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Compatative Catalytic Study of Oxidation of Thiourea by Chromium (VI) in Presence of Different Catalysts and Micelles

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Abstract

The series of catalysts like acetate, oxalate, EDTA, the varies micelles viz, CTAB, SDS, TRITON X-100 was carried out in the kinetic study of oxidation of Thiourea by Cr(VI) as an oxidant in water medium. The effect of catalytic efficiency has been study for varies catalyst and micelles by volumetric method and UV spectroscopic methods. The product was confirmed by IR studies. UV study reveals shows that higher catalytic efficiency has been studied in the presence of oxalate, SDS medium. The effect of catalytic efficiency also has been study for ionic strength, solvent variation, polymer, different temperatures, and Thermodynamic parameters and varied the [Thiourea] in the presence of different micelles at constant concentration. The UV–Visible spectroscopic results revealed that the oxidation reaction exhibited significantly enhanced catalytic efficiency in the presence of oxalate as a catalyst and SDS as the micellar medium, indicating their superior ability to accelerate the oxidation process compared with other tested systems. In addition to catalyst and micelle variation, the influence of several physicochemical parameters on the reaction kinetics was also examined in detail. These included ionic strength, solvent composition, polymer additives, temperature variation, and thermodynamic parameters to understand their role in modulating the oxidation mechanism. Furthermore, the concentration of thiourea was systematically varied under constant catalyst and micelle concentrations to investigate substrate dependency and reaction order in different micellar environments.

Keywords: Chromium, thiourea, micelles, ligands, spectral studies

INTRODUCTION

Thiourea one of the simplest of the thio compounds and has various industrial, agricultural, analytical applications. This material is widely used in photography as a fixing agent and also removes stains from negative. In agriculture it, is used as fungicides, herbicides, and rodenticides [1] and also to decrease the content of nitrifying bacteria in soil [2]. Thiourea is also used induction early ripening in several fruits [3]. In analytical chemistry Thiourea is used as a spectrophotometric reagent for the determination of several metals [4]. Thiourea is also used as reagent for copper electrolytes refinery [5]. Thiourea and its derivatives have also been screened as allergenic and carcinogenic factors [6]. Thiourea is poorly volatile and is not easily analyzed by gas chromatography [7]. For the determination of Thiurea by titrimetry by iodine [8], by kinetic measurements [9] were proposed by many researchers. Thiourea has many applications study by another many researchers [10, 11].

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Recently the radolysis of Thiourea and its derivatives has been studied in the connection with their uses as corrosion inhibitors in nuclear reactors [12, 13, 14]. The radiolytic oxidation of thioureas to the corresponding formamidine disulphides represents a special case within a whole class of oxidation reactions leading to the same dimer [15], among them anodic oxidation [16]. In radiolysis, the intermediacy, over a large pH range, of the dimeric thiourea radical cation now has been unequivocally established. It can be fairly assumed that this species plays a dominant in many of these other process as well. Thiourea is toxic [17] and cancer support agent [18]. There and other environment concerns have promoted studies on the destruction of Thiourea[19]. Thiourea can be oxidized by variety of oxidizing agents [20–27]. The reaction pathways and final product of oxidation reaction depend on the pH and the condition of the reaction mixtures. Reaction involving Sulphur containing compounds are generally known to be quite complex. The complexity is highlighted by free radical mechanism [28], auto oxidation [29] and formation of Sulphur – Sulphur bonds leading to various polymeric Sulphur species [30].

Polarity and water content in different regions of the micelle plays an important role in the rate of reactions in these regions. The Surface layer of micelle resembles a concentrated electrolyte solution with a dielectric constant lower than that of the bulk water. The micelle phase is less polar than water and the ionic micelles have a polarity near to that of pure ethanol even at the stern layer [31–35]. An increase in the aggregation number causes a decrease in the surface polarity [36].

Micelle catalyzed reactions had become an area of rapidly increasing interest and a number of extremely important thermodynamic and kinetic studies of organic reactions have been performed in micellar solutions. There is extensive evidence on the ability of aqueous micelles and other associated colloids to influence reaction rates and equilibria, and concentration, or depletion, of the reactants in the interfacial region have major effects o the rate of reaction [37–43].

Cr (VI) is known to function as a one electron, two electron depending upon the substrate and its used extensively for the analytical, and preparative purposes. Chromium exists in many oxidation states. Due to this redox chemistry among the different oxidation state Cr(VI) is more stable. Among the oxidation states from the Cr(VI) is the most stable and generally important are Cr(VI), Cr(II), Cr(III). The rate of reaction of Cr(VI) to Cr(III) was analyzed by many researchers[44–49].

Even though the Cr-S interaction is important in several systems in the attention has been paid to study of the chemistry of this system. For the Cr(VI) oxidation of Thiourea we have proposed a mechanism involving complex formation between Cr(VI) and sulphur in thiouryl cation. In this report we established that Cr(VI) behave different from Cr(V) andCr(IV) in the oxidation of Thiourea [50].

Oxalate is an efficient catalyst for in the oxidation of Thiourea and enhanced the reactivity in the presence of oxalate is attributed to the formation of more reactive Cr(VI)- Oxalate complex. Therefore we thought it would be interested to test the catalytic activity of acetate, oxalate, EDTA on the oxidation of Thiourea .We also worked here on result on the catalyzed oxidation of Thiourea by Cr(VI) in the presence of varies micelles like CTAB, SDS, TRITON X-100, ionic strength, solvent effect, temperature study and free radical formation and Thermodynamic parameters also studied.

EXPERIMENTAL STUDIES

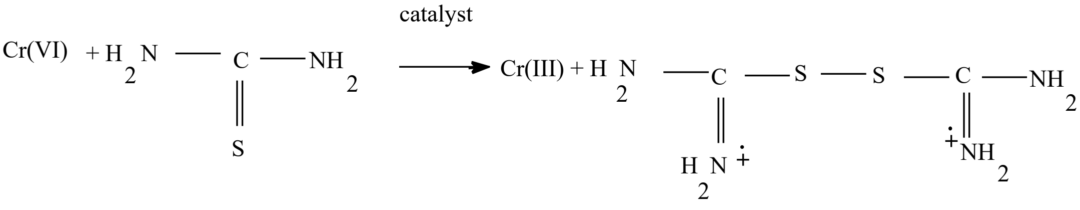
Potassium dichromate (Aldrich 99%) and Thiourea (Merck, AR grade) are used in this kinetic studies. The product was formed by addition of Thiourea, Cr(VI) in different catalysts over a period of 24 hours. HPLC grade Acetic acid, Ethanol, Dimethyl sulphoxide, Perchloric acid and double distilled water were used in all the kinetic runs performed. Sodium acetate, Calcium oxalate, Ethylene di-ammine tetra acetate, Cetyl tributyl ammonium Bromide, Sodium lauryl sulphate, Triton X-100 were purchased from (Aldrich 99% purity) and used as received.

All other reagents were Analar grade. Rate of reaction determined by Iodimetrically. So we used sodium thio sulphate, copper sulphate, pure starch, potassium iodide and dilute sulhuric acid are used.

The standardized sodium thio-sulphate solution is used to find the rate constant. All the above substance are Analar Grade.

STOICHIOMETRY

The reaction was carried out between potassium dichromate (1×10^{-2}M) and Thiourea (1×10^{-2}M), in the presence of catalysts keeping other conditions similar to kinetic studies. After completion of the reaction, examination of the products the mole ratio of the oxidant and Thiourea by volumetrically shows that one mole of Thiourea consumes one mole of Cr(VI). The stoichiometry is 1:1. Thus type of stoichiometry already proposed by Olatungi [48]. Thus the net reaction can be represented by equation (1)



$$\mathrm{Cr(VI)} + H_2N-\underset{\underset{S}{\|}}{C}-NH_2 \xrightarrow{\text{catalyst}} \mathrm{Cr(III)} + H_2N-\underset{\underset{H_2\dot{N}^{+}}{\|}}{C}-S-S-\underset{\underset{{}^{+}\dot{N}H_2}{\|}}{C}-NH_2 \quad ---- \ (1)$$

PRODUCT ANALYSIS

A mixture of Thiourea (0.01M), Catalyst (0.01M), Cr(VI) (0.01M) in double distilled water at pH 2.44 was allowed to stand until completion of the reaction. The same pH was also worked done many researchers [51–54]. The reaction product was filtered and dried. The residue was analyzed by recording the IR spectrum using Shimadzu 408 IR spectrometer. The spectrum shows that the peaks corresponding to the Formamidine disulphide. The same product also observed by many researchers [15, 45, 48–49, 51, 54–68]. The remaining Cr(III) product was analyzed by adsorption spectroscopy. The adsorption spectrum of sample shows the adsorption intensity for the product is 3.5 indicated the disulphide-Cr(III) was most efficiently. The absorption spectrum maximum for the product 400–420nm indicating the product formation [69].

KINETIC MEASUREMENTS

The kinetics of the reaction was followed by pH 2.44 by measuring the absorbance intensity (3.3) at Cr(VI) alone employing a Hitachi-200 UV Spectrometer having thermostated cell compartment attached to a circulating constant temperature bath. The absorbance intensity for Cr(VI)-Thiourea-Catalyst (SDS) is 8.0 in the presence of catalyst like SDS the absorbance intensity will shift higher. The absorbance intensity for product formamidine sulphide was observed as 3.5. In all reaction, at least 10 fold stoichiometry excess of substrate over the oxidant was used ensures pseudo first order conditions. Rate constants were evaluated by using the logarithmic plots of volume of thiourea consumed against time in first order equation (2). The rate constants (k_1) collected in tables (1–6) were computed by the equation,

$$k = \frac{2.303}{t} log \left(\frac{v_o}{v_t}\right) \qquad (2)$$

SPECTRAL STUDIES

In the present study we noticed that an initial increased in absorbance followed by slow decay of Cr(VI) with absorbance intensity was noted. During the course of the reaction the colour changed red colour to brown colour indicating the formation of Cr(III) – product complex. The disappearance of red colour at the end of reaction indicated that Cr(VI) leading to the formation of product. When we recorded the absorption spectrum of Cr(VI) is alone we observed the sharpening of the peak at absorption intensity is 3.4. How ever when the absorbance spectrum was recovered in the presence of oxidant Cr(VI) – catalyst – Thiourea (product) the peak absorbed at 3.5. The sharp peak in the UV absorption spectra shows the evidence for the Cr(III)- product formation. It has been established that the peak corresponds to the Cr-S bond formation [69]. The absorbance intensity also increased from 3.4 to 8.0 when we recorded in the presence of SDS micelle medium.

During our kinetic studies we realized the possibility of the existence of two intermediate complexes Cr(IV) and Cr(V).

RESULTS AND DISCUSSION

In order to understand the role of catalysts on the Cr(VI) oxidation of Thiourea, it is essential to understand the mechanism of uncatalyzed reaction. The uncatalyzed reaction is first order with respect to Cr(VI) and fractional order with respect to substrate and catalysts (Figure 1).

UV Adsorption Studies

By the help of Hitachi-200 UV Spectrophotometer was used to analyzed the absorbance intensity was various catalysts and micelles .According to the [substrate] it shows absorbance intensity was exhibits at 3.0, for oxidant [Cr(VI)] exhibits at 3.4, while in the product was exhibits at 3.5.In catalytic studies in presence of ligands like acetate ligand shows the absorbance intensity was exhibits at 5.6, while in presence of oxalate ligand shows the absorbance intensity was exhibits at 5.8, and then in presence of EDTA ligand shows the absorbance intensity was exhibits at 6.3 (Figure 2).

In catalytic studies in presence of micelles like CTAB shows the absorbance intensity was exhibits at 6.5 (Figure 3), while in presence of SDS shows the absorbance intensity was exhibits at 8.0, and then in presence of TRITON X-100 shows the absorbance intensity was exhibits at 7.4.

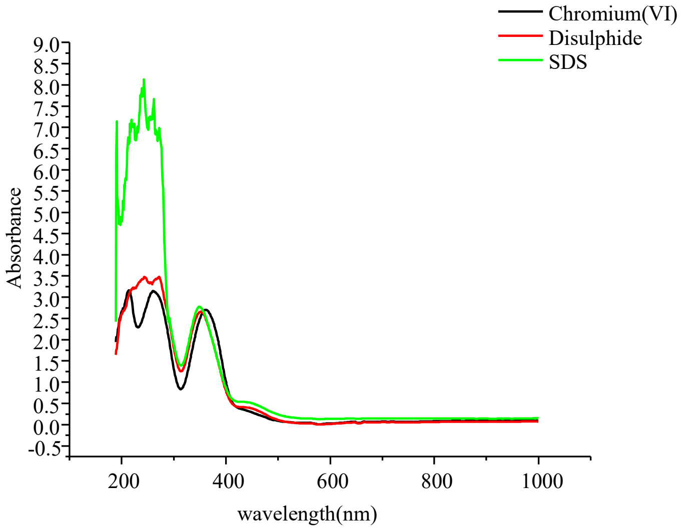


Figure 1. The UV absorption spectra for a) Cr(VI) (0.01M) only b) Product- Formamidine disulphideC) Cr(VI) (0.01M), SDS (0.01M) and Thiourea (0.01M)

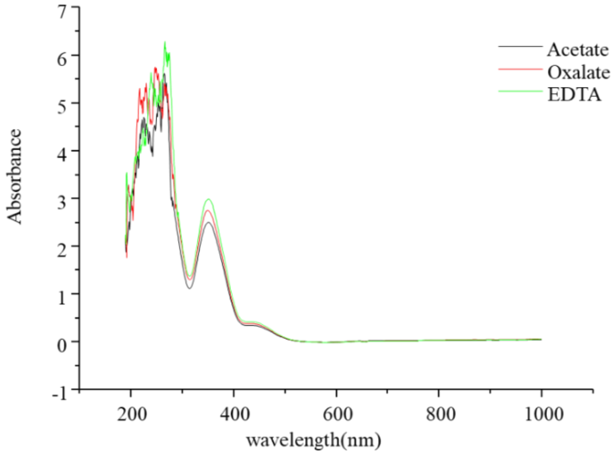


Figure 2. The UV absorption spectra for a) Cr(VI) (0.01M), Acetate ligand (0.01M) and Thiourea (0.01M)b) Cr(VI) (0.01M), Oxalate ligand (0.01M) and Thiourea (0.01M)c) Cr(VI) (0.01M), EDTA ligand (0.01M) and Thiourea (0.01M)

Then we compare the catalytic efficiency was maximum in oxalate ligand than among the ligands, as well as the catalytic efficiency was maximum at SDS has maximum absorbance intensity was greater than other micelles. Pseudo first order k_1 and second order rate constant k_2 values for Cr(VI) oxidation of Thiourea in double distill water medium at 303K.

[Oxidant] = 0.001M, pH 2.44, 303 K. Second order rate constants were calculated from $k_2 = k_1$ /[Thiourea]

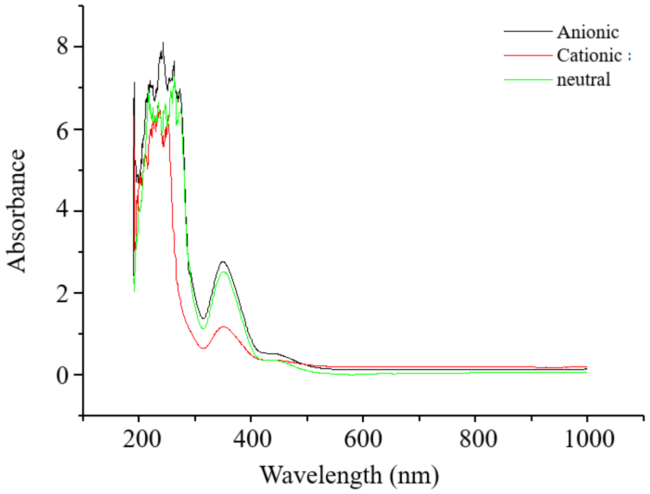
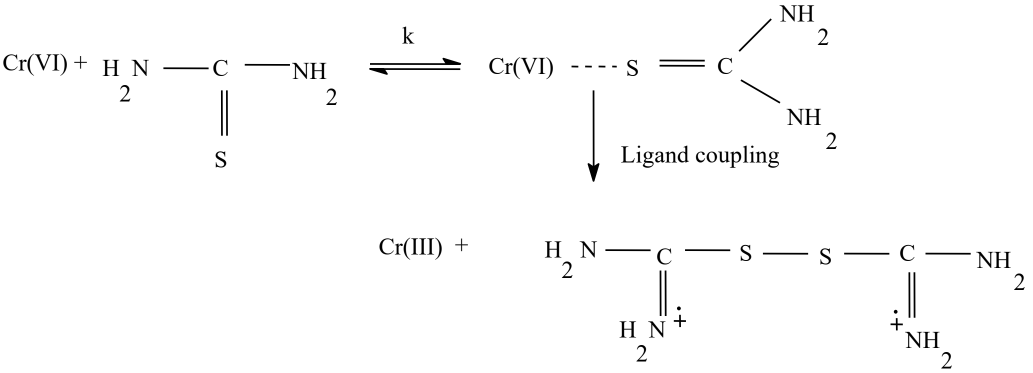


Figure 3. The UV absorption spectra for a) Cr(VI) (0.01M), Cationic micelle (0.01M) and Thiourea (0.01M)b) Cr(VI) (0.01M), Anionic micelle (0.01M) and Thiourea (0.01M) c) Cr(VI) (0.01M), Neutral micelle (0.01M) and Thiourea (0.01M) (Table 1).

Table 1. Oxidation of Thiourea in double distill water medium at 303K.

[THIOUREA]	**[$k_1 \times 10^{-3}$] S^{-1}**	**[$k_2 \times 10^{-1}$] $M^{-1} S^{-1}$**
0.01	0.902	0.902
0.03	1.385	0.462
0.07	1.944	0.277
0.10	2.244	0.224

The saturation kinetics was explained in terms of complex formation between Cr(VI) and Thiourea in the uncatalyzed reaction. The mechanism proposed for the uncatalyzed reaction scheme is,

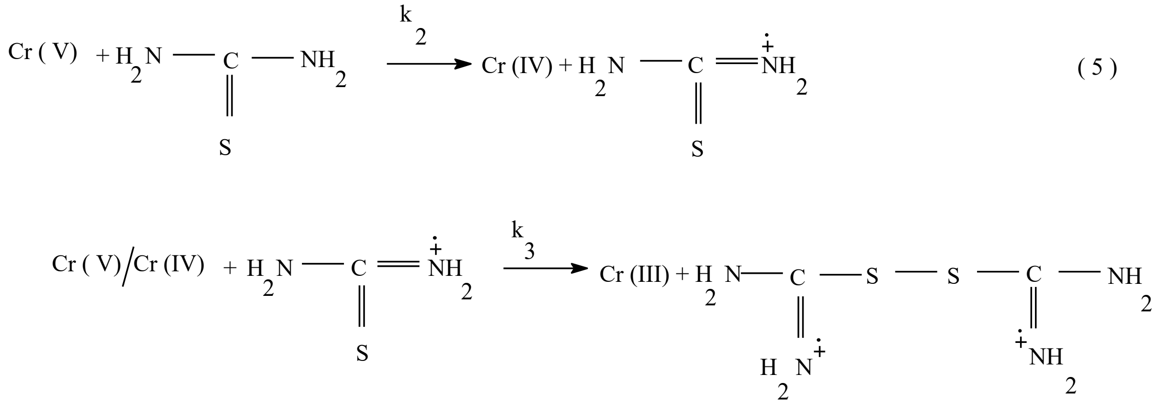


(Scheme I)

According to scheme – I, the oxidant forms a formamidine disulphide. The formation of product, formamidine disulphide can be visualized due to ligand coupling of thiouryl cation in the complex [15, 48, 51, 55, 57, 60, 62–68].

However the alternative formulation is in terms of inner sphere electron from Cr(VI) to Thiourea in the complex laeding to the formation of Cr(IV) and Cr(V) and thiouryl cation radical [70]. Thus the equations (3–6) represents the alternative mechanism [71]. (scheme-II)

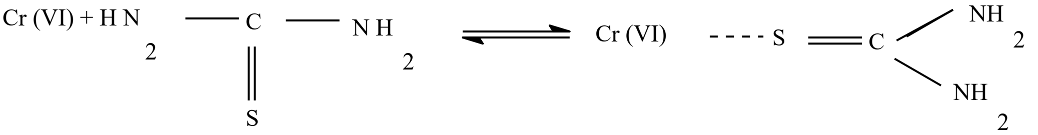
The Cr(VI) oxidation of thiourea is catalysed by the ligands such as sodium acetate,calcium oxalate, Ethylene diammine tetra acetic acid, CTAB, SDS, Triton X-100 and the rate constant values obtained for the oxidation of Thiourea at different [catalyst] are given in Table 2.



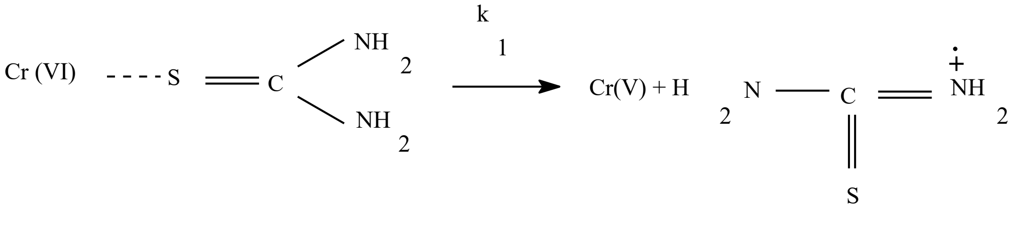
$$\mathrm{Cr(V)} + H_2N-\underset{\underset{S}{\|}}{C}-NH_2 \xrightarrow{k_2} \mathrm{Cr(IV)} + H_2N-\underset{\underset{S}{\|}}{C}=\overset{\bullet +}{N}H_2 \qquad (5)$$

$$\mathrm{Cr(V)/Cr(IV)} + H_2N-\underset{\underset{S}{\|}}{C}=\overset{\bullet +}{N}H_2 \xrightarrow{k_3} \mathrm{Cr(III)} + H_2N-\underset{\underset{H_2\overset{\bullet +}{N}}{\|}}{C}-S-S-\underset{\underset{\overset{\bullet +}{N}H_2}{\|}}{C}-NH_2$$

(Scheme II)



(Complex ii)



The Cr(VI) highly stable in the pH 3.0 to 4.0. In the present study the catalyst- Cr(VI) at pH 2.44 has been measured through the reaction is catalysed by all catalysts, the catalytic efficiency varies, when the catalyst concentration is 1 × 10^{-2} M, the rate enhancement is 1.1 time lower with acetate ligand, when as in oxalate ligand the rate enhancement is 1.3 times is increased, and in the presence of Ethylene diammine tetra acetic acid ligand rate enhancement is lower with 1.5 times. Since acetate, Ethylene diammine tetra acetic acid ligands they tend to co-ordinate to complex catalyst- Cr(VI) and try to stabilize the oxidant. This fact was confirmed by the least reactivity observed with these ligands was carried out in the pH 2.44. Thus the oxalate ligand seems to be the superior catalysts among these ligands.

Thus in the present study also carried out in the present of different catalysts like CTAB, SDS, Triton X-100 through the reaction is catalysed by all the micelles the catalytic efficiency varies. When the cationic micelle (CTAB), neutral micelle (Triton X-100) the catalysts concentration is 1 × 10^{-2}M, the rate enhancement is decreased with 6.6 times with CTAB, Triton X-100. Where as rate enhancement in SDS is about increased with 1.32 times. Since CTAB, Triton X-100 are cationic, neutral micelle are they tend to co-ordinate catalyst- Cr(VI) and try to stabilize the oxidant. This fact was confirmed by least reactivity observed with these micelle the reaction was carried out at in pH 2.44. Thus SDS seems to be the superior micelles among these micelle.

Micellar Medium Studies

At constant micellar medium, the substrate concentration was varied about 10 times, the reaction was carried out at in pH 2.44.At constant [CTAB] medium, the rate of reaction at 1 × 10^{-2}M of [Thiourea] was 9.6 times decreased. When at constant [Triton X-100] medium, the rate of reaction at 1 × 10^{-2}M of [Thiourea] was 5.8 times decreased. At constant [SDS] medium, the rate of reaction at 1 × 10^{-2}M of [Thiourea] was 1.1 times increased.

Thus the rate of reaction at different micelle at constant [micelle] medium, rate enhancement is 9.6 times decreased at constant [CTAB] medium, rate enhancement is 5.8 times decreased at constant [Triton X-100] medium, rate enhancement is 1.1 times increased at constant [SDS] medium. This fact was confirmed by the least reactivity observed with these micelle CTAB, Triton X-100 which is try to stabilize the oxidant. Thus SDS seems to be the superior micelles among these micelle.

The order with respect to found to be unity from the linearity of the plots of log absorbance Vs log [concentration] under our experimental conditions, all the substrate exhibits fractional order dependence. The complex kinetics could be explained only in a terms of Michalelis-menton type mechanism. The order with respect to found to be in the presence of catalyst and micelles studies is also found to be fractional order in this presence study.

Catalytic Efficiency

Pseudo first order rate constant k_1 values for the catalytic oxidation of Thiourea by Cr(VI) in double distilled water medium in pH 2.44, at 303K (Table 2 & 3).

Table 2. Values for the catalytic oxidation of Thiourea.

Catalyst	**Concetration (M)**	**$k_1 \times 10^{-3}$ S^{-1}**
Acetate	0.001	0.786
	0.003	1.129
	0.007	1.711
	0.010	1.974
Oxalate	0.001	0.883
	0.003	1.563
	0.007	2.428
	0.010	2.922
EDTA	0.001	0.758
	0.003	0.883
	0.007	1.063
	0.010	1.383
CTAB	0.001	0.923
	0.003	0.567
	0.007	0.387
	0.010	0.330
SDS	0.001	0.775

	0.003	1.114
	0.007	1.473
	0.010	1.657
Triton X-100	0.001	0.790
	0.003	0.521
	0.007	0.377
	0.010	0.330
Acrylonitrile	0.001	0.832
	0.003	0.840
	0.007	0.843
	0.010	0.845

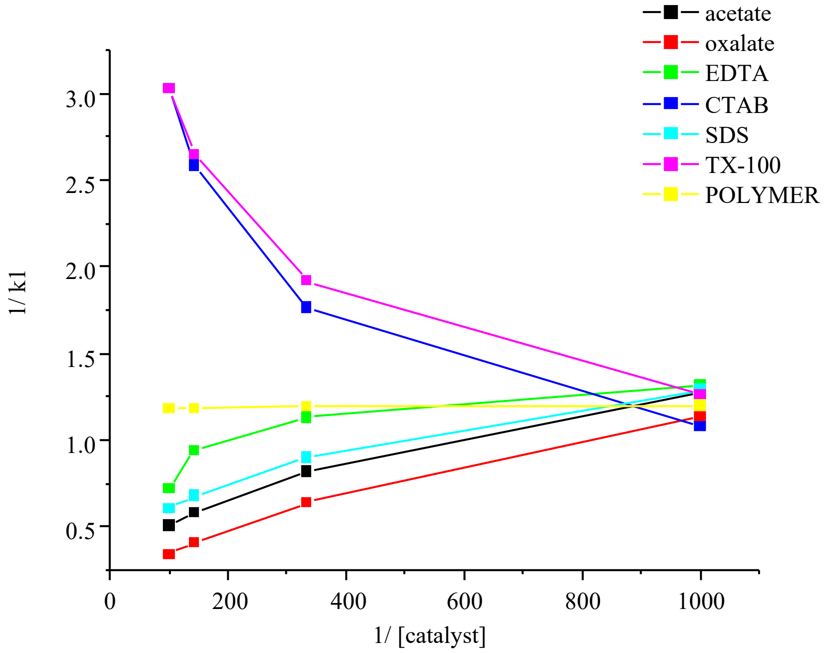


Figure 4. Michaelisment on plot for catalysts.

Table 3. Michaelisment on plot for catalysts.

[Micelle] (M)	**[Thiourea] (M)**	**$k_1 \times 10^{-3}$ S^{-1}**	**$K_2 \times 10^{-1}$ M^{-1} S^{-1}**
CTAB	0.01	0.923	0.923
	0.03	0.410	0.136
	0.07	0.325	0.046
	0.10	0.239	0.024
SDS	0.01	0.775	0.775
	0.03	1.243	0.414
	0.07	1.789	0.255
	0.10	2.086	0.208
TRITON X-100	0.01	0.790	0.790
	0.03	0.556	0.185
	0.07	0.424	0.061
	0.10	0.378	0.038

Micellar Studies

Pseudo first order rate constant k_1 and second order rate constant k_2 value for the different micelles in constant [micelle] in the oxidation of Thiourea at different [Thiourea] in double distill water medium at 303K.

[Oxidant] = 0.001M, [Thiourea] = 0.01M, pH 2.44, 303 K.

The kinetic study also followed by mixing of Thiourea- Cr(VI) with addition of monomer like acrylonitrile was induced and turbity was observed in reaction with in 10 miniutes. Hence, we conclude the radical intermediate was involved in the reaction [67]. The rate of reaction wasslight increased with increasing [acrylonitrile]. It was zero order reaction, but it helps to leading the product (Figure 4).

Second order rate constant listed were calculated from $k_2=k_1$ / [Thiourea], [CTAB] = 0.001M, [SDS] = 0.001M, [TRITON X–100] = 0.001M, Cr(VI) = 0.001M, pH 2.44, 303K (Figure 5).

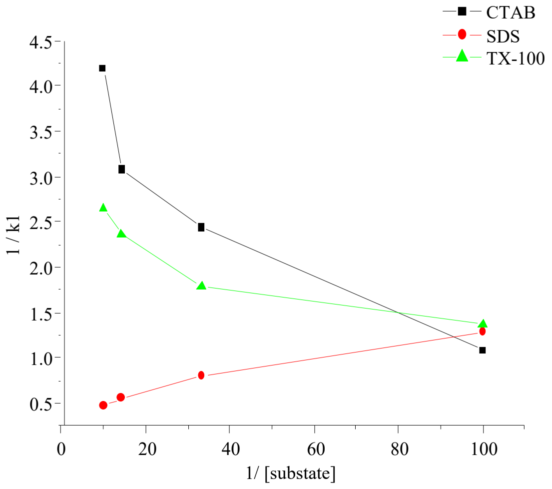


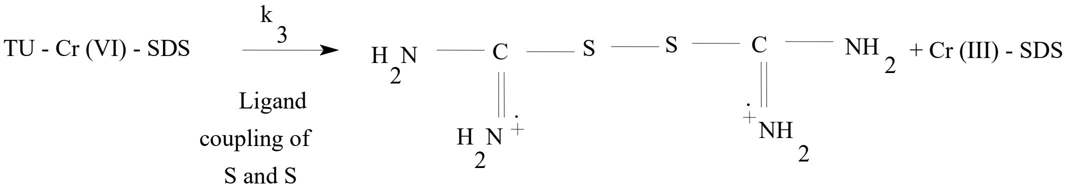
Figure 5. Michaelismenton plot for [Thiourea].

$$\text{Cr (VI) + SDS} \overset{k_1}{\rightleftharpoons} \text{Cr (VI) - SDS} \qquad (7)$$

(Complex 3)

$$\text{Cr (VI) - SDS + TU} \overset{k_2}{\rightleftharpoons} \text{TU - Cr(VI) - SDS} \qquad (8)$$

(Complex 4)



$$\text{TU - Cr (VI) - SDS} \xrightarrow[\text{Ligand coupling of S and S}]{k_3} H_2N-\overset{\overset{+}{N}H_2}{\underset{}{C}}-S-S-C(=\overset{+}{N}H_2)-NH_2 + \text{Cr (III) - SDS} \qquad (9)$$

(Scheme III)

This fractional order dependence of catalysts indicate the reversible complex formation between oxidant Cr(VI) and catalyst. Thus the catalytic activity can be explained in terms of the formation of more reactive Cr (V / IV) catalyst complex. If all the assumptions are valid one expects spectral evidence for the formation of a complex between oxidant and the catalyst and also for the other complex formation involving oxidant, substrate, and catalyst. Indeed the spectral evidence for the formation 3, 4 have been observed. Thus we propose the following mechanism scheme (III), for sodium lauryl sulphate catalyzed Cr(VI) complex-4. A similar mechanism may operate in the presence of other catalyst also.

Thus the reaction is initiated by the formation of Cr(VI) – SDS (complex-3), which is more reactive oxidant than Cr(VI). This complex-3 forms another complex-4 with the substrate as shown in the scheme (III). The formation of the product Foramidine disulphide and Cr(III) – SDS complex can be visualized as due to the ligand coupling between Cr and $S^{+\cdot}$ in hypervalent intermediate complex-4. The concept of ligand coupling involving hypervalent Cr(V) intermediate has been extensively applied and review by Oae Uchida [72]. The formation of product may be formulated in terms of an alternative mechanism inner sphere electron transfer with in the complex-4 as shown in the equation (10–12). However it is difficult to distinguish these alternative mechanism by kinetic measurements. The importance of these two alternative mechanismis the reaction of nucleophiles has been highlighted already [71, 73–74].

The rate of reaction is not appreciably affected by the change in [Acrylonitrile]. On the other hand the reaction is highly influenced by the change $[H^+]$ and solvent composition.

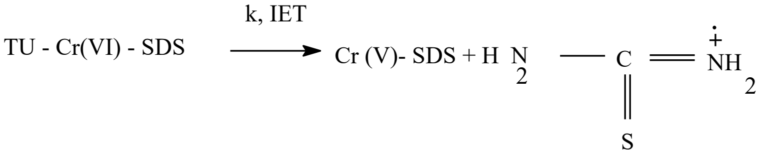
Effect of Ionic Strength

Effect of varying $[H^+]$ on the oxidation of Thiourea by Cr(VI) in double distilled water medium Cr(VI) = 0.001M, [Thiourea] = 0.01M, pH 2.44, at 303K.

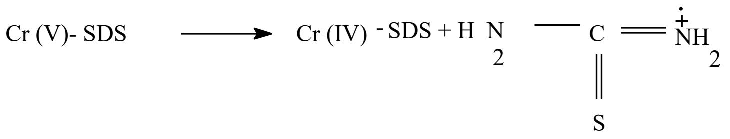
Effect of Solvent Variation

Effect of solvent variation in the oxidation of Thiourea by Cr(VI) in double distilled water medium.

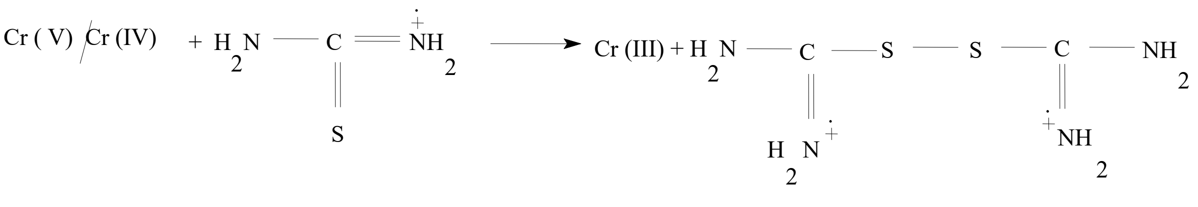
A plot of log k_1 Vs 1/D is fairly linear with a positive slop pointing to an intermediate between a positive ion and molecule in the rate determination step (Table 4 & 5).



$$\mathrm{TU - Cr(VI) - SDS} \xrightarrow{k,\ \mathrm{IET}} \mathrm{Cr\ (V)\text{-}\ SDS} + \mathrm{H_2N} - \underset{\underset{\displaystyle S}{\|}}{C} = \overset{\cdot}{\overset{+}{N}}H_2 \qquad (10)$$



$$\mathrm{Cr\ (V)\text{-}\ SDS} \longrightarrow \mathrm{Cr\ (IV)\ \text{-}SDS} + \mathrm{H_2N} - \underset{\underset{\displaystyle S}{\|}}{C} = \overset{\cdot}{\overset{+}{N}}H_2 \qquad (11)$$



$$\mathrm{Cr\ (V)/Cr\ (IV)} + \mathrm{H_2N} - \underset{\underset{\displaystyle S}{\|}}{C} = \overset{\cdot}{\overset{+}{N}}H_2 \longrightarrow \mathrm{Cr\ (III)} + \mathrm{H_2N} - \underset{\underset{\displaystyle H_2\overset{\cdot}{N}^{+}}{\|}}{C} - S - S - \underset{\underset{\displaystyle {}^{+}\overset{\cdot}{N}H_2}{\|}}{C} - NH_2$$

Table 4. Effect of Hydrogen Ion Concentration $[H^+]$on the Observed First-Order Rate Constant $(k_1)$of the Reaction.

$[H^+]$ M	$k_1 \times 10^{-3}$ S^{-1}
0.001	0.746
0.003	2.114
0.005	3.506
0.010	7.687

Table 5. Effect of solvent composition (water–solvent mixtures) on the pseudo-first-order rate constant ($k_1 \times 10^{-3}\ s^{-1}$) for the reaction in ethyl alcohol, acetic acid, and dimethyl sulphoxide media at varying solvent concentrations**.**

Solvent	**% of composition (water – solvent)**	**$k_1 \times 10^{-3}\ S^{-1}$**
Ethyl alcohol	0-100	0.955
	30-70	0.910
	50-50	0.850
	30-70	0.794
Acetic acid	0-100	0.905
	30-70	0.861
	50-50	0.833
	30-70	0.794
Dimethyl sulphoxide	0-100	0.870
	30-70	0.865
	50-50	0.852
	30-70	0.841

Table 6. Effect of temperature on the rate constant *($k_1 \times 10^{-3}\ s^{-1}$)* for the studied reaction, showing an increase in reaction rate with rising temperature from 303 K to 323 K.

TEMPERATURE (K)	**$k_1 \times 10^{-3}\ S^{-1}$**
303	0.902
313	1.820
323	2.732

The substantial acid hydrolysis of the reaction may be ascribed to facile the formation of Cr(VI)-SDS complex in the presence of [H^+] and the increased electrophilicity of the protonated oxidation. Similar explanations have been already offered by Agarwal [75]. The catalyzed oxidation was carried out at three different temperatures and the thermodynamic parameters evaluated using the Eyring equation along with k_1 values are collected in Table 6.

Temperature, and Thermodynamic Studies

Pseudo first order rate constant are calculated at three different temperatures, thermodynamic parameters Enthalpy ($\Delta H^{\#}$), entropy ($\Delta S^{\#}$), and free energy ($\Delta G^{\#}$) are calculated in the kinetic study oxidation of thiourea by Cr(VI) in double distilled water medium.

[SDS] = 0.001M, [Cr(VI)] = 0.001M, [Thiourea] = 0.01M, pH 2.44.

THERMODYNAMIC PARAMETERS

($\Delta H^{\#}$) = 41.49 KJ/mol, ($\Delta s^{\#}$) = -51.754 J/mol K, ($\Delta G^{\#}$) = 51.68 KJ/mol.

The thermodynamic parameters are given in above table follow the trend for catalyzed reaction is ($\Delta H^{\#}$) is small and ($\Delta s^{\#}$) value is more negative. By applying michaleis menton kinetics in scheme (III). We have derived as the expression for k_1 equation (13).

Rate Law

Our kinetics and spectral evidence observations point out the formation of Cr(VI)-Catalyst and Cr(VI)-Catalyst -Thiourea complex are intermediates application of a steady state approximation to these complexes in scheme (III) lead to the rate law,

$$k_1 = \frac{-d[(Cr(VI)]}{dt} \times \frac{1}{Cr(VI)} \quad \text{- - - - - - - - - - - -} \qquad (13)$$

$$= \frac{k_1 \, k_2 \, k_3 \, [Thiourea] \, [cat\text{- } Cr(VI)]_0}{[k_1 (cat) + 1] \, [k_2 \, (Thiourea) + 1]}$$

This rate law explains the first order dependence of oxidant Cr(VI) and fractional order with respect to substrate and catalysts. The value of k_1, k_2 and k_3 values has been estimated from the slope and intercept of 1/ k_1 vs 1 / [catalyst], and 1/ k_1 vs 1 / [substrate]. Theseresults given point out that the reversible step in equation(8) may be by rate controlling. Since the reaction is fractional order with respect to the catalysts and substrate.

CONCLUSION

The comparative catalytic study of oxidation of thiourea by Chromium (VI) in the presence of different catalysts and micelles demonstrates that both catalysts and surfactant media significantly influence the reaction kinetics and efficiency of oxidation. Among the catalysts investigated, acetate, oxalate, and EDTA showed notable enhancement in the oxidation rate due to their ability to facilitate electron transfer and stabilize intermediate complexes during the reaction. Similarly, micellar media such as CTAB, SDS, and Triton X-100 altered the reaction environment by modifying substrate–oxidant interactions, thereby affecting the reaction mechanism and rate. The kinetic results indicate that cationic and anionic micelles exhibit varying catalytic efficiencies based on their charge interactions with the reacting species. Spectroscopic and product analysis confirmed the successful oxidation of thiourea and formation of the expected oxidation products. Overall, the study highlights the importance of catalyst selection and micellar environment in optimizing oxidation reactions, offering valuable insights for designing efficient catalytic systems in analytical and industrial chemical processes.

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