.30	4.00
	0.4	1.84	3.20
	0.8	1.38	2.39
	1.2	1.38	2.40
	1.6	0.92	1.59
	2.0	0.69	1.20
NO_3^-	0	2.30	4.00
	0.4	1.38	2.40
	1.2	1.15	1.99
	1.6	0.92	1.60
	2.0	0.69	1.20

Figure 4: Plot of dependence of k_2 on $[NO_3^-]$ for the redox reaction of CV^+ and $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6x10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 4.0x10^{-3}$ mol dm^{-3}, $[H^+] = 1.0x10^{-2}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max} = 580$ nm, $T = 25 \pm 1.0^oC$
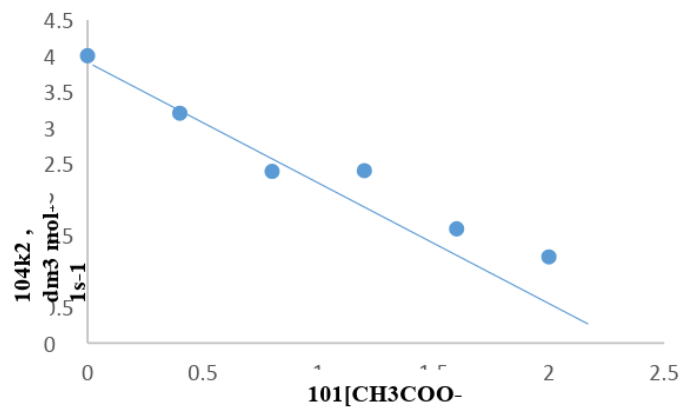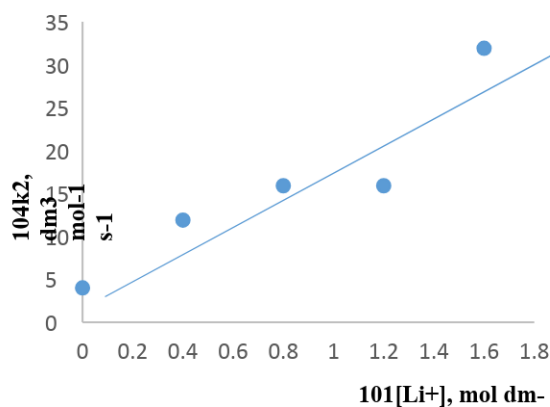
Figure 5: Plot of dependence of k_2 on $[CH_3COO^-]$ for the redox reaction of CV^+ and $[Co(NO_2)_6^{3-}]$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max} = 580$ nm, $T = 25 \pm 1.0^oC$
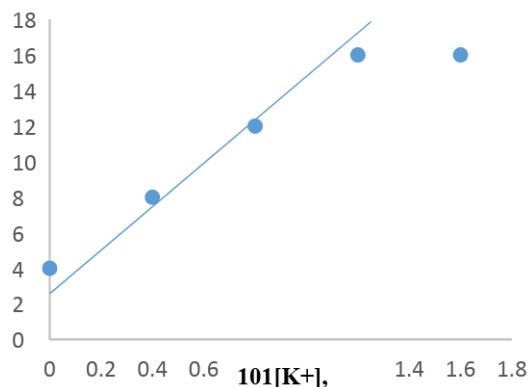

Figure 6: Plot of dependence of k_2 on $[Li^+]$ for the redox reaction of CV^+ and $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{2-}] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max} = 580$ nm, $T = 25 \pm 1.0^oC$

Figure 7: Plot of dependence of k_2 on $[K^+]$ for the redox reaction of CV^+ and $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 2.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max} = 580$ nm, $T = 25 \pm 1.0^oC$

Dielectric Constant Effect

The effect on change in medium dielectric constant was carried out using a binary solvent (acetone and water) in the range of 1 - 30% at concentration for $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, and any other condition kept constant. The effect

of dielectric constant D was found to increase the rates constant of reactions with decrease in dielectric constant (Table 3). The relationship between rate constant k_2 against $1/D$ are presented in Figure 8, and the mathematical method for calculation of dielectric constant [4] and [5].

Table 3: Effect of changes in dielectric constant for the reaction of CV^+ by $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 4.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-3}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max} = 580$ nm, T = $26 \pm 1°C$

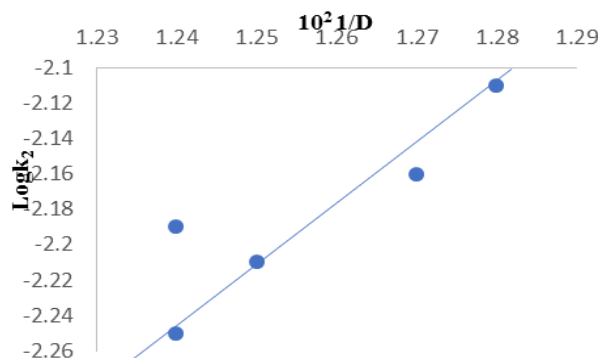| D	$10^2 1/D$	$10^3 k_1 (s^{-1})$	$10^3 k_2$
80.3	1.24	5.07	08.8
79.6	1.25	5.53	09.6
79.2	1.26	5.76	10.0
78.5	1.27	6.22	10.8
77.7	1.28	6.91	11.9

Figure 8: Plot of log k_2 versus $1/D$ for the reduction reaction of CV^+ by $Co(NO_2)_6)^{3-}$ at $[CV^+] = 1.6 \times 10^{-5}$ mol dm^{-3}, $[Co(NO_2)_6)^{3-}] = 1.92 \times 10^{-2}$ mol dm^{-3}, $[H^+]=1.0 \times 10^{-2}$ mol dm^{-3}, $\mu = 1.0$ mol dm^{-3} (NaCl), $\lambda_{max}= 580$ nm, T= 27±1°C

Test for Intermediate Complex Formation
Spectroscopic Test
The results spectroscopic test were obtained after passing the mixture of the reactants over the wave length range of 400 – 700 nm. The electronic spectra of the reaction which was obtained were compared with the spectra of the dye alone within the same range. The results of the spectroscopic studies indicated a bathochromic shift in the λ_{max} from 580 nm to 590 nm respectively (Figure 9). This is a suggestion that intermediate complex may be formed prior to electron transfer.
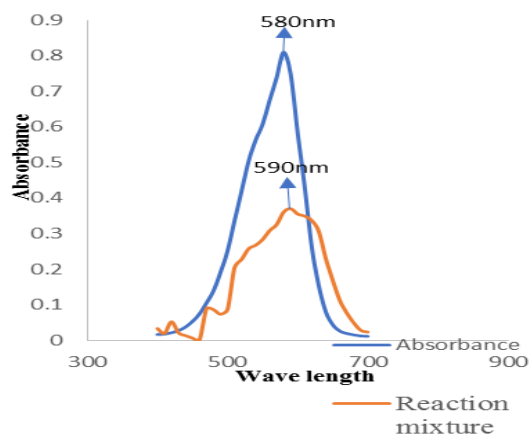

Figure 9: Spectra of the reaction mixture of CV^+ and $Co(NO_2)_6)^{3-}$ after two minutes of reaction Kinetic Test (Michaelis-Mentens Plot)

The result of the Michaelis-Mentens test was obtained by plotting $1/k_1$ against $1/[Reductant]$. The Michaelis-Mentens plot for $1/k_1$ against $1/[Co(NO_2)_6]^{3-}$ show a significant intercept.

Test for Free Radicals

Acrylamide solution was added to the partially oxidized reaction mixture of CV^+ and $Co(NO_2)_6^{3-}$ ions in large excess of methanol. The mixture shows no formation of gel or precipitate, which indicate the absence of free radical formation.

Product Analysis

Product analysis was carried out using qualitative analysis and Fourier Transformation Infrared (FTIR) test.

Qualitative Analysis

Co^{2+} was qualitative tested by adding a few drops of ammonium chloride solution to the product, followed by the addition of 2 cm^3 of ammonia solution, H_2S gas was pass in to solution. Black precipitate was obtained when H_2S gas was passed in to the product. This is an indication for presence of Co^{2+}.

Black precipitate remains after the addition of 2 cm^3 of dilute HCl and warming, further confirmed the presence of Co^{2+} as part of the product formed.

The FTIR spectra of crystal violet and cobaltinitrite before the reaction, were compared with the one after the reaction for possible shift in stretching/vibrational frequencies (Figure 10 and 11).
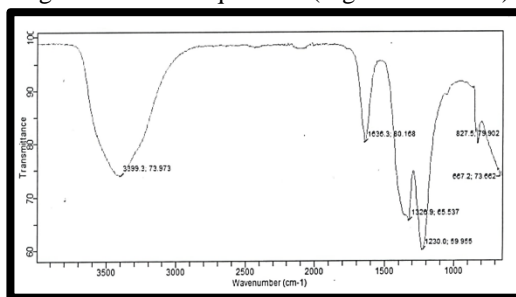

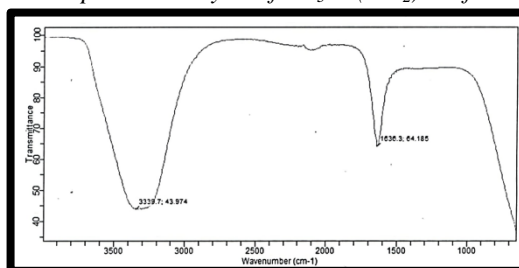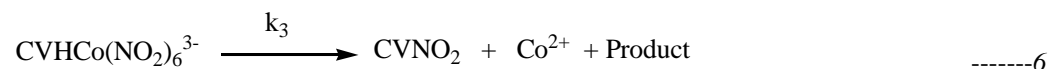*Figure 10: FTIR spectral analysis of $Na_3Co(NO_2)6$ before the reaction*

Figure 11: Typical infrared spectral analysis of the   reaction product of $CV^+ Co(NO_2)_6)^{3-}$

Mechanism of the Reaction

The following plausible mechanisms were proposed from the data obtained and experimental results coupling with steps from literature

$$CV^+ + H^+ \overset{k_1}{\rightleftharpoons} CVH^{2+} \qquad\qquad \text{-------}4$$

$$CVH^{2+} \overset{k_2}{\longrightarrow} CVHCo(NO_2)_6^{3-} \qquad\qquad \text{-------}5$$

$$CVHCo(NO_2)_6{}^{3-} \xrightarrow{k_3} CVNO_2 + Co^{2+} + Product \qquad \text{------6}$$

From equation 5

Rate = $k_3[CVHCo(NO_2)_6^-]$ ------7

$[CVHCo(NO_2)_6^-] = [Co(NO_2)_6{}^{3-}]\,[CVH^{2+}]$ ------ 8

Substituting equation 8 in to equation 7

Rate = $k_3\,k_2[Co(NO_2)_6{}^{3-}][CVH^{2+}]$ ------ 9

Recall from equation 2

$CV^{2+} = CV^+ + H$ ------ 10

Substituting equation 9 in to equation 8 and rearranged

Rate = $k_2[CV^+][H^+]$ ------ 11

From the results gathered for all the perimeters and mechanism of the reactions, the following conclusion were drawn:

(a) Result from stoichiometry studies was 1:1.
(b) the reaction was catalyze with increase in hydrogen ion concentration.
(c) neutral effect of ionic strength on rate constants suggest that one of the species reacting on the activated
(d) complex is neutral
(e) qualitative analysis carried out on the product formed confirmed the presence of Co^{2+}
(f) spectroscopic test and Michaelis-Mentens plot gave the evidence intermediate complex formation.

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