REDOX KINETICS OF MONOMETHYL FUCHSIN BY DITHIONITE ION IN AQUEOUS HYDROCHLORIC ACID

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ABSTRACT

The kinetics and mechanism of the reduction of monomethyl fuchsin (hereafter mmf⁺) by dithionite ion ($S_2O_4^{2-}$) have been studied in aqueous hydrochloric acid I = 0.25M (LiCl), [H⁺] = 3 x 10^{-4}M (HCl), T = 30°C. The reaction was first order in both [mmf⁺] and [$S_2O_4^{2-}$]. The rate of the reaction showed inverse dependence on [H⁺] with the empirical rate law

$$-\frac{d[mmf^+]}{dt} = a[H^+][mmf^+][S_2O_4^{2-}]$$

and displayed negative salt effect while spectroscopic investigation and Michaelis - Menten plot showed evidence of intermediate complex formation. A plausible mechanism has been proposed for the reaction.

INTRODUCTION

Monomethyl fuchsin is a triphenyl methane dye with a methylated benzene ring. It is one of the dyes simply called basic fuchsin and it is used mainly as a biological stain[1]. Monomethyl fuchsin is also one of the constituents of Schiff's reagent often employed for the detection of aldehydes and aldehyde - like cell constituents.

In preparing the reagent, basic fuchsin is reduced by sulphite or metabisulphite ions to a colourless form. The characteristic test of the reagent is in the restoration of violet colour to the basic fuchsin in the presence of aldehydes. The chemical reaction for this observation was hitherto obscure and was ascribed to the restoration of the quinoid structure of the fuchsin[1]. Iyun and Lawal[2] however reported that the observed restored colour was not due to the restoration of the quinoid structure of the fuchsin but the formation of a new dye with a cyanic chromophoric group.

Redox studies of monomethyl fuchsin is gaining ground. We have earlier reported our finding on the reduction of the dye by nitrite[3] and chlorite[4] ions. Given the importance of monomethyl fuchsin as stain and dye, adequate understanding of the mechanism of its redox reaction is important for extending it uses. We herein report our findings on the redox reaction of monomethyl fuchsin with dithionite ion.

EXPERIMENTAL

Reagents

All reagents used were of 'Analar' grade. Stock solutions of mmf⁺ and dithionite ion were prepared by dissolving a known amount of each reagent and making up to a known solution volume with distilled water. The λ_{max} (545nm) of mmf⁺ was determined by running the electronic spectrum of the solution of mmf⁺ in the wavelength range 380 - 580nm.

A stock solution of hydrochloric acid was made by diluting commercial acid (36%, specific gravity 1.8) and standardizing the solution using trioxocarbonate (IV). Stock solutions of lithium chloride, sodium formate, sodium acetate were prepared and standardized gravimetrically.

Kinetic measurements

The rate of the reaction of mmf⁺ with dithionite ion was studied by observing the decrease in absorbance of mmf⁺ at 545nm on a spectronic 20 colorimeter. All kinetic measurements were carried out under pseudo-first order conditions with dithionite ion concentration in excess over the mmf⁺ concentration at 30°C and 0.25M (LiCl) ionic strength. The pseudo-first plots of $\log(A_t - A_\infty)$

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versus time were made. From the gradient of the plots, the pseudo-first order rate constant, k_1, was determined. The second order rate constant, k_2, was obtained from k_1 as $k_1/[S_2O_4^{2-}]$. The results are presented in Table 1.

The effect of H⁺ on the rate

The influence of H^+ on the rate was investigated using hydrochloric acid in the range $(9 - 100) \times 10^{-5}M$ while the $[mmf^+]$ and $[S_2O_4^{2-}]$ were kept constant. The reaction was carried out at 30°C and $I = 0.25M$ (LiCl). The results are presented in Table 1.

The effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range $I = 0.14 - 0.30M$ (LiCl) while the concentration of other reagents were kept constant. The results are presented in table 1.

Test for intermediate complex formation

Spectrophotometric test was carried out by comparing the electronic spectra of the reaction mixture and that of mmf⁺ alone within 440 - 580nm. Michaelis - Menten plot vs $[S_2O_4^{2-}]$ was also done (Figure 1) (545nm). The λ_{max} determined by running the electronic spectrum of the solution...580nm.

RESULTS AND DISCUSSION

Kinetic measurements

The pseudo-first order plots of $\log(A_t-A_\infty)$ versus time for these reactions were linear for about 70% of the reaction. The linearity of these plots indicates that these reactions are first order with respect to $[mmf^+]$. Plots of $\log k_1$ vs $\log[S_2O_4^{2-}]$ gave a gradient of unity showing that the reaction is also first order with respect to $[S_2O_4^{2-}]$. Thus the rate equation for the reaction is

$$-\frac{d[mmf^+]}{dt} = k_2[mmf^+][S_2O_4^{2-}] \quad ....(1)$$
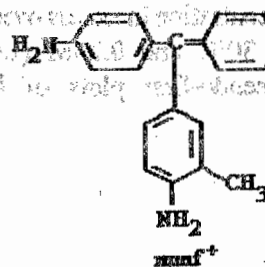
The orders of one or half have been reported for some $S_2O_4^{2-}$ reactions[5-8]. The nature of the order suggests whether the reactive specie in the equilibrium $S_2O_4^{2-} \rightleftharpoons 2SO_2^-$ is $S_2O_4^{2-}$ or SO_2^- [9-11]. For the reactions in which the order is half the SO_2^- radical has been implicated as the reducing specie while $S_2O_4^{2-}$ is the reducing specie for reactions in which the order is one[6]. An order of one was obtained with respect to $[S_2O_4^{2-}]$ in the reaction of mmf⁺ with $S_2O_4^{2-}$; thus the mechanism of the reaction should involve $S_2O_4^{2-}$. The mechanism is further supported by the lack of acrylamide polymerization of the reaction. Acrylamide polymerization of the reaction would have indicated the presence of radical species in the reaction medium.

Effect of H⁺

From the result in Table I, it is observed that the rate constant of the reaction decreased with increase in $[H^+]$. The plots of k_2 vs $[H^+]$ was linear with zero intercept (Figure 2). The acid dependence rate constant is given as

$$k_2 = a[H^+]^{-1}, \quad a = 3.33 \times 10^{-4} s^{-1} \quad ....(2)$$

Substituting equation (2) in equation (1), the rate of the reaction becomes

$$-\frac{d[mmf^+]}{dt} = a[H^+]^{-1}[mmf^+][S_2O_4^{2-}] \quad ....(3)$$

The nature of H^+ dependence observed for the reactions suggests the release of proton in a pre-equilibrium step and that the deprotonated form of the mmf⁺ is reactive.
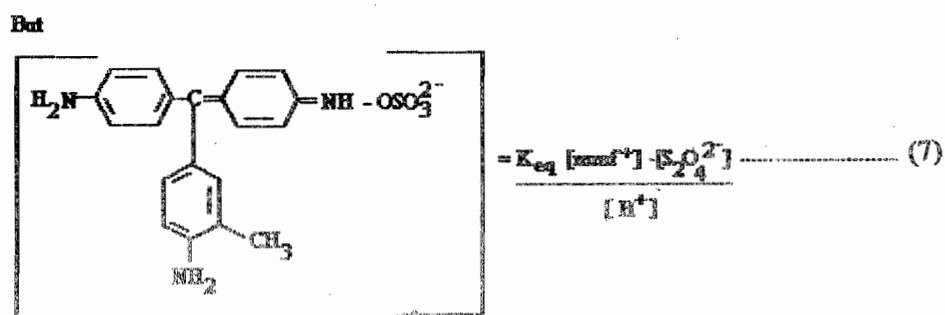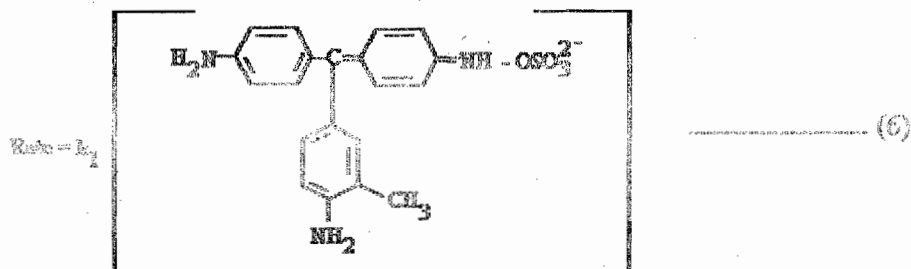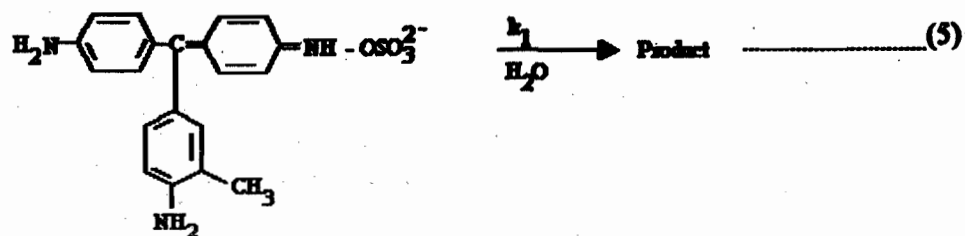
A plausible mechanism consistent with the result is

$$H_2N-\bigcirc-\bigcirc=NH_2^+ + S_2O_4^{2-} \overset{K_{eq}}{\rightleftharpoons} H_2N-\bigcirc-C-\bigcirc=NH - OSO_3^{2-} + H^+ \quad ....(4)$$

$$\text{(structure)} \quad \xrightarrow[\;H_2O\;]{k_1} \quad \text{Product} \quad \text{————————(5)}$$

$$Rate = k_1 \left[\text{(structure)} \right] \quad \text{————————(6)}$$

But

$$\left[\text{(structure)} \right] = \frac{K_{eq}\,[mmf^+]\,[S_2O_4^{2-}]}{[H^+]} \quad \text{————(7)}$$

Table 1. Pseudo-first order and second order rate constants for the reaction of mmf^+ and $S_2O_4^{2-}$ $[mmf^+] = 4 \times 10^{-6}M$, $I = 0.25M$ (LiCl), $T = 30^{\circ}C$, and $\lambda_{max} = 545nm$.

$10^3[S_2O_4^{2-}]$M	$10^5[H^+]$M	I (LiCl)M	$10^4 k_1 s^{-1}$	$10^1 k, M^{-1}s^{-1}$
1.0	30.0	0.25	8.90	8.90
2.4	30.0	0.25	22.14	11.07
3.0	30.0	0.25	33.48	11.16
4.0	30.0	0.25	46.06	11.51
5.0	30.0	0.25	55.98	11.20
6.0	30.0	0.25	55.07	9.18
8.0	30.0	0.25	79.17	9.90
3.0	9.0	0.25	100.89	33.63
3.0	20.0	0.25	47.37	15.79
3.0	30.0	0.25	32.91	10.97
3.0	40.0	0.25	24.00	8.00
3.0	50.0	0.25	18.03	6.01
3.0	60.0	0.25	20.31	6.77
3.0	100.0	0.25	9.09	3.03
3.0	30.0	0.14	48.10	16.11
3.0	30.0	0.17	41.41	13.80
3.0	30.0	0.21	36.36	12.12
3.0	30.0	0.25	32.24	10.75
3.0	30.0	0.30	22.16	7.39
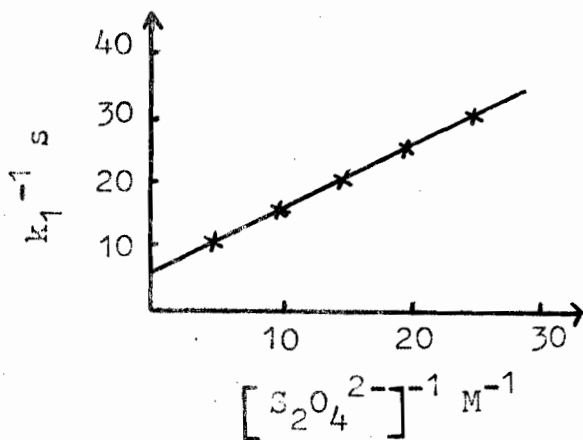
Figure 1. Michaelis - Menten plot for the reaction between mmf^+ and $S_2O_4^{2-}$.

Figure 2. Plot of k_2 vs $[H^+]^{-1}$ for the redox reaction between mmf^+ and $S_2O_4^{2-}$.

putting equation (7) into (6)

$$rate = \frac{k_1 K_{eq} [mmf^+][S_2O_4^{2-}]}{[H^+]} \qquad ....(8)$$

If $k_1 K_{eq} = a$, then

$$rate = a[H^+]^{-1}[mmf^+][S_2O_4^{2-}] \qquad ....(9)$$

Equation (9) conforms to the observed rate law, equation (3).

The reaction displayed negative salt effect as the second order rate constant decreased with increasing ionic strength. This observation is suggestive of interaction of unlike charges in the activated complex[12]. This agrees with equation (4) of the reaction scheme.

The Michaelis - Menten plot gave an intercept (Figure 1) and also the spectra of the reaction mixture showed a hypsochromic shift from 54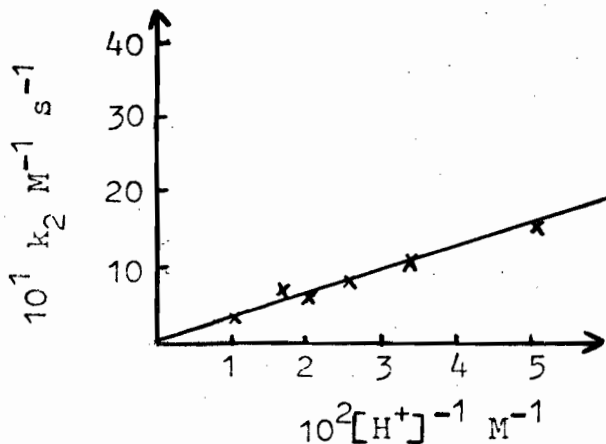5nm to 530nm. Both evidences suggest the formation of an intermediate complex. Intermediate complex formation has been adduced in favour of the innersphere mechanism.

The catalytic effect of the anions, $HCOO^-$ and CH_3COO^-, on the reaction rate is unexpected vis-a-vis the evidences from kinetic and spectroscopic analyses that favour the innersphere mechanism. Ion catalysis of reaction rate has been reported to be characteristic of the outer-sphere mechanism[13-15]. The catalysis of the reaction rate by the anions may be due to medium effect.

However, the shift of 15nm in λ_{max} and the significant intercept in the Michaelis - Menten plot for the reaction are strong evidence in favour of the innersphere mechanism which is probably operating in the $S_2O_4^{2-}$ - mmf^+ reaction.

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