

OXIDATION OF 1, 3-DIMETHYL-2-THIOUREA BY 3, 7-BIS(DIMETHYLAMINO)PHENAZOTHONIUM CHLORIDE IN AQUEOUS HYDROCHLORIC ACID

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ABSTRACT

The stoichiometry, kinetics and mechanism of oxidation of 1,3-dimethylthiourea by 3,7-bis(dimethylamino)phenazothionium chloride have been studied in aqueous hydrochloric acid in the $(8 - 70) \times 10^{-2} \text{ mol dm}^{-3}$ range. The rate shows a first order dependence on the substrates, a linear first order dependence on $[\text{H}^+]$ and a positive salt effect. One mole of the oxidant is consumed per mol of the reductant to give the corresponding urea derivative and other products. A mechanism consistent with the experimental data has been proposed.

Keywords: Kinetics, mechanisms, stoichiometry, 1,3-dimethyl-2-thiourea.

INTRODUCTION

It has been reported that the reactivity of the sulphur center is heavily dependent upon its environment and its oxidation state and, these reactivity is greatly simplified if the sulphur center is bonded to an organic molecule¹. Much insight into sulphur chemistry can be gained from a study of thiocarbonyl compounds, $\text{R}_1\text{R}_2\text{C}=\text{S}$. Small molecules such as thiourea, substituted thioureas, and thiosemicarbazides are moderately soluble in water, making it possible for the studies to be carried out in aqueous media. While focusing on the sulphur center, it is important to evaluate the effect of substitution on the rate of oxidation and the ease of the C-S bond cleavage to form SO_4^{2-} . Taking a cue from several authors²⁻⁶, the importance of sulphur chemistry in the environment, biology, and industry made us recently embark on a series of research studies aimed specifically at kinetics and mechanisms of sulphur oxidations using, initially, sulphur atoms bonded to small organic molecules. We report in this paper on the oxidation of a substituted thiourea: 1,3-dimethyl-2-thiourea(DMTU). This is

with the hope that the study will provide support for the mechanism proposed for the oxidation of thiourea⁷, and 1,-methyl-2-thiourea⁸. DMTU, is one of the most efficient scavengers of reactive, toxic oxygen species in vitro, and reduces oxidative injury in many biological systems⁹⁻¹². DMTU is used in the textile industry as an antioxidant¹³. It is an extremely diffusible, potent scavenger of hydroxyl radical, hydrogen peroxide, and hypochlorous acid, with a long half-life of 43 hours¹⁴⁻¹⁷. It has been used to test the involvement of OH^\cdot in several animal models of human diseases.

MATERIAL AND METHODS

The following reagent grade chemicals (B.D.H.) were used without further purification: sodium chloride, sodium acetate, hydrochloric acid (36%), magnesium chloride, 3,7-bis(dimethylamino)phenazothionium chloride (methylene blue) and 1,3-dimethyl-2-thiourea (Sigma-Aldrich). Neither of the major reactants (methylene blue, MB^+ and 1,3-dimethyl-2-thiourea) was standardized; they were assumed to be of high enough purity. Hydrochloric acid, used

to furnish hydrogen ions, was standardized by standard sodium carbonate with methyl orange as indicator. Solutions were prepared by dissolving the requisite amounts of the sample in singly distilled water. The ionic strength of the reaction mixtures was maintained constant at 0.5 mol dm⁻³ using NaCl.

Stoichiometry

The stoichiometry was determined by spectrophotometric titrations under the conditions of [H⁺] = 0.2 mol dm⁻³, μ = 0.5 mol dm⁻³ (NaCl), [MB⁺] = 8 x 10⁻⁶ mol dm⁻³, [DMTU] = (24.0 x 10⁻⁵ – 96.0 x 10⁻⁴ mol dm⁻³), T = 31.0 ± 1.0°C and λ_{max} = 660 nm. A plot of absorbance versus [DMTU] was made from which the stoichiometry was determined.

Kinetic measurement

All kinetic measurements were performed under pseudo-first-order conditions, where DMTU was present in a large excess over that of MB⁺ at T = 31.0 ± 1.0°C, [H⁺] = 0.20 mol dm⁻³ and 0.50 mol dm⁻³ (NaCl) ionic strength, using a JENWAY 6405 UV-Vis spectrophotometer. The course of reaction was followed by recording the decrease in absorbance of MB⁺ at its absorption

maximum (660 nm) as a function of time. It was verified that there was no interference from other reagents at this wavelength. The procedure of the kinetic measurements was the same as described earlier⁷.

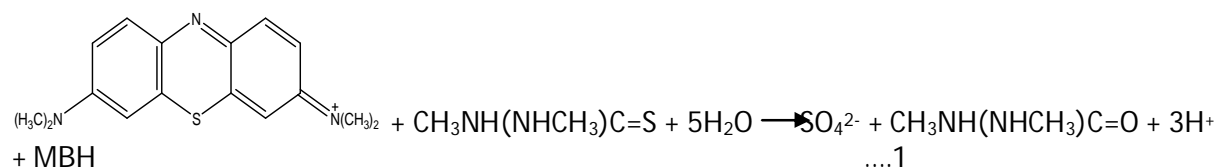
Product analysis

Likely products tested for were leucomethylene blue (the reduced form of MB⁺) and SO₄²⁻. Mixtures of glucose/NaOH solution were added to the product in order to oxidize back the colourless solution to blue. The presence of SO₄²⁻ was qualitatively tested for with dilute acidified solution of BaCl₂. Urea derivatives were tested for by the addition of few drops of dilute alkaline CuSO₄ solution.

RESULTS AND DISCUSSION

Stoichiometry and product analysis

Spectrophotometric estimation of the reaction revealed that 1 mol of methylene blue consumed 1 mol of 1,3-dimethylthiourea. Product analyses indicated the formation of sulphate ion, a urea derivative and leucomethylene blue acid as the oxidation products. This result suggests that the stoichiometry of the reaction conforms to the following stoichiometric equation:



where MBH is the reduced methylene blue. Similar mole ratio has reported for the reaction with thiourea⁷, mercaptoacetic acid and L- ascorbic acid¹⁸ and thiosulphate¹⁹.

[MB⁺] and [DMTU] dependences

Pseudo-first-order plots of log (A_∞ - A_t) versus time were found to be linear for more than 70% of reaction completion. This result indicates that the reaction is first-order with respect to [MB⁺]. The values of pseudo-first-order rate constants, k₁, were

calculated from the gradients of these plots at a variety of initial MB⁺ and 1,3-dimethylthiourea concentrations. The first-order dependence was confirmed not only by the observed linearity of the pseudo-first-order plots but also by the independence of the obtained rate constants, k₂, on different initial concentrations of the oxidant ranging between (24.0 – 96.0) x 10⁻³ mol dm⁻³ (Table 1). The reaction is therefore second order overall as represented in the rate law below:

$$-d[MB^+]/dt = k_2[MB^+][DMTU] \quad \dots 2$$

at $[H^+] = 0.2 \text{ mol dm}^{-3}$ and $T = 31.0 \pm 1.0^\circ\text{C}$, and $k_2 = 11.44 \times 10^{-2} \pm 0.04 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The second order rate constants were determined as $k_1/[DMTU]$. A similar order has been reported by Jonnalagadda *et al.*,¹.

Acid dependence

To clarify the influence of the $[H^+]$ on the rate of reaction and to elucidate a reaction mechanism, some kinetic measurements were performed at different $[H^+] = (8 - 70) \times 10^{-2} \text{ mol dm}^{-3}$ and constant ionic strength of 0.5 mol dm^{-3} and temperature $T = 31.0 \pm 1.0^\circ\text{C}$. The results are summarized in Table 1. An increase in acid concentration was found to be accompanied by an increase in the observed first-order-rate constant. This means that the reaction is acid-catalyzed. From the result, it is proposed that the observed acid catalysis may be due to the successive protonation of methylene blue and this seems to agree with similar findings reported for reduction of methylene blue by bromate ion²⁰, β -mercaptoethanol²¹, thiosulphate ion¹⁹ and permanganate ion and thiourea^{7,8}.

The order with respect to $[H^+]$ was found to be one (obtained from $\log k_1$ versus $\log [H^+]$ plots) and a plot of k_{H^+} against $[H^+]$ gave a positive intercept (Figure 1). Therefore the acid dependent rate constant is of the form

$$k_{H^+} = a + b[H^+] \dots\dots\dots 3$$

Hence, the rate of the reaction as function of acid can be represented by the general equation:

$$\text{Rate} = (a + b[H^+])[MB^+][DMTU] \dots\dots\dots 4$$

where $a = 9.39 \times 10^{-2} \text{ s}^{-1}$, and $b = 2.43 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

Ionic strength dependence

The rate constant of the reaction increased with increase in ionic strength (Table 1) suggesting a positive Bronsted – Debye salt effect²² within the range $\mu = 0.30 - 1.00 \text{ mol dm}^{-3}$ (NaCl) while the concentration of other reagents were kept constant. Plot of $\log k_2$ versus $\sqrt{\mu}$ is linear with slope 0.78. This suggests that there is most likely no bond formation at the transition state and the reaction involves two similar charges. This result is similar to those we observed for reduction of methylene blue by thiourea and 1-methyl-2-thiourea^{8, 23}.

Ions dependence

At constant reactant concentrations ionic strength and $[H^+] = 0.2 \text{ mol dm}^{-3}$, reactions were increased for added Mg^{2+} , but decreased with added CH_3COO^- in the range $0.2 < [X] < 1.00 \text{ mol dm}^{-3}$ (Table 2). This is suggestive of an outer-sphere mechanism²⁴.

Free radical test

The addition of a solution of acrylamide to the partially reacted mixture did not give any gel in the presence of excess methanol. This is suggestive of the probable absence of free radical in the reaction mixture²⁵.

Intermediate complex formation

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 MB^+ within a wavelength of 400 - 700 nm. The result shows that the absorption maxima did not deviate from 660 nm indicating likely absence of stable precursor complexes. This suggests operation of outer-sphere electron transfer mechanism. This is further supported by the fact that Michaelis-Menten plot of $1/k_1$ against $1/[DMTU]$ was linear with a zero intercept (Figure 2) suggesting that formation constant for such intermediates must be small.

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 method²⁶.

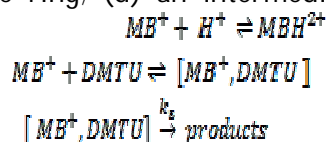
Product analysis

The result of the analysis carried out shows that leucomethylene blue, SO_4^{2-} ion and a urea derivative are major products of the reaction.

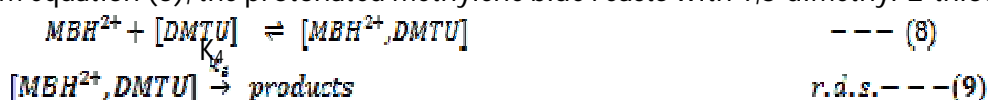
Mechanism

Under the experimental condition employed in this investigation, the following facts are inferred: (a) 1 mole of MB^+ reacts with 1 mole of DMTU; (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, DMTU; (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



From equation (5), the protonated methylene blue reacts with 1,3-dimethyl-2-thiourea



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

$$\text{Rate} = k_3[MB^+, DMTU] + k_4[MBH^+, DMTU] \quad --- (10)$$

From equation (6)

$$\text{Rate} = k_3K_2[MB^+][DMTU] + k_4[MBH^{2+}, DMTU] \quad --- (11)$$

But from equation 5 and 8

$$\text{Rate} = k_3K_2[MB^+][DMTU] + k_4K_1K_4[MB^+][H^+][DMTU] \quad --- (12)$$

Let $k_3K_2 = k'$ and $k_4K_1K_4 = k$

$$\text{Rate} = k'[MB^+][DMTU] + k[MB^+][H^+][DMTU] \quad \text{--- 13}$$

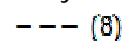
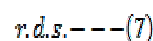
$$\text{Rate} = (k' + k[H^+])[MB^+][DMTU] \quad --- (14)$$

Equation 14 conforms to equation 3 with $a = k_3K_2 = 9.39 \times 10^{-2} \text{ mol dm}^{-3} \text{ s}^{-1}$, and $b = k_4K_1K_4 = 2.43 \times 10^{-1} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ thus suggesting that the proposed mechanism is plausible.

The pathway to this reaction can be assessed as follows:

- 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.
- 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-

complex is formed that carries a positive charge which further react with protonated methylene blue and/or with more molecules of 1,3-dimethyl-2-thiourea; (e) the complex fragments to give the products. Thus based on this, the following mechanism is proposed:



association step. This also favours an outer-sphere mechanism.

- Enhancement of the rate of reaction by cations and its inhibition by anions also points to an outer-sphere pathway in the electron transfer processes for this reaction.
- 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 negligible²⁷.

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 thiourea and 1-methyl-2-thiourea (MTU). A 10-step mechanism was proposed for the methylene blue - thiourea reaction⁷ and the methylene blue - MTU system²³. The reaction with thiourea is slower than the reaction with MTU and DMTU. 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 center¹. This change in rate of reaction could be attributed to the inductive effect of the 2

methyl groups in DMTU. 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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Table 1: Pseudo-first order and second order rate constants for the oxidation of DMTU by MB^+ at $[MB^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 660 \text{ nm}$ and $T = 31.0 \pm 1.0^\circ\text{C}$

$10^3[DMTU]$ (mol dm^{-3})	$10^2[H^+]$ (mol dm^{-3})	μ (mol dm^{-3})	10^3k_1 (s^{-1})	10^2k_2 ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
24	20	0.5	2.76	11.52
32	20	0.5	3.69	11.53
40	20	0.5	4.61	11.52
48	20	0.5	5.53	11.51
56	20	0.5	6.22	11.10
64	20	0.5	7.39	11.16
72	20	0.5	8.06	11.20
80	20	0.5	9.21	11.52
88	20	0.5	10.36	11.78
96	20	0.5	11.05	11.51
40	8	0.5	2.30	5.76
40	10	0.5	3.22	8.06
40	20	0.5	4.61	11.52
40	30	0.5	6.91	17.28
40	40	0.5	9.44	23.61
40	50	0.5	11.75	29.38
40	60	0.5	14.51	36.28
40	70	0.5	17.96	44.90
40	20	0.3	2.99	7.50
40	20	0.4	3.68	9.20
40	20	0.5	4.61	11.52
40	20	0.6	5.06	12.67
40	20	0.7	5.53	13.82
40	20	0.8	5.99	14.97
40	20	0.9	6.45	16.12
40	20	1.0	6.91	17.27

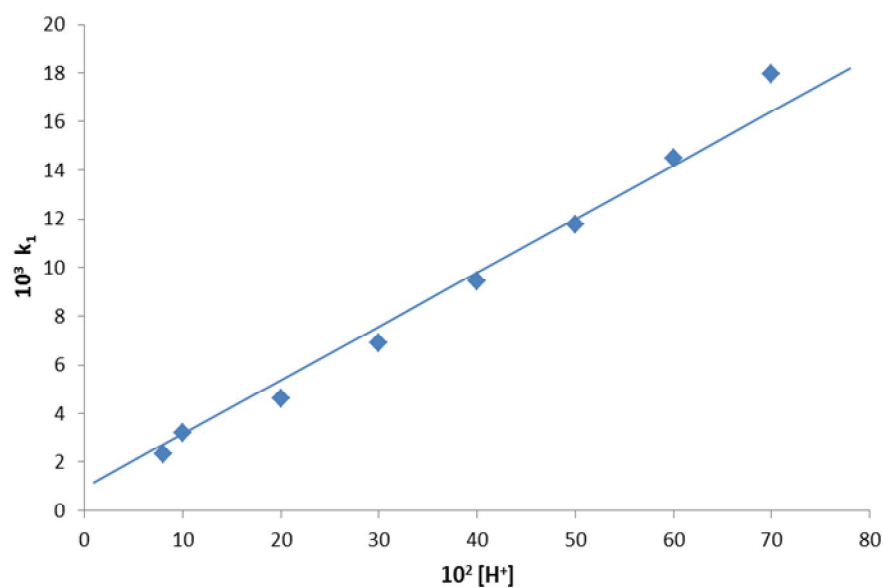


Fig. 1: k_{H^+} versus $[H^+]$ for the redox reaction of MB^+ and DMTU
 $[MB^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$; $[DMTU] = 40 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = (8 - 70) \times 10^{-2} \text{ mol dm}^{-3}$,
 $\mu = 0.5 \text{ mol dm}^{-3}$ (NaCl), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

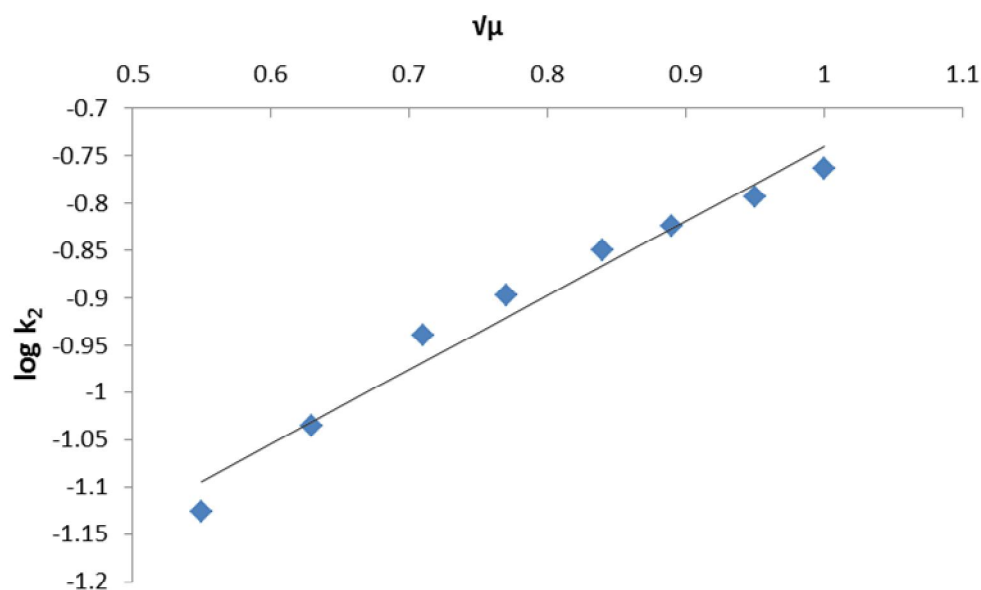


Fig. 2: $\log k_2$ versus $\sqrt{\mu}$ for the redox reaction of MB^+ and DMTU
 $[MB^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$; $[DMTU] = 40 \times 10^{-3} \text{ mol dm}^{-3}$, $[H^+] = 0.20 \text{ mol dm}^{-3}$,
 $\mu = 0.5 \text{ mol dm}^{-3}$ (NaCl), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$

Table 2: Rate data for the effect of Mg^{2+} and CH_3CHOO^- on the second order rate constant for MB^+ and DMTU reaction at $[\text{MB}^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{DMTU}] = 40 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 660 \text{ nm}$ $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ and $T = 31.0 \pm 1.0^\circ\text{C}$

X	$10^2[\text{X}] \text{ mol dm}^{-3}$	$10^3k_1(\text{s}^{-1})$	$10^2k_2(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$
Mg^{2+}	0	4.61	11.52
	20	4.84	12.09
	30	5.30	13.24
	60	5.55	13.82
	80	5.87	14.68
	100	6.22	15.55
CH_3CHOO^-	0	4.61	11.52
	20	4.15	10.36
	40	3.45	8.64
	60	3.22	8.06
	80	2.07	5.18
	100	1.84	4.61

Table 3: Effect of changes in dielectric constant for MB^+ and DMTU reaction at $[\text{MB}^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$, $[\text{DMTU}] = 40 \times 10^{-3} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 660 \text{ nm}$ $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$ and $T = 31.0 \pm 1.0^\circ\text{C}$

D	$10^2 1/D$	$10^3k_1(\text{s}^{-1})$	$10^2k_2(\text{dm}^3\text{mol}^{-1}\text{s}^{-1})$
81.00	1.23	4.61	11.53
79.80	1.25	3.45	8.63
78.59	1.27	2.99	7.48
77.36	1.29	2.76	6.90
76.20	1.31	2.30	5.75
75.00	1.33	2.07	5.18

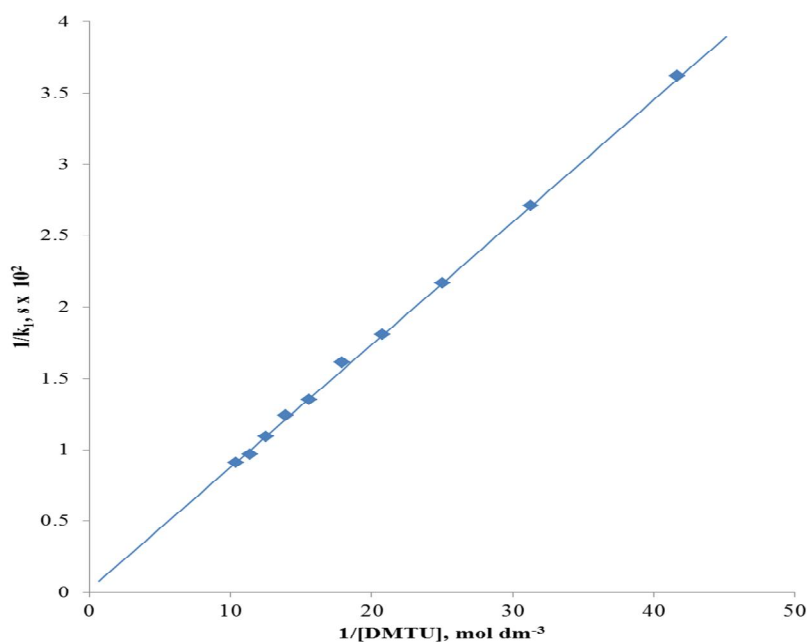


Fig. 3: Michealis-Menten plot of $1/k_1$ versus $1/[\text{DMTU}]$ for the redox reaction of MB^+ and DMTU at $[\text{MB}^+] = 8 \times 10^{-6} \text{ mol dm}^{-3}$; $[\text{DMTU}] = (24.0 - 96.0) \times 10^{-3} \text{ mol dm}^{-3}$ $[\text{H}^+] = 0.20 \text{ mol dm}^{-3}$, $\mu = 0.50 \text{ mol dm}^{-3}$ (NaCl), $T = 31.0 \pm 1.0^\circ\text{C}$ and $\lambda_{\text{max}} = 660 \text{ nm}$.

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