

Kinetic Probe of Azure-b Eosin Y Reaction with Thiourea in an Acid Medium

Sa'adatu Auwal Hamza, Madina Imam, Safiyya Abdulsalam

Department of Chemistry,
Ahmadu Bello University Zaria,
Kaduna State.

ABSTRACT

Kinetic probe of the azure-b eosin Y reaction with thiourea in an acid medium was executed using a spectrophotometric approach at 299 K. The reaction proceeded with the active form eosin Y that was actualized by deprotonation, leading to a decrease in reaction rate with the elevation of acid concentration. The reaction assumed a 1:1 stoichiometry (EY: TU) with the inclusion of free radical species. The concentration of the reaction species assumed first order kinetics. The reaction rate elevation was experienced in increasing the ionic strength and was decelerated as the medium polarity was altered with acetone. This demonstrated the effect of ion species distribution at the rate-controlling phase. There was a glaring catalytic effect on the inclusion of additional ion (Mg^{2+}) to the system. The involvement of a steady intermediate moiety was ruled out as shown by kinetic evidence from the Lineweaver-Burk modification of the Michaelis-Menten plot.

ARTICLE INFO

Article History

Received: November, 2023

Received in revised form: January, 2024

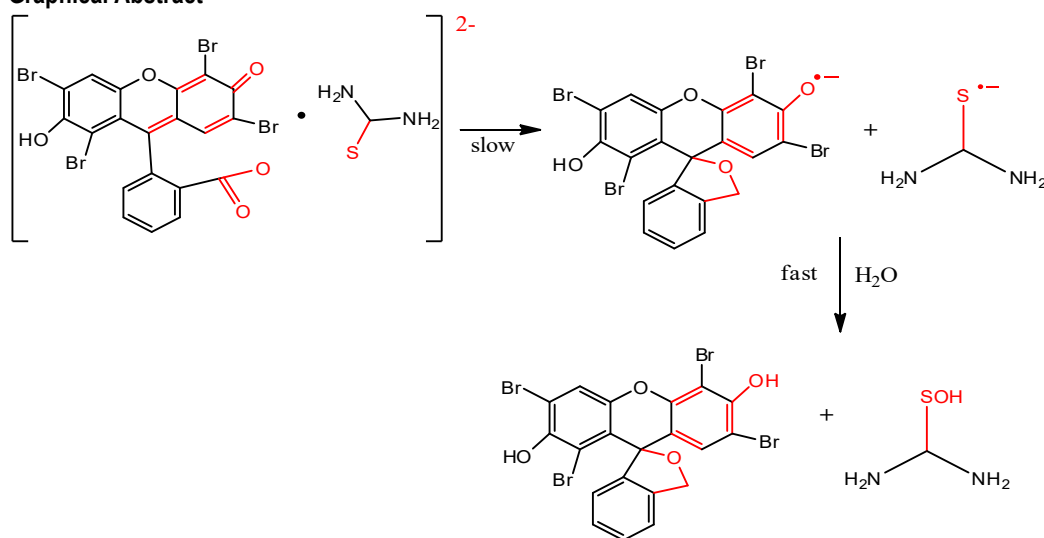
Accepted: March, 2024

Published online: June, 2024

KEYWORDS

Eosin Y, Mechanism, Kinetics, Thiourea, Catalysis

Graphical Abstract



INTRODUCTION

The degradation of dyes from industries into innocuous species is paramount in ensuring a cleaner atmosphere and environment. Some of the dyes are carcinogenic in nature, and they

affect the ecosystem [1]. Photocatalysis and Fenton oxidation have been deployed to degrade dye-containing effluents. Azures are basic dyes that bind to the acid nuclei. Azure-b eosin Y (eosin Y) is an acidic anionic dye and it is a derivative of

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved

methylene blue dyes with attachment of a benzoate substituent as a major substituent [2]. It has found application in the examination of various blood cells and cellular components for parasitic infections that are linked to malaria and leukaemia disorders. It is also applied in the production of intermediate species such as thiocyanation of imidazoheterocycles [3], aerobic oxidative cyclization of 2-aminobenzothiazole [4], carboxylation of styrenes [5], carbonylation of arene diazonium salts [6], reductive deoxygenation [7], reductive desulfonylation [8], reductive dehalogenation [9], and photosensitizer in organic synthesis [10]. Its disposal into the ecosystem has health hazard implications, hence, the need to investigate its reduction reaction.

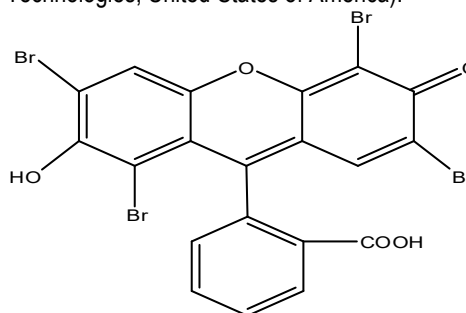
Conversely, thiourea has been confirmed to be a free radical scavenger of the peroxide radical and one of the metabolites in people unprotected from carbon disulphide exposure. Persistent exposure of people to it can likely cause bone marrow mutilation which may lead to a reduction in the level of red and white blood cells. It has been known to impede fatty acid peroxidation, and counter the unnecessary activity of the thyroid gland. Also, it has served as a component of hair preparations and photographic toning agents via its redox effect [11–14]. Its derivatives have various agricultural, biological, pharmaceutical, and analytical applications which include applications in rubber industries as accelerators, silver taint removers, anti-corrosion, and in agriculture as fungicides, herbicides, and rodenticides [15–18]. The reactions of thiourea with dioxygen [19], chlorine dioxide [20], hydrogen peroxide [21], and tris-(1,10-phenanthroline)iron(III) [22] have been archived in order to understand its non-oncogenic species and mechanistic pathways. Our interest in this study is to probe the reactivity mode of the eosin dye with a thiol moiety and kinetically interpret the effect of solvent polarity on the reaction.

EXPERIMENTATION

Materials

Merck provided azure-b eosin Y (2-(2,4,5,7-tetrabromo-6-oxido-3-oxo-3H-xanthen-9-yl)benzoate), Scheme 1, and thiourea (TU). HCl

(BDH) was used to initiate H⁺ ion catalysis. NaCl and acetone (BDH) were used to adjust the ionic strength and polarity of the reaction system respectively. NaNO₃ and MgCl from BDH were used to investigate the effect of added ion catalysis on the reaction. Acrylamide and methanol (BDH) were used to probe the presence of free radicals in the system. The reaction product was tested classically with sodium nitroprusside and sodium ascorbate (Merck) and spectroscopically with a UV-visible spectrophotometer (Cary 300 series, Agilent Technologies, United States of America).



Scheme 1: Azure-b eosin Y (Eosin Y)

Methods

The reaction stoichiometry was checked as reported formerly [23,24] by spectrophotometric titration at constant ionic strength and 299 K. An inflexion point on the curve of absorbance versus mole ratio was obtained from the absorbance obtained after eleven hours. Sulphenic acid product formed was checked by the addition of 0.3 cm³ of 0.2 mol/dm³ sodium ascorbate solution to the product mixture and two drops of 0.2 mol/dm³ sodium nitroprusside [22,25,26], and the colourless lactone form of eosin Y was identified with a UV-visible spectrophotometer [27].

Kinetic measurements were conducted using a Corning colorimeter model 254 at a wavelength of 539 nm by noting the decline in absorbance of the dye under a pseudo condition with [TU] in 250-fold excess over the [dye] at fixed temperature and ionic strength [28-30]. The variation in the ionic strength (μ) and medium polarity (D) of the reaction medium was examined by varying each at a time while keeping the

remaining factors constant [31,32]. The first order rate constant (k_{obs}) was obtained from the gradient of the plot of $\ln A$ against time, and the second order rate constant (k_2) was obtained from the ratio of k_{obs} with $[TU]$. The addition of 0.5 cm³ of acrylamide solution with excess methanol into the reaction mixture was used to examine the contribution of free radicals [33,34].

RESULTS AND DISCUSSION

Stoichiometry and Product Study

A 1:1 stoichiometry was observed as illustrated from the point of inflexion in Figure 1, confirming the reaction mole contributions.

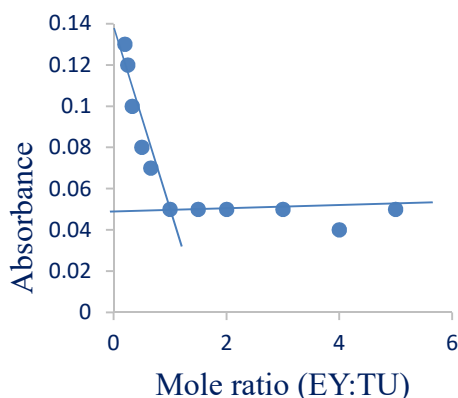
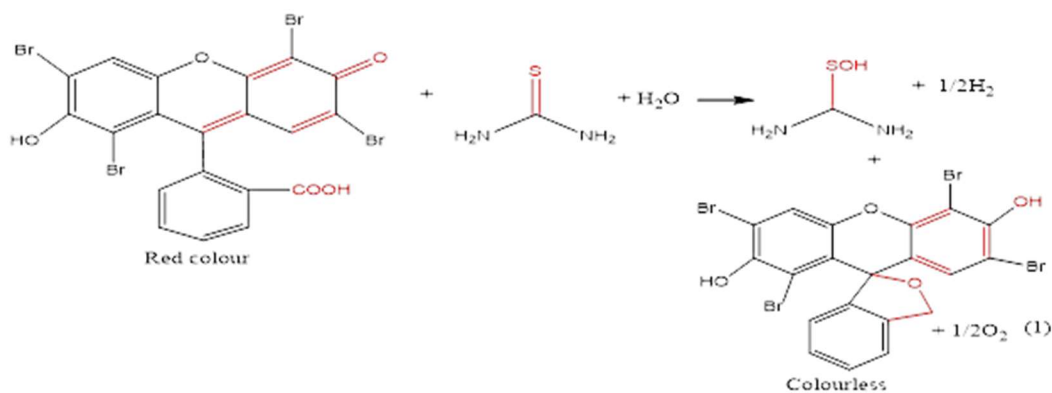


Figure 1: Stoichiometric curve of the reaction of Azure-b eosin Y and thiourea



Determination of Kinetic Parameters

The linearity of the pseudo-first order plot obtained from the absorbance-time traces (Figure 2) suggests that there is no inhibition by the product of the reaction and that the order of

Involvement of a mole of Eosin Y (EY) and thiourea in the reaction occasioned the formation of a colourless lactone form of eosin Y and sulphenic acid products. A 316 nm wavelength was obtained from the UV-visible spectrophotometer, revealing the formation of a colourless lactone form of eosin Y with the absence of its chromophore (π * transitions). The resulting red colouration on the addition of two drops of sodium nitroprusside to a portion of the product mixture treated with 0.3 cm³ of 0.2 mol/dm³ sodium ascorbate solution indicated the formation of sulphenic acid (Equation 1).

reaction with respect to the concentration of eosin Y is unity, and the slope (1.0012) of the plot of $\log k_{obs}$ against $\log [TU]$ (Figure 3) suggests first order with respect to $[TU]$. The reaction was largely characterized by the deprotonation of TU

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved

and EY (Equations 2 and 3) which resulted in a decrease in the reaction rate as $[H^+]$ was increased (Table 1). Rate of the reaction was influenced positively by the adjustment of ionic strength in the reaction medium (Figure 4) due to the interaction of similar charge species that formed an activated complex with a charge magnitude of -2 (Equation 4), and this is supported by a deceleration in the reaction rate as the medium polarity is decreased with acetone (Table 2).

Introduction of Mg^{2+} and NO_3^- ions catalyzed and inhibited the reaction (Table 3) due to the interplay of similar charges at the slow step (Equation 5), implicating an electrostatic process within the reacting moieties. Also, polymerization of acrylamide on addition of excess methanol into the reaction in progress reveals the input of free radical in formation of sulphenic acid. The existence of a stable intermediate moiety was not significant as shown by the zero intercept from the Michaelis-Menten plot of k^{-1}_{obs} versus $[TU]^{-1}$ (Figure 5).

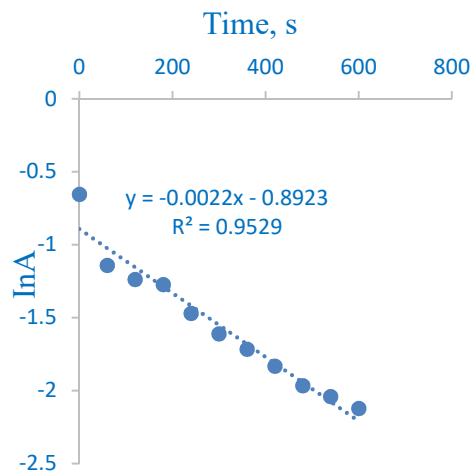


Figure 2: A Pseudo-first order curve for the reaction of EY and TU

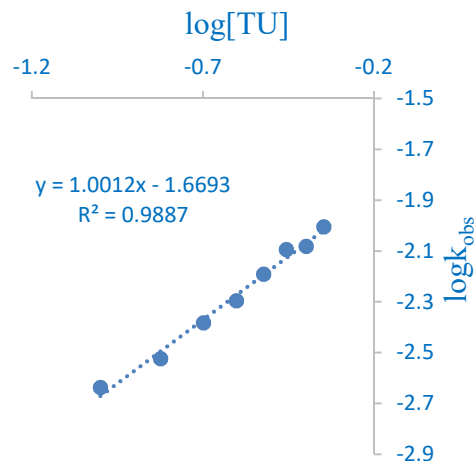


Figure 3: Plot of $\log k_{obs}$ against $\log [TU]$ for the reaction of EY and TU

Table 1: Kinetic constants of the reaction at $[EY] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 539 \text{ nm}$, and $T = 299 \text{ K}$

$10^2 [TU]_{\text{obs}}$ mol dm^{-3}	μ , mol dm^{-3}	$10^4 [H^+]$, mol dm^{-3}	$10^3 k_{\text{obs}}$, s^{-1}	$10^2 k_2$, $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
10.00	0.50	1.00	2.53	2.30
15.00	0.50	1.00	2.99	2.00
20.00	0.50	1.00	4.14	2.07
25.00	0.50	1.00	5.06	2.02
30.00	0.50	1.00	6.44	2.14
35.00	0.50	1.00	8.06	2.30
40.00	0.50	1.00	8.29	2.07
45.00	0.50	1.00	9.90	2.20
25.00	0.50	1.00	5.06	2.02
25.00	0.50	2.00	4.60	1.84
25.00	0.50	3.00	4.14	1.65
25.00	0.50	4.00	3.45	1.38
25.00	0.50	5.00	2.99	1.19
25.00	0.50	6.00	2.30	0.92
25.00	0.50	7.00	1.84	0.73
25.00	0.50	8.00	1.38	0.55
25.00	0.20	1.00	1.15	0.46
25.00	0.25	1.00	1.84	0.73
25.00	0.30	1.00	2.30	0.92
25.00	0.35	1.00	2.99	1.19
25.00	0.40	1.00	3.45	1.38
25.00	0.45	1.00	3.91	1.56
25.00	0.50	1.00	5.06	2.02
25.00	0.55	1.00	5.52	2.21

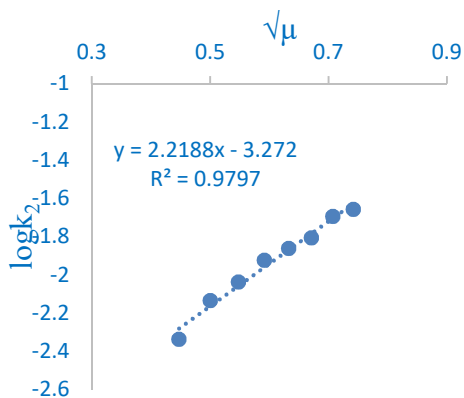


Figure 4: Plot of $\log k_2$ against $\sqrt{\mu}$ for the reaction of EY and TU

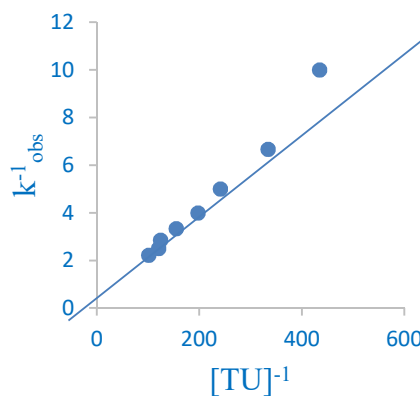


Figure 5: Michaelis-Menten plot of k_{obs}^{-1} versus $[TU]$

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved

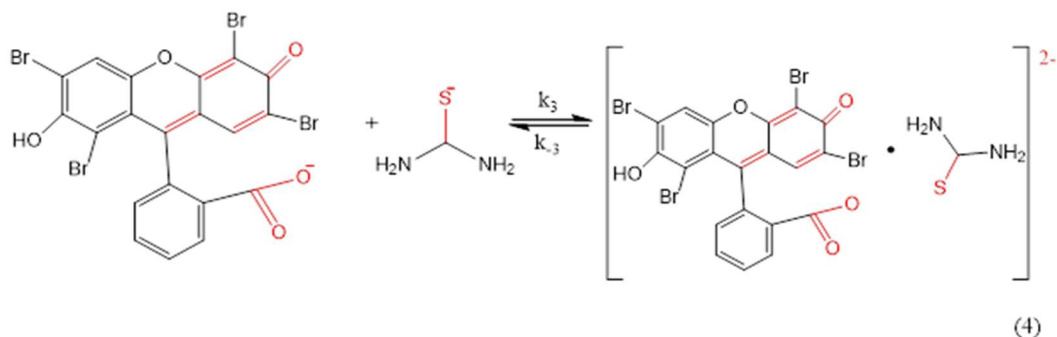
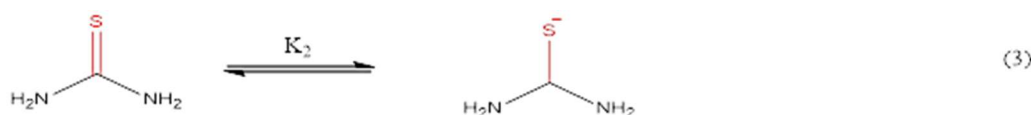
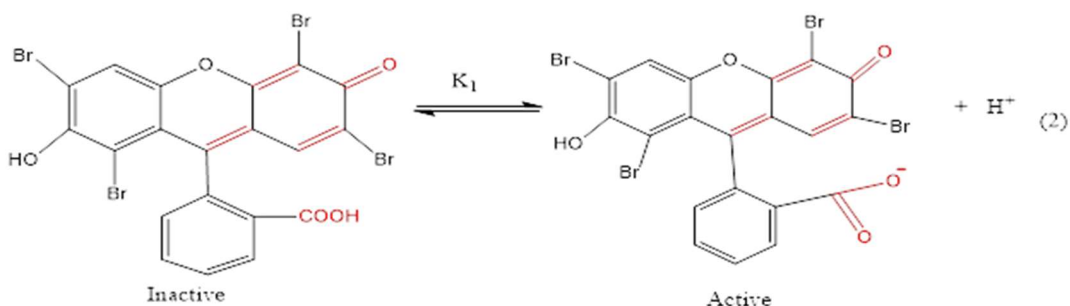
Table 2: Effect of medium polarity on the reaction rate of EY and TU

D	80.1	77.4	74.7	72.1	69.4	66.7	64.1	61.4
$10^3 k_{obs} (s^{-1})$	5.06	4.60	3.91	3.22	2.76	2.30	1.84	1.15
$10^2 k_2 (dm^3 mol^{-1} s^{-1})$	2.02	1.84	1.56	1.28	1.10	0.92	0.73	0.46

Table 3: Effect of added on the rate constants for the reaction of EY and TU

Ion	$10^2 [Ion], mol dm^3$	$10^3 k_{obs}, s^{-1}$	$10^2 k_2, dm^3 mol^{-1} s^{-1}$	Ion	$10^2 [Ion], mol dm^3$	$10^3 k_{obs}, s^{-1}$	$10^2 k_2, dm^3 mol^{-1} s^{-1}$
Mg^{2+}	0.00	5.06	2.02	NO_3^-	0.00	5.06	2.02
	1.00	5.98	2.39		1.00	4.37	1.75
	2.00	6.67	2.67		2.00	3.91	1.56
	3.00	7.60	3.04		3.00	3.22	1.28
	4.00	8.06	3.22		4.00	2.53	1.01
	5.00	8.75	3.50		5.00	2.07	0.08

Reaction Mechanism

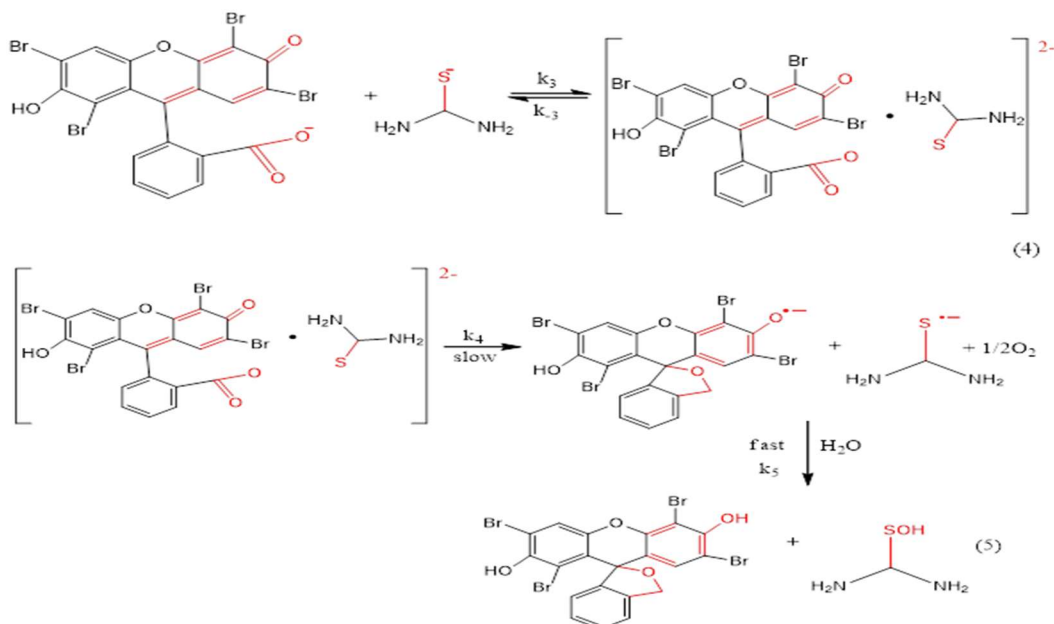


Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education, ATBU Bauchi. All rights reserved



Scheme 2: Mechanistic pathway of the reaction of eosin Y and thiourea

From Scheme 2, the electric charge of eosin Y varies with pH and its large aromatic system provides a hydrophobicity region and polarizable electrons contribute to dye-thiol affinity. The kinetic evidence showed that the reacting species are similarly charged; ion catalysis and acid hydrolysis were paramount.

CONCLUSION

The reaction of azure-b eosin Y with thiourea in an acid medium was characterized by the activation of eosin Y by a deprotonation process, initiating the involvement of π * transition in its hydrophobic interaction with the thiourea. This suggested that its cellular and blood activities could be more effective in non-acid media. A 1:1 stoichiometric ratio was obtained with a reaction order of first order in the [EY] and [TU]. Increase in medium ion concentration suggested a reliable means of degrading the dye, and the inclusion of counter-ions contributed to the fast product realization. Medium polarity enhances the energy hurdle of the activated complex by decreasing its breakdown to product. The reaction is in similitude to the ion exchange that takes place between eosin Y and positive ions of proteins and the

hydrophobic effects that exist when eosin Y and biopolymer co-exist. Non-detectable intermediate moiety suggested the intervention of an outer-sphere mechanistic path according to the mechanism of complexes from Taube's theory.

FIGURE LEGEND

Fig. 1. Stoichiometric curve of the reaction of EY and TU at [EY] = 2.0×10^{-4} mol dm⁻³, μ = 0.5 mol dm⁻³ (NaCl), D = 80.1, [TU] = (4.0 – 100.0) $\times 10^{-5}$ mol dm⁻³, [H⁺] = 1.0×10^{-4} mol dm⁻³, λ_{\max} = 539 nm, and T = 299 K

Fig. 2. A Pseudo-first order curve for the reaction of EY and TU at [EY] = 2.0×10^{-4} mol dm⁻³, μ = 0.5 mol dm⁻³ (NaCl), D = 80.1, [TU] = 2.5×10^{-1} mol dm⁻³, [H⁺] = 1.0×10^{-4} mol dm⁻³, λ_{\max} = 539 nm, and T = 299 K

Fig. 3. Plot of $\log k_{\text{obs}}$ against $\log [TU]$ for the reaction of EY and TU at [EY] = 2.0×10^{-4} mol dm⁻³, μ = 0.5 mol dm⁻³ (NaCl), D = 80.1, [TU] = (1.0 – 4.5) $\times 10^{-1}$ mol dm⁻³, [H⁺] = 1.0×10^{-4} mol dm⁻³, λ_{\max} = 539 nm, and T = 299 K

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved

Fig. 4. Plot of $\log k_2$ against $\sqrt{\mu}$ for the reaction of EY and TU at $[EY] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = (0.10 - 0.55) \text{ mol dm}^{-3}$ (NaCl), $D = 80.1$, $[TU] = 2.5 \times 10^{-1} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 539 \text{ nm}$, and $T = 299 \text{ K}$

Fig. 5. Michaelis–Menten plot of k_{obs}^{-1} versus $[TU]$ at $[EY] = 2.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\mu = 0.5 \text{ mol dm}^{-3}$ (NaCl), $D = 80.1$, $[TU] = (1.0 - 4.5) \times 10^{-1} \text{ mol dm}^{-3}$, $[H^+] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$, $\lambda_{\text{max}} = 539 \text{ nm}$, and $T = 299 \text{ K}$

REFERENCES

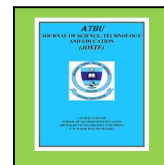
1. El-Sikaily A, Khaled A, El Nemr A (2012) Textile dyes xenobiotic and their harmful effect. In, pp. 31-64
2. Zheng H, Pan Y, Xiang X (2007) Oxidation of acidic dye eosin Y by the solar photo-fenton processes. *J Hazard Mater* 141(3):457-464
3. Mitra S, Ghosh M, Mishra S, Hajra A (2015) Metal-free thiocyanation of imidazoheterocycles through visible light photoredox catalysis. *J Org Chem* 80(16):8275–8281
4. Srivastava V, Singh PK, Singh PP (2015) Eosin Y catalyzed visible-light-promoted aerobic oxidative cyclization of 2-aminobenzothiazole. *Croat Chem Acta* 88(3):227–233
5. Song C, Chen P, Tang Y (2017) Carboxylation of styrenes with CBr_4 and DMSO via cooperative photoredox and cobalt catalysis. *RSC Adv* 7(19):11233–11243
6. Majek M, Wangelin AJ (2014) Metal-free carbonylations by photoredox catalysis. *Angew Chem Int Ed* 54(7):2270-2274
7. Gazi S, Ananthkrishnan R (2011) Metal-free-photocatalytic reduction of 4-nitrophenol by resin-supported dye under the visible irradiation. *Appl Catal B* 105:317–325
8. Yang D, Meng Q, Zhong J, Xiang M, Liu Q, Wu L (2013) Metal-free desulfonylation reaction through visible light photoredox catalysis. *Eur J Org Chem* 2013(33):7528–7532
9. Neumann M, Földner S, König B, Zeitler K (2011) Metal-free, cooperative asymmetric organophotoredox catalysis with visible light. *Angew Chem Int Ed* 50:951–954
10. Yan DY, Zhao Q, Rao L, Chen J, Xiao W (2018) Eosin Y as a redox catalyst and photosensitizer for sequential benzylic C-H amination and oxidation. *Chem Eur J* 24(63):16895-16901
11. Wang S, Lin J, Chen F, Hu M, Hu X, Han Y, Gao Q (2004) Kinetics and mechanism of the reaction between thiourea and iodate in unbuffered medium. *Sci China Series B: Chem* 47:480–491
12. Ni S, Bai F, Pan X (2020) Atmospheric chemistry of thiourea: nucleation with urea and roles in NO_2 hydrolysis. *Phys Chem Chem Phys* 22(15):8109–8117
13. Naz S, Zahoor M, Umar MN, Alghamdi S, Sahibzada MUK, UIBari W (2020) Synthesis, characterization, and pharmacological evaluation of thiourea derivatives. *Open Chem* 8:764–773
14. Sahu S, Sahoo PR, Patel S, Mishra BK (2011) Oxidation of thiourea and substituted thioureas: a review. *J Sulphur Chem* 32(2):171–197
15. Mohite AR, Phatake RS, Dubey P, Agbaria M, Shames AI, Lemcoff Ng, Reany O (2020) Thiourea-mediated halogenation of alcohols. *J Org Chem* 85(20):12901–12911
16. Saad IR, Abdel-Gaber AM, Younes GO, Nsouli B (2018) Thiourea and n-methylthiourea as corrosion inhibitors for steel in phosphoric acid. *J Fail Anal Preven* 18(5):1293–1299
17. So H., Lee H, Lee GD, Kim M, Lim MH, Kim K, Kim C (2020) A thiourea-based fluorescent chemosensor for bioimaging hypochlorite. *J Ind Eng Chem* 89:436–441
18. Azizi N, Farhadi E (2017) Rapid and highly efficient synthesis of thioureas in

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved



- biocompatible basic choline hydroxide. *J Sulfur Chem* 38(5):548–554
19. Kudrik EV, Theodoridis A, Eldik RV, Makarov SV (2005) Kinetics and mechanism of the Co(II)-assisted oxidation of thioureas by dioxygen. *Dalton Trans* 6:1117-1122
20. R'abai G, Wang RT, Kustin K (1993) Kinetics and mechanism of the oxidation of thiourea by chlorine dioxide. *Int J Chem Kinet* 25(1):53–62
21. Chatterjee D, Rothbart S, Eldik R (2013) Selective oxidation of thiourea with H₂O₂ catalysed by [RuIII(edta)(H₂O)]: kinetic and mechanistic studies. *Dalton Trans* 13:4725–4733
22. Nkole, I.U., Idris, S.O., Onu, A.D. (2021) Redox reactions of tris-(1,10-phenanthroline)iron(III) complex with thiourea and N-methylthiourea in an aqueous acidic medium: kinetics and mechanism. *Inorg Chem Comm* 133:108930
23. Arthur, D.E., Nkole, I.U., Osunkwo, C.R. (2020) Electron transfer reaction of tris-(1,10-phenanthroline)cobalt(III) complex and iodide ion in an aqueous acidic medium. *Chem Afr* 4(1):63-69
24. Abdulsalam, S., Idris, S. O., Shallangwa G. A, Onu, A. D. (2020) Reaction of n, n¹ - phenylenebis(salicylideneiminato)cobalt(III) and l-cysteine in mixed aqueous medium: kinetics and mechanism. *Heliyon* 6 e04621
25. Gupta V, Carroll, K.S. (2014) Sulfenic acid chemistry, detection and cellular lifetime. *BBA* 1840 (2):847–875
26. Nkole, I.U., Osunkwo, C.R., Onu, A.D., Idris, S.O. (2018) Kinetics and mechanism of the reduction of n-(2-hydroxyethyl)ethylenediaminetriacetato iron(III) complex by thioglycol in bicarbonate buffer medium. *Int J Adv Chem* 6(1):102-107
27. Acharya, S, Rebery, B. (2009) Fluorescence spectrometric study of eosin dye-surfactant interactions. *Arabian J Chem* 2(1):11-19
28. Nkole IU, Idris SO, Abdulkadir I, Onu AD (2022) Redox reaction of bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex with thiosulphate ion in aqueous acidic and surfactant media. *Inorg Chem Comm* 140:109468
29. Dennis CR, Van Zyl GJ, Fourie E, Basson SS, Swarts JC (2021) A kinetic study of the oxidation of the tetrakisoxalatoironate(IV) ion by the hexacyanoferrate(III) ion in an oxalate buffer medium. *Reac Kinet Mech Catal* 132:599-615
30. Arthur DE, Nkole IU, Osunkwo CR (2020) Electron transfer reaction of tris-(1,10-phenanthroline)cobalt(III) complex and iodide ion in an aqueous acidic medium. *Chem Afr* 4(1):63-69
31. Idris SO, Suleiman JO, Iyun JF, Osunlaja AA (2015) Reduction of 3,7-bis(dimethylamino)phenazothionium chloride by benzene thiol in aqueous nitric acid medium: a mechanistic approach. *Am Chem Soc J* 5(4):313-321
32. Ibrahim I, Idris SO, Abdulkadir I, Onu AD (2019) Kinetics and mechanism of the redox reaction of n, n¹-phenylenebis-(salicylideneiminato)iron(III) with oxalic acid in mixed aqueous medium. *Transit Met Chem* 44(3):269-273
33. [Nkole IU, Idris SO \(2021\) Thermodynamics and kinetic investigation of reaction of acriflavine with l-cysteine in aqueous medium. *Chem Afr* 4:731-740](#)
34. Nkole, I.U., Idris, S.O., Onu, A.D., Abdulkadir, I. (2022) The study of piskiewicz's and berezin's models on the redox reaction of allylthourea and bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex in an aqueous acidic medium. *Beni-Suef Uni J Basic Appl Sci* 11:68

Corresponding author: Sa'adatu Auwal Hamza

✉ saadahm82@yahoo.com

Department of Chemistry, Ahmadu Bello University Zaria, Nigeria.

© 2024. Faculty of Technology Education. ATBU Bauchi. All rights reserved