

Original Research Article

Reduction of 3,7-Bis(dimethylamino)phenazothionium Chloride by Benzenethiol in Aqueous Nitric Acid: A Mechanistic Approach

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ABSTRACT

The kinetics of the reduction of 3,7-bis(dimethylamino)phenazothionium chloride (MB^+) by benzenethiol in aqueous solution has been investigated in the acid range $0.3 \leq [H^+] \leq 0.9$ mole dm^{-3} , ionic strength $0.4 \leq \mu \leq 1.0$ mole dm^{-3} ($NaNO_3$) and temperature, $T = 29^\circ C$. The reaction is first order in both [oxidant] and [reductant] and display an inverse order acid dependence with an overall reaction that conforms to the rate law:

$$\frac{-d}{dt} [MB^+] = (Kk_4[H^+]^{-1} + k_6)([MB^+][C_6H_5SH])$$

at $[H^+] = 0.3$ mole dm^{-3} and $\mu = 1.0$ mole dm^{-3} ($NaNO_3$). The rate of the reaction increased with increase in the ionic strength of the reaction medium and also with the decrease in dielectric constant. Added $HCOO^-$ and Cl^- enhanced the rate of the reaction. Spectroscopic investigation did not reveal the formation of any stable reaction intermediate. Test for free radical was positive and a plausible mechanism consistent with these observations has been proposed.

Keywords: 3,7-bis(dimethylamino)phenazothionium chloride, benzenethiol, kinetics, stoichiometry, maximum absorbance (λ_{max}), Michaelis-Menten plot, outersphere.

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1. INTRODUCTION

A recent review of methylene blue (here and thereafter represented by MB^+ for convenience, Fig. 1) by Schirmer *et al.*,^[1] reveals an array of its many uses especially in medicine. It is reported to be the first fully synthetic drug in medicine. In recent years, there was a surge of interest in MB^+ as an anti-malarial agent and as a potential treatment of neurodegenerative disorders such as alzheimer's disease, possibly through its inhibition of the aggregation of tau protein. However, in most of these applications of methylene blue, literature on the mechanism of its reactions is scanty. In the last two decades, it has been shown that, reduction of MB^+ can be achieved with BrO_3^- ^[2], SCN^- ^[3], H_2O_2 ^[4], $\text{UV-H}_2\text{O}_2$ ^[5,6], ascorbic acid^[7-11], Ce(IV) ^[12], thiosulphate^[13], β -mercaptoethanol^[14], photo-decomposition on TiO_2 ^[15,16], photo-reduction by the ureas and thioureas^[17]. This work reports an investigation in to the dynamics of the oxidation of benzenethiol by methylene blue, with the aim of gaining insight and understanding of the mechanistic pathway of methylene blue reaction with benzenethiol.

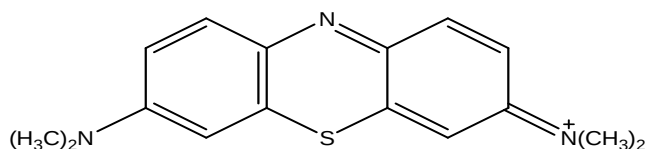


Figure 1: Structure of 3,7-bis(dimethylamino)phenazothionium chloride (methylene blue, MB^+)

2. MATERIALS AND METHODS

All the reagents used were of analytical grade and were used as supplied. Standard solution of methylene blue was prepared by dissolving accurate weight amount of the dye in a known volume of water. The spectrum of the solution was determined over the wavelength range 400 – 700 nm. The λ_{max} which is the wavelength of maximum absorption was found to be 665 nm (Fig. 2). This agrees with the value reported by Busari *et al.*,^[18] Snehalatha *et al.*,^[8] Ukoha^[14], Sarah and Paul^[7], and Mishra *et al.*,^[19]. A stock solution of benzenethiol ($\text{C}_6\text{H}_5\text{SH}$) was prepared by mixing a known volume of $\text{C}_6\text{H}_5\text{SH}$ with little cm^3 of concentrated nitric acid and made up to the mark of volumetric flask with distilled water. Standard solutions of sodium formate, sodium

chloride and sodium nitrate were prepared by dissolving a known weight of respective salts in known volume of distilled water.

2.1 Stoichiometric Studies

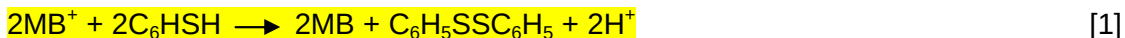
The stoichiometry of the reaction of methylene blue with benzenethiol was determined at $\lambda_{\max} = 665 \text{ nm}$ by spectrophotometric titration using the mole ratio method. The concentration of benzenethiol range was $(4.68 - 93.5) \times 10^{-6} \text{ mole dm}^{-3}$ with a constant concentration of methylene blue $(1.87 \times 10^{-5} \text{ mole dm}^{-3})$, $[\text{H}^+] = 0.3 \text{ mole dm}^{-3}$ and $T = 29^\circ\text{C}$. The absorbance of the solutions was measured at $\lambda_{\max} = 665 \text{ nm}$, the wavelength of maximum absorption, after the reaction has been allowed to go to completion.

2.2 Determination of Order

The rate of reaction was studied by monitoring the decrease in absorbance of the methylene blue at $\lambda_{\max} = 665 \text{ nm}$ using Corning 252 Colorimeter. Kinetic measurements were carried out under pseudo-first order condition with the $[\text{C}_6\text{H}_5\text{SH}]$ in at least 100 - fold excess over $[\text{MB}^+]$ at 29°C . Ionic strength as well as hydrogen ion concentration were maintained constant for each of the runs.

3. RESULTS AND DISCUSSION

The result of the stoichiometry determination for the reduction of methylene blue by benzenethiol shows that one mole of benzenethiol was consumed per mole of methylene blue according to equation 1



Similar stoichiometry have been reported for the reactions between methylene blue with thiosulphate ion^[13], mercaptoacetic acid^[14], L-ascorbic acid^[20], thiourea^[21], and 1-methyl-2-thiourea^[22].

Pseudo-first order plots of $\log (A_t - A_\infty)$ against time (where A_t and A_∞ are the absorbances at time, t and at infinity respectively) were linear to more than 90% extent of the reaction. The linearity of the plots suggests that the reaction is first order with respect to $[\text{MB}^+]$. The order of the reaction with respect to $[\text{C}_6\text{H}_5\text{SH}]$ was determined by plotting $\log k_1$ against $\log [\text{C}_6\text{H}_5\text{SH}]$ from

Table 1. The gradient of the linear graph was about unity. The order with respect to methylene blue is in accord to that which has been reported in the literature^[10,18,21-24].

Table 1: Pseudo-first order and second order rate constant for the reaction of [MB⁺] and [C₆H₅SH] at [MB⁺] = 1.87 x 10⁻⁵ mole dm⁻³, [H⁺] = 0.3 mole dm⁻³, T = 29⁰C, μ = 1.0 mole dm⁻³ and λ_{max} = 665 nm

10 ³ [C ₆ H ₅ SH], mole dm ⁻³	10 ³ k ₁ , s ⁻¹	k ₂ , dm ³ mole ⁻¹ s ⁻¹
1.300	0.77	5.89
1.496	0.86	5.75
1.683	0.99	5.88
1.870	1.08	5.78
2.057	1.19	5.76
2.244	1.28	5.71
2.430	1.37	5.64
2.618	1.56	5.46

Within the hydrogen ion concentration range $0.3 \leq [\text{H}^+] \leq 0.9$ mole dm⁻³ at a constant ionic strength, μ = 1.0 mole dm⁻³ and T = 29⁰C while keeping the [oxidant] and [reductant] constant, the reaction exhibited an inverse acid dependence. The nature of H⁺ dependence in this study, suggests release of proton in a pre-equilibrium step and that the deprotonated form of benzenethiol is non-reactive. This observation is in agreement with those reported for the reaction of this dye with ascorbic acid^[8] but at variance with its reduction with thiol compounds such as mercaptoacetic acid^[14], whose rate constant increases with increase in [H⁺]. The pseudo-first order rate constants, k₁, and the acid dependence second order rate constants k₂, determined are reported in Table 2. Linear plot of k₂ versus [H⁺]⁻¹ produced a straight line with an intercept (Fig. 3), suggesting that the two rate determining steps (equations) are preceded by a rapid deprotonation equilibrium²⁵. Both the deprotonated and the native species are reactive. A slope of 0.495 was obtained with R=0.996, when a linear plot of log k₁ versus log[H⁺] was made (Fig. 4),

an indication that order with respect to deprotonation of benzenethiol is probably one (equation 3). We suspect that other interactions within the reaction medium might have taken place to account for the non-integral value.

Table 2: Pseudo-first order rate constant k_1 and the acid dependence rate constants for the reaction of $[MB^+]$ and $[C_6H_5SH]$ at $[MB^+] = 1.87 \times 10^{-5} \text{ mole dm}^{-3}$, $[C_6H_5SH] = 1.87 \times 10^{-3} \text{ mole dm}^{-3}$, $T = 29^\circ\text{C}$, $\mu = 1.0 \text{ mole dm}^{-3}$ and $\lambda_{\text{max}} = 665 \text{ nm}$

$[H^+]$, mole dm^{-3}	$10^2 k_1$, s^{-1}	k_2 , $\text{dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
0.3	1.081	5.78
0.4	0.964	5.16
0.5	0.847	4.53
0.6	0.773	4.13
0.7	0.724	3.87
0.8	0.679	3.63
0.9	0.625	3.34

The observed first order and second order rate constants (k_1 and k_2 respectively) were determined as a function of ionic strength of reaction medium in the range $0.4 \leq \mu \leq 1.0 \text{ mole dm}^{-3}$ (NaNO_3) and are reported in Table 3. The plot of $\log k_2$ against $\sqrt{\mu}$ (Fig. 5) indicate a positive Debye salt effect. This result suggests an interaction of species carrying same charge signs in the activated complex. According to Snehalatha *et al.*,^[8] reactions between two pairs of ions of like charge are usually accelerated by increasing ionic strength because of the favorable interactions of the activated complex with the denser ionic environment.

Table 3: Pseudo-first order and the ionic strength, μ dependence rate constants for the reaction of $[MB^+]$ and $[C_6H_5SH]$ at $[MB^+] = 1.87 \times 10^{-5} \text{ mole dm}^{-3}$, $[C_6H_5SH] = 1.87 \times 10^{-3} \text{ mole dm}^{-3}$, $T = 29^\circ\text{C}$ and $\lambda_{\text{max}} = 665 \text{ nm}$

μ , mole dm^{-3}	$10^3 k_1$, s^{-1}	k_2 , $\text{dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
0.4	4.47	2.39

0.5	5.39	2.88
0.6	6.34	3.39
0.7	7.44	3.98
0.8	8.36	4.47
0.9	9.16	4.90
1.0	10.81	5.78

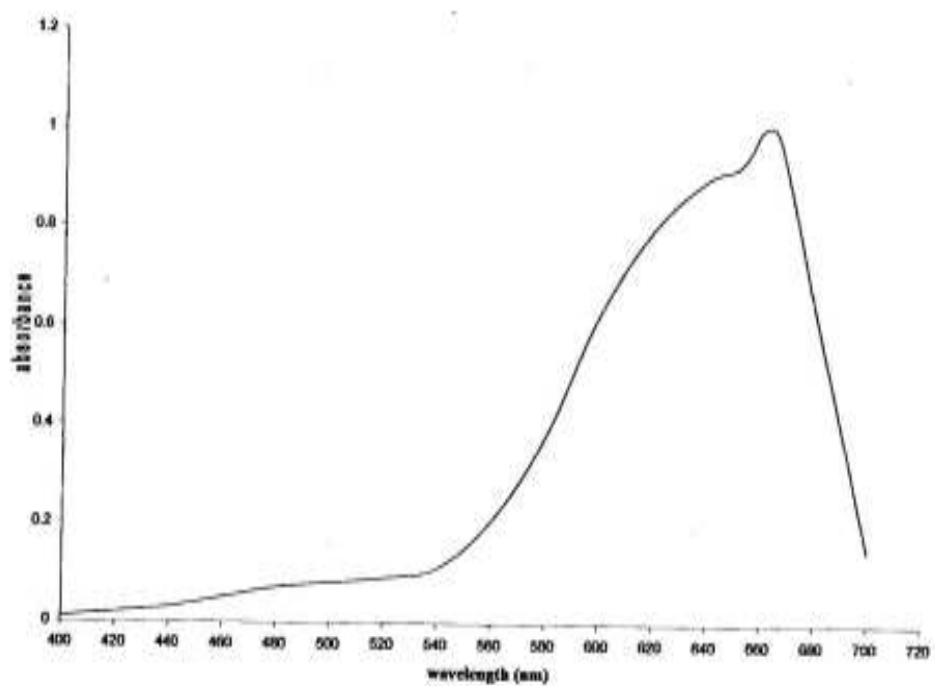


Figure 2: Spectrum of MB⁺

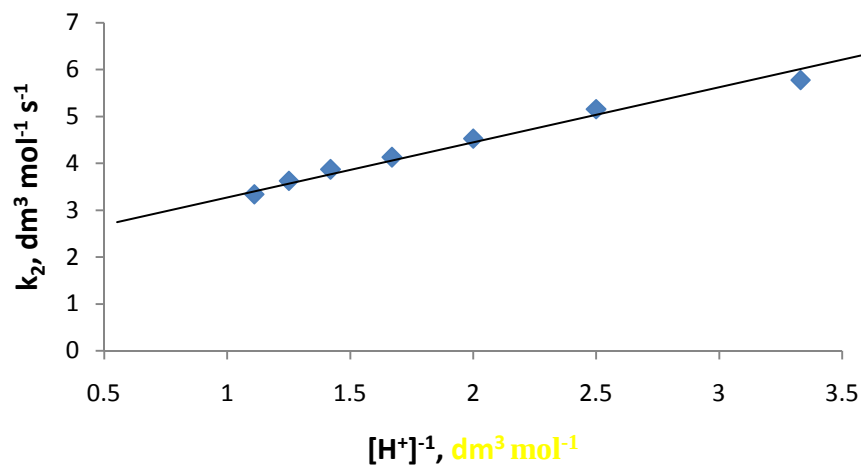


Figure 3: Plot of the dependence of hydrogen ion concentration on second order rate constant of $\text{MB}^+ - \text{C}_6\text{H}_5\text{SH}$ reaction

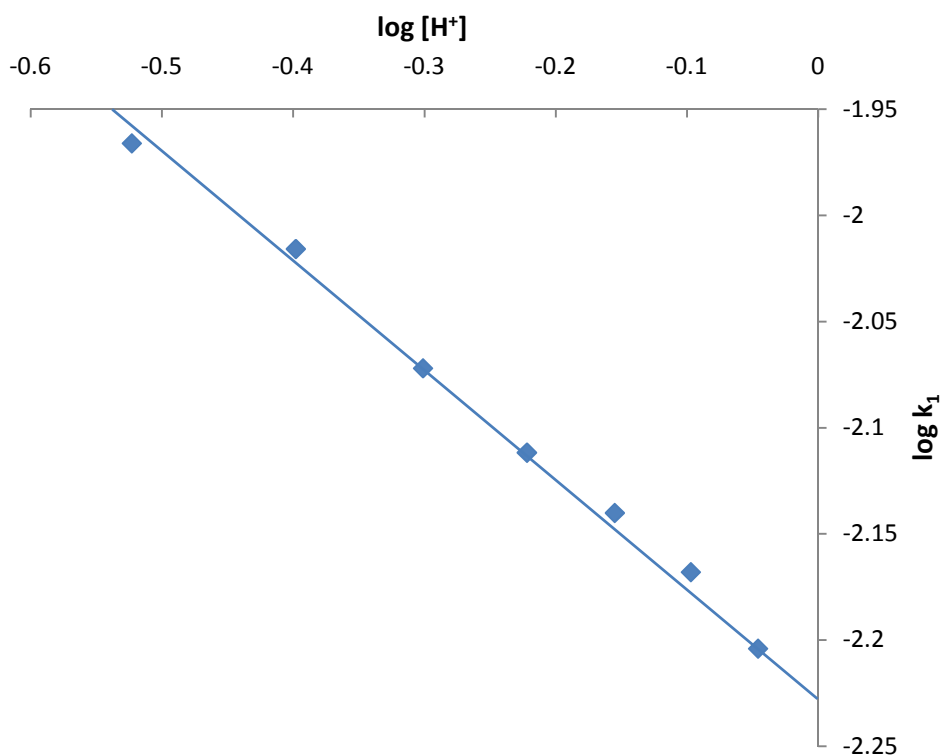


Figure 4: Plot of $\log k_1$ versus $\log [\text{H}^+]$ of $\text{MB}^+ - \text{C}_6\text{H}_5\text{SH}$ reaction

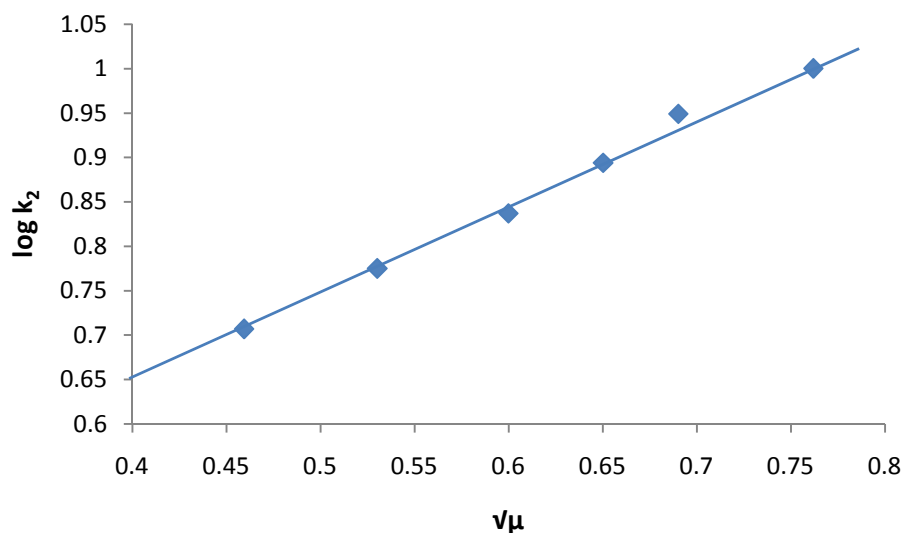


Figure 5: Effect of ionic strength on MB^+ - $\text{C}_6\text{H}_5\text{SH}$ reaction rate

3.1 Effect of Added Anions on Reaction Rate

Table 4 shows increase in reaction rate with increase in concentration of the anions (HCOO^- and Cl^-). Plots of k_2 against [anions] for this reaction were found to be linear (Figs. 6 & 7).. Ion catalysis of reaction rate has been reported as being characteristic of the outersphere reaction mechanism because of the possibility of the intervention of these ions in the activated complex^[26]. In this investigation the anions HCOO^- and Cl^- were found to catalyzed the reaction. This suggests that the coordination integrity of the reactants are intact prior to and during the electron transfer process implying the possibility of an outersphere reaction mechanism.

3.2 Effect of Change in Dielectric Constant on Reaction Rate

The effect of change in dielectric constant (D) on the rate of the MB^+ - $[\text{C}_6\text{H}_5\text{SH}]$ reaction was investigated at constant [oxidant], [reductant], μ and temperature. This was done by varying the % of acetone in acetone-water mixture as shown by equation 2. The decrease in rate

constants with increase in D of reaction medium is presented in Table 5. Observation of this nature is consistent with interaction of species of unlike charges or charged – neutral molecule in the rate determining step. This assertion conforms with equations 4 and 6. However, this is in contrast to the increase in reaction rate obtained upon increase in ionic strength of reaction medium. Therefore, we suspect that other interaction could be taking place in the reaction medium to account for the latter observation.

Table 4: The Effect of Added HCOO^- and Cl^- on the Rate of the Reaction of Methylene Blue and Benzenethiol at $[\text{MB}^+] = 1.8 \times 10^{-5} \text{ mole dm}^{-3}$, $[\text{C}_6\text{H}_5\text{SH}] = 1.87 \times 10^{-3} \text{ mole dm}^{-3}$, $\mu = 1.0 \text{ mole dm}^{-3}$, $[\text{H}^+] = 0.3 \text{ mole dm}^{-3}$, $T = 29^\circ\text{C}$ and $\lambda_{\text{max}} = 665 \text{ nm}$

[HCOO⁻]		
$10^3[\text{HCOO}^-], \text{mole dm}^{-3}$	$10^2k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mole}^{-1} \text{s}^{-1}$
20	1.38	7.40
40	1.43	7.65
80	1.60	8.54
120	1.68	8.99
180	1.81	9.67
200	1.92	10.27
300	2.10	11.23

[Cl⁻]		
$10^3[\text{Cl}^-], \text{mol dm}^{-3}$	$10^2k_1, \text{s}^{-1}$	$k_2, \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$
20	1.30	6.97
40	1.37	7.31
80	1.46	7.80
120	1.57	8.39
180	1.69	9.06
200	1.75	9.36
300	2.98	10.59

Table 5: The Effect of Variation of Dielectric Constant on the Rate Constants of MB⁺ - C₆H₅SH Reaction at [MB⁺] = 1.8 × 10⁻⁵ mole drn⁻³, [C₆H₅SH] = 1.87 × 10⁻³ mole drn⁻³, μ = 1.0 mole drn⁻³, [H⁺] = 0.3 mole drn⁻³, T = 29⁰C and λ_{max} = 665 nm

D	% acetone	10 ² k ₁ , s ⁻¹	k ₂ , dm ³ mole ⁻¹ s ⁻¹
81.0	0	1.197	5.79
80.4	1	1.244	6.65
79.8	2	1.403	7.54
79.2	3	1.533	8.20
78.6	4	1.621	8.67
78.0	5	1.733	9.27
77.4	6	1.907	10.20
76.8	7	2.019	10.80
76.2	8	2.132	11.40
75.6	9	2.289	12.20

$$D_{\text{reaction medium}} = \frac{D_{H_2O} \times V_{H_2O} + D_{\text{acetone}} \times V_{\text{acetone}}}{\text{total volume of solution}} \quad [2]$$

where D_{H_2O} , V_{H_2O} , D_{acetone} and V_{acetone} are dielectric constant of water, volume of water, dielectric constant of acetone and volume of acetone respectively.

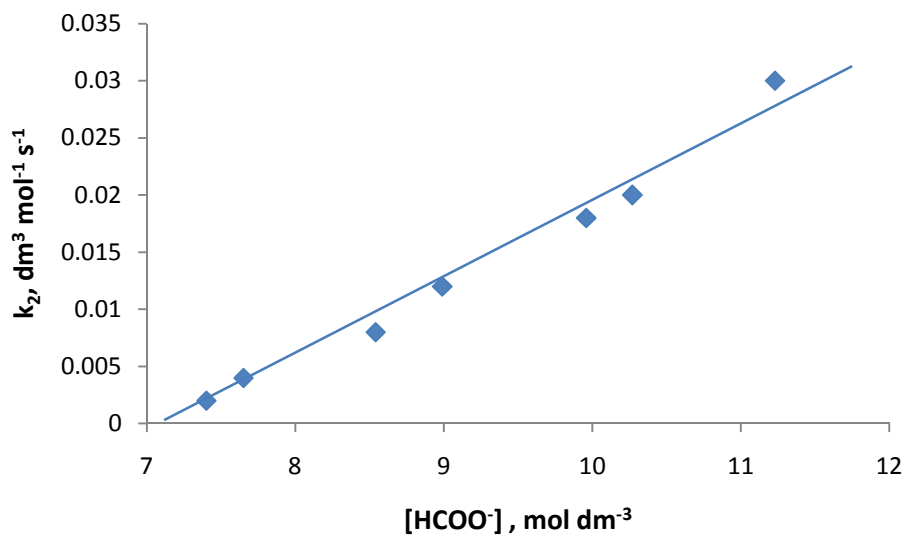


Figure 6: Plot of $[\text{HCOO}^-]$ dependence on second order rate constants of $\text{MB}^+ - \text{C}_6\text{H}_5\text{SH}$ reaction

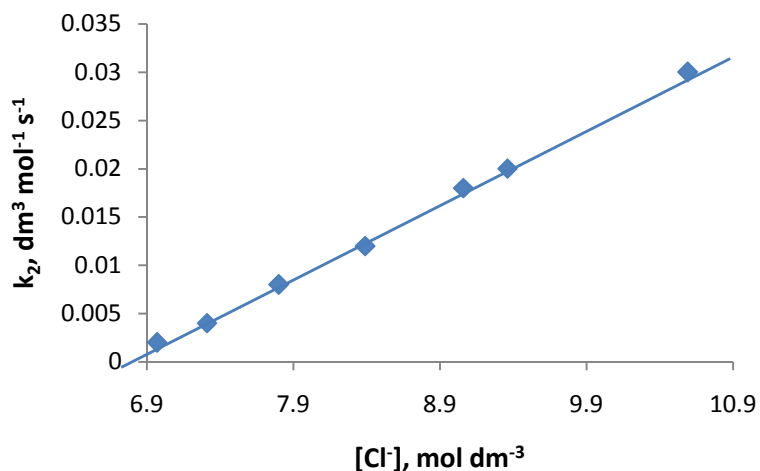


Figure 7: Plot of $[\text{Cl}^-]$ dependence on second order rate constants of $\text{MB}^+ - \text{C}_6\text{H}_5\text{SH}$ reaction

A linear plot of $1/k_1$ against $1/[\text{C}_6\text{H}_5\text{SH}]$, also called Michaelis- Menten plot (Fig.8) which passed through the origin showed that there was no binuclear complex formation of significant stability during the course of the reaction, affirming that an outersphere mechanism for this reaction is probable.

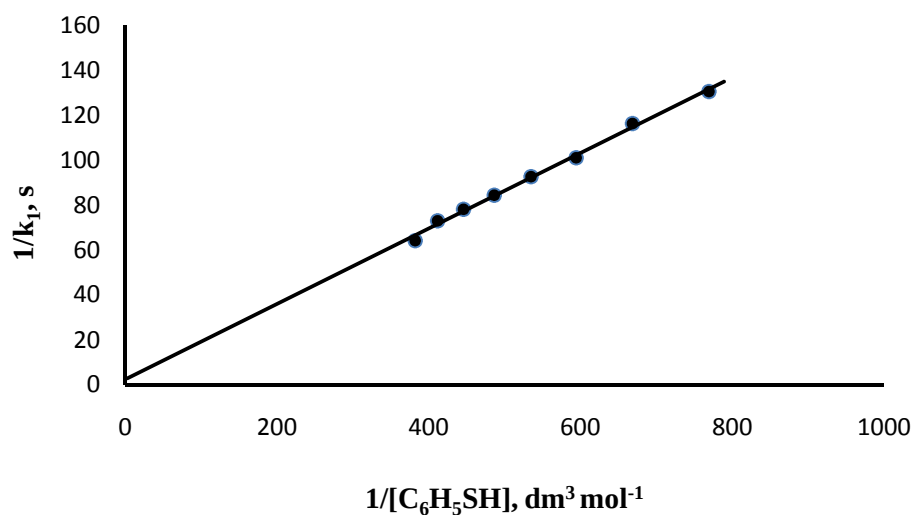


Figure 8: Plot of $1/k_1$ versus $1/C_6H_5SH$ of $MB^+ - C_6H_5SH$ reaction

3.3 Reaction Mechanism

Taking recourse to the above findings, the following possible mechanism is proposed:



From equations 4 and 6 which are the rate determining steps, the rate law can be written as

$$\frac{-d}{dt} [MB^+] = k_4 [MB^+] [C_6H_5S^-] + k_6 [MB^+] [C_6H_5SH] \quad [8]$$

and from equation 3

$$[C_6H_5S^-] = \frac{K[C_6H_5SH]}{[H^+]} \quad [9]$$

Making the substitution of equation 9 into equation 8, the rate of the $MB^+ - C_6H_5SH$ reaction can be represented by the expression

$$\frac{-d}{dt} [MB^+] = \frac{k_4 K [MB^+] [C_6H_5SH]}{[H^+]} + k_6 [MB^+] [C_6H_5SH] \quad [10]$$

$$\frac{-d}{dt} [MB^+] = k_4 K [MB^+] [C_6H_5SH] [H^+]^{-1} + k_6 [MB^+] [C_6H_5SH] \quad [11]$$

$$\text{Therefore, } \frac{-d}{dt} [MB^+] = (Kk_4 [H^+]^{-1} + k_6) [MB^+] [C_6H_5SH] \quad [12]$$

Investigation of intermediate complex formation gave a negative result, suggesting that such species is not important in the reaction. Free radicals test carried out by adding about 1g of acrylamide to a partially oxidized mixture in excess methanol revealed some suspension, an indication of formation of some free radicals in the reaction medium. This is consistent with the proposed mechanism (equations 5 and 6). It is worth noting, however, that the proposed formation of $[MB^+, C_6H_5S^-]$, an ion-pair in one of the pre-electron transfer equilibrium step did not lead to a shift in the λ_{max} of 665 nm for methylene blue. This suggests that MB^+ and this ion-pair absorb at the same λ_{max} . It is therefore proposed, based on the above results that, the reaction of methylene blue with benzenethiol occurs by the outersphere mechanism.

4. CONCLUSION

The kinetics and the mechanism of electron transfer reaction of methylene blue with the benzenethiol have been investigated in acidic nitrate. The reaction displayed a stoichiometry of 1:1. It shows inverse first order hydrogen ion dependence and is catalyzed by added anion. The rate of the reaction increased with increasing ionic strength and decreasing dielectric constant respectively. The test for radicals was positive. The reaction is therefore believed to occur by the outersphere mechanism and plausible mechanism consistent with these observations has been proposed.

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COMPETING INTERESTS

We Have No Conflicting Interest

REFERENCES

1. Schirmer, R. H., Adler, H., Pickhardt, M. and Mandelkow, E. "Lest we forget you - methylene blue . . ." *Neurobiology of Aging*. 2011; 32(12): 2325.e7 – 2325.e16
2. Iyun, J.F. and Asala, M. Mechanism of bromate oxidation of 3,7-bis (dimethylamino) phenazothio-5-ium chloride. A paper presented at the 18th Annual Conference of the Chemical Society of Nigeria, Kano. 1994; 29th May – 2nd June.
3. Pande, S., Ghosh, S.K., Nath, S., Praharaj, S. Jana, S., Panigrahi, S., Basu, S. and Pal, T.. Reduction of methylene blue by thiocyanate: kinetics and thermodynamics aspects. *Journal of Colloid and Interface Science*. 2006; 299(1):421-427
4. Salem, A. and El-Maazawi, M.S. Kinetics and mechanism of colour removal of methylene blue with hydrogen peroxide catalyzed by some supported alumina surfaces. *Chemosphere*. 2000; 41:1173 – 1180.
5. Banat, F., Al Ashesh, S., Al Rawashedeh, M. and Nusair, M. Photodegradation of methylene blue by the UV/H₂O₂ and UV/acetone oxidation processes. *Desalination*. 2005; 181:225 – 232.
6. Jian-xiano, L.V., Ying, C., Guo-hong, X., Ling-yun Z. and Su-Fen. Decolouration of methylene blue simulated wastewater using a UV-H₂O₂ combined system. *Journal of Water Reuse and Desalination*. 2011; 1(1): 45 – 51.
7. Sarah, M. and Paul, J.O. Kinetics of methylene blue reduction by ascorbic acid. *Journal of Chemical Education*. 1999; 76(7). 970 - 973.
8. Snehathatha, T., Rajanna, K.C. and Saiprakash, P.K. Methylene blue – ascorbic acid – an undergraduate experiment in kinetics. *Journal of Chemical Education*. 1997; 74(2): 228 - 233.
9. Pietkiewicz-Graczyk, A., Impert, O., Katafias, A. and Kita, P. Reactivity of two protolytic forms of methylene blue in reaction with ascorbic acid. *Polish Journal of Chemistry*. 2003; 77(4): 475 – 480.

10. Khan, M.N. and Sarwar A. The influence of transition metal ions on the kinetics of ascorbic acid oxidation by methylene blue in strongly acidic media. *Turk Journal of Chemistry*. 2001; 25: 433 - 400.
11. Tawani, B.B. Dehydrogenation studies of ascorbic acid with methylene blue in the presence of copper hexacyanoferrate(III) complex and light. *Bulletin of the Chemists and Technologists of Macedonia*. 2005; 24(2): 109 – 115.
12. Katafias, A., Kita, P., Wrzeszez, G. and Mills, A. Kinetics of the methylene blue oxidation by cerium(IV) in sulphuric acid solutions. *Transition Metal Chemistry*. 2006; 32: 31 – 37.
13. Bugaje, B.M. and Iyun, J.F. Methylene blue oxidation of thiosulphate ion: kinetics and mechanism. *ChemClass Journal*. 2008; 5:120 – 125.
14. Ukoha P.O. Kinetics and mechanism of some redox reactions of μ -oxo-bridged iron III complex ion $[(\text{Fe}(\text{HEDTA})_2\text{O})]^{2-}$ and of some oxyanions and thiols. *Ph.D. Thesis*, 1999; Chemistry Department, A.B.U, Zaria.
15. Mills, A. and Wang, J. Photobleaching of methylene blue sensitized by TiO_2 : an ambiguous system?. *Journal of Photochemistry and Photobiology. A.Chemistry*. 1999; 127(1): 123 – 134.
16. Randorn, C., Wongnawab, S. and, Boonsin, P. Bleaching of methylene blue by hydrated titanium dioxide. *ScienceAsia*. 2004; 30:149 – 156.
17. Khalid, Z. Studies of the photochemical kinetics of methylene blue with reductants. *Ph.D thesis*. 2001; Department of Chemistry. University of Karachi, Karachi, Pakistan.
18. Busari A., Iyun, J.F. and Idris, S.O. Kinetics and mechanism of silver(I) catalysed oxidation of 3,7-bis (dimethylamino) phenazothionium chloride (methylene blue) by peroxydisulphate ion in aqueous nitric acid. *International Journal of Pure and Applied Chemistry*, 2008; 2(1): 10-16.
19. Mishra, R., Mukhopadhyay, S. and Banerjee, R. Reduction mechanism of a coordinated superoxide by thiols in acidic media. *Dalton Transaction*. 2010; 39: 2692-2696.
20. Ukoha, P.O. and Iyun, J.F. Kinetic and mechanisms of oxidation of L-ascorbic acid by 3,7-bis (dimethylamino) phenazothionium chloride in aqueous acid media. *Journal of Chemical Society of Nigeria*, 2000; 25: 39 - 42.
21. Osunlaja, A.A., Idris, S.O. and Iyun, J.F. Mechanism of the reduction of methylene blue by thiourea in aqueous acidic medium. *International Journal of ChemTech Research*. 2012a; 4(2): 609 – 617.
22. Osunlaja, A.A., Idris, S.O. and Iyun, J.F. Kinetic analysis of the oxidation of 1-methyl-2-thiourea by methylene blue in acid medium. *Der Chemica Sinica*. 2012b; 3(6): 1428 – 1437.
23. Adamcikova, A., Pavlikova, K. and Sevcik, P. The decay of methylene blue in alkaline solution. *Reaction Kinetics and Catalysis Letters*. 2000; 69(1): 91 – 94.
24. Tabbari, M.A. and Jamal, M.M. A kinetic study of the discolouration of methylene blue by Na_2SO_3 , comparison with NaOH . *Journal of the University of Chemical Technology and Metallurgy*. 2012; 47(3): 275 – 282.

25. Gupta, K.S. and Gupta Y.K. Hydrogen ion dependence of reaction rates and mechanism. *Journal of Chemical Education*. 1984; 61(11):972-977.
26. Adegite, A., Iyem, J. F., and Ojo, J. F. Kinetics and Mechanism of electron transfer reactions between Uranium (III) and some ruthenium (III) amine complexes. *J. Chem. Soc. Dalton*. 1977; 115-117.