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Kinetic analysis of the oxidation of 1-methyl-2-thiourea by methylene blue in acid medium

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ABSTRACT

The kinetics of the oxidation of 1-methyl-2-thiourea (MTU) by methylene blue (MB^+) in acid medium has been investigated. The oxidation is first order in both oxidant and reductant and the reaction rate showed dependence on acid concentration. The reaction obeys the rate law:

$$-d[MB+]/dt = (a + b\,[H^+]^{0.5})[MB^+][MTU]$$

where $a = 4.19 \times 10^{-2}$ *mol* dm^{-3} s^{-1}, $b = 4.52 \times 10^{-1}$ dm^6 mol^{-2} s^{-1} *at* $29.0 \pm 0.5\,^{o}C$, $[H^+] = 0.20$ *mol* dm^{-3}, *0.5 mol* dm^{-3}*(NaCl) ionic strength and* $\lambda_{max} = 660$ *nm.*

The rate of reaction increased with increase in ionic strength and decreased as the dielectric constant of the medium increased. Added cations catalyzed the reaction. The result of spectroscopic and kinetic investigation did not indicate intermediate complex formation in the course of the reaction. Plausible mechanism for the reaction has been proposed in line with the outer-sphere reaction pathway.

Key words: Kinetics, reaction mechanisms, stoichiometry, catalysis, 1-methyl-2-thiourea, methylene blue.

INTRODUCTION

Previous studies on the simplest thiocarbonyl, thiourea, had shown that the C=S double bond is extremely polar , much more so than the corresponding C=O double bond due to the mismatch of size between the carbon and sulfur atoms which results in an incomplete ð-bond overlap [1]. Thus a permanent negative dipole resides on the sulfur atom, making it extremely vulnerable to electrophilic attack [2]. We have previously investigated the reduction of methylene blue (MB^+) by thiourea [3]. In this paper, we report on the oxidation of a substituted thiourea: 1-methyl-2-thiourea by methylene blue. 1-methyl-2-thiourea, also called N-methylthiourea, is a proximate toxicant and a ring cleavage metabolite [4]. It is used as a convenient reagent for the hydrogenolysis of bicyclic endoperoxide in combination with polystyrene [5].

MATERIALS AND METHODS

All materials were of analytical grade and were used without further purification. Stock solutions of methylene blue and 1-methyl-2-thiourea, hereafter referred to as MB^+ and MTU respectively, were prepared by dissolving a known amount of each reagent and making up to a known solution volume with distilled water. The λ_{max} (660 nm) of MB^+

was determined by running the electronic spectrum of the solution of MB^+ in the wavelength range 400-700 nm. Standard hydrochloric acid was used as a source of hydrogen ions while the ionic strength of the medium was maintained constant at 0.50 mol dm^{-3} using sodium chloride. Standard salt solutions were made by dissolving known amounts of $MgCl_2$, KCl, $NaNO_3$ and CH_3COONa in a given volume of distilled water and were used to probe the effect of cations and anions respectively on the reaction rate.

Stoichiometry

The stoichiometries of the reactions were determined at λ= 660 nm characteristic of MB^+ by spectrophotometric titration using the mole ratio method. Solutions containing known concentrations of MB^+ and varying concentrations of MTU (0.40 – 46) x 10^{-5} mol dm^{-3} were reacted at $[H^+]$ = 0.2 mol dm^{-3}, μ = 0.5 mol dm^{-3} (NaCl) and T = 29.0 ± 0.5°C. The absorbance of the reaction mixture was measured until the completion of the reaction was indicated by a constant absorbance value. A plot of absorbance versus [MTU] was made from which the stoichiometry was determined.

Kinetics

The rate of reactions were determined under the pseudo-first order conditions with [MTU] in excess by monitoring the decrease in the absorbance of $[MB^+]$ at λ = 660 nm, T= 29.0 ± 0.5°C, $[H^+]$ = 0.20 mol dm^{-3} and 0.50 mol dm^{-3}(NaCl) ionic strength, using a Spectronic 20 colorimeter. The MTU and the products of the reaction had no significant absorbance at this wavelength. The pseudo-first order rate constants k_1 were obtained from a plot log $(A_t - A_\infty)$ versus time (where A_t and A_∞ are the absorbance at time t and infinity respectively).The second order rate constants were determined as k_1/[MTU].

The effect of $[H^+]$ on the rate

The effect of $[H^+]$ on the reaction rate was studied using hydrochloric acid in the range (6 – 70) x 10^{-2} mol dm^{-3} while the concentration of MB^+ and MTU were constant at μ = 0.50 mol dm^{-3} (NaCl) and T = 29.0 ± 0.5^0C. The results are presented in Table I.

The effect of ionic strength

The effect of ionic strength on the rate of the reaction was investigated in the range μ = 0.30 - 1.00 mol dm^{-3} (NaCl) while the concentration of other reagents were kept constant. The results are presented in Table I.

Effect of changes in the dielectric constant

The effect of medium dielectric constant on the rate of reaction was investigated by using a binary solvent mixture of water and acetone (2-10%) (Table III). A plot of log k_1 against $\frac{1}{D}$ gave the relationship between the second order rate constant and the total dielectric constant of the reaction medium.

Effect of added ions

At constant concentration of all other reactants, the effect of added ions (Mg^{2+}, K^+ , NO_3^- or CH_3COO^-) on the rates of the reactions was investigated in the range (3.0 – 16.0) x 10^{-2} mol dm^{-3} (Table II).

Test for formation of intermediate complex

Spectroscopic test was carried out by comparing the electronic spectrum of the reaction mixture one minute after the start of the reaction with that of the final product within a wavelength of 400 - 700 nm.

Michaelis-Menten's plots of $1/k_1$ versus 1/ [MTU] were also made (Figure IV).

Test for free radicals

The presence of free radicals were tested for by adding acrylamide to a partially oxidized reaction mixtures followed by addition of a large excess of methanol. Control experiment was carried out by adding acrylamide to solutions of MB^+ and MTU separately at the stated conditions of $[H^+]$, μ and temperature in Table I. Gel formation indicates presence of free radicals.

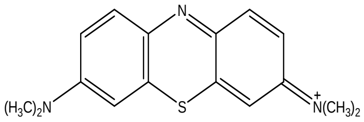
Product analysis

Likely products tested for were leucomethylene blue (the reduced form of MB^+) and SO_4^{2-}**.** Mixtures of glucose/NaOH solution were added to the product in order to oxidize back to blue the colourless solution at the end of the reaction. The presence of SO_4^{2-} was qualitatively tested for with dilute acidified solution of $BaCl_2$. Urea derivatives were tested for by the addition of few drops of dilute alkaline $CuSO_4$ solution.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

The stoichiometry of the reaction between the methylene blue and 1-methyl-2-thiourea was found to be in the ratio 1:1, the overall reaction is given by equation 1:



$+ CH_3NH(NH_2)C{=}S + 5H_2O \rightarrow SO_4^{2-} + CH_3NH(NH_2)C{=}O + 3H^+ + MBH$ ….1

Where MBH is the reduced methylene blue. Similar mole ratio was reported for the reaction with thiourea [3] and thiosulphate [6].

Kinetics

The pseudo-first order plots of log (A_∞ -A_t) versus time were linear for about 80% of the reaction. The linearity of these plots indicates that this reaction is first order with respect to [MB^+]. Plots of log k_1 versus log [MTU] gave a gradient of 1.00 showing that the reaction is also first order with respect to [MTU]. Thus the rate law for the reaction is

$$-\frac{d[MB^+]}{dt} = k_2[MB^+][MTU] \qquad …..2$$

at [H^+] = 0.2 mol dm^{-3} and T = 24 ±1.0°C, and k_2 = 13.22 ± 0.003 $dm^3\ mol^{-1}\ s^{-1}$

A similar order has been reported by [1].

Table I: Pseudo-first order and second order rate constants for the reduction of MB^+ by MTU.
[MB^+] = 8 x 10^{-6} mol dm^{-3}, λ_{max} = 660 nm and T = 29.0 ±0.5°C

10^3[MTU] (mol dm^{-3})	10^2[H^+] (mol dm^{-3})	μ (mol dm^{-3})	10^3k_1 (s^{-1})	10^2k_2 ($dm^3\ mol^{-1}\ s^{-1}$)
8	20	0.5	1.04	12.95
16	20	0.5	2.12	13.24
24	20	0.5	3.22	13.21
32	20	0.5	4.15	13.00
40	20	0.5	5.30	13.24
48	20	0.5	6.45	13.43
56	20	0.5	7.37	13.16
64	20	0.5	8.52	13.33
72	20	0.5	9.67	13.43
64	6	0.5	4.84	7.56
64	8	0.5	5.47	8.55
64	10	0.5	6.08	9.50
64	20	0.5	8.52	13.31
64	30	0.5	10.59	16.55
64	40	0.5	12.21	19.08
64	50	0.5	15.89	24.83
64	60	0.5	22.57	35.27
64	20	0.3	7.37	11.52
64	20	0.4	8.06	12.59
64	20	0.5	8.52	13.31
64	20	0.6	9.21	14.39
64	20	0.7	9.90	15.47
64	20	0.8	10.36	16.19
64	20	0.9	10.70	16.63
64	20	1.0	11.28	17.63

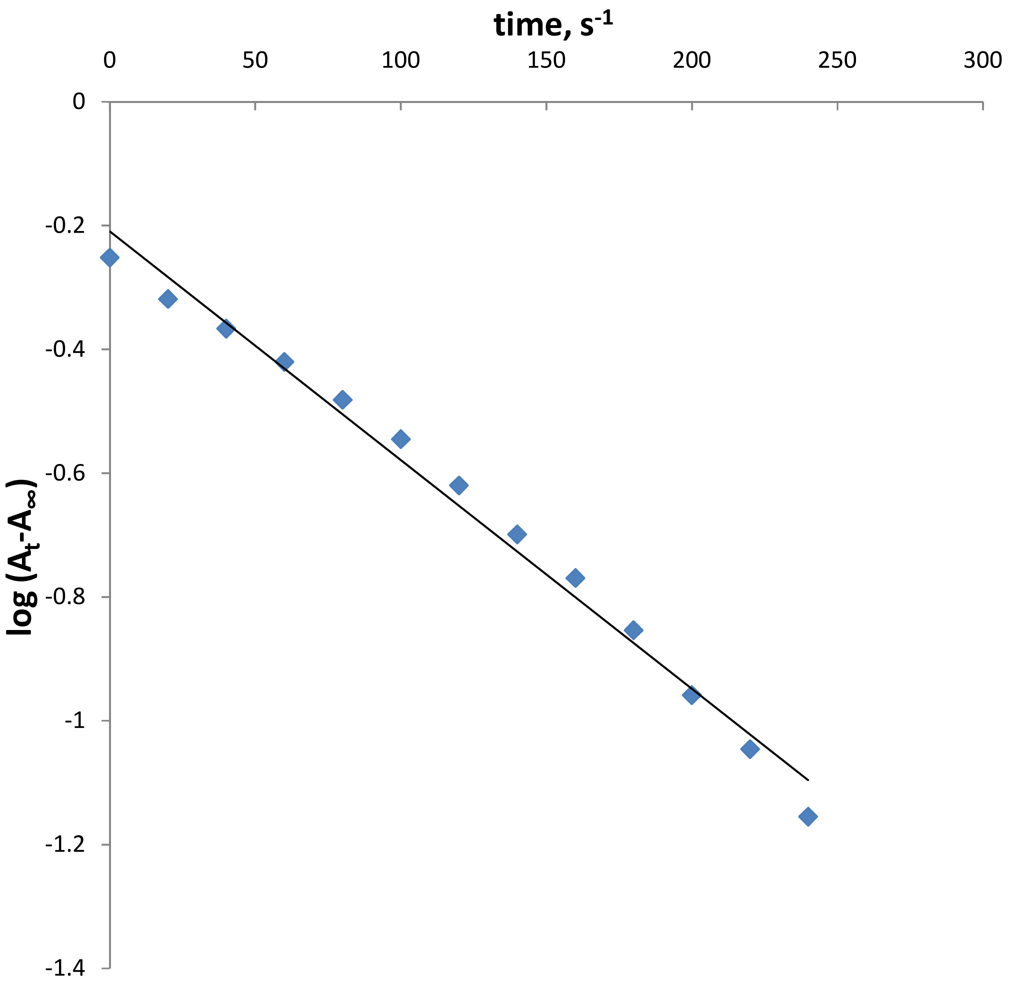


Figure I: Typical Pseudo-first order plot for the redox reaction of MB^+ with MTU
$[MB^+]$ = 8 x 10^{-6} mol dm^{-3}, [MTU] = (8.0 – 72.0) x 10^{-3} mol dm^{-3}
$[H^+]$ = 0.20 mol dm^{-3}, μ = 0.50 mol dm^{-3} (NaCl), T = 29.0 ±0.5°C and λ_{max} = 660 nm

Acid dependence

At constant [MTU] and $[MB^+]$ and $[H^+]$ = (6 – 70) x 10^{-2} mol dm^{-3} (Table I), the rate of reaction is strongly catalyzed by acid with a fractional order of 0.5 from a plot of log $[H^+]$ against log k_1. Equation 1 show that acid is not a reactant, but a product. The catalytic effect of acid must be through the formation of a reactive intermediate either with MB^+ or with MTU. Plots of k_2 versus $[H^+]$ were also linear with a slope of 4.52 x 10^{-1} and intercept of 4.19 x 10^{-3}. Hence the acid dependence of the rate constant for the reaction could be given as

$k_2 = a + b\,[H^+]^{0.5}$ …..3

and the rate of the reaction as a function of $[H^+]$ can now be written as:

$-d[MB+]/dt = (a + b\,[H^+]^{0.5})[MB^+][MTU]$ -----4

where a = 4.19 x 10^{-3} mol dm^{-3} s^{-1}, b = 4.52 x 10^{-1} dm^6 mol^{-2} s^{-1}

From the result, it is proposed that the observed acid catalysis may be due to the successive protonation of methylene blue and this seem to agree with similar findings reported for reduction of methylene blue by bromate ion [7], β-mercaptoethanol [8], thiosulphate ion [6] and permanganate ion and thiourea [9,3].

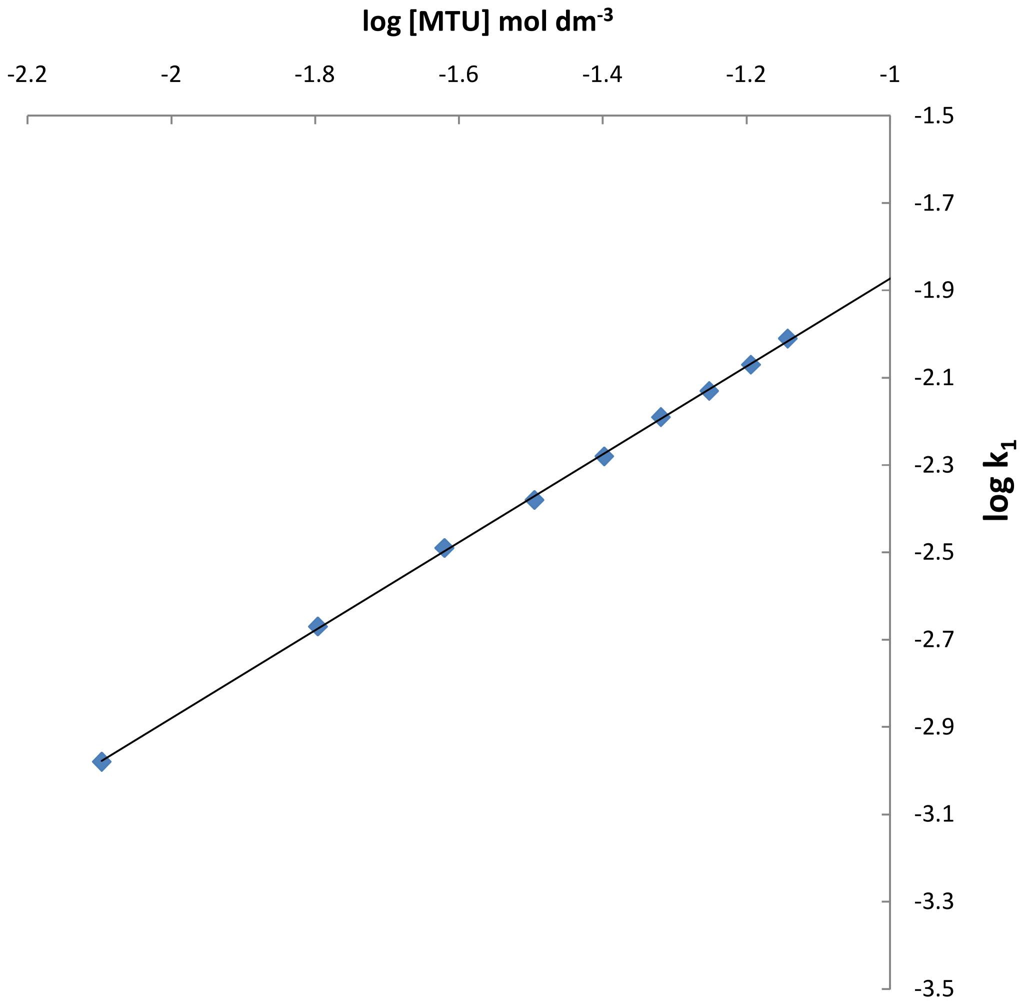


Figure II: Plot of log k_1 versus log [MTU] for the redox reaction of MB^+ with MTU
$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, [MTU] = (8.0 – 72.0) x 10^{-3} mol dm^{-3}
$[H^+] = 0.20$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3} (NaCl), T = 29.0 ±0.5°C and $\lambda_{max} = 660$ nm

Cation and anion dependence

Added cations led to enhancement of the rate of reaction while anions inhibited the rate of reaction. This is suggestive of the outer–sphere mechanism operating in this reaction. However, it was observed that the enhancement of the rate is in the order of k (Mg^{2+}) > k (K^+).

Effect of changes in ionic strength and total dielectric constant of the reaction medium

The results presented in Table1, show that the rate constant increases with increase in ionic strength suggesting a positive Bronsted – Debye salt effect. Plot of log k_2 versus $\sqrt{\mu}$ for the reaction gave a slope of 0.402 (Figure III). This positive salt effect suggests an interaction of species carrying same charge signs in the activated complex. 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 [10]. This fact is also buttressed by the observed effect of varying the dielectric constant, D, of the reaction medium (Table III) on the rate of reaction. These results are similar to those we observed for reduction of methylene blue by thiourea [3].

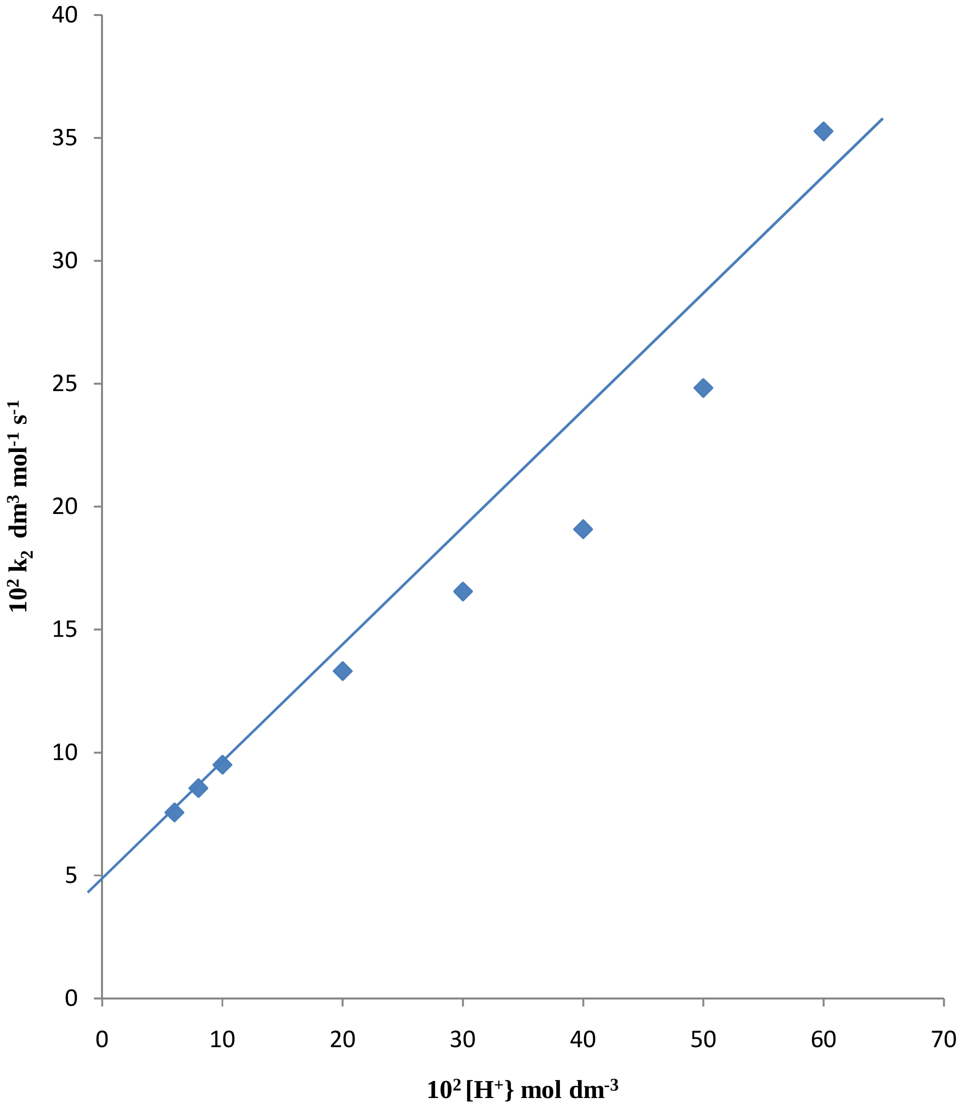


Figure III: Plot of k_2 versus [H^+] for the redox reaction of MB^+ and MTU
[MB^+] = 8 x 10^{-6} mol dm^{-3}; [MTU] = 64 x 10^{-3} mol dm^{-3} [H^+] = (6-60) x 10^{-2} mol dm^{-3},
μ = 0.5 mol dm^{-3} (NaCl), T = 29.0 ± 0.5 °C and λ_{max} = 660 nm

Spectroscopic evidence of intermediate
The results of the spectroscopic studies indicate no significant shifts from the absorption maxima of λ_{max} = 660 nm. This suggests the absence of the formation of an intermediate complex in the reaction. Alternatively, if any such intermediate was formed, it must have a small formation constant.

Plots of $1/k_1$ versus 1/[MTU] were linear with zero intercept (Figure IV). Both results suggest the absence of intermediate complex formation prior to electron transfer in the reactions.

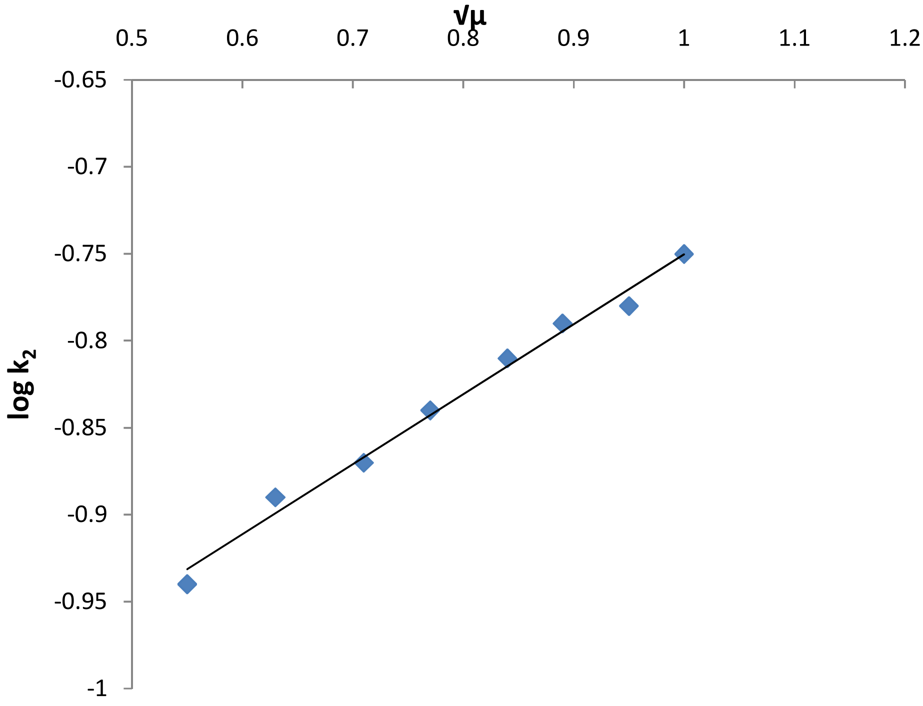


Figure IV: log k_2 versus √μ for the redox reaction of MB^+ and MTU
$[MB^+]$ = 8 x 10^{-6} mol dm^{-3}; [MTU] = 64 x 10^{-3} mol dm^{-3} $[H^+]$ = 0.20 mol dm^{-3}, μ = (0.3-1.0) mol dm^{-3} (NaCl), T = 29.0 ±0.5°C and λ_{max} = 660 nm

Table II: Rate data for the effect of cations and anions on the second order rate constant for MB^+ and MTU reaction.
$[MB^+]$ = 8 x 10^{-6} mol dm^{-3}, [MTU] = 64 x 10^{-3} mol dm^{-3}, λ_{max} = 660 nm $[H^+]$ = 0.20 mol dm^{-3} and T = 29.0 ±0.5°C

X	10^2[X] mol dm^{-3}	10^3k_1 (s^{-1})	10^2k_2 (dm^3 mol^{-1} s^{-1})
Mg^{2+}	0	8.52	13.31
	20	10.13	15.83
	30	12.21	19.07
	60	14.27	22.31
	80	17.27	26.99
	100	21.65	33.82
K^+	0	8.52	13.31
	20	8.98	14.03
	40	9.67	15.11
	60	10.69	16.55
	80	11.05	17.27
	100	12.43	19.43
NO_3^-	0	8.52	13.31
	20	8.06	12.59
	40	7.37	11.52
	60	6.91	10.80
	80	5.07	7.92
	100	2.53	3.96
CH_3CHOO^-	0	8.52	13.31
	20	8.29	12.95
	40	7.83	12.23
	60	7.14	11.16
	80	6.44	10.76
	100	5.30	8.28

Table III: Effect of changes in total dielectric constant

$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}, $[MTU] = 64 \times 10^{-3}$ mol dm^{-3}, $\lambda_{max} = 660$ nm, $\mu = 0.50$ mol dm^{-3} and T=29.0 ±0.5°C

D	10^2 1/D	$10^3k_1(s^{-1})$	$10^2k_2(dm^3mol^{-1}s^{-1})$
81.00	1.23	8.52	13.31
79.80	1.25	8.06	12.60
78.59	1.27	6.91	10.80
77.36	1.29	6.22	9.72
76.20	1.31	5.07	7.92
75.00	1.33	3.22	5.03

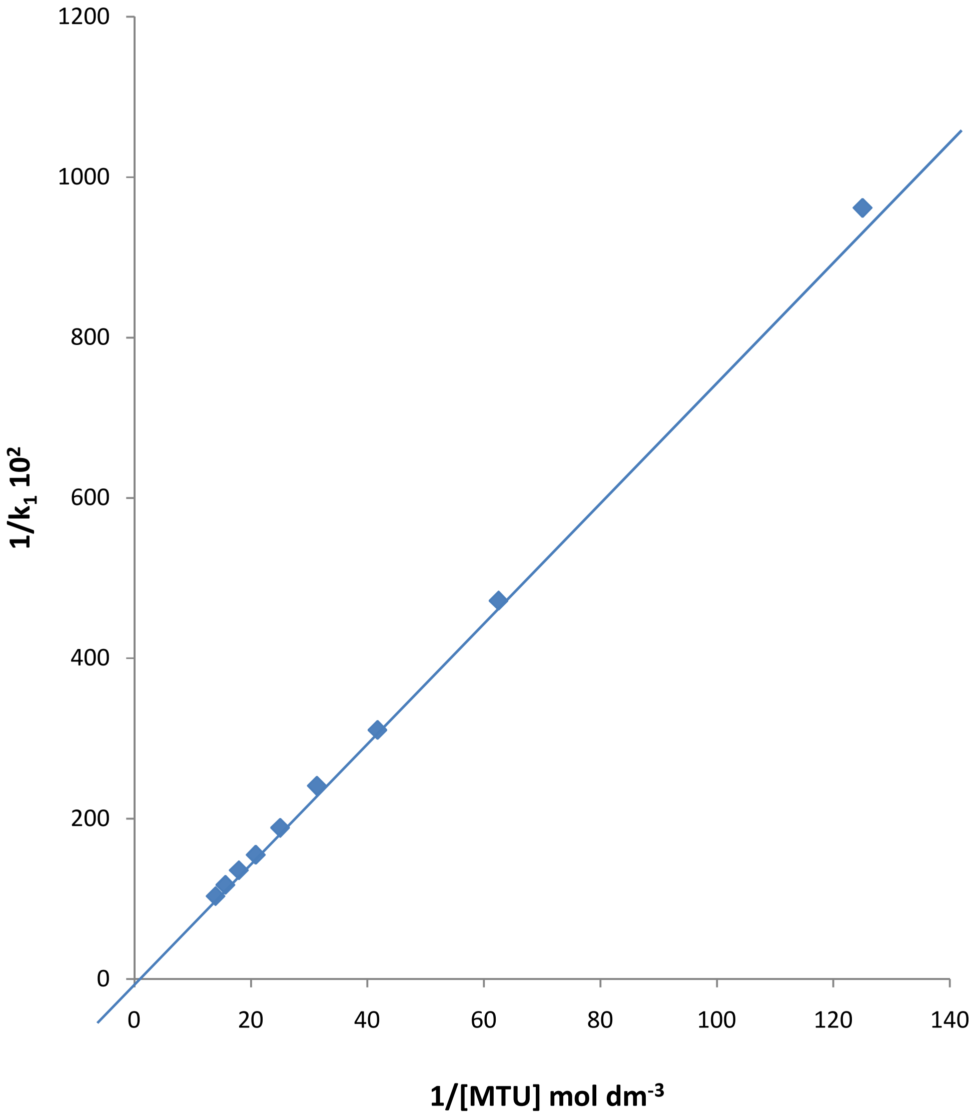


Figure V: Michealis-Menten plot of $1/k_1$ versus 1/[MTU] for the redox reaction of MB^+ and MTU.

$[MB^+] = 8 \times 10^{-6}$ mol dm^{-3}; $[MTU] = (8.0 – 72.0) \times 10^{-3}$ mol dm^{-3}
$[H^+] = 0.20$ mol dm^{-3}, $\mu = 0.50$ mol dm^{-3} (NaCl), T = 29.0 ±0.5°C and $\lambda_{max} = 660$ nm

Product analysis

The blue colour of MB^+ was regenerated on the addition of NaOH/glucose mixture, showing the presence of leucomethylene blue. Addition of acidified $BaCl_2$ solution gave a white precipitate; an indication that SO_4^{2-} ion was one of the reaction products.

Test for radicals

Addition of acrylamide to partially oxidized reaction mixture followed by excess methanol showed no gel formation. This suggests the probable absence of a radical intermediate in the reaction. The other probability is that the radical may be formed and consumed so fast that it cannot be detected by this method [10].

A pinkish-violet colour which gradually turned bluish was obtained with the addition of dilute alkaline $CuSO_4$ solution. This shows the presence of urea derivatives [11].

Mechanism

Under the experimental condition employed in this investigation, the following results were pertinent to the proposed mechanism: (a) 1 mole of MB^+ reacts with 1 mole of MTU; (b) the organic molecule is left intact, and the only activity in term of oxidation (electron transfer and/or hydrolysis) is occurring at the sulphur center of the thiocarbonyl compound, MTU; (c) there is successive electron transfer from the sulphur center to the nitrogen atom in the center of the methylene blue ring; (d) an intermediate complex is formed that carries a positive charge which further react with protonated methylene blue and/or with more molecules of 1-methyl-2-thiourea; (e) the complex fragments to give the products. Thus based on this, the following plausible mechanism is proposed:

$$MB^+ + H^+ \rightleftharpoons MBH^{2+} \qquad ---(5)$$

$$MB^+ + MTU \rightleftharpoons [MB^+, MTU] \qquad ---(6)$$

$$[MB^+, MTU] \overset{k_3}{\rightarrow} products \qquad r.d.s.---(7)$$

From equation (5), the protonated methylene blue reacts with 1-methyl-2-thiourea

$$MBH^{2+} + [MTU] \rightleftharpoons [MBH^{2+}, MTU] \qquad ---(8)$$

$$[MBH^{2+}, MTU] \overset{k_5}{\rightarrow} \overset{K_4}{products} \qquad r.d.s.---(9)$$

From equations 7 and 9, which are the rate determining step, the rate law can be written as

$$\text{Rate} = k_3[MB^+, MTU] + k_5[MBH^+, MTU] \qquad ---(10)$$

From equation (6)

$$\text{Rate} = k_3K_2[MB^+][MTU] + k_5[MBH^{2+}, MTU] \qquad ---(11)$$

But from equation 5 and 8

$$\text{Rate} = k_3K_2\left[[MB^+][MTU]\right] + k_5K_1K_4[MB^+][H^+][MTU] \qquad ---(12)$$

Let k_3K_2=k$'$ and $k_5K_1K_4$ = k

$$\text{Rate} = k'[MB^+][MTU] + k[MB^+][H^+][MTU] \qquad ---(13)$$

$$\text{Rate} = (k' + k[H^+])[MB^+][MTU] \qquad ---(14)$$

Equation 14 conforms to equation 3 with a = k_3K_2 = 2.71×10^{-3} mol dm^{-3} s^{-1}, and b = $k_5K_1K_4$ = 2.87×10^{-1} dm^{6} mol^{-2} s^{-1} thus suggesting that the proposed mechanism is plausible.

The basis for this proposal are:

(a) Absence of spectroscopic evidence suggests that a precursor complex is probably not formed prior to the act of electron transfer and that the electron transfer may occur by the outer-sphere path.

(b) Michaelis-Menten's plot of $1/k_1$ versus 1/[MTU] was found to be linear without positive intercept suggesting the absence of a pre-association step. This also favours the outer-sphere mechanism.

(c) Enhancement of the rate of reaction by cations and its inhibition by anions also point to the outer-sphere pathway in the electron transfer processes for this reaction.

(d) The negative result of polymerization test suggests the absence of free radical intermediate in the reaction or the equilibrium constant for the formation of such radicals can be assumed to be negligible [12].

Based on the above evidences, an outer-sphere mechanistic pathway is proposed for the reaction.

CONCLUSION

The mechanism reported here shows similar steps in relation to the mechanism that was reported for the reduction of methylene blue by the unsubstituted thiourea (Osunlaja *et al.*, 2012a). A 10 -step mechanism was proposed for the methylene blue - thiourea reaction so also the mechanism proposed for the methylene blue - MTU system has 10–steps.The reaction with thiourea is slower than the reaction with MTU. This finding supports earlier assertion that changing the substituents on the nitrogen may affect the rate of reaction but not the mechanism since the major reaction is at the sulphur center[1]. This change in rate of reaction could be attributed to the inductive effect of the methyl group in MTU. However, increases in $[H^+]$ and μ shows the same effect in both reactions i.e. a linear dependence within the concentrations range studied.

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