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The study of Piszkiewicz's and Berezin's models on the redox reaction of allylthiourea and bis-(2-pyridinealdoximato) dioxomolybdate(IV) complex in an aqueous acidic medium

I. U. Nkole[1*], S. O. Idris[1], A. D. Onu[2] and I. Abdulkadir[1]

Abstract

Background: The study of Piszkiewicz's and Berezin's models on the redox reaction of allylthiourea and bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex ($[Mo^{IV}O_2(paoH)_2]^{2-}$) in an aqueous acidic medium is suggested. The Piszkiewicz's and Berezin's models are applied, and their parameters are used to explain the redox behaviour of allylthiourea with Mo(IV) complex in the presence of surfactants.

Results: The reaction followed a high cooperativity pattern that reflects a strong interaction between the two redox partners in the presence of cetyltrimethylammonium bromide (CTAB) which is reinforced by a notable binding constant at the Stern layer of the micelle. The effect of cationic counter-ion (Ca^{2+}) on the reaction rate further confirmed the effectiveness of the interaction at the rate-limiting step. The presence of sodium dodecyl sulphate (SDS) in the reaction medium resulted in reaction inhibition which reveals the interplay of electrostatic repulsion at the electrophilic polar head of the surfactant and the redox species. The effect of ionic strength on the reaction rate shows that one of the reacting species is not charged (neutral) which kept the rate of the reaction uniform at different salt concentrations studied. The change in the medium polarity buttressed the effect of ionic strength on the reaction which is explained better by Piszkiewicz's and Berezin's models. Free radical was actively engaged in the reductive process of the Mo(IV) complex, and this revealed that the hydrophobic region is a possible location for the interaction of the redox partner in the presence of SDS micelle.

Conclusions: The models depict well the microenvironments of enzymatic reactions involving bimolecular interactions with significant binding constants and cooperativity indexes that show the strength of the interaction between the substrates and surfactant molecules.

Keywords: Allylthiourea, Piszkiewicz model, Molybdenum(IV) complex, Berezin model, Redox

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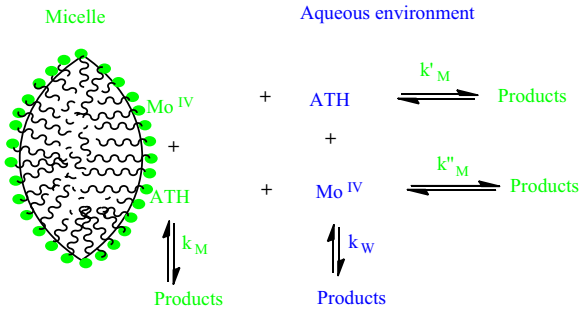
Graphical Abstract



1 Background

Allylthiourea (ATH) is a metabolic inhibitor that selectively inhibits ammonia oxidation. It selectively inhibits ammonia oxidation at low concentrations and probably acts by chelating the copper of the ammonia monooxygenase active site. It is able to produce soluble methane monooxygenase in the presence of copper [1]. Allylthiourea is a precursor of anticancer agents because of its pharmacophore (thiol group) and primary amine group that is responsible for its bio-activities [2–7]. The oxidation of allylthiourea by acidified Chloramine-T has been studied at 278 K. The oxidative process followed first-order kinetics in the concentrations of the reacting species. The reaction rate was unaffected by variation in the ionic strength of the reaction medium and the inclusion of a counter-ion (halide). The variation of the solvent polarity by the addition of methanol in the reaction medium retarded the reaction rate, and the oxidation was an enthalpy controlled process that produced a disulphide product [8]. The study of corrosion inhibition of cold-rolled steel in a phosphoric acid medium by allylthiourea resulted in a significant inhibitory effect on the steel and fitted well with Langmuir adsorption isotherm [9]. The kinetics of methylthiourea and allylthiourea oxidation in buffer solution with μ-oxo-tetrakis(1,10-phenanthroline)diiron(III) complex gave first order in the complex and allylthiourea concentrations but zero order in methylthiourea concentration. The reactions were observed to be independent of variations in pH and salt concentration. The reactions were also characterised by the negative participation of free radicals and intermediate complexes. The result suggested that the reactivity of methylthiourea is greater than allylthiourea due to the increase in electron density provided within the reaction medium [10].

On the other hand, molybdenum being the only member of the second transition metal series with biological activities has been attracting a lot of interest among many researchers. The oxidation of octacyanomolybdate(IV) with nitrous acid showed first order in redox species concentrations. The reaction featured pH dependence which could be an indication of two rate-determining steps where protonated and deprotonated nitrous ions are involved. It was observed that the deprotonated specie reacts slowly and ion catalysis is implicated [11]. In contrast, the oxidation of hydroxide ion by octacyanomolybdate(V) ions followed first-order kinetics in both oxidant and reductant concentrations, a positive salt effect on the reaction rate, and free radical intervention in the oxidative process [12]. Studies have also shown that all molybdenum enzymes followed two-electron redox processes, and Mo(IV) happened to be a strong competitor for one of the redox species. Even in the xanthine oxidase enzyme, evidence has shown that the Mo(IV) form is realistic and suggests its involvement in the catalytic sequence [13] and hence the need to gain a more detailed understanding of its mechanistic pathways that will stand alongside other findings in the advancement of the chemistry of molybdenum.

The influence of surfactant micelles on the reaction has been an area of great interest in medicine, pharmaceutical, biochemical, and chemical industries [14]. Piszkiewicz's and Berezin's models are among other kinetic models that numerically reveal the reliance of the observed reaction rate on the surfactant concentration with the efforts of their unique features like binding constant, cooperativity index, and micellar pseudo-phase rate constant [14, 15]. It is of great interest to ascertain the relevancy of the models on the redox reaction of allylthiourea and the bis-(2-pyridinealdoximato)dioxomolybdate(IV) complex in dissimilar micellar media.

2 Methods

The $[Mo^{IV}O_2(paoH)_2]^{2-}$ complex was prepared and characterised by using the method of Konidaris et al. [16] and FTIR (FTIR-8400S Fourier Transform Infrared Spectrophotometer, Shimadzu, Double Beam) and UV–Visible (Cary 300 Series UV–Vis Spectrophotometer, Agilent Technologies, USA), respectively. 2-Pyridinealdoxime and molybdenum dioxide obtained from Sigma-Aldrich were used to prepare it. The oxime-based complex was prepared by stirring the ligand paoH (2.4424 g, 0.02 mol) in ethanol (15 cm^3) followed by adding a dark violet solution (5 cm^3) of MoO_2 (1.4394 g, 0.01 mol) in drops into the stirring ligand solution. The resulting mixture was stirred at 70 °C with a magnetic stirrer for 3 h, and the solution was transferred to an ice bath and was allowed to slowly evaporate at ambient temperature for two days. Well-formed, quality light yellow crystals of the product appeared. The crystals were collected by filtration, washed with cold 50% ethanol (2×3 cm^3), and dried in the air. Yield: 2.464 g (63%).

Hydrochloric acid (BDH) was used to supply H^+ ions in the reaction. Allylthiourea (Merck) was used as a reducing agent. The variation of ionic strength was achieved by using sodium chloride salt (Merck), and ethanol (BDH) was used to vary the reaction medium polarity. Cetyltrimethylammonium bromide and sodium dodecyl sulphate acquired from Sigma-Aldrich were used to obtain micellar media. Calcium chloride and sodium formate obtained from Merck were used to inspect the effect of counter-ion on the observed rate. Acrylamide and methanol (BDH) were used to test for the presence of free radicals in the reaction medium. The products formed were analysed classically by using diethyl ether (BDH), sodium ascorbate (BDH), sodium nitroprusside (Merck), potassium thiocyanate (Merck), sulphuric acid (BDH), tin chloride (BDH), and potassium thiocyanate (Merck).

The stoichiometry of the reaction was inspected as documented previously [17, 18] by spectrophotometric mole ratio titration at fixed salt concentration and 300 K. The point of inflexion on the graph of absorbance against mole ratio was obtained from the absorbance observed after twelve hours. The products formed were probed accordingly. The addition of three drops of sodium ascorbate into a 2 cm^3 of the extracted organic layer of the reaction product followed by the addition of one drop of sodium nitroprusside was carried out to check the presence of sulphenic acid [19–23]. The addition of 0.1 cm^3 of concentrated sulphuric acid, boiled to a dense white fume and allowed to cool, followed by the addition of 0.5 cm^3 of distilled water and 0.5 cm^3 of 1.0 mol dm^{-3} potassium thiocyanate solution and one drop of acidified 0.25 mol dm^{-3} tin(II) chloride was used to determine the presence of Mo(II)/(III) ion in the reaction product mixture [24].

The kinetic measurements were conducted using a UV–visible Spectrophotometer (Model 721 PEC Medical) at a wavelength of 560 nm by observing the decrease in absorbance of the oxidant under the pseudo-first-order situation with [ATH] in a tenfold excess over the oxidant concentration while keeping the temperature and the ionic strength fixed [25–28]. The change in the medium polarity (D), acid concentration, and ionic strength (μ) of the reaction was studied by altering either one of them while keeping other parameters constant [29, 30]. The gradient of the plot of InA versus time was used to obtain the observed rate constant (k_{ob}) according to Eq. 1, and the second-order rate constant (k_2) was obtained from the ratio of k_{ob} with ATH concentration (Eq. 2). The addition of 0.2 cm^3 acrylamide to the reaction mixture with excess methanol was carried out to check the participation of free radicals in the reaction [31, 32].

$$\mathrm{InA} = \mathrm{InA}_0 + k_{ob}t \tag{1}$$

$$k_2 = k_{ob}/[\mathrm{ATH}] \tag{2}$$

The Piszkiewicz's and Berezin's models were probed in the reaction from their mathematical Eqs. 3 and 4, respectively.

$$k_{ob} = \frac{k_W K_D + k_M [D]^n}{K_D + [D]^n} \tag{3}$$

where $[D]^n = [D]$—CMC and $[D]$ is the concentration of surfactant. k_W and k_M are the pseudo-first-order rate constants for aqueous (absence of surfactant) and micelle medium, respectively. n is a number of surfactant molecules (D), and K_D is the dissociation constant of this micelle back to its free components. k_{ob} is the pseudo-first-order rate constant [14, 15].

$$k_{ob} = \frac{k_M K_a K_b C V + k_W}{(1 + K_a C)(1 + K_b C)} \tag{4}$$

where C = [Surfactant]—critical micelle concentration (CMC), the subscripts "a" and "b" denote quantities relating to the oxidant and reductant, respectively, K_a and K_b stand for the binding constants of Mo(IV) complex and allylthiourea separately, k_W and k_M stand for the rate constants of aqueous and micellar phases, respectively, C stands for surfactant concentration, and V is the molar volume of the surfactant [11, 27].

3 Results

The graph of absorbance against mole ratio is displayed in Fig. 1 which shows the stoichiometric amount involved in the reaction, and it is supported by Eq. 1.

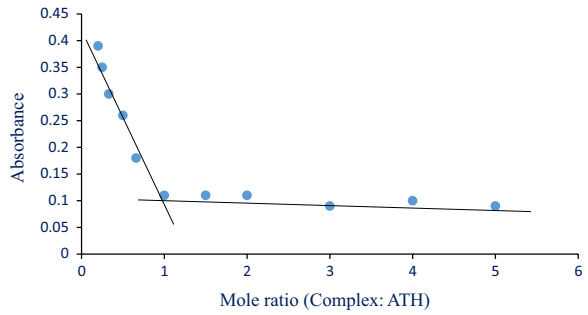


Fig. 1 Stoichiometric plot of the reaction of $[Mo^{IV}O_2(paoH)_2]^{2-}$ and ATH at $[Mo^{IV}O_2(paoH)_2{}^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, $D = 77.9$, [ATH] = (3.0—75.0) × 10^{-4} mol dm^{-3}, $\lambda_{max} = 560$ nm, and $T = 300$ K

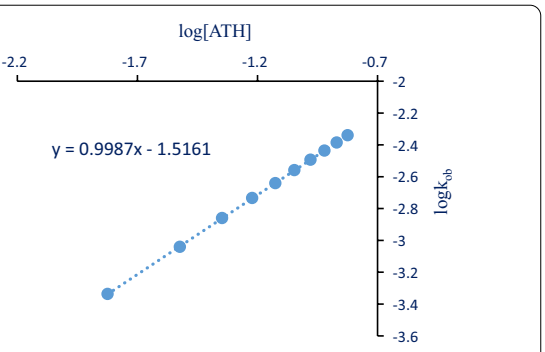


Fig. 3 Plot of logk_{ob} versus log[ATH] for the reaction of $[Mo^{IV}O_2(paoH)_2]^{2-}$ and ATH at $[Mo^{IV}O_2(paoH)_2{}^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, $D = 77.9$, [ATH] = (1.5—15.0) × 10^{-2} mol dm^{-3}, $\lambda_{max} = 560$ nm, and $T = 300$ K

$$2[Mo^{IV}O_2(paoH)_2]^{2-} + 2 \; \text{(allylthiourea)} + 2H_2O \longrightarrow 2[Mo^{II}O_2(paoH)_2]^{4-} + 2 \; \text{(sulphenic acid)} + 4H^+ \quad (5)$$

The pseudo-first-order plot and the logarithmic plot of the observed rate constant with the concentration of the reducing agent which reveals the order of the substrate concentrations in the reaction are presented in Figs. 2 and 3, respectively. The observed rate and second rate constants for the kinetic measurement are shown in Table 1.

The medium polarity and the counter-ion effects on the reaction rate are displayed in Tables 2 and 3, and Piszkiewicz's and Berezin's parameters which explain the micellar effect of the surfactants on the reaction rate are presented in Table 4.

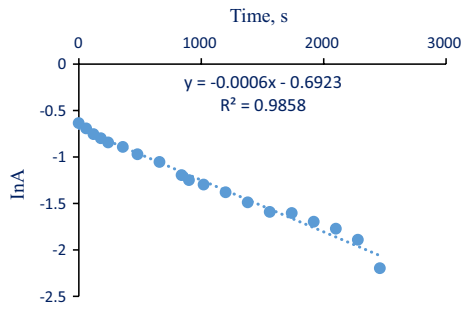


Fig. 2 Typical pseudo-first-order plot for the reaction of $[Mo^{IV}O_2(paoH)_2]^{2-}$ and ATH at $[Mo^{IV}O_2(paoH)_2{}^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, $D = 77.9$, [ATH] = 4.5×10^{-2} mol dm^{-3}, $\lambda_{max} = 560$ nm, and $T = 300$ K

4 Discussion

The stoichiometry followed a two-electron transfer from two moles of the allylthiourea to the two moles of the Mo(IV) complex. The point of inflexion in Fig. 1 confirmed the mole contribution in the course of the reaction.

The contribution of two moles of allylthiourea and two moles of the complex in the reaction leads to the formation of sulphenic acid and Mo(II) products. The appearance of red colouration on the addition of the sodium nitroprusside solution into the organic layer of the reaction product containing sodium ascorbate points to the presence of sulphenic acid. A red colour formation on the addition of 0.5 cm^3 of 1.0 mol dm^{-3} potassium thiocyanate solution and one drop of acidified 0.25 mol dm^{-3} tin(II) chloride among other reagents indicates the presence of Mo^{2+} ion in the reaction product. However, the existence of colouration ruled out the presence of Mo^{3+} ions in the product mixture (Eq. 5).

The determination of the first-order rate constant, k_{ob}, from the plot of absorbance versus time (Fig. 2) showed remarkable linearity that validates the reaction proceeding with a first-order in the [complex], and the slope (0.9987) of the plot of logk_{ob} against log[ATH] (Fig. 3) inferred the first order with respect to the [ATH]. The reaction was largely characterised by the deprotonation of ATH (Eq. 6) which gave rise to a decrease in the reaction rate as the [H^+] was increased (Table 1). The rate of the reaction was unaffected by the adjustment

Table 1 Pseudo-first-order and second-order rate constants for the reaction of $[Mo^{IV}O_2(paoH)_2^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, $D = 77.9$, $\lambda_{max} = 560$ nm, and $T = 300$ K

10^2[ATH] mol dm^{-3}	μ mol dm^{-3}	[H +] mol dm^{-3}	$10^4 k_{ob}$ s^{-1}	$10^2 k_2$ dm^3 mol^{-1} s^{-1}
1.50	0.10	0.01	5.00	3.07
3.00	0.10	0.01	9.10	3.03
4.50	0.10	0.01	13.82	3.07
6.00	0.10	0.01	16.39	3.07
7.50	0.10	0.01	18.94	3.05
9.00	0.10	0.01	23.29	3.06
10.5	0.10	0.01	27.00	3.05
12.0	0.10	0.01	30.46	3.05
13.5	0.10	0.01	33.84	3.05
15.0	0.10	0.01	37.27	3.04
4.50	0.10	0.01	13.82	3.07
4.50	0.10	0.15	09.36	2.08
4.50	0.10	0.20	07.47	1.66
4.50	0.10	0.25	06.84	1.52
4.50	0.10	0.30	06.62	1.47
4.50	0.10	0.35	05.94	1.32
4.50	0.10	0.40	04.68	1.04
4.50	0.10	0.45	04.11	0.91
4.50	0.10	0.50	03.74	0.83
4.50	0.10	0.55	02.30	0.51
4.50	0.10	0.20	07.47	1.66
4.50	0.10	0.01	13.82	3.07
4.50	0.20	0.01	14.05	3.12
4.50	0.30	0.01	13.82	3.07
4.50	0.40	0.01	13.82	3.07
4.50	0.50	0.01	13.82	3.07
4.50	0.60	0.01	13.82	3.07
4.50	0.70	0.01	13.82	3.07
4.50	0.80	0.01	13.82	3.07
4.50	0.90	0.01	14.05	3.07

of the ionic strength in the reaction medium due to the interaction of charged and uncharged species (Eq. 7), and this is supported by the lack of effect of medium polarity on the reaction rate (Table 2). Furthermore, the consistency of second-order rate constant (k_2) for the change in [ATH] at constant [H$^+$] and μ in Table 1 reinforced the first order in allylthiourea concentration, while at constant [ATH] and [H$^+$], the consistency of k_2 obtained at varying μ buttressed a reaction proceeding without salt effect on the reaction rate. Busari et al. [10] on the study of oxidation of methylthiourea and allylthiourea by μ-oxo-tetrakis(1,10-phenanthroline) diiron(III) complex generated similar data which depict first in [ATH] and neutral salt effect on the reaction rate. The oxidation of octacyanomolybdate(IV) by nitrite ions showed a linear dependence on [H$^+$] and zero ionic strength effect on the reaction rate [11]. The reduction of octacyanomolybdate(V) ion by hydroxide ion observed similar first order in both octacyanomolybdate(V) ion and hydroxide ion concentrations with a positive effect of [H$^+$] and ionic strength on the reaction rate [12]. The oxidation of formaldehyde by octacyanomolybdate(V) ion in an aqueous alkaline medium yielded first order with respect to formaldehyde and octacyanomolybdate(V) ion concentrations. The influence of hydroxide ion concentration was positive, with an increase in reaction rate [33]. More et al. [34] obtained a similar outcome on the reduction of thiosemicarbazide by a Waugh-type 9-molybdomanganate(IV) complex that showed first order in both redox species concentrations, a positive acid effect, and a zero ionic strength effect on the reaction rate. From Table 2, the consistency of the first- and second-order rate constants reinforced a reaction with zero dielectric constant effect on the reaction rate due to the interaction of neutral and charged species at the rate-controlling step, which is similar to the studies of More et al. [34] and Busari et al. [10].

Table 3 shows increase in reaction rate with an increase in Ca^{2+} ion concentration and a zero effect on reaction rate with an increase in $HCOO^-$ ion concentration. Hence, the reaction rate was unaffected and catalysed by the introduction of Ca^{2+} and $HCOO^-$ counter-ions, respectively, due to the interplay of charged and unchanged charged species at the rate-limiting step, respectively (Eq. 7). Also, the generated free radical was imperative in the formation of sulphenic acid.

Table 4 features Piszkiewicz's and Berezin's parameters which quantitatively explain the effect of surfactants on

Table 2 Influence of medium polarity on the reaction rate of $[Mo^{IV}O_2(paoH)_2]^{2-}$ with ATH at $[Mo^{IV}O_2(paoH)_2^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, $\mu = 0.1$ mol dm^{-3}, $[ATH] = 4.50 \times 10^{-2}$ mol dm^{-3}, $[H^+] = 1.0 \times 10^{-2}$ mol dm^{-3}, $\lambda_{max} = 560$ nm, and $T = 300$ K

D	77.9	77.4	76.9	76.5	76.1	75.7	75.2	74.8	74.3	73.9
$10^4 k_{ob}$ (s^{-1})	13.82	13.82	13.82	13.82	14.28	13.82	14.05	13.82	13.82	14.05
$10^2 k_2$ (dm^3 mol^{-1} s^{-1})	3.07	3.07	3.07	3.07	3.17	3.07	3.12	3.07	3.07	3.12

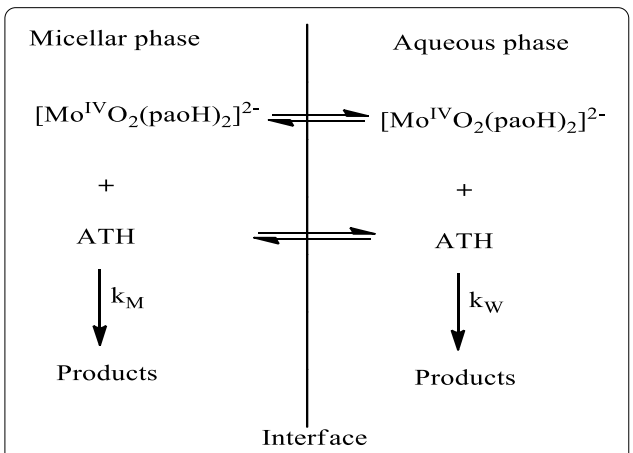
Table 3 Effect of counter-ions on the rate constants for the reaction of $[Mo^{IV}O_2(paoH)_2]^{2-}$ and ATH at $[Mo^{IV}O_2(paoH)_2{}^{2-}] = 1.5 \times 10^{-3}$ mol dm^{-3}, [ATH] = 4.50×10^{-2} mol dm^{-3}, and $\mu = 0.1$ mol dm^{-3}

Ion	10^3[Ion], mol dm^3	$10^4 k_{ob}$, s^{-1}	$10^2 k_2$, dm^3 mol^{-1} s^{-1}	Ion	10^3[Ion], mol dm^3	$10^4 k_{ob}$, s^{-1}	$10^2 k_2$, dm^3 mol^{-1} s^{-1}
Ca^{2+}	0.00	10.13	3.81	$HCOO^-$	0.00	13.82	13.82
	8.00	11.05	7.16		8.00	13.82	3.07
	12.0	12.67	8.19		12.0	13.36	2.96
	16.0	13.82	9.72		16.0	13.82	3.07
	20.0	14.51	10.74		20.0	13.59	3.07
	24.0	17.04	12.79		24.0	13.36	2.96
	28.0	18.19	13.82		28.0	13.82	3.07
	32.0	20.49	16.89		32.0	13.82	3.07

Table 4 Piszkiewicz's and Berezin's model parameters

Piszkiewicz's parameters						
Surfactant	n	K_D	$1/K_D$	k_M (dm^3 mol^{-1} s^{-1})	r^2	k_W (dm^3 mol^{-1} s^{-1})
CTAB	1.4882	0.3999	2.5006	0.9065	0.9854	0.0067
SDS	0.8725	0.5541	1.8047	0.7388	0.9182	0.0025
Berezin's parameters						
	k_M	K_a	K_b (dm^3 mol^{-1} s^{-1})	r^2	k_W (dm^3 mol^{-1} s^{-1})	
CTAB	0.7899	0.8004	0.7793	0.9814	0.0037	
SDS	0.4537	0.2008	0.7066	0.9674	0.0005	

the reaction rate. The observed relative coefficient (r^2) showed the degree of agreement of the reaction rate constants of CTAB and SDS with respect to the rate constants of the aqueous medium. The dissociation constants (K_D) represent the slow deactivation of the activated complex to possible products. The effect of CTAB on the observed reaction rate through which the Piszkiewicz's and Berezin's models were analysed revealed that there are a significant binding constant ($1/K_D$) and positive cooperativity ($n > 1$) existing between the redox partners, which is a result of the much increased reaction rate (Table 4). This effect may be due to the interaction of the hydrophilic polar head of CTAB with the charged Mo(IV) complex at the Stern layer of the surfactant aggregates, which are considered to have a high ionic concentration of CTAB with low polarity. The distribution of the redox species at the micellar and aqueous phases of the reaction medium (Scheme 1) results in a catalytic reduction of the Mo(IV) complex by the nucleophile with $k_M > k_W$. The nonlinear least-squares approach was used to obtain the parameters of Eqs. 3 and 4 (Table 4). Similar studies



Scheme 1 The distribution of redox species in the aqueous and micellar phases

by Laguta et al. [14, 15] showed agreeable fitting of Piszkiewicz's and Berezin's models into the observed reaction

rate. The reaction of *L*-tyrosine and ninhydrin in the presence of CTAB showed a catalytic effect on the reaction rate [35]. On the other hand, the reaction kinetics of the ethylene glycol and periodate in the presence of CTAB showed an inhibitory effect on the reaction rate due to the association of one of the substrates with the micelles, leaving the other substrate in the aqueous phase [36]. Likewise, the kinetics of the oxidation of tris-(1,10-phenanthroline)iron(II) by azido-pentacyanocobaltate(III) complex in the presence of CTAB had a inhibitory effect on the oxidation process [37].

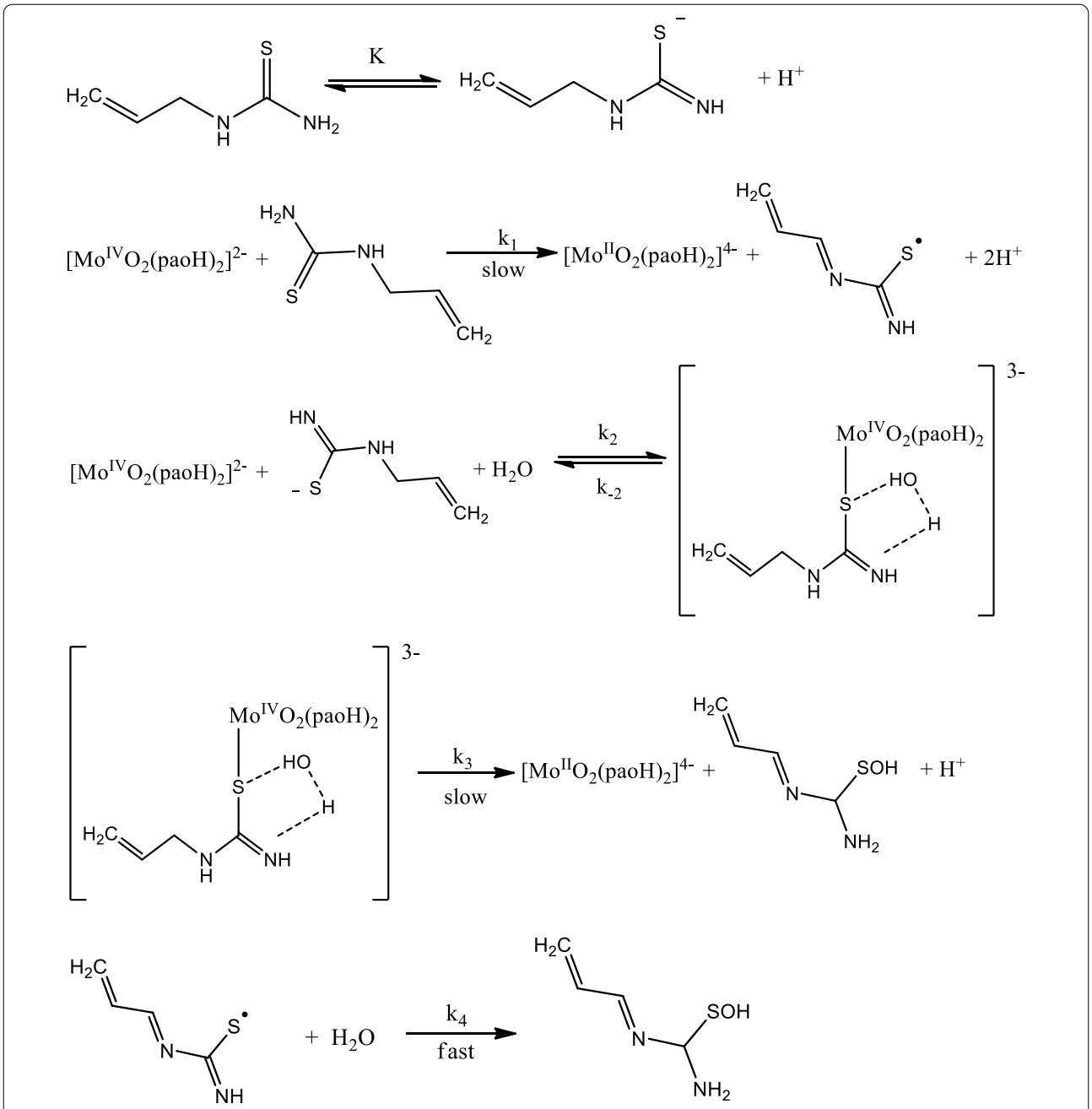
On the other hand, the impact of SDS on the reaction rate through which the Piszkiewicz's and Berezin's models were analysed showed that there are weak hydrophilic and hydrophobic interactions between the surfactant and the substrates at the Gouy–Chapman layer region of the micelle. This is probably related to the charges of the substrates at the rate-controlling step (Eq. 7). It is observed that the substrates bind weakly with the micelles, leading to an unfavourable interaction between them and the free radical generated in the process. The dominance of inhibitory effects over the catalytic effect of SDS on the reaction rate is reinforced by the observed low binding constant (0.7066) of the substrates with the micelle compared to the binding constant (0.8004) of the substrates with the CTAB micelle according to Berezin's model, and the layer of this activity can be considered as a region of low ionic concentration and low medium polarity. The outcome suggests that Piszkiewicz's and Berezin's approaches are appropriate and applicable in this redox process. The treatment of the models gives significant values of the evaluation coefficients (r^2), and the estimated k_M values of the surfactants are higher than the analogous k_W value, which makes the models valid here.

Comparative result was reported by Singh and Luwang [38] on the reactions of triphenylmethyl carbocations with cyanide ion in the presence of SDS. The reaction rate was inhibited with change in the [SDS] and suggestive of a hydrophobic interaction between the reacting species. The electron transfer reactions of iron(III)-polypyridyl complexes with organic sulphides recorded a catalytic effect with change in concentration of SDS and CTAB in the reaction medium on the reaction rate [39].

On the basis of the above result, an outer-sphere mechanistic route for the reaction has been proposed (Eqs. 6–10) as presented in Scheme 2;

5 Conclusions

The study of Piszkiewicz's and Berezin's on the redox reaction of bis-(2-pyridinealdoximato) dioxomolybdate(IV) complex with allylthiourea ion followed a 2:2 stoichiometric and first-order in both reacting species concentrations. The formation of sulphenic acid products is necessitated by the emergence of a free radical and an energised activated complex. The influence of ionic strength on the reaction rate occasioned no salt effect, which indicates a reaction arising from neutral and charged species at the limiting phase of the reaction, and the decrease in the medium polarity had no control on the rate of reaction. The catalysis originating from the presence of counter-ion (Ca^{2+}) is possible due to the participation of an unlike charged species at the rate-limiting step. Change in the concentration of CTAB and SDS in the reaction medium catalysed and inhibited the reaction rate. The probing of the Piszkiewicz's and Berezin's models on the reaction established that a high binding constant was responsible for the high efficiency observed in the redox activity, and the positive cooperativity order observed among the substrates and the surfactants implicated the electrostatic and hydrophobic interactions. Piszkiewicz's and Berezin's models are applicable to this reaction as they aid in revealing the mode and factors associated with enzymatic reactions in biological systems. The study also established the likelihood of interaction between the complex in the SDS micelle phase and the ATH in the bulk water phase, which resulted in the dominance of an inhibitory factor. The use of other kinetic models such as Menger and Portnoy, Raghavan and Srinivasan, and pseudo-phase ion exchange (PIE) models should also be used for further possible interpretation of the reaction rate in the presence of the surfactants.



Scheme 2 Elementary pathways of $[Mo^{IV}O_2(paoH)_2]^{2-}$ and ATH reaction

Abbreviations

A_t: Absorbance at time "t"; A_∞: Absorbance at infinity; CTAB: Cetyltrimethylammonium bromide; SDS: Sodium dodecyl sulphate; DNA: Deoxyribonucleic acid; CMC: Critical micelle concentration; k_{ob}: Observed rate constant; k_2: Second-order rate constant; *K*: Equilibrium constant; ob: Observed; μ: Ionic strength; *D*: Dielectric constant; *T*: Temperature; λ_{max}: Wavelength of maximum absorption; UV: Ultraviolet; ATH: Allylthiourea; BDH: British drug house; FTIR: Fourier-transform infrared.

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Author contributions

Category 1 IUN, SOI, and IA contributed to conception and design of study; ADO and IUN were involved in acquisition of data; and IUN, SOI, and ADO contributed to analysis and/or interpretation of data. *Category* 2 IUN, SOI, and IA were involved in drafting the manuscript; IUN, ADO, and IA revised the manuscript critically for important intellectual content. All authors read and approved the final manuscript.

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We have no conflicts of interest to disclose.

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