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KINETICS OF THE OXIDATION OF ORANGE II BY NITRITE ION IN AQUEOUS ACIDIC MEDIUM

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ABSTRACT

The kinetics of the electron transfer reaction between Orange II(here and thereafter referred to as OII^-) and nitrite ion in aqueous acidic solution has been studied spectrophotometrically ($\lambda = 484$ nm) at $T = 27 \pm 1^oC$in the acid range $1.0 \times 10^{-2} \leq [H^+] \leq 10.0 \times 10^{-2}$ mol dm^{-3}, ionic strength $0.1 \leq [I] \leq 0.7$ mol dm^{-3} (NaCl). The reaction shows a first order dependence on [oxidant] and [reductant].The rate of the reaction increases with increase in $[H^+]$. Plot of $k_2$versus $[H^+]$ was linear with an intercept. The overall reaction conforms to the rate law:

$$-d[OII^-]/dt = (a + b[H^+])[OII^-][NO_2^-]$$

The stoichiometry of the reaction is 1:2 (OII^- : NO_2^-). Added cations and anions speed up the rate of the reaction. The results of spectroscopic investigation indicate that no intermediate complex is probably formed in the course of this reaction. The reaction is believed to proceed via the outersphere mechanistic pathway.

Keywords: *Kinetics, Nitrite, Mechanism, Orange II*

INTRODUCTION

Nitrite ion is a physiologically inorganic ion which yields bioactive NO in the blood and tissues when reduced in biological systems. It is also involved in Neurotransmission, respiration and fighting of infections (Onu *et al.,* 2008). Although NO_2^- is essential in life, its over production can be deadly. Fortney has established that the toxic shocks resulting from over productionof NO_2^- during infection can cause a fatal drop in blood pressure. Redox reaction involving nitrite ions are well known. Nitrite ions have been observed to reduce riboflavin, ascorbic acid and enzymes. In the reduction of riboflavin, H_2O_2 was obtained as the product while NH_3 wasthe product for the reaction involving ascorbic acid and enzyme from cucurbita pepo (Cresswell *et al.,* 1965).

More than one million tons of dyes produced annually in the world are azo dyes. The dyes are widely used in the textile industry and are the largest and most versatile group of synthetic organic dyes, with a tremendous number of industrial applications (Ollgaard *et al.,* 1998). They are usually strongly coloured compounds which can be intensily yellow, red, orange, blue or even green, depending on the exact structure of the molecule. As a result of their colour, azo compounds have tremendous importance as dyes and also as pigments for a long time(Ebenso *et al.,* 2008). However, in spite of these and other uses, the knowledge on their redox kinetics is scanty. This study is aimed at obtaining kinetic and non-kinetic data, which will assist in the understanding of its reaction mechanism.

MATERIALS AND METHODS

The chemicals used were of analytical grade and were used without further purification. Standard solution of OII^- was prepared by dissolving accurate weight of orange II dye in a known volume of distilled water. Sodium nitrite solution was prepared by dissolving known quantities in distilled water. All other reagents used were of analytical grade.

The stoichiometry of the reaction was determined spectrophotometrically using the mole ratio method by keeping the concentration of the dye constant at 5×10^{-5} mol dm^{-3}, $[H^+]=5.0 \times 10^{-2}$ mol dm^{-3}, I = 0.5 mol dm^{-3}, λmax = 484nm, T = 27 ± 1ºC and $[NO_2^-] = (0.25 - 2.5) \times 10^{-4}$mol dm^{-3}. The stoichiometry was determined from the plot of absorbance versus [reductant]/ [oxidant] after the reaction had gone to completion by the observation of a steady zero absorbance value over a period of two days.

A UV-Vis spectrophotometer 6405 was used to follow the decrease in absorbance of the dye at 484nm. The kinetic runs were conducted under pseudo – first order conditions with $[NO_2^-]$in at least 80-fold excess over OII-. Temperature, ionic strength and hydrogen ion concentration were maintained constant as follows: T = 27± 1°C, I = 0.5 mol dm^{-3} (NaCl) and $[H^+]$ = 7.0 ′ 10^{-2} mol dm^{-3}(HCl). The pseudo-first order plots of log $(A_t - A_\infty)$ versus time, were made (where A_t and A_∞ are the absorbance at time t and at the end of the reaction respectively). From the slope of the plots, the pseudo-first order rate constant (k_1) was determined (Mohammed *et al.,* 2009).

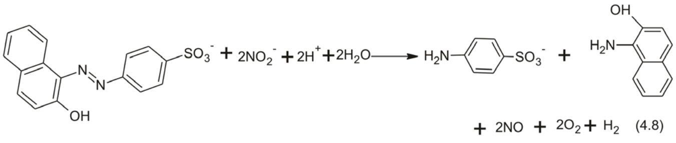
The effect of hydrogen ion concentration on the rate of reaction was investigated by varying $[H^+]$ in the range $1.0 \times 10^{-2} \leq [H^+] \leq 10.0 \times 10^{-2}$ mol dm^{-3}, while $[OII^-]$ and $[NO_2^-]$ were kept constant at 27± 1°C and I = 0.1 mol dm^{-3} (NaCl) respectively.

The effect of ionic strength on the rate of the reaction was carried out in the range $1.0 \leq [I] \leq 7.0$ mol dm^{-3} (NaCl) while the concentration of $[H^+]$ and $[NO_2^-]$ were kept constant at 27± 1°C.

The effect of added cations and anions were investigated by keeping the concentration of other reactants constant while varying theions concentrations as follows: $[X^-] = (1.0 \times 10^{-3} - 100 \times 10^{-3})$ mol dm-3, where X = ($HCOO^-$ and Cl^-) and [X] = $(10.0 \times 10^{-3} – 150 \times 10^{-3})$ mol dm^{-3}, where X = (Ca^{2+} and Mg^{2+})

RESULTS AND DISCUSSION

The result of stoichiometry study for the oxidation of OII^- by nitrite ion shows that one mole of OII^- consumed two moles of nitrite ion. Hence the overall equation for the reaction is shown in equation (1).



However, astoichiometry of 1:1 has been reported for the redox reactions of rosaniline monochloride and parafuchsin by nitrite ion (Onu *et al.,* 1998; Babatunde, 2009).

Sulphanilic acid was confirmed as one of the organic products on addition of few drops of Conc. HCl to the reaction solution, followed by solution of sodium nitrite. This formed a diazonium ion. The reaction was carried out in an ice-bath at 3^{O}C . On addition of the solution of 2-naphthol to the diazonium ion , an orange II dye was formed (Stephanie, 2008).

On addition of $FeCl_3$ to the reaction solution, a faint green colour was observed. This indicates the presence of 2-naphthol

Pseudo-first order plots of log (A_t-A_∞)versus time were linear to more than 80% extent of the reaction. The linearity of the pseudo-first order plots to more than 80% suggests that the reaction is first order with respect to OII^-. The order of the reaction with respect to $[NO_2^-]$ was also determined by plotting logk1 against $\log[NO_2^-]$ (Fig.1). Slope of one was obtained which indicate that the order of reaction with respect to $[NO_2^-]$ is first order.

This reaction therefore conforms to the rate law:

$$-d[OII^-]/dt = k_2[OII^-][NO_2^-] \quad \text{.................} (2)$$

where k_2 is the second order rate constant.

Effect of changes in ionic strength of the reaction medium had no effect on the rate of the reaction (Table 1). This obeys a zero Bronsted Debye salt effect, implying that the activated complex is formed from charged and neutral molecule (Edokpayi *et al.,* 2010). This observation is consistent with equation (6) in the reaction mechanism.

The result in Table 1 shows that the rate of reaction increases with increase in $[H^+]$in the range $1.0 \times 10^{-2} \leq [H^+] \leq 10.0 \times 10^{-2}$mol dm^{-3}. Plot of logk1 versus $\log[H^+]$ gave a gradient of approximately one, an indication that the order with respect to acid is first order. Also plot of $k_2$versus $[H^+]$ was linear with an intercept conforming with equation (3).

$$k_2 = a + b[H+] \quad ....(3)$$

The acid dependence of this nature shows that there is a rapid pre-equilibrium between the protonated and non-protonated forms in which both forms are reactive (Idris *et. al.,* 2015).

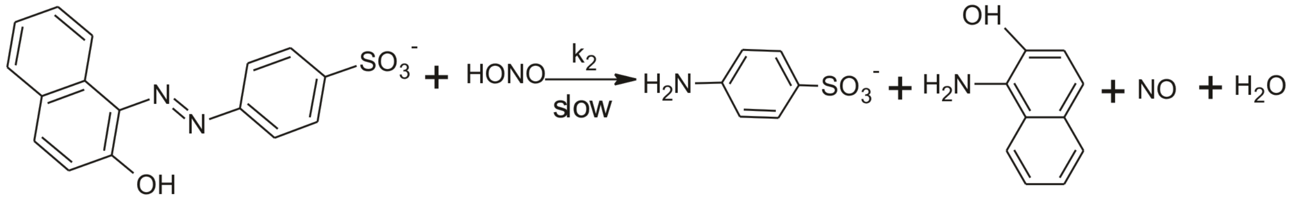
The overall rate equation in the acid rangeinvestigated is given as:

$$-d[BPR^{2-}]/dt = (a + b[H^+])[OII^-][NO_2^-] \quad ...(4)$$

Added cations and anions catalysed the rate of the reaction (Table 2 and 3). Michaelis – Menten's plot of $1/k_1$ versus $1/NO_2^-$ (Fig. 2) and spectrophotometric test suggest absence of an intermediate in the rate determining step. Free radical test did not yield gel formation. Based on the results obtained, this reaction is probably operating through the outersphere mechanism.

Nitrite ion exists in acidic medium as HONO, NO^+ and forms the following equilibra (Onu *et al.*, 2008).

$$NO_2^- + H^+ \overset{K_1}{\rightleftharpoons} HONO \quad .....(5)$$



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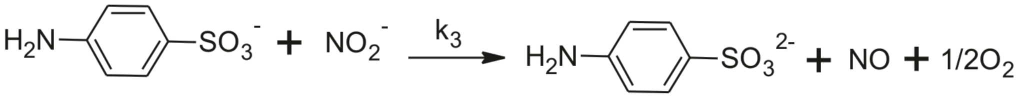

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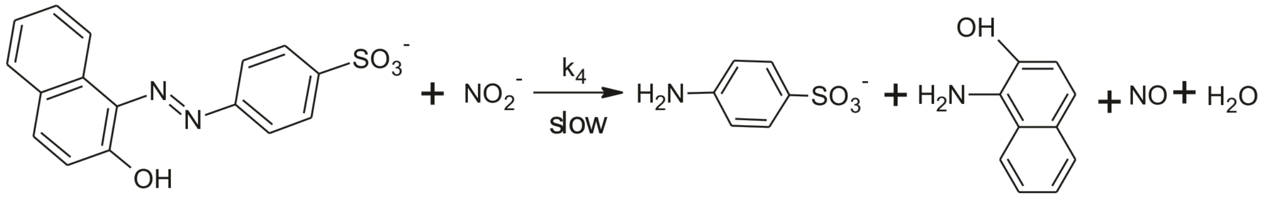

...(8)

$$NO_2^- + H_2O \xrightarrow{k_5} HNO_2 + OH^- \quad ...(9)$$

$$\text{Rate} = k_2[OII^-][HONO] + k_4[OII^-][NO_2^-] \quad ...(10)$$

$$\text{Rate} = k_2K_1[OII^-][NO_2^-][H^+] + k_3[OII^-][NO_2^-] \quad ...(11)$$

$$= (k_3 + k_2K_1[H^+])[OII^-][NO_2^-] \quad ...(12)$$

Table 1: Table 1: Pseudo – first order and second order rate constants for the reaction of Orange II and NO_2^- at [OII-] = 5.0 × 10^{-5} mol dm^{-3},
λ = 484 nm and T = 27 ± 1°C

$10^3[NO_2^-]$,	**$10^2[H+]$,**	**10^1I,**	**$10^4k_1,k_2$,**	
mol dm^{-3}	**mol $dm^{-3}C^2$mol $dm^{-3}s_{-1}dm^3$ mol^{-1} s^{-1}**			
4.0	5.0	5.0	2.66	0.067
5.0	5.0	5.0	3.07	0.061
6.0	5.0	5.0	3.84	0.064
7.0	5.0	5.0	4.37	0.062
8.0	5.0	5.0	5.07	0.063
9.0	5.0	5.0	5.78	0.064
7.0	1.0	5.0	1.73	0.025
7.0	2.0	5.0	2.25	0.032
7.0	4.0	5.0	3.58	0.051
7.0	5.0	5.0	4.30	0.061
7.0	6.0	5.0	5.10	0.073
7.0	10.0	5.0	5.76	0.082
7.0	5.0	1.0	4.35	0.062
7.0	5.0	2.0	4.22	0.060
7.0	5.0	3.0	4.40	0.063
7.0	5.0	4.0	4.20	0.060
7.0	5.0	5.0	4.34	0.062
7.0	5.0	6.0	4.26	0.061
7.0	5.0	7.0	4.28	0.061

Table 2: Rate data for the effect of added cations (Ca^{2+} and Mg^{2+}) on the rate of reaction of orange II and NO_2^-at [OII^-] = 5.0 × 10^{-5} mol dm^{-3}, [NO_2^-] = 7.0 × 10^{-3} mol dm^{-3}, [H^+] = 5.0 × 10^{-2}mol dm^{-3},
I = 0.50 C^2mol dm^{-3}, λ = 484 nm and T = 27 ± 1 °C

Ion	10^3[ion], mol dm-3	10^4k_1, s^{-1}	k2, dm^3 mol^{-1} s^{-1}
	0.0	4.27	0.061
Ca2+	10.0	4.80	0.069
	20.0	5.47	0.078
	40.0	5.83	0.083
	80.0	6.91	0.099
	100.0	7.37	0.105
	150.0	8.20	0.117
	0.0	4.32	0.062
Mg2+	10.0	5.87	0.084
	20.0	6.14	0.089
	40.0	6.40	0.091
	60.0	7.68	0.110
	80.0	8.25	0.118
	100.0	9.60	0.137
	150.0	10.7	0.153

Table 3: Rate data for the effect of added anions (CH3COO-and SO42-) on the rate of reaction of orange II and NO2–at [OII-] = 5.0 × 10–5 mol dm–3, [NO2–] = 7.0 × 10–3 mol dm–3, [H+] = 5.0 × 10–2mol dm–3, I = 0.50 C2mol dm–3, λ = 484 nm and T = 27 ± 1 °C

Ion	**10^3 [ion], mol dm^{-3}**	**10^4k_1, s^{-1}**	**k_2, dm^3 mol^{-1} s^{-1}**
	0.0	4.27	0.061
CH_3COO^-	1.0	4.99	0.071
	10.0	6.55	0.094
	20.0	7.29	0.104
	40.0	9.21	0.132
	60.0	12.3	0.179
	80.0	19.2	0.274
	0.0	4.34	0.062
SO_4^{2-}	10.0	5.76	0.082
	20.0	6.14	0.088
	40.0	7.29	0.104
	60.0	7.68	0.110
	80.0	8.44	0.121
	100.0	9.21	0.132

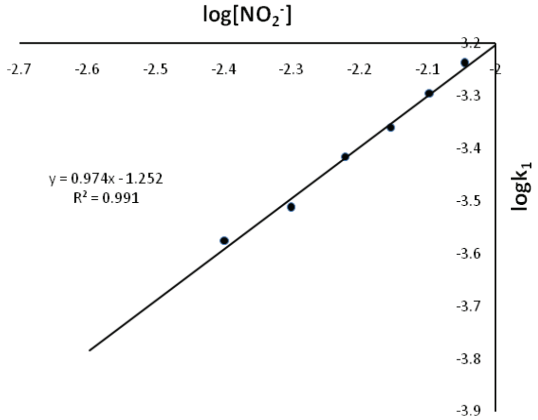

Figure 10:Plot of log k1 versus log[NO_2^-] for the redox reaction of OII^- with NO_2–at [OII^-] = 5.0 × 10–5 mol dm^{-3}, [NO_2^-] = (4.0 – 9.0) × 10^{-3} mol dm^{-3}, [H^+] = 5.0 × 10^{-2}mol dm^{-3}, I = 0.50 C^2mol $dm^{-3,}$ λ = 484 nm and T = 27 ± 1°C

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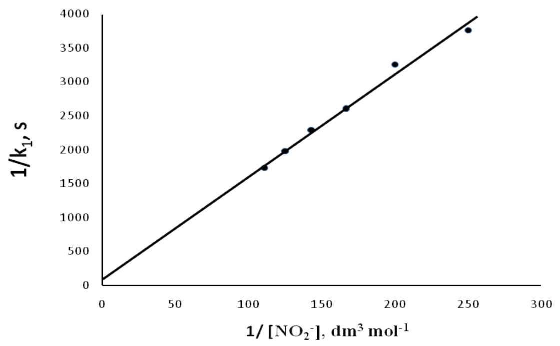

Figure 3:Michaelis - Menten plot for the redox reaction between orange II and NO_2^-at [OII^-] = 5.0 x 10^{-5} mol dm^{-3}, [NO_2^-] = (4.0 – 9.0) x 10^{-3} mol dm^{-3}, [H^+] = 5.0 x 10^{-2}mol dm^{-3}, I = 0.50 mol dm $^{-3}$, λ = 484 nm and T= 27 ± 1 °C

CONCLUSION

The redox reaction of OII$^-$ and nitrite ion in aqueous acidic medium showed a stoichiometry of 1:2, a first order was observed for OII$^-$ and NO_2^- ion.The rate constant increases with increase in acid concentration. The spectrum of the reaction mixture when compared to that of the dye (OII$^-$) alone showed no shift in λmax suggesting absence of an intermediate complex during the reaction.Added ionsspeed up the rate of the reaction. Michaelis – Mentein's plot of $1/k_1$ versus $1/[N_2H_4.2HCl]$ had negligible intercept.Based on the above results, it is proposed that the reaction operates probably through the outersphere mechanism.

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REFERENCES

Onu, A. D., Iyun, J. F and Idris, S.O. Redox reaction of [Co(II)HEDTA]2 with NO_2^- in Aqueous perchloric acid medium: Kinetics and mechanism (2008) *Chemclass Journal,*5:55-61

Cresswell, C. F, Hageman,R. H, Hewit, E. Jand Hucklesby, D. P(1965).The reduction of nitrite and hydroxylamine to ammonia by enzymes from cucurbita pepo in the presence of reduced benylviolegen as electron donor. *Biochemistry Journal 94:1*, 40.

Ollgaard, H. Frost, L and Galster J. C (1998). Survey of azo-colorants in Denmark: consumption, use, health and environmental aspects, Ministry of Environment and Energy, Denmark and the Danish Environmental Protection Agency.No. XX, p. 147

Ebenso, E. E., Alemu, H., Umoren, S. A and Obot, I. B (2008).Inhibition of mild steel corrosion in Sulphuric Acid using Alizarin yellow G.G. Dye and Synergistic Iodide Additive.*International Journal of Electrochemistry,3.1325-1339.*

Mohammed, Y., Iyun, J. Fand Idris, S. O.(2009).Kinetic approach to the mechanism of the redox reaction of malachite green and permanganate ion in aqueous acidic medium. *African Journal of Pure Applied Chemistry, 3: 12, 269.*

Onu, A. D and Iyun, J. F (1998). Kinetics and mechanism for oxidation of rosaniline monochloride by nitrite ions. *Journal of ChemicalResearch, 3:* 25-26.

Babatunde, O (2009). Kinetics and mechanism of reduction of parafushin by nitrite ions in aqueous medium. *World Journal of Chemistry4(1)*:39-44.

Edokpayi, J. N.,Iyun, J. F and 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. Unpublished M.Sc.\Thesis, Ahmadu Bello University, Zaria Nigeria

Idris, S. O,Samson, V. Oand Myek, B (2015).Kinetics of the Oxidation of Bromopyrogallol Red by Nitrite Ion in Aqueous Acidic Medium. *International Frontier ScienceLetters,(3)*32-38

Stephanie (2008). Practical organic chemistry, 3rd year students' part 1, Jazan University, Faculty of science, Chemistry Department, Pp 38