

Oxidation of α -Thio acids by QxBC in the Presence of Surfactants - A Kinetic Study

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ABSTRACT-The kinetics of oxidation Cobalt (III) complexes of α -Thio acids and free α -Thio acids by Quinoxalium bromo chromate (QxBC) in the presence of various surfactants have been studied in aqueous acetic acid 50% (v/v) medium. The rate of oxidation of the reaction was increased with the increasing perchloric acid and substrate concentration in the presence of various surfactants of both Co(III) complexes of α -Thio acids and free α -Thio acids under pseudo first order conditions. Also the rate of oxidation of the reaction was increased with increasing various Temperature. The reaction was followed by observing the decrease in the absorbance at 365nm for remaining Cr (IV) for free α -Thio acids and Co (III) complexes of α -Thio acids by spectrophotometer. The added CTAB enhances the rate of oxidation of reaction much more than TRITON-X 100 and NaLS.

KEYWORDS: Cetyltrimethylammoniumbromide (CTAB), PentaammineCo(III)complexes, Quinoxaliumbromochromate (QxBC), Induced Electron Transfer

I. INTRODUCTION

The kinetics of oxidation reactions and the elucidation of the reaction mechanisms from the kinetic data have always been the most fascinating subjects in chemistry [1]. In any kinetic investigation one may be interested to arrive at the relationship between the rate and various factors like concentration of the reactants, temperature, reaction medium etc., [2]. A number of new Cr (VI) containing compounds, with heterocyclic bases like pyridinium chlorochromate (PCC)[3], Quinoliniumchlorochromate(QCC)[4], Imidazolium fluoro chromate(IFC)[5] have been developed to improve the selectivity of oxidation of organic compounds. The kinetics of oxidation of α -Thio acids by QxBC, a Cr (VI) reagent has not yet been studied. This inspired us to tackle the present investigation. The present study describes the kinetics of oxidation of α -Thio acids by QxBC and evaluates the rate constants. Mechanistic aspects are also discussed. The literature survey reveals that no report is available on the kinetics of oxidation of α -Thio acids by QxBC. In this article, the kinetics and mechanism of oxidation of α -Thio acids by QxBC is reported.

II. MATERIALS AND METHODS

Materials

Thio Lactic acid (98%, s.d. fine), Thio Glycolic acid (95%, Sigma Aldrich) Quinoxaline (99%, Sigma Aldrich) CrO₃ (99%, Merck, India), Hydrobromic acid (47%, Merck, India), HClO₄ were used as supplied and their stock solutions were prepared in double distilled (first time from alkaline KMnO₄), Deionized and CO₂ free water. Acetic acid was purified by standard method and the fraction distilling at 118^oC was collected. Quinoxalium Bromochromate has been prepared [6]. QxBC is a mustard yellow, non-hygroscopic, but moderately light-sensitive solid which should be protected from light during preparation and storage. The purity of QxBC was checked by the iodometric method. The Micelles used in the present work are Sodium laurylsulphate (NaLS) [7], Cetyltrimethyl ammonium bromide (CTAB) [8] and TRITON X-100. The Micelles were purified by adopting earlier procedure [9-10]. Pentaamminecobalt (III) complexes of α -Thioacids were prepared by reporting methods [11].

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

Vol. 5, Issue 1, Januray 2016

Kinetic Measurements

All kinetic measurements were carried out An Evolution 60 Thermo spectrophotometer fitted with recording and thermo stating arrangement was used to follow the rate of the reaction. The total volume of the reaction mixture in the spectrophotometric cell was kept as 2.5ml in each kinetic run The progress of the reaction was followed at 365 nm by monitoring the decreases of Cr(IV) in free α -thio acids and Co(III) complexes. The required α -Thio acids, HClO₄, and QxBC were premixed in a reaction vessel, thermo stated in an oil bath, and thermally equilibrated QxBC solution was then added prior to the absorbance measurements. Under pseudo-first order conditions of α -Thio acids, the plots of log Absorbance *versus* time were linear up to 75% completion of the reaction with an average of linear regression coefficients, $r \geq 0.996$. The Cobalt (III) complexes of α -Thio acids were prepared using the method of Fan and Gould [12]. Kinetic measurements of the oxidation of cobalt(III) complexes of α -Thio acids and unbound ligands were carried out under pseudo first order conditions in 50%(v/v) acetic acid-water medium at various Temperatures. Table-1 shows the results of Thio glycolic acid oxidation by QxBC in presence of NaLS as surfactant in acidic medium at 323K in the below concentrations of reactants and Rate constants k_1 were calculated.

Table-1

[QxBC] = $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, [HClO₄] = 0.1 mol dm^{-3} , ThioGlycolic acid = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$, [NaLS] = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$

Time(s)	log(Absorbance)	$10^4 k_1 \text{ (s}^{-1}\text{)}$
0	-0.211	0
310	-0.240	1.641
613	-0.265	1.644
908	-0.292	1.625
1204	-0.319	1.667
1507	-0.345	1.620
1810	-0.375	1.636
2114	-0.400	1.671
2411	-0.434	1.675
2708	-0.469	1.679
3015	-0.506	1.587

Figure 1 shows the oxidation of Thio glycolic acid by QxBC in presence of NaLS as surfactant in acidic medium at 323K. The first order plots of log absorbance versus Time in seconds were linear and regression (r) is 0.998 and average rate constant k_1 is $1.645 \times 10^{-4} \text{ s}^{-1}$ from the Table-1.

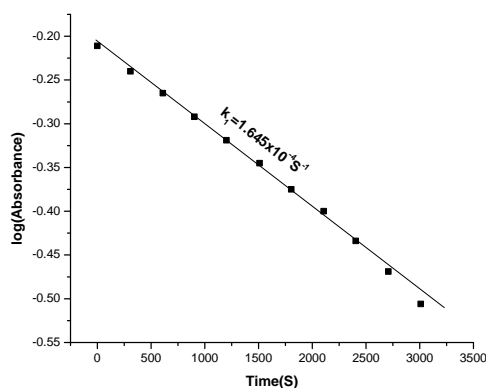


Fig. 1

International Journal of Innovative Research in Science, Engineering and Technology

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Vol. 5, Issue 1, Januray 2016

Stoichiometric studies

The stoichiometric studies for the oxidation of pentaammine cobalt (III) complexes of α - Thio acids and unbound ligands by QxBC were carried out with the oxidant in excess. The H⁺ ion concentration and ionic strength were maintained every bit in the corresponding rate measurements. After nine half lives when the reaction was nearing completion, the concentration of unreacted was determined by spectrophotometrically from the change in absorbance measured at 365 nm for free ligands and Co(III) complexes. The stoichiometry was calculated from the ratio between reacting oxidant and substrate from the decrease in the absorbance measured for the cobalt (III) complex, the amount of Cr(VI) reduced was calculated. This value was then compared to the amount of Cr (IV) and formed compound. Table-2 shows the stoichiometric data for QxBC oxidation of Co(III) bound and unbound α -Thio acids in presence of 0.02M of Cetyl Trimethyl ammonium Bromide(CTAB) at 323K in 0.1M perchloric acid medium. Stoichiometry was calculated from the ratio between reacted QxBC and free α -thio acids and Co (III) of α -Thio acids.

Table-2

10^2 [Compound] mol dm ⁻³	10^2 [QxBC] _{Initial} mol dm ⁻³	10^2 [QxBC] _{Final} mol dm ⁻³	$\Delta 10^2$ [QxBC] mol dm ⁻³	[Compound]: Δ [QxBC]
Thio Lactic acid				
1.0	10.0	9.28	0.74	1.00:0.74
2.0	10.0	8.52	1.48	1.00:0.74
3.0	20.0	17.84	2.16	1.00:0.72
Thio Glycolic acid				
1.0	10.0	9.28	0.72	1.00:0.72
2.0	10.0	8.50	1.50	1.00:0.75
3.0	20.0	17.81	2.19	1.00:0.73
Co(III) Thio Lactato				
1.0	10.0	9.26	0.74	1.00:0.74
2.0	10.0	8.50	1.50	1.00:0.75
3.0	20.0	17.72	2.28	1.00:0.76
Co(III) Thio Glycolato				
1.0	10.0	9.29	0.71	1.00:0.71
2.0	10.0	8.56	1.44	1.00:0.72
3.0	20.0	17.90	2.10	1.00:0.70

Product Analysis

Product analysis was carried out under kinetic conditions *i.e.*, with excess of the reductant over QxBC. In a typical experiment, Thio Lactic acid (0.10 mol), perchloric acid (0.10mol) and QxBC (0.01 mol) were dissolved in acetic acid – water mixture (50%- 50%) and the solution was allowed to stand in the dark for about 24 h to ensure completion of the reaction. The residue was treated with an excess (200 mL) of a saturated solution of 2,4-dinitro phenylhydrazine in 1mol HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitro phenyl hydrozone (DNP) was filtered off, dried and recrystallised from ethanol. The product was identical with melting point and mixed melting point to an authentic sample of the DNP of Thio pyruvic acid.

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III. RESULTS AND DISCUSSION

Dependence of rate on α -Thio acids in Surfactants

The concentration of the substrates, free ligand of Thio Lactic acid and Thio Glycolic acid were varied in the range of 1.0×10^{-2} to 3.0×10^{-2} mol dm⁻³ at 323 K and keeping all other reactant concentrations as constant and the rates were measured. The rate constants were calculated by the integrated rate equation. The graph of logarithms was concentration versus time linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows a first order dependence plot on α -Thio acids. The rate of oxidation increased progressively with increasing the concentration of α -Thio acids. The plot of $\log k_1$ versus $\log [\alpha\text{-Thio acids}]$ gave the slope of 0.998 under pseudo-first-order conditions. Table -3 shows the kinetic data for the oxidation of free α -thio acids and Co(III) complexes of α -Thio acids by QxBC in the presence of NaLS, CTAB and TRITON with varying substrate concentrations and keeping all other reactant concentrations as constants and rates were measured at 323K.

Table-3

$$[QxBC] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}, [HClO_4] = 0.1 \text{ mol dm}^{-3}, \text{Surfactants} = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$$

$10^2 [\alpha\text{-Thio acids}] / [\text{Co(III)} \alpha\text{-Thio acids}]$ mol dm ⁻³	NaLS	CTAB	TRITON	NaLS	CTAB	TRITON
	$10^4 k_1$ (s ⁻¹)	$10^4 k_1$ (s ⁻¹)	$10^4 k_1$ (s ⁻¹)	$10^4 k_1$ (s ⁻¹)	$10^4 k_1$ (s ⁻¹)	$10^4 k_1$ (s ⁻¹)
Thio Lactic acid			Thio Lactato			
1.0	2.420	2.884	2.668	2.608	3.012	2.810
1.5	3.675	4.305	3.989	3.927	4.535	4.314
2.0	4.938	5.780	5.376	5.238	6.036	5.696
2.5	6.190	7.260	6.683	6.525	7.550	7.135
3.0	7.368	8.682	7.950	7.884	9.042	8.583
Thio Glycolic acid			Thio Glycolato			
1.0	1.645	2.360	2.105	1.834	2.712	2.328
1.5	2.475	3.552	3.284	2.744	4.065	3.531
2.0	3.296	4.754	4.312	3.700	5.430	4.730
2.5	4.138	5.870	5.415	4.613	6.800	5.825
3.0	4.983	7.050	6.510	5.571	8.124	7.068

Figure 2 shows the plot of \log of α -Thio acids versus $\log k_1$ for the oxidation of α -Thio Lactic acid and α -Thio Glycolic acid by QxBC in the presence of CTAB at 323K. The rate of oxidation increased progressively with increasing the concentration of α -Thio acids. The slope is 0.998 measured.

International Journal of Innovative Research in Science, Engineering and Technology

(A High Impact Factor, Monthly Peer Reviewed Journal)

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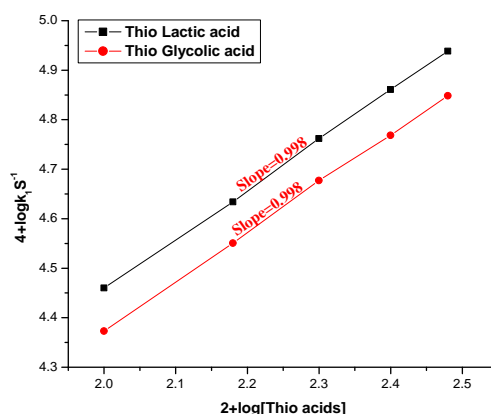


Fig. 2

Dependence of rate on Co(III) bound ligands in surfactants

The concentration of the substrates, bound Co (III) ligands of Thio Lactato and Thio Glycolato were varied in the range of 1.0×10^{-2} to 3.0×10^{-2} mol dm⁻³ at 323 K and keeping all other reactant concentrations as constant and the rates were measured. The rate constants were calculated by the integrated rate equation. The graph of logarithms was concentration versus time linear and the rate constants calculated from the slope of the graph agreed with the experimental value. This shows a first order dependence plot on Co (III) complexes of α -Thio acids. The rate of oxidation increased progressively with increasing the concentration of Co (III) complexes of α -Thio acids. The plot of $\log k_1$ versus $\log [Co (III)]$ gave the slope of 0.998 under pseudo-first-order conditions. Figure 3 shows the plot of \log of Co (III) complexes α -Thio acids versus $\log k_1$ for the oxidation of Co (III) of α -Thio Lactato and Co(III) of α -Thio Glycolato by QxBC in the presence of CTAB at 323K. The rate of oxidation increased progressively with increasing the concentration of Co (III) Complexes of α -Thio acids. The slope is 1.000 measured.

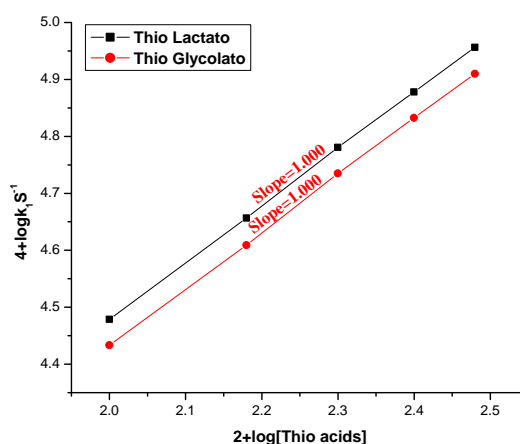


Fig. 3

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Dependence of rate on perchloric acid in surfactants

Perchloric acid has been used as a source of H^+ in the reaction medium. The concentration of perchloric acid was varied in the range 0.06 to 0.14 mol dm^{-3} keeping all other reactant concentration as constant at 323 K as well as Cobalt(III) complexes and the rates were measured. The acid catalysed nature of this oxidation is confirmed by an increase in the rate with the addition of perchloric acid. The plot of $\log kI$ versus $\log [H^+]$ is a straight line with a slope of 0.999 .

Dependence of rate on Surfactant concentration

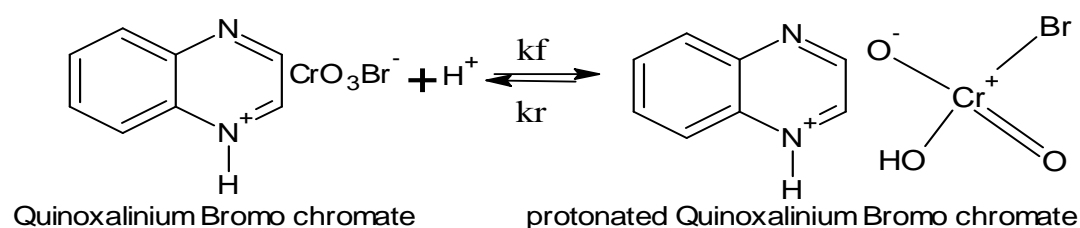
The concentration of surfactants, sodium laryl sulphate, cetyltrimethylammoniumbromide and Triton X 100 were varied in the range of 1.0×10^{-4} to $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ at 323 K as well as Cobalt (III) complexes and keeping all other reactant concentrations as constant and the rates were measured. The rate of oxidation increased with increasing the concentration of surfactants. When formation of surfactants on the substrates the rate of reaction was observed constantly. A plot of specific rate constant versus Surfactants concentration is sigmoidal in shapes both free ligand and cobalt (III) complexes. The rate of the reaction is increased by the addition of NaLS, CTAB and TRITON. The catalytic effect is more in CTAB than TRITON and NaLS. Also observed in the rate of oxidation of reaction enhances with increasing TRITON than NaLS[13].

Dependence of rate on Varying Temperature in Surfactants

The rate of oxidation of reaction was observed in varying the temperature from 323 K to 343 K and keeping all other reactant concentrations as constant. The rate of oxidation of reaction increased with increasing the Temperature in both free ligands and Co(III) complexes.

Mechanistic Aspects

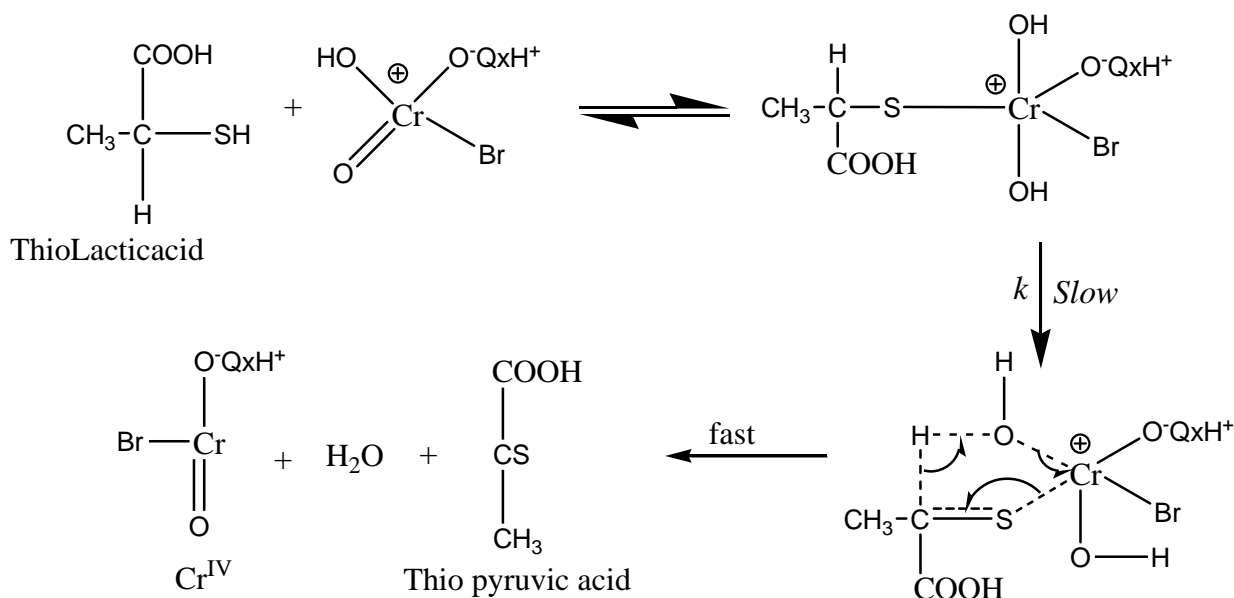
The oxidation of α -Thio acids and their complexes by QxBC in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile which discounts the possibility of any radical formation. The oxidation of α -Thio acids and their complexes was catalysed by perchloric acid, which may well be attributed to protonation of QxBC to give a stronger oxidant and electrophile. The formation of a protonated Cr(VI) species has been postulated earlier. The kinetic and absence of aldehydes as a product leads to a mechanism involving two electron transfer from Cr(VI) with C-H cleavage. It was confirmed by product analysis, that formation of 2,4-dinitro phenyl hydrazone. Hence, synchronous C-H fission and hydride ion transfer are rate determining step was suggested [Scheme-1]. Similar trend was proposed for Co (III) of Thio lactate complexes [Scheme-2].



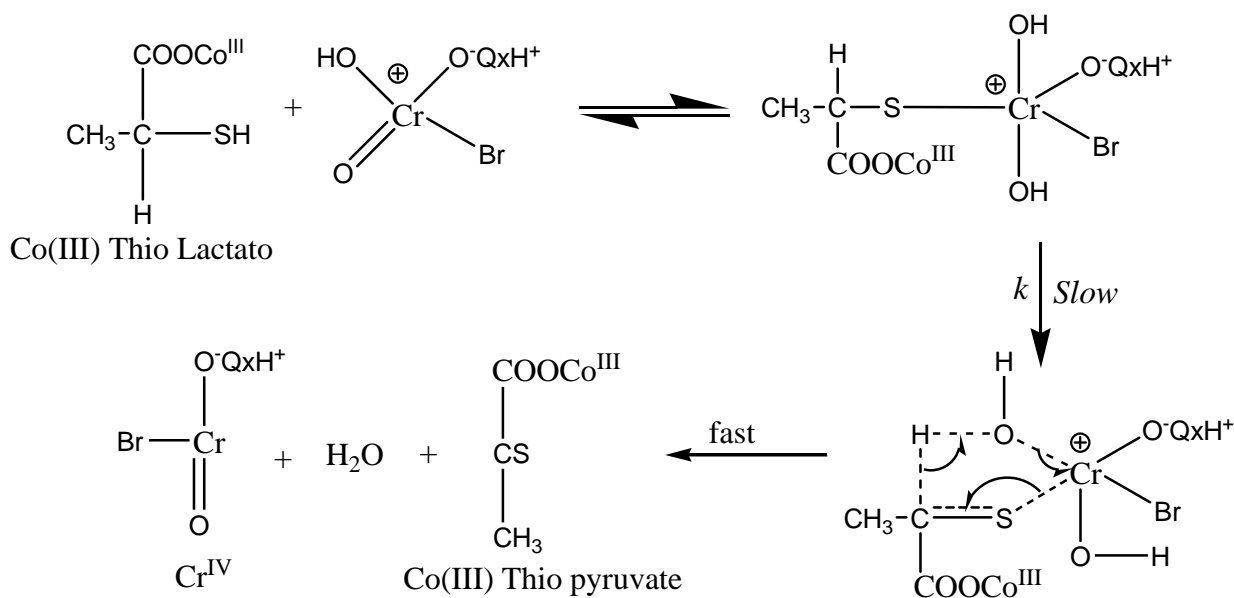
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Scheme-1



Scheme-2

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Vol. 5, Issue 1, Januray 2016

IV.CONCLUSION

The kinetics of oxidation of α -thio acids and Co(III) complexes of α -thio acids have been investigated in aqueous acetic acid medium in the presence of perchloric acid on the surfactants by spectrophotometrically at 323K. The rate of reaction increases with increasing substrate, Perchloric acid, Temperatue and surfactants. The reaction does not show the polymerization, Which indicates the absence of free radical intermediate in the oxidation. A suitable mechanism is proposed involving the hydride ion transfer in the rate determining step. The added CTAB enhances the rate of oxidation of a reaction much more than Triton and NaLS. Similar trends have been observed in Thio glycolic acid and Co (III) complexes of thio lactato and thio glycolato.

ACKNOWLEDGEMENT

Authors are thanks to the Management of Vaniyambadi Muslim Educational Society and PG & Research Department of Chemistry, Islamiah College Vaniyambadi for providing the necessary facilities for the successful completion of this research work.

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