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Kinetics and Mechanism of Reduction of Parafuchsin by Nitrite Ions in Aqueous Acid Medium

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Abstract: The kinetics and mechanism of reduction of parafuchsin (hereafter referred to as pf^+) by nitrite ion have been studied in aqueous acidic medium under the pseudo-first order condition of excess $[NO_2^-]$ at 28 ±0.1°C, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3} and ionic strength (I) = 1.0 mol dm^{-3} (NaCl). The stoichiometry of the reaction was observed to be 1:1 in terms of mole ratio of parafuchsin and nitrite ions consumed. The redox reaction follows second order kinetics at constant hydrogen ion concentration and the rate also shows first order dependence on acid ion concentration. The overall reaction conforms to the rate law

$$-\frac{d}{dt}[pf^+] = a[H^+][pf^+][NO_2^-]$$

Where $a = 1.44 \times 10^{-1}$ dm^6 mol^{-2} s^{-1}

The rate of reaction increases with increase in ionic strength while it decreases with increase in dielectric constant of the reaction mixture. There were no free radicals in the reaction. The results from kinetics studies, spectroscopic investigation and Michaelis- Mentens plot did not indicate complex formation. A plausible mechanism is proposed for the reaction.

Key words: Parafuchsin · Nitrite

INTRODUCTION

Parafuchsin (triaminotriphenylmethane chloride) is a basic fuchsin (Fig 1) and one of the most powerful nuclear dyes with many biological uses [1]. Basic fuchsin is the main constituents of Schiff's reagent, it is often employed by the biologist as bacteriostatic agent and sometimes it assists in differentiation of species. This reagent is also employed by the chemist as an indicator for detecting the presence of aldehydes [2]. Basic fuchsin is also used in cotton tannin, mordant, printing and dyeing in textile industries.

The quiniod stucture of the fuchsin is easily reducible where the chromophore group is destroyed and the compound loses its colour to form leuco-fuchsin which is an important reagent to the biologist [3]. Redox reactions of pararosaniline (Parafuchsin) by sulphite ions have earlier been reported by Iyun and Lawal [3].

Nitrite ions have been reported to act either as oxidant and reductants in redox reactions involving nitrite ions [4-9].

Consequently, knowledge of the kinetics and mechanisms that characterise the redox reaction of parafuchsin is highly desirable so as to enhance its applicability in the textile industry and laboratory. This paper reports on kinetics and mechanism of reduction of parafuchsin by nitrite ions in aqueous acid medium.

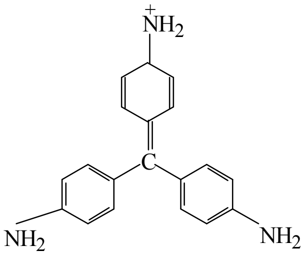

Fig. 1: Parafuchsin (Pararosaniline Chloride, Pf^+)

EXPERIMENTAL

Materials: Stock solutions of parafuchsin and sodium nitrite were prepared by dissolving known quantities in distilled water. The λ_{max} = 540nm of pf^+ was determined by running the electronic spectrum of solution of pf^+ in the wavelength range of 400 – 600nm. Sodium chloride (BDH) was used to maintain the ionic strength of the medium

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Table 1: Pseudo-first order and second order rate constants for reaction of parafuchsin and nitrite ions. $[pf^+] = 1 \times 10^{-4}$ mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl), T = 28°C, λ_{max} = 540 nm.

$10^3[NO_2^-]$ mol dm^{-3}	10^4 $[H^+]$, mol dm^{-3}	I (NaCl), mol dm^{-3}	k_o s^{-1}	10^3k_2 dm^3 $mol^{-1}s^{-1}$
2.0	1.0	1.0	3.14	1.57
3.0	1.0	1.0	4.96	1.66
4.0	1.0	1.0	7.19	1.77
5.0	1.0	1.0	8.70	1.74
6.0	1.0	1.0	10.30	1.72
7.0	1.0	1.0	11.80	1.69
8.0	1.0	1.0	13.06	1.63
4.0	1.0	0.5	5.28	1.32
4.0	1.0	0.6	5.64	1.44
4.0	1.0	0.7	6.90	1.73
4.0	1.0	0.8	7.20	1.80
4.0	1.0	1.0	7.00	1.75
4.0	1.0	1.1	8.28	2.07
4.0	1.0	1.2	9.00	2.25
2.0	0.5	1.0	1.32	0.66
2.0	1.0	1.0	3.12	1.56
2.0	2.0	1.0	6.00	3.00
2.0	3.0	1.0	8.40	4.20
2.0	4.0	1.0	10.05	5.53
2.0	5.0	1.0	13.80	6.96
2.0	6.0	1.0	17.05	8.52
2.0	7.0	1.0	19.80	9.96
2.0	8.0	1.0	22.80	11.40

constant and solution of hydrochloric acid (BDH) was also prepared (36%, specific gravity 1.18) to investigate the effect of hydrogen ions on the rate of reaction. All other reagents used were of analar grade.

Stoichiometry: The stoichiometry of the reaction was determined by Spectrophotometric titration using the mole ratio method by keeping the concentration of the dye constant at 1×10^{-4} mol dm^{-3},$[H^+] = 1 \times 10^{-4}$ mol dm^{-3}, I = 1.0mol dm^{-3}, λ_{max} = 540nm, T = 28.0±1°C and $[NO_2^-]$ was varied from $1.0 \times 10^{-4} - 10.0 \times 10^{-3}$mol dm^{-3}. The absorbance of the reacting mixture was measured after the reaction had gone to completion by steady zero absorbance value over a period of two days. A point of inflexion on the curve of absorbance versus mole ratio corresponds to the stoichiometry of the reaction.

Kinetic Measurements: The kinetics of the reaction was monitored using a Corning Spectrophotometer Model.252 at 28±0.1°C, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3} and I=1.0 mol dm^{-3} (NaCl). The progress of the reaction was monitored by following the decrease in absorbance of the dye at 540nm. All kinetic experiments were performed under pseudo-first order conditions with the concentration of the nitrite ions at least 20 fold greater than that of the dye.

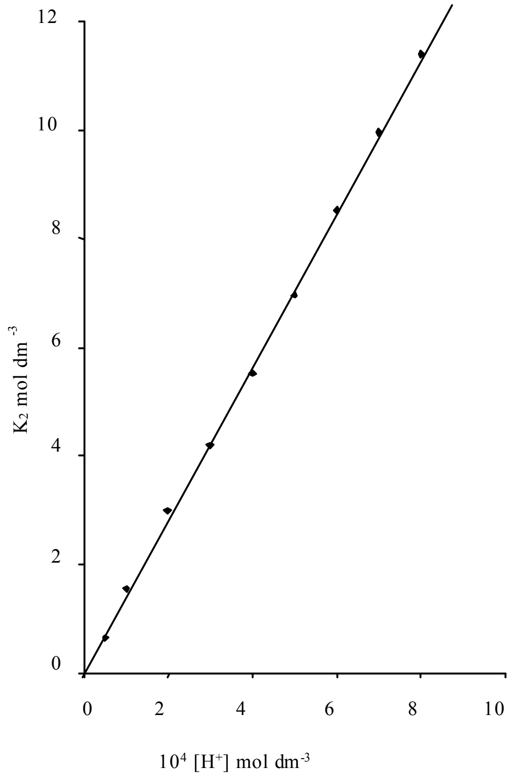

Fig. 2: Plot of k_2 versus $[H^+]$ for the redox reaction between parafuchsin and nitrite

The pseudo-first order plots of the log (A_t-A_∞) versus time t were made (where A_∞ and A_t are the absorbance at the end of the reaction and at time, t) and from the slope of the plots, the pseudo-first order rate constant (k_o) was determined. The second order rate constant (k_2) was obtained from k_o as k_2 / $[NO_2^-]$.

Effect of Ionic Strength: The effect of ionic strength on the rate of the reaction was investigated in the range of 0.5-1.2 mol dm^{-3} (NaCl) while the concentration of other reactants were kept constant at 28±1°C.The results are presented in Table 1.

Effect of Added Cation and Anion: The effect of added cation and anion were investigated for X= 1.0×10^{-3} -4.0×10^{-3} mol dm^{-3} (X =Li^+, Ba^{2+}, K^+, SO_4^{2-}, CH_3COO^-) and the concentration of other reactants were kept constant at 28.0±1°C and ionic strength of 1.0 mol dm^{-3} (NaCl).

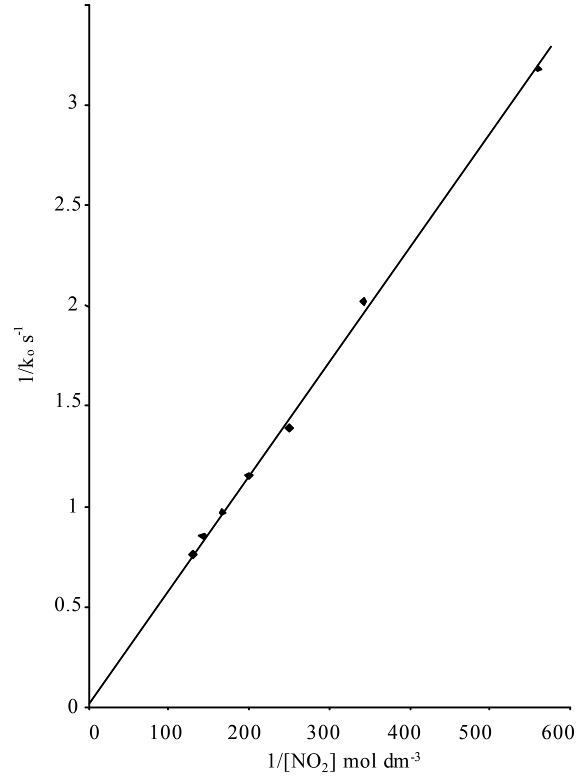

Fig. 3: Michaelis-Menten's plot for the reaction of parafuchsin and nitrite ion

Effect of Acid on the Reaction Rate: The effect of acid on the rate of the reaction was studied in the range of $0.5x10^{-4}$ -$1x10^{-3}$ mol dm^{-3} while concentration of the dye and nitrite were kept constant at 28.0±1.0°C and I =1.0 mol dm^{-3} (NaCl).

Test for Intermediate Complex: The spectra of the reaction mixture were obtained after five minutes.The spectra of the dye alone were compared over a range of wavelength 400 nm-600 nm.

Michaelis-Mentens plot of $1/k_o$ versus$1/[NO_2^-]$ was made (Fig. 2).

Test for Free Radical: Acrylonitrile was added to the partially oxidized reaction mixture of dye and the nitrite ions in a large excess of methanol and to each of the reactants separately.

RESULTS AND DISCUSSION

Stoichiometry and Product Analysis: A stoichiometric study showed that one mole of the dye was consumed by one mole of the nitrite ion.

Table 2: Effect of added ions on the second order rate constants for parafuchsin and nitrite ion reaction. $[pf^+] = 1 \times 10^{-4}$ mol dm^{-3}, I = 1.0 mol dm^{-3} (NaCl), $[NO_2^-] = 40 \times 10^{-4}$ mol dm^{-3}, T = 28±1°C and λ_{max} = 540 nm

X	10^4 [X]mol dm^{-3}	10^2 k_o s^{-1}	$10^{-1}k_2$ dm^3mol s^{-1}
K^+	10	5.71	1.43
	20	5.04	1.26
	30	4.80	1.20
	40	4.44	1.11
Li^+	10	6.05	1.51
	20	5.28	1.32
	30	4.51	1.13
	40	4.18	1.04
Ba^{2+}	10	5.90	1.48
	20	5.30	1.33
	30	4.90	1.22
	40	4.15	1.04
SO_4^{2-}	10	5.76	1.44
	20	5.51	1.38
	30	5.18	1.30
	40	4.92	1.23
CH_3COO^-	10	6.26	1.57
	20	6.13	1.53
	30	6.19	1.55
	40	5.57	1.40

$$Pf^+ + NO_2^- \rightarrow \text{Product} \qquad (1)$$

Similar stoichiometry has been reported for the parafusin with sulphite ions [3] and for another triphenyl methane dye, Leucomalachite green with Cr (iv) ions [10].

The product analysis was carried out by reacting equimolar amount of dye and NO_2^- at 28±0.1°C, $[H^+] = 1 \times 10^{-4}$ mol dm^{-3} and I = 1.0 mol dm^{-3} [NaCl].

After the completion of the reactions a colourless solution was obtained and UV visible spectra of the product showed no absorption peak at λ_{max} 540 nm.

This indicates the destruction of the quinoid (chromophore) group.

Kinetics: The pseudo-first order of log $(A_t-A_{\bullet})$ versus time for these reactions were linear for about 80% of the reaction. The linearity of these plots indicates that these reactions are first order with respect to $[pf^+]$. A plot of log k_o vs. log $[NO_2^-]$ was linear with a slope of 0.84 showing that the reaction is also first order with respect to $[NO_2^-]$. This is also supported by the constancy of k_2 values. Thus the reaction is second order at constant $[H^+]$ and the rate equation for the reaction is

$$-\frac{d}{dt}[pf^{+}] = k_2[pf^{+}][NO_2^{-}] \qquad (2)$$

where $k_2 = (1.69\pm0.01) \times 10^{-2} dm^3 mol^{-1}s^{-1}$

The order of one in both reactants in the reaction conforms with already reported redox reaction of rosaniline monochloride by nitrite ions [11] and parafuchsin by sulphite ions [3].

Effect of Acid: From the result in Table 2, it is observed that the value of reaction rate constant of the reaction increasing with increase in $[H^+]$. The plot of k_2 versus $[H^+]$ was linear with no intercept. The acid dependence rate constant is given as

$$k_2 = a [H^+] \qquad (3)$$

Combining equations 2 and 3, the rate of reaction becomes

$$-\frac{d}{dt}[pf^{+}] = a[H^{+}][pf^{+}][NO_2^{-}] \qquad (4)$$

where $a = (1.44 \times 10^{-1}) dm^6 mol^{-2} s^{-1}$

The nature of $[H^+]$ dependence observed for this reaction suggests that the equilibrium between protonated and deprotonated form of nitrite ion prior to the rate-determining step is so rapid that the equilibrium constant for deprotonated form is small and is not complete even at high acidities, only the protonated form is reactive [12]. The acid dependent component in the reduction of dioxomanganese complex by NO_2^- is similar to one observed in this reaction [13].

Effect of Ionic Strength: According to Bronsted-Debye salt effect [14] the reaction displayed a positive salt effect as the second order rate constant increased with increasing ionic strength. This suggests that the activated complex is formed from two ions of like charges (equation 7). A plot of k_2 versus $\sqrt{I}$ gave a slope of 0.59. This suggests that some other interactions must be taking place to account for this non-integral value of the slope for product species at the transition state.

Effect of Added Species: Inclusion of K^+, Li^+, Ba^{2+}, SO_4^{2-}, CH_3COO^- ions decreases the rate of the reaction. Although lack of catalysis in the presence of added ions could be indicative of inner-sphere mechanism [15]. This inhibition effect by the anions and cations suggested that there is interference of these ions in the transition state, which shows that an outersphere mechanism might be in operation [16].

Free Radical Test: The acrylamide did not polymerise either of the reactant alone or reaction mixture. This suggests that free radicals are not involved in this reaction. However, according to Bexenddle and Hardy [17] there could be formation of semiquione radical in the reaction, which is difficult to observe experimentally because it is very reactive.

Intermediate Complex Formation: The results of the spectroscopic studies indicated no significant shift from the absorption maxima of 540 nm characteristic of pf^+. This suggests the formation of an intermediate complex during the reactions is very unlikely.

Plots of $1/k_o$ vs. $1/[NO_2^-]$ gave a straight line which passed through the origin. (Fig 3) This further suggests the absence of formation of intermediate complex thereby supporting the domination of outer-sphere mechanism [18].

Reaction Mechanism: From the observed experimental data, the mechanism proposed below accommodates all the experimental findings for the reaction of pf^+ with NO_2^-.

$$NO_2^- + H^+ \xrightleftharpoons{K_1} HNO_2 \qquad (5)$$

$$HNO_2 + H \xrightleftharpoons{K_2} H_2O + :\overset{+}{N} = 0 \qquad (6)$$

$$RNH_2^+ + :\overset{+}{N}=0 \xrightleftharpoons{K_3} [RNH_2//NO]^{2+} \qquad (7)$$

$$[RNH_2//NO]^{2+} \xrightarrow{k_4} Product \qquad (8)$$

$$Rate = k_4 [RNH_2//NO]^{2+} \qquad (9)$$

From equation 7

$$-\frac{d}{dt}[RNH_2//NO]^{2+} = k_3[RNH_2^{+}][\overset{+}{N} = 0] \qquad (10)$$

Putting equation 10 in 9

$$Rate = K_4 K_3 [RNH_2^{+}][:\overset{+}{N}=0] \qquad (11)$$

From equation 5 & 6

$$[:\overset{+}{N}=0\,] = K_2K_1\ [H^+][NO_2^-] \qquad (12)$$

Substituting equation 12 in 11

$$\text{Rate} = k_4K_3K_2K_1\ [H^+]\ [RNH_2^+][NO_2^-] \qquad (13)$$

Therefore

$$\text{Rate} = k[H^+]\ [RNH_2^+][NO_2^-] \qquad (14)$$

Equation 14 is analogous to equation 4

Where $k = k_4K_3K_2K_1 = a$ and $RNH_2^+ = pf^+$

CONCLUSION

At constant $[H^+]$, the order of the reaction is second order as represented by equation 2. And the rate also shows a first order dependence on acid ion concentration therefore the overall rate law becomes

$$-\frac{d}{dt}[pf^+]=k[H^+][pf^+][NO_2^-]$$

The actual mechanism of the reaction can then be only arrived at if the following points are considered:

Absence of free radicals in the reaction mixture suggests the contribution of outer-sphere mechanism[19].

The absence of a spectrophotometric evidence (Absence of a shift in the λ_{max} 540 nm of pararosaniline chloride (parafuchsin) in the reaction) suggests that a precursor complex is probably not formed prior to act of electron transfer and that the electron transfer may occur by the outer-sphere mechanism.

Michaelis- Mentes plot of 1/ k_o versus 1/ $[NO_2^-]$ was linear with no significant intercept. This greatly favours the outer-sphere mechanism [15].

The above reasons suggest that the reaction is most probably occurring by outer-sphere mechanism

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