Original Contribution

HEXAMETHYLPARAROSALININE CHLORIDE (CRYSTAL VIOLET) OXIDATION BY CHLORATE IONS IN AQUEOUS ACIDIC MEDIUM : KINETIC APPROACH TO THE MECHANISM OF REACTION

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ABSTRACT
The redox kinetic studies of the reaction of crystal violet (CV^+) and ClO_3^- were carried out in aqueous acidic medium, at a temperature of 32 ± 1 C; $= 0.50$ mol dm^{-3} (NaCl), $[H^+] = 1.00 \times 10^{-2}$ mol dm^{-3} (HCl). In the stoichiometry, one mole of the dye was consumed by two moles of ClO_3^-. The reaction is first order in both [dye] and the [oxidant]. The rates of redox reaction showed dependence on acid concentrations (in the acid range used). Rate equation for the reaction has been proposed as: $-d[MG^+]/dt = (b[H^+])[CV^+][ClO_3^-]$. At $[H^+] = 1.00 \times 10^{-2}$ mol dm^{-3}, the second order rate constant for the crystal violet $- ClO_3^-$ reaction was found to be 3.88 dm^3 mol^{-1} min^{-1}. The rate of reaction displayed zero salt effect and was not affected by changes in the dielectric constant of the reaction medium. Added anions and cations catalysed the crystal violet/ ClO_3^- reaction. Results of the Michaelis- Menten analysis gave no evidence of intermediate complex formation. Based on the results obtained experimentally, the outer sphere mechanism is proposed for the crystal violet $- ClO_3^-$ reaction and a plausible mechanism of the reaction is proposed.

Key words: kinetics, mechanism, catalysis, salt effect.

INTRODUCTION

Crystal violet is a triphenyltmethane dye that is antimicrobial [1, 2], mutagenic [3, 4] and used to prevent fungal growth in poultry feed [1, 2]. It is used as a bacteriostatic agent in medical solutions [5, 6], and to treat skin infections by *staphylococcus aureus* [7, 8]. It has been reported to undergo electrochemical oxidation in liquid sulphur dioxide [9], oxidation with $N_3^.$ and $OH^.$ radicals [10].

Chlorate is a synthetic chloroxyanion that is strongly oxidizing [11, 12]. Earlier studies have shown that chlorate undergoes reduction in bovine ruminal fluid [13]. Chlorate, ClO_3^- (oxidation state +5), during its reduction to chloride, Cl^- (oxidation state -1), intermediates such as chlorite, ClO_2^- (oxidation state +3) and hypochlorite, ClO^- (oxidation state +1) could be formed [13]. Hypochlorite is not stable enough to be detected as an intermediate

form, because it is an extremely strong oxidizing agent [14]. Chlorate, though, can be oxidized to the perchlorate [15]. It has a potential in preharvest food safety applications [16].

This work is carried out to obtain relevant kinetic data for redox reactions involving crystal violet and the mechanisms for such reactions, which would give an idea on the conditions best suitable for the use of crystal violet for whatever purpose. The knowledge would be very beneficial to pharmaceutical chemists in improving its use for medicinal purposes.

EXPERIMENTAL

HCl was used to investigate the effect of hydrogen ion concentration on the reaction, $KClO_3$ was used as the oxidant and NaCl was used to maintain a constant ionic strength for each run. Crystal violet, the oxidant and the other solutions were prepared with distilled water.

The rate of reactions of the oxidant (ClO_3^-) and the reductant (crystal violet) were studied by

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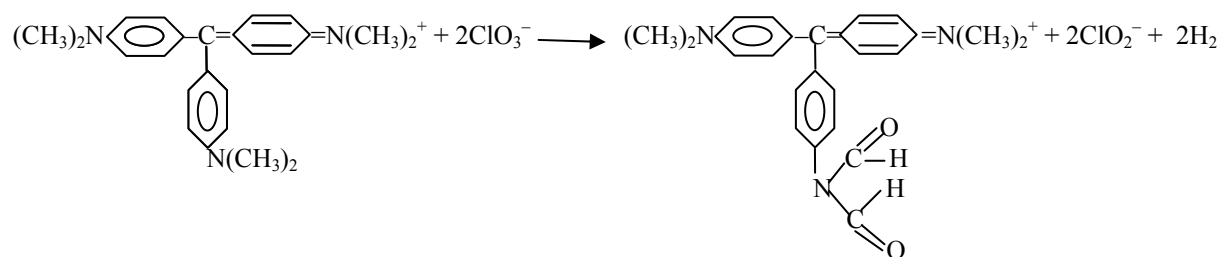
monitoring the decrease in absorbance of the reductant at its λ_{max} (530 nm) using Seward digital biomedical colorimeter. All kinetic measurements were carried out under pseudo-first order conditions with oxidant concentrations at least 50 fold in excess of the reductant concentration at temperature of $32 \pm 1°C$, ionic strength of 0.50 mol dm^{-3} (NaCl) and $[H^+] = 7.5 \times 10^{-3}$ mol dm^{-3} (HCl). The pseudo-first order plots of log (A_t –

A_∞) against time were made and the slope of the plots gave the pseudo- first order rate constant, k_1. The second – order rate constants, k_2, were determined from k_1 as $k_1/ [ClO_3^-]$.

RESULTS AND DISCUSSION
Stoichiometry
Stoichiometric studies show that one mole of dye is consumed by two moles of the oxidant, which is consistent with the equation below:

$$(CH_3)_2N\text{—}\langle\bigcirc\rangle\text{—}C=\langle\bigcirc\rangle=N(CH_3)_2^+ + 2ClO_3^- \longrightarrow (CH_3)_2N\text{—}\langle\bigcirc\rangle\text{—}C=\langle\bigcirc\rangle=N(CH_3)_2^+ + 2ClO_2^- + 2H_2$$

Order of reaction
Plots of log ($A_t - A_\infty$) versus time obtained under pseudo-first order conditions were linear for about 100% of the reactions. (A_t and A_∞) are the absorbances of the complex at time 't' and at the end of the reaction respectively), suggesting that the reaction is first order with respect to $[CV^+]$. Pseudo-first order rate constants, k_1, for the plots were obtained from the slope of the plots of log ($A_t - A_\infty$) versus time. Order of reaction in $[ClO_3^-]$ was obtained

from the slope of the plot of log k_1 versus log $[ClO_3^-]$, which was 1.03 ± 0.02 **(Figure 1)**, suggesting that the reaction is first order in $[ClO_3^-]$, meaning that the reaction is second order overall. The second order rate constants, k_2, calculated from $k_1/ [ClO_3^-]$ were fairly constant and reported in **Table 1** and the average was found to be 3.88 dm^3 mol^{-1} min^{-1}. The rate law can therefore be represented by equation (2) below:

$$\frac{-d[CV^+]}{dt} = k_2 [CV^+][ClO_3^-] \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

Effect of acid
In the acid range used ($1.00 \times 10^{-4} \leq [H^+] \geq 1.00 \times 10^{-2}$ mol dm^{-3}), rate of reaction increased with increase in $[H^+]$. **(Table 1)**. Plot of k_{H+} versus $[H^+]$ is linear without an
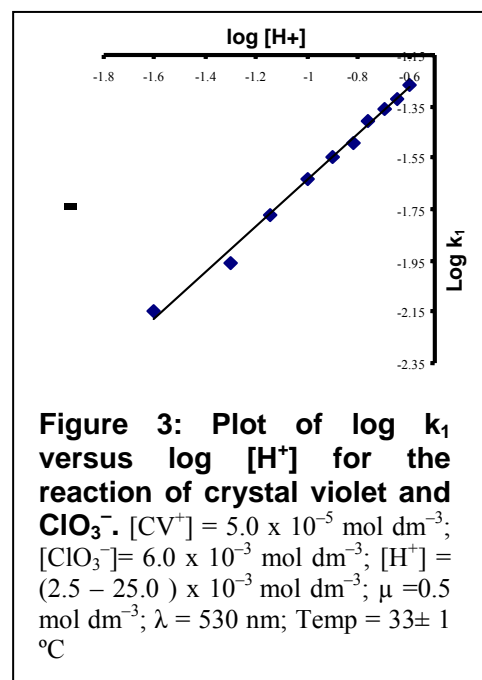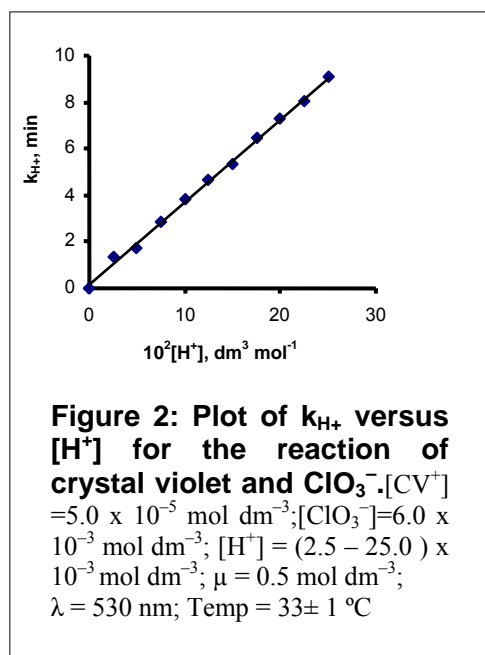
intercept and with a slope of 36.0 dm^6 mol^{-2} min^{-1} **(Figure 2)** The H^+ dependent second order rate constant can thus be presented by equation (3) below:

$$k_{H+} = a[H^+] \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(3)$$

Order of reaction with respect to $[H^+]$ is obtained from the slope of the plot of log k1 versus log $[H^+]$ and was obtained as 0.98 **(Figure 3)**, suggesting a first order in $[H^+]$

In the range of $[H^+]$ used, the overall rate equation is represented by equation (4) below:

$$-d[MG]/dt = a[H^+][CV^+][ClO_3^-] \quad\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(4)$$

log [ClO$_3^-$]

-3.05 -2.85 -2.65 -2.45 -2.25 -2.05 -1.85

-1.25
-1.45
-1.65
-1.85
-2.05
-2.25
-2.45

log k$_1$

Figure 1: Plot of log k$_1$ versus log ClO$_3^-$ for the reaction of crystal violet and ClO$_3^-$. [CV$^+$] = 5.0 x 10^{-5} mol dm^{-3}; [ClO$_3^-$] = (1.5 – 13.5) x 10^{-3} mol dm^{-3}; [H$^+$] = 10 x 10^{-3} mol dm^{-3}; μ = 0.5 mol dm^{-3}; λ = 530 nm; Temp = 32 ± 1 ºC

k$_{H+}$, min

10
8
6
4
2
0

0   10   20   30

10^2[H$^+$], dm^3 mol^{-1}

Figure 2: Plot of k$_{H+}$ versus [H$^+$] for the reaction of crystal violet and ClO$_3^-$. [CV$^+$] =5.0 x 10^{-5} mol dm^{-3};[ClO$_3^-$]=6.0 x 10^{-3} mol dm^{-3}; [H$^+$] = (2.5 – 25.0) x 10^{-3} mol dm^{-3}; μ = 0.5 mol dm^{-3}; λ = 530 nm; Temp = 33± 1 ºC

log [H+]

-1.8 -1.6 -1.4 -1.2 -1 -0.8 -0.6

-1.15
-1.35
-1.55
-1.75
-1.95
-2.15
-2.35

Log k$_1$

Figure 3: Plot of log k$_1$ versus log [H$^+$] for the reaction of crystal violet and ClO$_3^-$. [CV$^+$] = 5.0 x 10^{-5} mol dm^{-3}; [ClO$_3^-$]= 6.0 x 10^{-3} mol dm^{-3}; [H$^+$] = (2.5 – 25.0) x 10^{-3} mol dm^{-3}; μ =0.5 mol dm^{-3}; λ = 530 nm; Temp = 33± 1 ºC

Effect of changes in ionic strength and dielectric constant of reaction medium on rates of reaction

The rate of reaction was neither affected by changes in the ionic strength (**Table 1**) nor the dielectric constant of the reaction medium (**Table 3**). These two observations suggest that one of the reactant ions in the rate determining step is neutral.

Effect of added ions

Added Mg^{2+} and NO$_3^-$ in the range 1 x 10^{-3} ≤ [M^{n+}] ≥ 1 x 10^{-1} mol dm^{-3} catalysed the reaction (**Table 3**). This is possibly due to coulombic bridging.
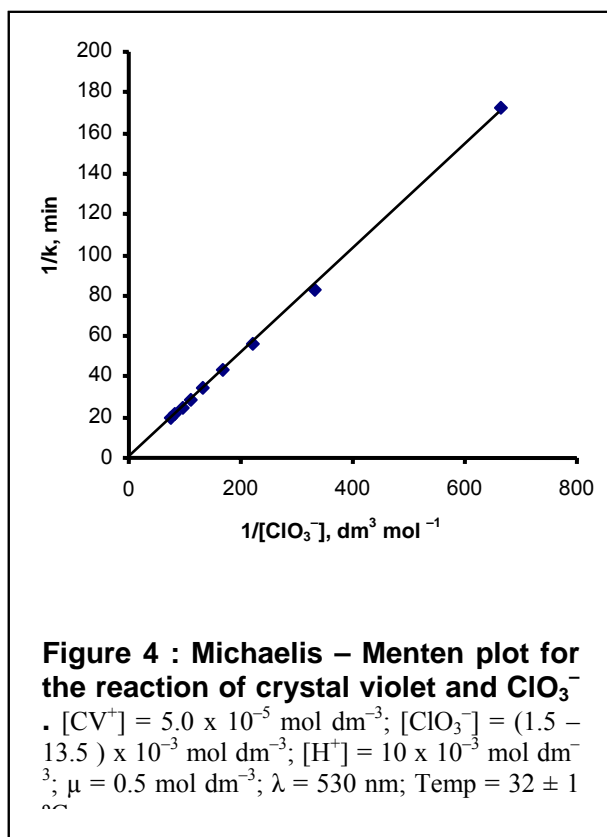
Test for intermediate complex

Michaelis – Menten plot of 1/k$_1$ versus 1/ [ClO$_3^-$] gave a straight line passing through the origin i.e. zero intercept (**Figure 4**), suggesting the absence of intermediate complex. Running the electronic spectrum of the reaction mixture after one minute of mixing, between the wavelengths 480 – 680 nm, after which a similar run was carried out for the crystal violet alone showed that there was no

significant shift in the λ_{max} further confirming the absence of intermediate complex.
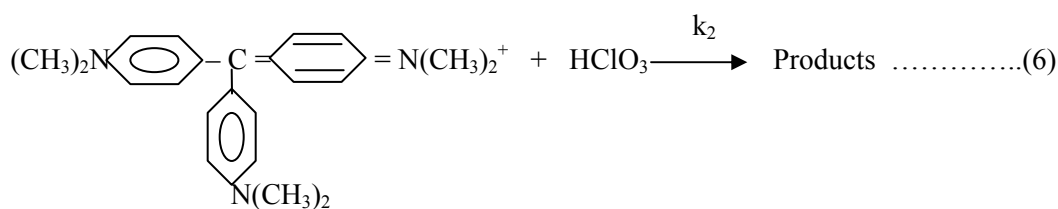
Test for free radicals
Addition of acrylamide (0.001 – 0.015 M) solution to partially oxidized reaction mixture with addition of excess methanol gave no gel indicative of the absence of free radicals in the reaction mixture.

Figure 4 : Michaelis – Menten plot for the reaction of crystal violet and ClO$_3^-$. $[CV^+] = 5.0 \times 10^{-5}$ mol dm^{-3}; $[ClO_3^-] = (1.5 - 13.5) \times 10^{-3}$ mol dm^{-3}; $[H^+] = 10 \times 10^{-3}$ mol dm^{-3}; $\mu = 0.5$ mol dm^{-3}; $\lambda = 530$ nm; Temp = 32 ± 1 °C

The acid dependence in this system showed only the acid dependent pathway, suggesting that the protonated species of the oxidant is the only reactive species.

Possible mechanism consistent with above result is :

$$ClO_3^- + H^+ \underset{}{\overset{K_1}{\rightleftharpoons}} HClO_3 \qquad \text{...........................(5)}$$

$$(CH_3)_2N\!\!-\!\!C = \!\!= N(CH_3)_2^+ + HClO_3 \xrightarrow{k_2} \text{Products} \quad \text{.............(6)}$$

$$N(CH_3)_2$$

$$\text{Rate} = k_2[CV^+][HClO_3] \qquad \text{...(7)}$$

But from equation (5),

$$[HClO_3] = K_1[ClO_3^-][H^+] \qquad \text{...(8)}$$

Substituting equation (8) into equation (7), we get equation (9) below

$$\text{Rate} = k_2K_1[CV^+][ClO_3^-][H^+] \qquad \text{..(9)}$$

TABLE 1. *PSEUDO – FIRST ORDER AND SECOND ORDER RATE CONSTANTS FOR THE REACTION OF CRYSTAL VIOLET AND CLO3– . [CV+] = 5.00 x 10–5 mol dm–3; λ = 530 nm; Temp. 32 ± 1 °C*

10^3 [ClO_3^-], dm³ mol⁻¹	10^3 [H^+], dm³ mol⁻¹	μ dm³ mol⁻¹	$10^2 k_1$, min	k_2, dm³ mol⁻¹ min
1.5	10.0	0.50	0.58	3.86
3.0	10.0	0.50	1.17	3.88
4.5	10.0	0.50	1.76	3.91
6.0	10.0	0.50	2.33	3.88
7.5	10.0	0.50	2.93	3.90
9.0	10.0	0.50	3.47	3.85
10.5	10.0	0.50	4.10	3.90
12.0	10.0	0.50	4.67	3.89
13.5	10.0	0.50	5.24	3.88
6.0	2.5	0.50	0.70	1.67
6.0	5.0	0.50	1.11	1.83
6.0	7.5	0.50	1.69	2.82
6.0	10.0	0.50	2.32	3.87
6.0	12.5	0.50	2.79	4.65
6.0	15.0	0.50	3.21	5.35
6.0	17.5	0.50	3.89	6.48
6.0	20.0	0.50	4.38	7.30
6.0	22.5	0.50	4.81	8.02
6.0	25.0	0.50	5.38	8.97
6.0	10.0	0.10	2.33	3.88
6.0	10.0	0.20	2.32	3.87
6.0	10.0	0.30	2.34	3.90
6.0	10.0	0.40	2.32	3.87
6.0	10.0	0.50	2.31	3.85
6.0	10.0	0.60	2.34	3.90
6.0	10.0	0.70	2.33	3.88
6.0	10.0	0.80	2.33	3.88
6.0	10.0	0.90	2.32	3.87

TABLE 2. *EFFECT OF CHANGES IN THE DIELECTRIC CONSTANT OF THE REACTION MEDIUM ON THE RATE OF REACTION OF CRYSTAL VIOLET AND ClO_3^- [CV+] = 5.00 x 10⁻⁵ mol dm⁻³; [ClO_3^-] = 6.0 x 10⁻³ mol dm⁻³; [H^+] = 10.0 x 10⁻³ mol dm⁻³; μ = 0.50 mol dm⁻³; λ = 530 nm; Temp. 32 ± 1 °C*

D	$10^2 k_1$, min	k_2, dm³ mol⁻¹ min
81.00	2.34	3.90
79.80	2.31	3.85
78.60	2.33	3.88
77.40	2.30	3.83
76.20	2.35	3.92
75.00	2.33	3.88
73.80	2.33	3.88
72.60	2.32	3.87
71.40	2.33	3.88

TABLE 3. *RATE DATA FOR THE EFFECT OF ADDED CATIONS (MG^{2+} AND NO_3^-) ON THE RATE OF REACTION OF CRYSTAL VIOLET AND CLO_3^- $[CV^+]$ = 5.00 x 10^{-5} mol dm^{-3}; $[ClO_3^-]$ = 6.0 x 10^{-3} mol dm^{-3}; $[H^+]$ = 1.0 x 10^{-2} mol dm^{-3}; μ = 0.50 mol dm^{-3}; λ = 530 nm; Temp. 32 ± 1 °C*

Ion	10^3 [ion] dm^3 mol^{-1}	$10^2 k_1$, min	k_2, dm^3 mol^{-1} min
Mg^{2+}	1.00	2.32	3.87
	20.00	2.17	3.62
	30.00	2.08	3.48
	40.00	2.03	3.38
	60.00	1.90	3.17
	80.00	1.73	2.88
	100.00	1.64	2.73
NO$_3^-$	1.00	2.24	3.90
	20.00	2.58	4.30
	30.00	2.72	4.53
	40.00	2.84	4.73
	60.00	3.08	5.13
	80.00	3.32	5.53
	100.00	3.57	5.95

Equation (9) is consistent with equation (4) which is the observed rate law, where $k_2 K_1$ = 'a' = 36 dm^3 mol^{-1} min^{-1}.

The zero salt effect is expected, since in the rate determining step (equation 6) a charged species and a neutral molecule are reacting (17). This assertion is buttressed by the fact that the reaction rate was not affected by changes in the dielectric constant of the reaction medium.

The Michaelis – Menten plot gave no intercept, suggesting the absence of intermediate complex formation. The spectra of the reaction mixture one minute after mixing gave no significant shift from 530 nm (λ_{max}).

The catalysis of added ions on the reaction rate is suggestive of the reaction proceeding through the outer – sphere mechanism (18,19,20).

Based on the above results, it is evident that the reaction is probably operating through the outer – sphere mechanism.

Conclusion

Based on the results obtained, it is evident that one mole of the CV$^+$ was consumed by one mole of ClO$_3^-$, stoichiometrically. The reaction is first order in both [CV$^+$] and [ClO$_3^-$] and the rates of redox reaction showed positive dependence on acid concentrations (in the acid range used). The zero salt effect displayed in the reaction and the lack of effect on the rate constants by changes in the dielectric constant of the reaction medium suggests that one of the reactant species reacting in the rate determining step was neutral. Lack of evidence of intermediate complex formation (from Michaelis- Menten plot analysis) and catalysis due to added ions strongly suggest that the CV$^+$ – ClO$_3^-$ reaction proceeded through the outer sphere pathway.

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