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Spectrophotometric Investigation of the Redox Reaction of Acid Green 1 with Periodate Ion in Aqueous Acid: Kinetics and Mechanistic Approach

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Abstract: *The redox reaction of acid green 1 (AG^{3-}) by periodate ion has been studied in aqueous acid at an ionic strength of $I = 0.50$ mol dm^{-3} (NaCl), $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, $T = 25 \pm 1^oC$ and $\lambda = 700$ nm. The redox reaction displayed a stoichiometry of 2:1. The reaction showed a first-order dependence on $[IO_4^-]$ and $[AG^{3-}]$. Investigation of the effect of ionic strength on the rate of the reaction showed that the rate of the reaction obeyed the positive Bronsted - Debye salt effect. This signified that the activated complex is composed of reactants of like charges. The rate of the reaction increases with an increase in hydrogen ion concentration in the range $(0.1 – 4.0) \times 10^{-4}$mol dm^{-3} investigated. The addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. This shows that the participation of free radicals in this reaction is unlikely. Based on the results obtained, the reaction probably obeyed the outer-sphere reaction mechanism.*

Keywords: Complex; Kinetics; Reaction; Redox

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1.0 Introduction

The first generally accepted theory of electron transfer, based on the transition theory approach, was developed by Rudolph A. Marcus (Marcus, 2006) to address outer-sphere electron transfer. The theory of electron transfer was then extended to include inner-sphere electron transfer by Noel Hush and Marcus (Reimers *et al.,* 2015). The resultant theory called the Marcus-Hush theory (Reimers *et al.,* 2015), has guided most discussions on electron transfer ever since. Both theories are, however, semi-classical in nature, although they have been extended following earlier work in non-radioactive transitions (Susan *et al.,* 1978). The Marcus theory (Marcus, 2006) was initially used for the calculation of absolute rate constants for homonuclear exchange reactions. It was later extended to cross-reactions. Despite some studies on the electron transfer reaction, a detailed investigation of the redox reaction of acid green 1 with periodate ion has not received much attention. This prompted the research in this aspect, for the investigation of the kinetics of its electron transfer reaction in aqueous acid.

The use of periodate as an oxidant has been extended to organic compounds especially in the oxidation of phenols (Radhakrishnan *et al.*, 1976), Azide (Vivekanandam and Ramachhandran, 1982) and esters (Sethuram *et al.*, 1983). In the oxidation of phenols (Radhakrishnan *et al.*, 1976), it is presumed that the periodate transfers a single oxygen and IO_3^- is the stable reduction product in an acidic medium. The effect of ethylamine pre-treatment on the oxidation of cellulose by periodate has been investigated (Nevell and Shaw, 1977). In this investigation, aqueous dimethyl formamide (DMF) was used as the oxidation medium. Due to the nature of the cellulose material, the oxidation could not take place uniformly throughout the fibre, but must occur in the accessible regions and then more slowly in the rest of the material as its crystalline structure gradually breaks down. Random attack on the 1, 2-diol groups by IO_4^- occurred.Despite the applications of periodate ion, its redox reaction with AG^{3-} is scanty. Hence, the present study is aimed at investigating the redox reaction of this dye with periodate ion in aqueous acid with the view establishing its reaction pathway.

2.0 Materials and Methods

2.1 Materials

All chemicals and reagents used in this work were analar grade and were used without further purification. $NaIO_4^-$ was used as the oxidant, AG^{3-} was used as the reductant and NaCl was used to maintain a constant ionic strength of the reaction medium. The dye, oxidant and other reagents were prepared with distilled water. The λ_{max} (700 nm) used for this work was determined by running the spectrum of the dye solution using UV-Vis spectrophotometer 6405.

2.2 Methods

The reaction stoichiometry was determined spectrophotometrically using the mole ratio method (Myek *et al,* 2014). This was accomplished by measuring the absorbance of solutions containing varying concentrations of the oxidant [IO_4^-], [H^+] = 1.0×10^{-4}mol dm^{-3}($HClO_4$) and I = 0.50 $moldm^{-3}$ at $\lambda = 700$ nm until a constant absorbance was obtained. A point on the curve of the absorbance versus mole ratio plot corresponds to the stoichiometry of the reaction.

The kinetic runs were performed under pseudo-first order conditions with the concentration of periodate ion at least 80-fold greater than that of the dye at T = 25 ± 1°C and ionic strength of reaction medium, I = 0.50 mol dm^{-3} (NaCl). The reaction was monitored spectrophotometrically by measuring the absorbance at 700 nm using UV-Vis spectrophotometer 6405. The pseudo-order plots of log (A_t - A_∞) versus time were made (where A_∞ and A_t are the absorbance at the end of the reaction and at the time, t respectively).The influence of [H^+] on the rate of reaction was investigated in the range (0.1 – 4.0) $\times 10^{-4}$ mol dm^{-3}, while the [AG^{3-}] and [IO_4^-] were kept constant at 25 ± 1°C and I = 0.50 mol dm^{-3} (NaCl).

The effect of the ionic strength of the reaction medium on the rate of the reaction was studied in the range of 0.1 - 0.7 mol dm^{-3} (NaCl), while the concentration of the reactants was kept constant. The effect of added ions was studied by keeping the concentration of other reactants constant while varying the concentrations of the ions as follows: [X^-] = (10.0 – 100) $\times 10^{-3}$mol dm^{-3}, where X^- = (CH_3COO^- and SO_4^{2-}) and [X^+] = (10.0 – 100) $\times 10^{-3}$mol dm^{-3}, where X^+ = (Ca^{2+} and Mg^{2+}).

The inorganic product of the reaction involving AG^{3-} and IO_4^- was qualitatively confirmed (Myek *et al.*, 2021).

3.0 Results and Discussion

The stoichiometric study indicates that two moles of AG^{3-}consumed by amole of periodate ion as indicated in equation (1) below.

$$2AG^{3-} + IO_4^- + H^+ \rightarrow IO_3^- + other\ products \qquad (1)$$

Similar stoichiometry has been reported for the reduction of IO_4^- by indigo carmine (Edokpayi *et al.*, 2010) and azide (Vivekanandam and Ramachandran, 1982) in aqueous acid medium. Iodate ion was confirmed qualitatively as one of the reduction products of the reaction of acid green 1 with IO_4^-(Jeffery *et al.*, 1991; Myek *et al.*, 2021).This observation is in accordance with the findings of Abdel-Khalek *et al* (1989); that IO_4^- is known to be reduced to IO_3^- in most of its reactions.

Kinetic studies of the reaction of AG^{3-} and IO_4^- showed that the reaction is first order in [AG^{3-}] and [IO_4^-].A similar order was reported for the oxidation of hexcyanoferrate(III) by IO_4^- (Kasim and Sulfab, 1997). The rate of this reaction is;

$$-\frac{d[AG^{3-}]}{dt} = (a + b[H^+])[AG^{3-}][IO_4^-] \quad (2)$$

The rate of the reaction increases with an increase in $[H^+]$. A plot of logk_1 versus log$[IO_4^-]$ gave a slope of approximately one (Fig. 2), signified that the reaction is first order in both oxidant and reductant concentrations. A plot of k_2 versus $[H^+]$ was linear (Fig. 1) with a positive intercept (R^2 = 0.91). The acid dependence of this nature shows that there is a rapid pre-equilibrium between the protonated and non-protonated forms in which both the protonated and unprotonated forms are reactive (Gupta and Gupta, 1984).

The result obtained for the effect of changes in ionic strength showed that the rate of reaction increases with an increase in the ionic strength of the reaction medium. This obeys a positive Bronsted - Debye salt effect, implying that the activated complex is composed of reactants of like charges (Bensen, 1969; Birk, 1978). A slope of 0.73(Fig. 3) was obtained from the plot of logk_2 against $I^{1/2}$ (R^2 = 0.98).

The effect of added Ca^{2+} and Mg^{2+} on the reaction rate (Table 2) was unexpected as the cations were expected to increase the rate of the reaction because anions are participating in the rate determining step. The inhibitive effect exerted by the introduction of CH_3COO^- and SO_4^{2-}(Table 3) was a surprise. Probably because there was an interference caused by the electrostatic interactions between these ions in the transition state; this observation excludes the possibility of a binuclear intermediate in the activated complex (Idris *et al*., 2005).

A plot of $1/k_1$ versus $1/[IO_4^-]$ gave an intercept suggesting a detectable binuclear intermediate formation (Fig. 4). Addition of acrylonitrile to a partially reacted mixture in the presence of excess methanol did not lead to gel formation. This shows that the participation of free radicals in this reaction is unlikely. The spectrum of the reaction mixture when compared to that of dye (AG^{3-}) alone showed no shift in λ_{max} suggesting the absence of an intermediate complex during the reaction.

Table 1: Pseudo-first order and second order rate constants for the reaction of acid green 1 and IO_4^- at $[AG^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, λ = 700 nm and T = 25 ± 1°C

$10^3[IO_4^-]$, mol dm^{-3}	$10^4[H^+]$, mol dm^{-3}	10^1, I mol dm^{-3}	10^3k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
3.50	1.0	5.0	1.76	0.503
4.00	1.0	5.0	2.00	0.500
4.80	1.0	5.0	2.42	0.504
6.00	1.0	5.0	3.00	0.500
7.50	1.0	5.0	3.72	0.496
8.00	1.0	5.0	4.05	0.506
6.00	0.1	5.0	2.90	0.483
6.00	0.5	5.0	2.95	0.492
6.00	1.0	5.0	3.00	0.500
6.00	1.5	5.0	3.25	0.541
6.00	3.0	5.0	4.00	0.667
6.00	4.0	5.0	4.30	0.717
6.00	1.0	0.5	1.15	0.192
6.00	1.0	1.0	1.52	0.253
6.00	1.0	2.0	1.95	0.325
6.00	1.0	3.0	2.54	0.423

6.00	1.0	5.0	3.01	0.502
6.00	1.0	6.0	3.55	0.591
6.00	1.0	7.0	3.60	0.600

Table 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on the rate of reaction of acid green 1 with IO_4^- at $[AG^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 700 nm and T = 25 ± 1 °C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
Ca^{2+}	10.0	3.10	0.517
	40.0	2.85	0.475
	60.0	2.52	0.420
	80.0	2.40	0.400
	100.0	2.20	0.367
Mg^{2+}	10.0	2.95	0.492
	40.0	2.62	0.437
	60.0	2.31	0.385
	80.0	2.25	0.375
	100.0	2.18	0.363

Table 3: Rate data for the effect of added anions (SO_4^{2-} and CH_3COO^-) on the rate of reaction of acid green 1 with IO_4^- at $[AG^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 700 nm and T = 25 ± 1°C

Ion	10^3 [ion], mol dm^{-3}	10^3 k_1, s^{-1}	k_2, dm^3 mol^{-1} s^{-1}
SO_4^{2-}	10.0	3.12	0.520
	30.0	2.72	0.492
	60.0	2.65	0.442
	80.0	1.98	0.330
	150.0	1.55	0.258
CH_3COO^-	10.0	2.98	0.497
	30.0	2.58	0.430
	40.0	2.35	0.391
	80.0	2.88	0.288
	100.0	1.35	0.225

Based on the results obtained, the effect of added ions and lack of shift from λ_{max}, also with the absence of free radicals ruled out the possibility of the innersphere. This evidence suggests that this reaction is probably operating by the outersphere mechanism. From the results, the mechanism proposed below accommodates all the experimental findings for the reaction of AG^{3-} with IO_4^-.

$$IO_4^- + H^+ \overset{K_1}{\rightleftharpoons} HIO_4 \qquad (3)$$

$$AG^{3-} + IO_4^- \xrightarrow{k_2} AG^{2-} + IO_4^{2-} \text{ slow} \qquad (4)$$

$$AG^{3-} + HIO_4 \xrightarrow{k_3} AG^{2-} + IO_4^{2-} + H^+ \text{ slow} \qquad (5)$$

$$AG^{3-} + IO_4^{2-} \xrightarrow{k_4} IO_3^- + \text{other products} \qquad (6)$$

$$\text{Rate} = k_2[AG^{3-}][IO_4^-] + k_3[AG^{3-}][HIO_4] \qquad (7)$$

$$= k_2[AG^{3-}][IO_4^-] + k_3K_1[AG^{3-}][IO_4^-][H^+] \qquad (8)$$

$$= (k_2 + k_3K_1[H^+])[AG^{3-}][IO_4^-] \qquad (9)$$

Equation (9) is similar to equation (2) where a = k_2 and b = k_3K_1

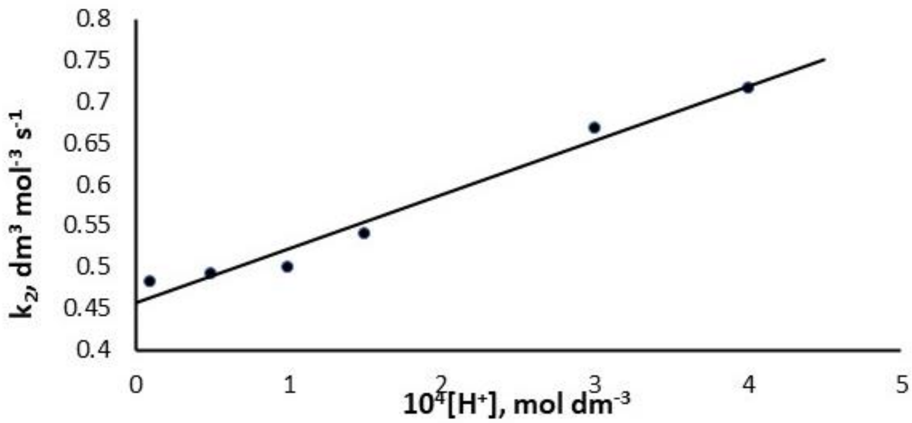

Fig. 1: Plot of k_2 versus $[H^+]$ for the redox reaction between Acid green 1 and IO_4^- at $[AG^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = 6.0 \times 10^{-3}$ mol dm^{-3}, $[H^+] = (0.1– 4.0) \times 10^{-4}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 700 nm and T = 25 ± 1°C

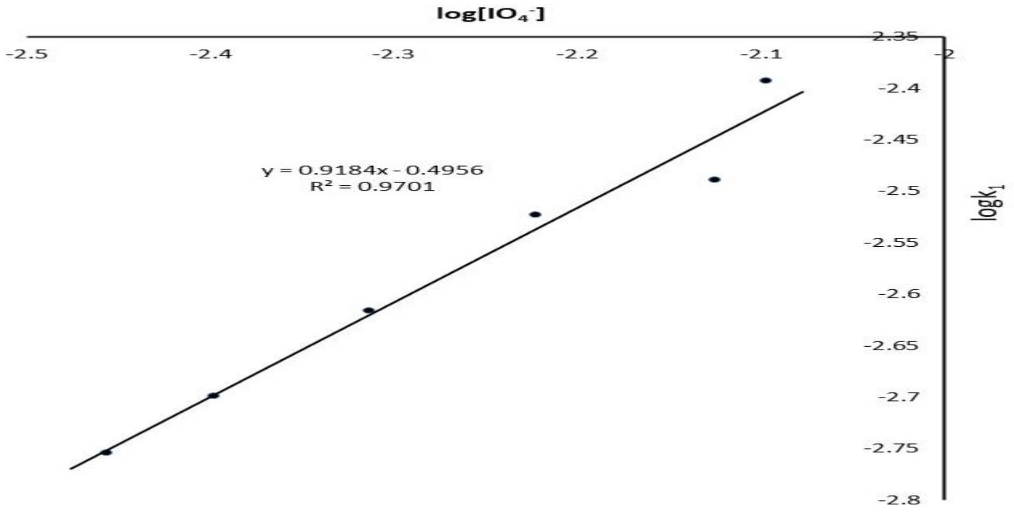

Fig. 2: Plot of log k_1 versus $\log[IO_4^-]$ for the redox reaction of acid green 1 with IO_4^- at $[AG^{3-}] = 4.0 \times 10^{-5}$ mol dm^{-3}, $[IO_4^-] = (3.5 – 8.0) \times 10^{-3}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-4}$ mol dm^{-3}, I = 0.50 mol dm^{-3}, λ = 700 nm and T = 25 ± 1 °C

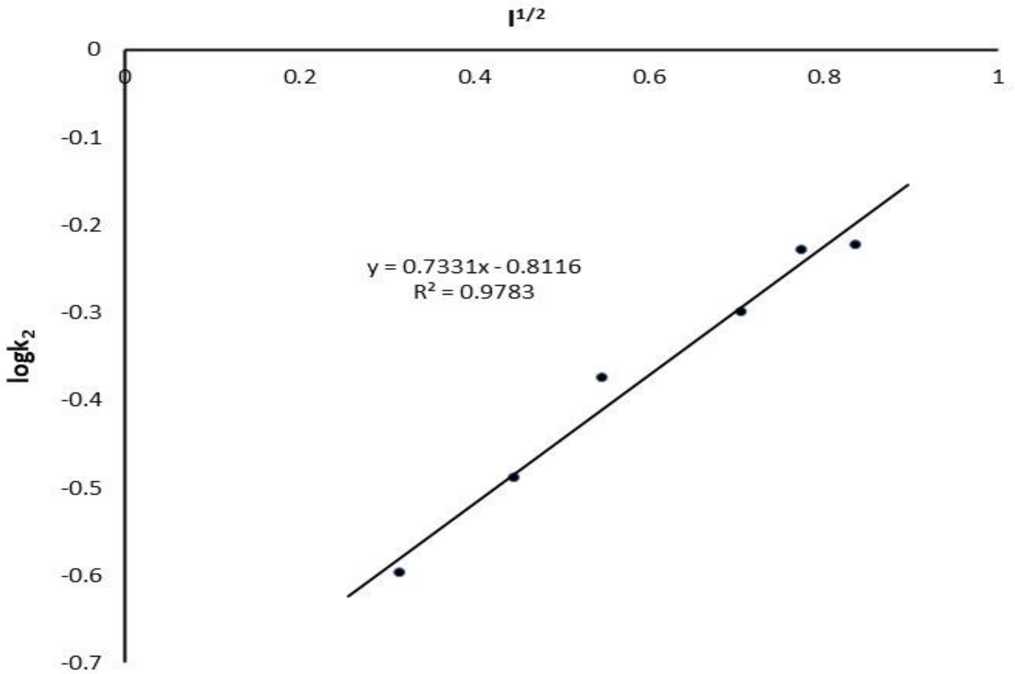

Fig. 3: Plot of logk_2 versus $I^{1/2}$ for the redox reaction between acid green 1 and IO_4^- at [AG^{3-}] = 4.0 × 10^{-5} mol dm^{-3}, [IO_4^-] = 6.0 × 10^{-3} mol dm^{-3}, [H^+] = 1.0 × 10^{-4} mol dm^{-3}, I = 0.05 – 0.7 mol dm^{-3}, λ = 700 nm and T = 25 ± 1°

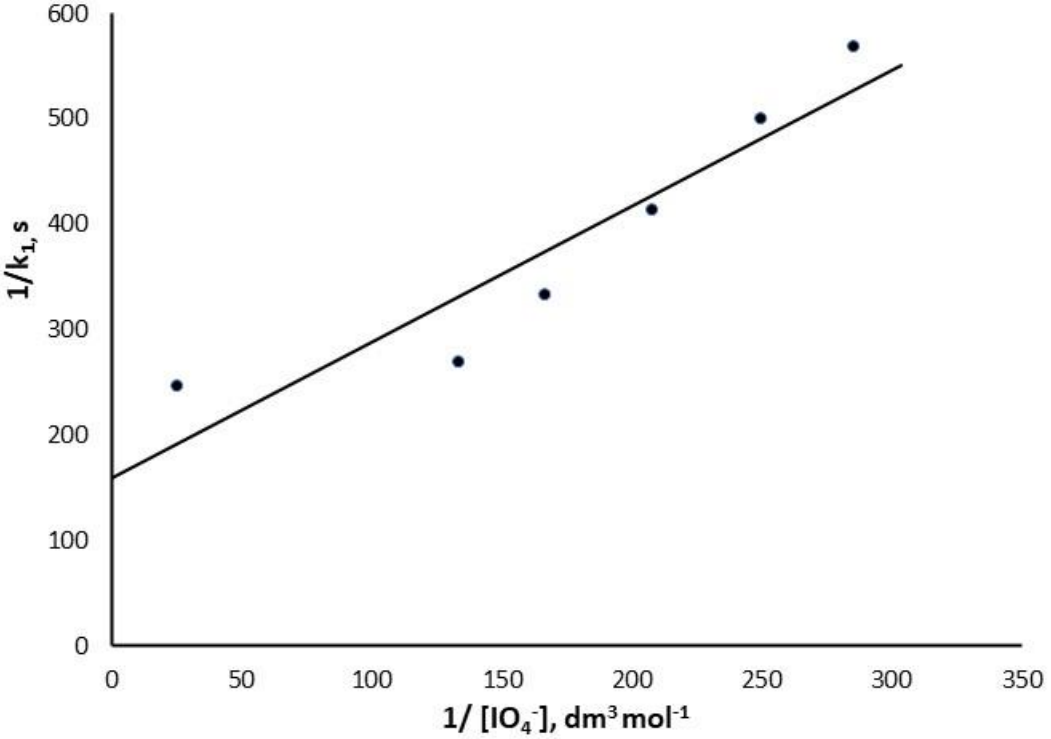

Fig. 4: Michaelis - Menten plot for the redox reaction between acid green 1 and IO_4^- at [AG^{3-}] = 4.0 × 10^{-5} mol dm^{-3}, [IO_4^-] = (3.5 – 8.0) ×10^{-3} mol dm^{-3}, [H^+] = 1.0 × 10^{-4} mol dm^{-3}, I = 0.50 mol dm $^{-3}$, λ = 700 nm and T= 25 ± 1 °C

4.0 Conclusion

The study of the redox reaction of AG^{3-} with IO_4^- in aqueous acid revealed a stoichiometry of 2:1, and first order with respect to oxidant and reductant concentrations. The rate of the reaction increases with an increase in acid concentration and ionic strength of the reaction medium. Added ions inhibited the rate of the reaction and there was no evidence of the formation of free radicals. The result from the spectroscopic study indicated no shift from the absorption maximum of 700 nm characteristic of AG^{3-}.The plot of $1/k_1$ versus $1/ [IO_4^-]$ gave an intercept suggesting a detectable binuclear intermediate formation. Based on the above results, it is proposed that the reaction is most probably operates through the outersphere mechanism.

5.0 References

Abdel-Khalek, A.A.&Elsemongy, M.M. (1989). Kinetics of the oxidation of diaqua(nitrilotracetato)-chromium(III) by periodate ion in aqueous solutions. *Trans. Met. Chem.*, 14, pp. 206-208.

Benson, D (1969). *Mechanism of Inorganic Reactions in Solution*. McGraw-Hill,UK, pp. 153-160.

Birk, J. P. (1978). Kinetics and mechanism of the reduction of bromated ion by hexachloroiridate(III). *Inorg. Chem.*, 17, pp. 504 – 506.

Edokpayi, J.N., Iyun, J.F.,& Idris, S.O. (2010). The kinetics of oxidation of disodium 3,3'-dioxobi-indoline-2, 2'-ylidene-5, 5' disulphonate by heptaoxodichtomate(VI) ion in aqueous acidic medium. *J. Appl .Sci. Res*. 2, 5, pp. 126-134.

Gupta, K.S.&Gupta, Y.K. (1984).Hydrogen ion dependence of reaction rates and mechanism.*J. Chem. Edu.*,61:972-978.

Idris, S.O., Iyun, J. F.&Agbaji, E.B. (2005).The kinetics and mechanism of reduction of propane-1,2,3-triol by Cr(VI) in aqueous perchloric acid medium. *Nig. J. Sci. Res.*, 5, 1, pp. 81-85.

Jeffery, G. H., Bassett, J., Mendham, J. &Denny, R.C. (1991). *Vogel's textbook of qualitative chemical analysis*, 5th edition, Longman, England, pp. 391.

Kasim A.Y.&Sulfab.Y. (1997). Kinetics and mechanism of oxidation of hexacynoferrate(II) periodate in acidic solution. Evidence for copper catalysis.*Inorg. Chem. Acta*, 11, pp. 169-173.

Marcus, R. A. (2006).Electron transfer reactions in chemistry.Theory and experiment.*Pure and Applied Chemistry*, 69, 1, pp. 13-29.

Myek, B., Idris, S. O.& Iyun, J. F. (2014). Kinetics and mechanism of the oxidation of naphthol Green B by peroxydisulphate ion In aqueous acidic medium. *InternationalJournal of Inorganic Chemistry*,https://doi.org/10.1155/2014/7-68575

Myek, B.,Idris, S. O., Onu, A. D., & Yakubu, M. K. (2021). Kinetics and Mechanism of the oxidation of Orange II by Periodate Ion in Aqueous Acid. *Ife Journal of Science*, , 23, 1, pp. 23-30

Nevell, T.P. &Shaw, I.S. (1973).Effect of ethylamine pretreatment on 293 – 296.the oxidation of cellulose by periodate. *Polymer*, 15, 9, pp. 553-558.

Reimers, J.R., Mckemmish, L., Mckenzir, R.H. &Hush, N.S (2015). A unified diabaticdescription for electron transfer reactions, isomerisation reactions, proton transferreactions and aromaticity, *Physical ChemistryChemical Physics*,17, 38, pp. 24598 - 24617.

Sethuram, B., Uma, V.&Rao, T.N. (1983). Kinetics of uncatalyzed and ruthenium(III) catalysed oxidation of esters by periodate ion in acid medium. *Indian J. Chem*., 22a, pp. 65-68.

Susan B. P, Elmars R. K. & Schatz P. N (1978). Vibronic coupling model for calculation of mixed valence absorption profiles;*Journal of American. Chemical Society*, 2996-3005.

Radhakrishnan, P.S., Pati, S.C.&Sriramulu, Y. (1976). Kinetics and mechanism of oxidation of phenol and substituted phenols by periodate: evidence for the participation of intermediate species. *Indian J. Chem.*,

Vivekanandam T.S. &Ramachandran M.S. (1983). Mechanism of oxidation of azide by periodate in acid medium. *Indian J. Chem.*,104-106.

Compliance with Ethical Standards

Declarations

The authors declare that they have no conflict of interest.

Data availability

All data used in this study will be readily available to the public.

Consent for publication

Not Applicable

Availability of data and materials

The publisher has the right to make the data Public.

Competing interests

The authors declared no conflict of interest.

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Authors' contributions

The entire work was carried out by the author