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Redox Reaction Between Synthesized Amino Heterocyclic Azo Dye and Heptaoxodichromate(VI) Ion in Aqueous Acidic Medium

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Abstract: *The kinetics and mechanism of the redox reaction between a synthesized amino heterocyclic azo dye (DYE) and heptaoxodichromate(VI) ion were investigated spectrophotometrically in aqueous hydrochloric acid medium at 30 ± 1 °C and ionic strength of 0.50 mol dm⁻³ (NaCl). The stoichiometry of the reaction, determined by the mole-ratio method, revealed a 1:1 relationship between DYE and $Cr_2O_7^{2-}$. Under pseudo-first-order conditions, the reaction exhibited first-order dependence on both the dye and dichromate ion concentrations, with a slope of 1.02 obtained from the plot of log k_{obs} versus log[$Cr_2O_7^{2-}$], indicating an overall second-order reaction. The second-order rate constant (k_2) remained relatively constant within the range of 3.05–3.14 dm³ mol⁻¹ s⁻¹. The reaction rate increased with increasing hydrogen ion concentration, giving a slope of 0.8645 from the plot of log k_{obs} versus log[H^+], while the plot of k_2 versus [H^+] was linear and passed through the origin, suggesting proton involvement in the rate-determining pathway. Increasing ionic strength from 0.1 to 1.3 mol dm⁻³ resulted in a decrease in reaction rate, and the plot of log k_2 versus $\sqrt{I}$ yielded a negative slope of –2.7464, indicating a negative salt effect and interaction of oppositely charged species in the activated complex. The reaction rate was unaffected by Ca^{2+} and Mg^{2+} ions but was inhibited by SO_4^{2-} and CO_3^{2-} ions. Spectroscopic scans showed no detectable intermediate species, while the Lineweaver–Burk plot passed through the origin, indicating the absence of a kinetically significant intermediate complex. Furthermore, acrylamide polymerization tests revealed no evidence of free-radical formation. The collective kinetic evidence supports an outer-sphere electron-transfer mechanism for the oxidation of the amino heterocyclic azo dye by heptaoxodichromate(VI) ion in aqueous acidic medium.*

Keywords*: Azo dye; Dichromate(VI); Kinetics; Outer-sphere mechanism; Redox reaction*

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1.0 Introduction

Azo dyes constitute one of the most important classes of synthetic colorants used extensively in textile, pharmaceutical, food, cosmetic, and analytical industries. Their widespread industrial applications have stimulated considerable interest in understanding their chemical reactivity, stability, degradation pathways, and redox behaviour under various environmental and laboratory conditions. Investigation of the oxidation kinetics of azo dyes provides valuable information on their reaction mechanisms and potential environmental fate.

In chemical kinetics, several techniques are employed in studying rates of reactions; some of these techniques involve the measurement of some physical property which is related to concentration. However, the property being measured must be different from reactants and products to a reasonable extent. Furthermore, the measured property should exhibit a direct and quantifiable relationship with the concentration of reactants or products. Where such a relationship is non-linear, appropriate calibration procedures must be employed to convert instrumental responses into concentration values (Atkins & de Paula, 2002). The techniques which relate the physical property to concentrations of reactants or products are: gas evolution technique, gas density technique, spectrophotometric methods colorimetry, optical rotation, galvanic cells, polarography, potentiometric method, magnetic susceptibility, refractive index, dielectric constants, viscosity, radiometric methods, thermal conductivity measurements, chromatography, tracer techniques and radiometric methods (Raj, 2012). However, spectrophotometry has been the most popular means of monitoring redox reactions. This technique applies Beer-Lambert's Law in its operations as long as the incident light is monochromatic in nature. In a spectrophotometric kinetic study it is possible to follow the course of the kinetic rate calculation at a particular wavelength as a function of time. Several authors have made use of the spectrophotometric technique in studying and analyzing redox reactions few of such reactions are: Redox dynamics of neutral red with bromate ion and nitrite ion in an acidic aqueous medium (Ibrahim & Hamza 2016; Ibrahim *et al.,* 2016), redox reaction of tetrakis (2, 2′- Bipyridine)-μ- oxodiiron(III) complex with thiourea and glutathione in aqueous acidic medium (Anweting *et al.,* 2017, 2021) and redox reactions of permanganate ion with theophylline and caffeine (Jones *et al.,* 2023a; Anweting *et al.,* 2023).

The popularity of spectrophotometric methods arises from their sensitivity, simplicity, rapidity, and ability to continuously monitor concentration changes without disturbing the reaction system. Consequently, they have become indispensable tools in mechanistic investigations of electron-transfer reactions.

Heptaoxodichromate (V1) is an oxyanion of chromium in the +6 oxidation state and it is a strong oxidant in organic, analytical and inorganic chemistry. Beyond its industrial applications, dichromate ion has attracted significant attention in kinetic and mechanistic studies because of its well-defined redox properties and its ability to oxidize a broad spectrum of organic and inorganic substrates. Studies on dichromate oxidation reactions have contributed substantially to the understanding of electron-transfer processes in solution chemistry.Dichromate ions are used for the inhibition of metallic corrosion in chrome plating for the protection of metal surfaces and enhancement of paint adhesion. The oxidizing potential of dichromate ion has been observed

in the oxidation of propane-1, 2, 3-triol, 2-methyl pentane-2,4-diol, napthol green, isoamyl alcohol, benzaldehyde and iodide ion (Idris *et al.,* 2005a, b; Myek *et al.,* 2014; Vellaisamy and Bhuvaneswari, 2015; Atolaiye *et al*., 2019; Nyong *et al.,* 2020). Previous investigations have demonstrated that reaction rates and mechanistic pathways of chromium(VI) oxidants are strongly influenced by substrate structure, medium acidity, ionic strength, and the presence of catalytic species. Depending on the nature of the reductant, both inner-sphere and outer-sphere electron-transfer pathways have been reported. These observations underscore the necessity of investigating each substrate system individually to establish its kinetic characteristics and mechanistic behaviour.

Although extensive kinetic investigations have been reported for the oxidation of various organic substrates by dichromate ion, little information is available regarding its reaction with amino heterocyclic azo dyes. Consequently, the kinetic behaviour, reaction orders, mechanistic pathway, and influence of reaction variables on the oxidation of such dyes remain largely unexplored.

The molecular structure of the synthesized amino heterocyclic azo dye employed in this investigation is presented in Fig. 1. Therefore, the aim of this study was to investigate the kinetics and mechanism of the redox reaction between a synthesized amino heterocyclic azo dye and heptaoxodichromate(VI) ion in aqueous acidic medium using spectrophotometric techniques. Particular attention was devoted to determining the stoichiometry, reaction orders, effects of acidity and ionic strength, and the probable electron-transfer mechanism. The findings of this study are expected to contribute to the fundamental understanding of electron-transfer reactions involving chromium(VI) oxidants and azo compounds. Furthermore, the mechanistic information generated may provide useful insights into the degradation, treatment, and environmental transformation of azo dye-containing wastes, thereby supporting future applications in environmental and industrial chemistry.

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2.0 Materials and Methods

2.1 Reagents and Instrumentation

All chemicals used in this study were of analytical reagent grade and were used without further purification. Distilled water was employed throughout the experiments. Absorbance measurements were obtained using a UV–Visible spectrophotometer equipped with 1 cm quartz cells. Temperature was maintained at 30.0 ± 1.0 °C using a thermostatically controlled water bath.

All chemicals used were analytical grade and required no further purification. Distilled water was used to prepare the solution. Absorbance of solutions was derived using a photoelectric spectrometer SM202 digital LED. Standard aqueous solution of the synthesized dye and hydrochloric acid, stock solutions of salts used in this research were prepared as recorded elsewhere (Adetoro *et al.,* 2024).

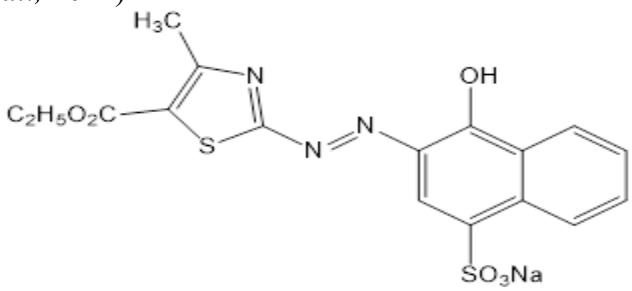

Fig. 1: Synthesized Amino Heterocyclic Azo Dye

2.1 Methods

2.1.1 Stoichiometric coefficient determination

"The stoichiometry of the reaction was determined spectrophotometrically using the mole-ratio method. (Anweting *et al.,* 2021; Jones *et al.,* 2023a; Adetoro *et al.,* 2024). The

the dye was concentration of were held constant at 1.0×10^{-4} mol dm $^{-3}$ while $Cr_2O_7^{2-}$ was adjusted between $(2.0 – 20.0) \times 10^{-5}$ mol dm $^{-3}$ at $[H^+] = 1.0 \times 10^{-3}$ mol dm $^{-3}$, I = 0.5 mol dm $^{-3}$(NaCl) and T = 30.0 ±1.0ºC. The reactions were allowed to run to 100% yield, and the absorbances of the reaction mixtures were recorded at completion (A_∞) using 530 nm on a photoelectric spectrometer. Absorbance readings were recorded and plotted as a function of reactant mole ratios.The stoichiometric ratio was obtained from the point of intersection of the two linear portions of the absorbance–mole ratio plot.

2.1.2 Kinetic measurements

The progression of the reaction was monitored by recording the sequential increase in the absorbance of the dye at 530 nm using a photoelectric spectrometer. All kinetic measurements were performed under pseudo-first-order conditions, with dichromate ion present in at least a 60-fold excess over dye. The kinetic plots obtained under this condition were exponential, and the rate constant was obtained from the logarithmic plot of $\ln(A_\infty - A_t)$ against time (t). Pseudo first-order rate constants were calculated from the slope of the plot, using equation 1:

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

where A_∞ = final absorbance, A_t = absorbance at time t, A_0 = Initial absorbance and k_{obs} = pseudo-first order rate constant as reported by (Anweting *et al.,* 2017, 2021). The second order rate constant (k_2) was evaluated as $k_{obs}/[Cr_2O_7^{2-}]$ at I = 0.50 mol/dm^3 (NaCl), $[Cr_2O_7^{2-}] = (6.0 – 18) \times 10^{-3}$ mol/dm^3, , λ_{max} = 530 nm, $[H^+] = 1 \times 10^{-3}$ mol/dm^3 and [DYE] = 1×10^{-4} mol/dm^3.

2.1.3 Proton concentration effects and ionic strength modulation

The effect of changes in the proton dependency profile on the reaction rate was determined by holding other reactant concentrations constant while varying the concentration of protons in the range $(2 – 14) \times 10^{-4}$ mol dm^{-3}. The effect of ionic strength was investigated over the range 0.1–1.3 mol dm−3 using sodium chloride as the inert electrolyte. (Anweting *et al.,* 2012a, b, c & d).

2.1.4 Impact of supplementary ions

The effects of Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-} ions on the reaction rate were investigated by varying their concentrations while maintaining constant concentrations of DYE, dichromate ion, hydrogen ion and ionic strength. The effects of Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-} ions on the reaction rate were investigated by varying their concentrations while maintaining constant concentrations of DYE, dichromate ion, hydrogen ion and ionic strength. mpact of supplementary added ions Ca^{2+}, Mg^{2+}, SO_4^{2-} and CO_3^{2-} was evaluated by systematically altering the concentration of cations and anions while keeping $[Cr_2O_7^{2-}]$, [Dye] ionic strength and concentration of hydrogen ion constant T = 30.0 ±1.0ºC and λ_{max} = 530nm (Osunlaja, *et al.,* 2012; Osunlaja, 2014; Myek *et al.,* 2024).

2.1.5 Spectroscopic and kinetic analysis of Intermediate complex formation

Screening for reaction intermediates was carried out spectroscopically by using the absorption spectrum of the reacting solutions obtained 180 s subsequent to the initiation of the reaction the DYE within the wavelength of 400 – 700 nm. Lineweaver-Burk plot of $1/k_{obs}$ versus $1/[Cr_2O_7^{2-}]$ was used for the kinetic test to probe intermediate during the reaction (Anweting *et al.*, 2012a & b; Imam *et al.,* 2018).

2.1.6 Investigation of transient free radicals

Investigation of free radicals was undertaken by adding 2 ml of acrylamide solution to a partially reacted reaction matrix comprising a variety of $[Cr_2O_7^{2-}]$, [Dye], and $[H^+]$. The reaction mixtures were treated with a large excess of methanol. Control experiment was

conducted via the addition of acrylamide to solutions of $Cr_2O_7^{2-}$ and DYE separately under the identical conditions of $[H^+]$, I and temperature. Any observed polymerization indicated by gelation implied that free radicals were present in the reaction mixture (Hamza *et al.,* 2012; Myek *et al.,* 2020).

3.0 Results and Discussion

3.1 Stoichiometry

Stoichiometry's result illustrated that one mole of $Cr_2O_7^{2-}$ was reduced by a mole of dye during the reaction, according to equation 2,

$$Dye + Cr_2O_7^{2-} \rightarrow Product \quad (2)$$

The first-order dependence on both reactants suggests that one molecule of dye and one molecule of dichromate participate in the rate-determining step.

Several reactions of some oxyanions and dyes have been reported to exhibit the stoichiometry of 1:1, these include: the reduction of permanganate ion with malachite green (Mohammed *et al.,* 2009), oxidation of pyrocatechol violet by iodate ion (Adetoro *et al.,* 2011), redox reaction of naphthol green and dichromate ion (Myek *et al.,* 2014), oxidation of neutral red by nitrite and bromate ions (Ibrahim *et al.,* 2016; Ibrahim and Hamza, 2016). The observed second-order overall rate law indicates a bimolecular electron-transfer process. Similar behaviour has been reported for several chromium(VI)-mediated oxidations where substrate oxidation occurs through direct interaction between the oxidant and reductant in the rate-determining step.

Similar stoichiometric coefficients result was also reported by Imam *et al.* (2018) in iodate-mediated oxidation of malachite green and Adetoro *et al.* (2024) in redox reaction of azo heterocyclic dye with iodate ion. Nevertheless, 3 moles of toluidine blue were consumed by 1 mole of nitrite ion in the redox reaction between toluidine blue and nitrite ion (Hamza *et al.,* 2012). In the redox reaction between orange II and thiosulphate ion, the reaction demonstrated a stoichiometry of 1:4 (orange II to thiosulphate ion).

3.2 Kinetic investigation

The plot of log $(A_t - A_\infty)$ versus time exhibited linearity up to approximate 80% reaction completion, suggesting that the reaction is first order with respect to [Dye]. The pseudo-first-order rate constants were obtained at different initial concentrations of $Cr_2O_7^{2-}$. The slope of the graph obtained by plotting log k_{obs} against log $[Cr_2O_7^{2-}]$ at $[H^+] = 1 \times 10^{-3}$ mol dm^{-3}, I = 0.5 mol dm^{-3} was 1.02 (Fig. 2) indicating first order in $[Cr_2O_7^{2-}]$. Relative consistency in the values of k_2 (Table 1) when each value of k_{obs} was divided by $[Cr_2O_7^{2-}]$ further affirmed the unity order of $[Cr_2O_7^{2-}]$, the reaction was second order overall, which fitted equation 3,

$$-\frac{d[dye]}{dt} = k_2[DYE][Cr_2O_7^{2-}] \quad (3)$$

Several authors have reported similar kinetic order in the following reactions: reduction of dichromate ion by benzaldehyde (Atolaiye *et al.,* 2019), redox reaction of orange II and thiosulphate ion (Myek *et al.,* 2020), reduction of permanganate ion by theophylline (Anweting *et al,* 2023), reduction of permanganate ion by theobromine (Jones *et al.,* 2023b) and redox reaction of iodate ion and azo heterocyclic dye (Adetoro *et al.,* 2024).

3.3 Proton concentration effects and ionic strength modulation

The rate of reaction was directly proportional to the fluctuation in hydrogen ion across the range of concentration studied as observed from the Plot of log k_{obs} versus log $[H^+]$ which gave a straight line graph with the slope of 0.8645 (Fig. 3) at $[H^+] = (2 – 14) \times 10^{-4}$ mol dm^{-3}, I = 0.5 mol dm^{-3} (NaCl), [DYE] = 1.0 x 10^{-4}mol dm^{-3}, $[Cr_2O_7^{2-}] = 1.2 \times 10^{-2}$mol dm^{-3}, λ_{max} = 530nm and T = 30 ± 1°C. Analysis of the graph of k_2 versus $[H^+]$ gave a linear plot

without any intercept (Fig. 4), and the relationship between k_2 and $[H^+]$ is given in equation 4

$$k_2 = a[H^+] \quad (4)$$

The positive dependence on hydrogen ion concentration indicates that protonation enhances the reactivity of one or both reacting species before electron transfer occurs. The absence of a significant intercept suggests that the proton-assisted pathway predominates throughout the investigated acidity range.

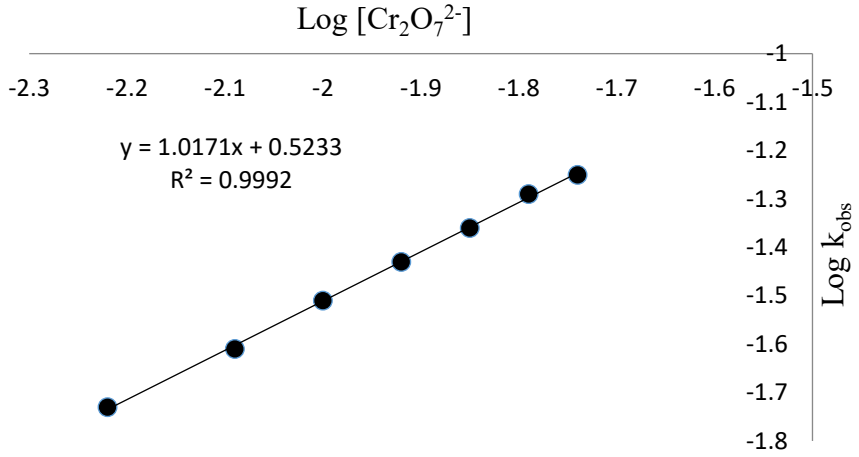

Fig. 2 : Variation of log k_{obs} as a function of log $[Cr_2O_7^{2-}]$

The result corresponds to the findings of Idris *et al.* (2005a & b) in the reduction of dichromate ion by butan-1,3-diol and 2-methyl pentane-2,4-diol in acidic medium, Edokpayi *et al.* (2010) in redox reaction between heptaoxodichromate(V1) ion and disodium 3,3-dioxobi-indolin-2,2'-ylidene-5,5-disulphonate and Anweting *et al.* (2012b) in the oxidation of L-cysteic acid by permanganate ion in acidic medium. There was an observable retardation of the kinetic rate when the system's ionic strength was varied from 0.1 to 1.3 mol dm^{-3}. The plot of $logk_2$ against $\sqrt{I}$ was linear (Fig. 5) with a negative slope of -2.7464, which suggests a negative salt effect, thus implicating the interaction of unlike charges at the activated complex. Comparable findings have been reported in redox reactions between monomethyl fuschin and dithionite ion in aqueous acidic media (Onu & Iyun, 2000), reduction of dichromate ion by 2-methyl pentane-2,4-diol in aqueous acidic media (Idris *et al.,* 2005b), oxidation of nicotinic acid and L-cysteic acid by permanganate ion in aqueous acidic media (Anweting *et al.,* 2012a & b), redox reaction between neutral red and nitrite ion in aqueous acidic media (Ibrahim *et al.,* 2016).

3.4 Influence of added ions

The kinetics rate was relatively constant when cations (Ca^{2+} and Mg^{2+}) were added but there was a retardation of the rate of reaction on addition of anions (SO_4^{2-} and CO_3^{2-}) (Table 2). Inhibition of rate is in accordance with outer sphere pathway (Myek *et al.,* 2020; Adetoro *et al.,* 2024).

The absence of cation catalysis and the inhibitory influence of anions suggest that electron transfer occurs without prior ligand substitution or bridge formation. The added anions likely stabilize the reactants through electrostatic interactions, thereby reducing reaction rates.

3.5 Spectroscopic and kinetic analysis of Intermediate complex formation

There was no bathochromic and hypsochromic shift when the partially reacted reaction mixture was scanned from 400-

800nm, suggesting that there was no spectroscopically detectable intermediate in the course of reaction, thus the coordination integrity of the coordination sphere of the reacting species was not distorted, consequently the reaction followed outer-sphere pathway. Kinetically, the Lineweaver-Burk plot of $1/k_{obs}$ versus $1/[Cr_2O_7^{2-}]$ (Fig. 6) gave a straight line graph that passed through the origin without any intercept to confirm further the absence of intermediate in the course of the reaction.

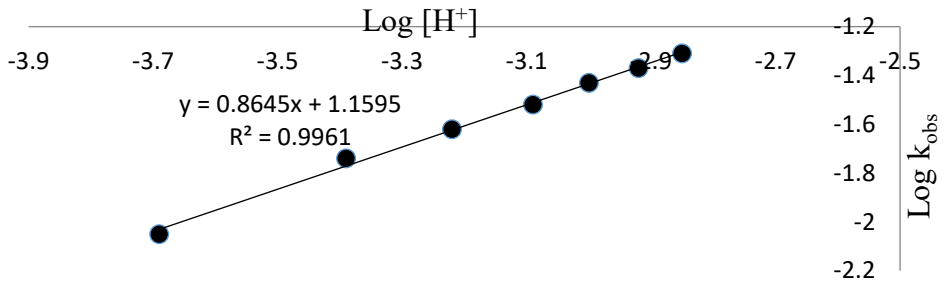

Fig. 3 : Variation of log k_{obs} as a function of log $[H^+]$

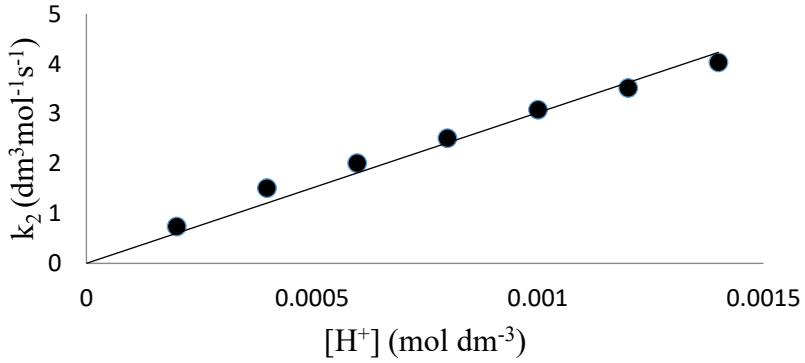

Fig. 4: Variation of k_2 ($dm^3mol^{-2}s^{-1}$) as a function of $[H^+]$

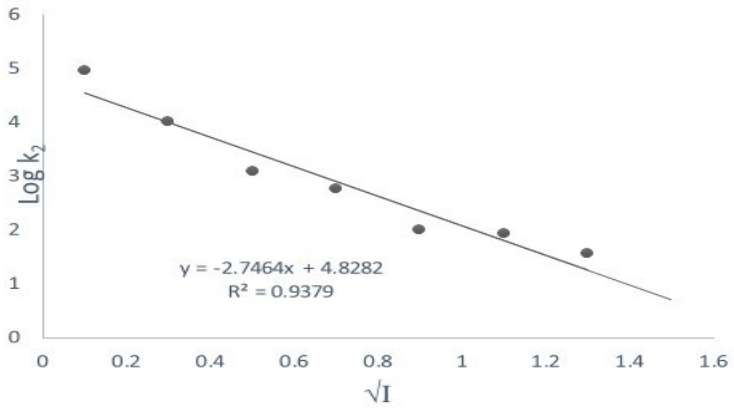

Fig. 5 : Variation of logk_2 as a function of √I

Table 1: Pseudo-first order and the corresponding second order rate constant for the oxidation – reduction reaction of DYE by $Cr_2O_7^{2-}$ in aqueous HCl medium, λ_{max}= 530nm, T = 30 ± 1°C, I = 0.50 mol dm-3 (NaCl), [DYE] = 1.0 x 10^{-4}mol dm^{-3}

$10^2[Cr_2O_7^{2-}]$ (mol/dm^3)	$10^3[H^+]$ (mol/dm^3)	$10[I^-]$ (mol/dm^3)	10^3 k_{obs} (/s)	k_2 (dm^3/mol/s)
0.6	1.0	5.0	18.66	3.11
0.8	1.0	5.0	24.40	3.05
1.0	1.0	5.0	31.00	3.10
1.2	1.0	5.0	36.96	3.08
1.4	1.0	5.0	43.40	3.10
1.6	1.0	5.0	50.24	3.14
1.8	1.0	5.0	54.90	3.05
1.2	0.2	5.0	8.88	0.74
1.2	0.4	5.0	18.12	1.51
1.2	0.6	5.0	24.12	2.01
1.2	0.8	5.0	30.12	2.51
1.2	1.0	5.0	36.96	3.08
1.2	1.2	5.0	42.24	3.52
1.2	1.4	5.0	48.36	4.03
1.2	1.0	1.0	59.52	4.96
1.2	1.0	3.0	48.12	4.01
1.2	1.0	5.0	36.96	3.08
1.2	1.0	7.0	33.24	2.77
1.2	1.0	9.0	24.12	2.01
1.2	1.0	1.1	23.28	1.94
1.2	1.0	1.3	18.84	1.57

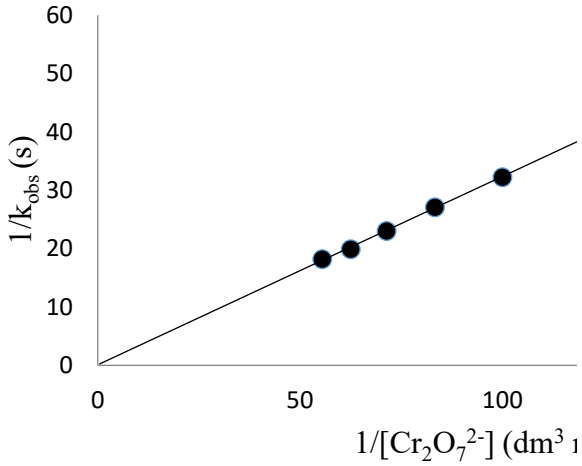

Fig. 6: Lineweaver-Burk variation of $1/k_{obs}$ as a function of $1/[Cr_2O_7^{2-}]$

Table 2: Cations and Anions Species for the synthesized Amino-heterocyclic dye [DYE]-$Cr_2O_7^{2-}$ system at I = 0.5mol dm^{-3} (NaCl), T = 30 ± 1°C, $[Cr_2O_7^{2-}]$ = 1.2 x 10^{-2}mol dm^{-3}, [DYE] = 1.0 x 10^{-4}mol dm^{-3}, λ_{max} = 530nm, $[H^+]$ = 1.0 x 10^{-3}mol dm^{-3}

$10^3[Ca^{2+}]$ (mol/dm^3)	10^3k_{obs} (/s)	k_2 (dm^3/mol/s)
00.0	36.96	3.08
30.0	36.72	3.06
50.0	36.96	3.08
70.0	36.48	3.04
90.0	36.84	3.07
120.0	36.60	3.05
150.0	36.36	3.03

$10^3[Mg^{2+}]$ (mol/dm^3)		
	36.96	3.08
00.0	36.84	3.07
30.0	36.24	3.02
50.0	36.48	3.04
70.0	36.60	3.05
90.0	36.24	3.02
120.0	36.36	3.03
150.0		
$10^3[SO_4^{2-}]$ (mol/dm^3)	36.96	3.08
	35.16	2.93
00.0	30.60	2.55
30.0	27.72	2.31
50.0	24.84	2.07
70.0	23.28	1.94
90.0	21.96	1.83
120.0		
150.0		
	36.96	3.08
$10^3[CO_3^{2-}]$ (mol/dm^3)	34.68	2.89
	30.12	2.51
00.0	25.56	2.13
30.0	21.00	1.75
50.0	16.56	1.38
70.0	12.48	1.04
90.0		
120.0		
150.0		

The absence of a positive intercept suggests that no kinetically significant precursor complex accumulated during the reaction.

3.6 Investigation for transient free radicals in the course of reaction

There was no gel formation when acrylamide was added to the individual reactants separately and the reaction mixture, which was subsequently treated with an excess of methanol, suggesting that the absence of free radicals during the reactions. The absence of acrylamide polymerization suggests that free radical intermediates were either absent or too short-lived to initiate polymerization under the experimental conditions.

3.7 Reaction mechanism

Plausible mechanism from the experimental result obtained from this research is proposed according to the following equations:

$$DYE + H^+ \underset{}{\overset{K}{\rightleftharpoons}} DYEH^+ \quad \textbf{(5)}$$

$$Cr_2O_7^{2-} + DYEH^+ \xrightarrow{k_6} \text{Products} \quad \textbf{(6)}$$

$$Rate = k_6[DYEH^+][[Cr_2O_7^{2-}] \quad (7)$$

The substitution of [DYEH$^+$] in (7) leads to equation 8

$$Rate = [Kk_6][DYE][Cr_2O_7^{2-}] \quad (8)$$

where Kk_6 in equation 8 is equal to k. Therefore, the rate of the reaction can also be written as $k[DYE][Cr_2O_7^{2-}]$

4.0 Conclusion

The kinetics and mechanism of the redox reaction between a synthesized amino heterocyclic azo dye and heptaoxodichromate (VI) ion have been successfully investigated in aqueous acidic medium using spectrophotometric techniques. The reaction exhibited a stoichiometric ratio of 1:1 (DYE:$Cr_2O_7^{2-}$) and was found to be first order with respect to both the dye and dichromate ion concentrations, resulting in an overall second-order rate law. The second-order rate constant remained relatively constant within the range of 3.05–3.14 dm^3 mol^{-1} s^{-1}, confirming the validity of the proposed kinetic model.

The reaction rate increased with increasing hydrogen ion concentration, indicating proton involvement in the oxidation process, while a negative salt effect was observed with increasing ionic strength, suggesting interaction between oppositely charged species in the activated complex. The reaction was unaffected by Ca^{2+} and Mg^{2+} ions but was

inhibited by SO_4^{2-} and CO_3^{2-} ions. Spectroscopic investigations revealed no detectable intermediate species, and the absence of an intercept in the Lineweaver–Burk plot further indicated that no kinetically significant intermediate complex was formed during the reaction. In addition, acrylamide polymerization tests showed no evidence of free-radical intermediates.

Collectively, the kinetic and spectroscopic evidence supports an outer-sphere electron-transfer mechanism involving a protonated form of the dye as the reactive species. The study contributes to the understanding of chromium(VI)-mediated oxidation processes and provides valuable mechanistic information on the redox behaviour of amino heterocyclic azo dyes in acidic aqueous media.

5.0 References

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Authors' Contributions

Ahmed Adetoro designed the research and carried out all the experiments in the research. Idongesit Bassey Anweting and Myek Bako compiled the manuscript, while Aderonke Ajibola Oloidi and Asiwe Thomas Ndidi read and revised the manuscript.