



Research Article

ISSN : 0975-7384
CODEN(USA) : JCPRC5

Effect of temperature on redox reaction of cobalt (III) complexes of α -thio acids by 2, 2'-bipyridinium bromochromate (BPBC) in Micellar medium kinetic study

C. Vijayakumar and K. Subramani

PG & Research Department of Chemistry, Islamiah College, Vaniyambadi, TamilNadu, India

ABSTRACT

Kinetics of investigation the redox reaction Cobalt (III) complexes of α -Thio acids by 2,2'-bipyridinium bromochromate(BPBC) in the presence of micellar medium at 328K in 50% acetic acid – 50 % water. The reaction the rate of oxidation shows pseudo first order kinetics. It rules out the synchronous C-C bond fission and one electron transfer to Cobalt (III) centre. The reaction was followed by observing the decrease in the absorbance at 365 nm for the Cr (VI) present in the reagent in a UV – Visible spectrophotometer. The rate of the reaction increases also temperatures increases. Product and stoichiometric analysis were carried out for the oxidation of complexes and free ligands. A mechanism involving one electron transfer for the ligand was proposed.

Keywords: α -Thio acids, 2, 2'-bipyridinium Bromochromate, Sodium lauryl sulphate, Cetyl trimethyl ammonium bromide, TRITON-X 100.

INTRODUCTION

Chromium has frequently and extensively been employed as an oxidizing agent both for preparative as well as analytical methods in chemistry. Chromic acid, aqueous dichromate, chromyl chloride, chromyl acetate and other substituted chromates have been employed in oxidation of organic as well as inorganic compounds in aqueous acid and alkaline media. Chromium compound play the most important role, in oxidative reaction. A number of Chromium reagents are readily available. Almost every oxidisable functional group may undergo Chromium oxidation. Chromium (VI) containing reagents include Chromium acid, dichromate ion, Chromyl chloride, chromyl acetate–butyl Chromate, Chromyl nitrate and Co-ordination complexes of Chromium Trioxide [1,2]. Recently some neutral or almost neutral Chromium (VI) reagents have been developed to effect oxidation under mild conditions. Pyridinium Chlorochromate (PCC) introduced by Corey et al [2] is widely used in the oxidation of alcohols. Pyridinium flourochromate has a less pronounced acidity and is an effective agent for the oxidation of polycyclic organic substitutes. PFC was developed by Bhattachargee and co-worker[3,4]. In 1986, Narayanan and Balasuramaniam[5] introduced Pyridinium Bromochromate. This is an efficient oxidant for alcohols and a brominating agent as well. Banerji *et al* [6]. Studied the kinetics of oxidation of thioglycolic acid, thiolactic acid and thiomalic acid by BPBC. The reaction is first order with respect to [BPBC] and Michaelis-Menten types of kinetics were observed with respect to all the α -thioacids. The rate was not affected by the addition of acrylonitrile indicates the absence of the free radical mechanism. 2, 2'-bipyridinium bromochromate (BPBC) has been used as a mild, efficient and selective oxidising reagent in synthetic organic chemistry [7]. There are only a few reports about the kinetics and mechanism of oxidation by BPCC, available in the literature [8,9] while the kinetics of oxidation of organic sulphides by BPCC has not been investigated.

EXPERIMENTAL SECTION

2, 2'-Bipyridine (A.R. Qualigens, India), chromium trioxide from (SD Fine chemicals, India 95%) Hydrobromic acid (47%, Merck, India) Preparation of BPBC to 16.75 ml of Hydrobromic acid (0.11mole) is added 10.0 g. (0.1 mole) of chromium trioxide rapidly while stirring. After dissolution of the chromium trioxide is complete, 15.6 g. (0.1 mole) of 2, 2'-bipyridine is added in portions while stirring vigorously. A yellow slurry results which is stirred for 1 hour at room temperature. The slurry is then collected on a sintered glass funnel and washed with two 15 ml portions of cold distilled water. The resulting solid yellow filter cake is dried for 3 hours in vacuum at room temperature. The resulting product is 2, 2'-bipyridinium bromochromate, its purity was checked by an iodometric method and is obtained in a typical yield of 26.8 g. which is 92% of the theoretical yield. Thiolactic, Thiomalic and Thioglycolic acids from (SD Fine chemicals, India 95%). The cobalt (III) complexes of alpha-Thio acids were prepared as their perchlorates using the method of Fan and Gould[10]. The surfactants used in the present work are sodium lauryl sulphate[11] (NaLS) and cetyl trimethylammonium bromide[12] (CTAB). The surfactants are purified by adopting earlier procedure [13,14,15].

Kinetic Measurements

All kinetic measurements were carried out on a Spectrophotometer. The progress of the reaction was followed at 365 nm by monitoring the changes in absorbance of remaining Cr (VI) and 502nm by monitoring the changes in absorbance of remaining Co (III). The required α -Thio acid, HClO₄ and BPBC were premixed in a reaction vessel, thermostated in an oil bath, and BPBC solution (thermally equilibrated) was then added prior to the absorbance measurements. Under pseudo-first-order conditions of α -Thio acid, the plots of $\log A$ versus time (A is absorbance intensity) were linear up to 80% completion of the reaction with an average of linear regression coefficients, $r \geq 0.998$ (Table-2 and Figure-1). Kinetic measurements of the oxidation of cobalt (III) complexes of α -Thio acid and free ligands of α -Thio acid were carried out under pseudo first order conditions in 50% acetic acid-50% water (v/v) medium at 328K.

Product Analysis

Product analysis was carried out under kinetic conditions *i.e.*, with excess of the reductant over BPBC. In a typical experiment, Thio lactic acid (0.10 mol), perchloric acid (0.10mol) and BPBC (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 phenyl hydrazine in 1mol HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitro phenyl hydrazone (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 aldehyde

Stoichiometry

Stoichiometric studies for the oxidation of pentaammine cobalt (III) complexes of α -Thio acid and free ligand of α -Thio acid by BPBC were carried out with the oxidant in excess. The [H⁺] and ionic strength were maintained as such in the corresponding rate measurements. After ten half-lives when the reaction was nearing 80% completion the concentration of unreacted BPBC was determined spectrophotometrically from the change in absorbance measured at 365 nm for Cr (IV) in free ligands and 502nm for Co (III) in 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 cobalt (III) reduced was calculated.

RESULTS AND DISCUSSION

The kinetics and oxidation of α -Thio acids by 2,2'-bipyridinium bromo chromate in micellar medium at 328K under pseudo first order condition of free ligand of α -Thio acid and their bound Co(III) complexes of α -Thio acid in the presence of perchloric acid of anionic and cationic micelles at 328K. An explanation for the higher reactivity of Thio lactic acid involving C-H cleavage was given based on the higher acidity of C-H proton. In the present investigation, the absence of such an observation leads to C-C cleavage. The product analysis confirmed the formation of aldehydes due to C-C cleavage and not keto acids as a product. Further the absence of keto complexes in the product and formation of aldehydes as the only organic product confirm the C-C cleavage. The reduction of Co (III) to Co (II) to an extent of 98% showed an induced one electron transfer from the ligand to the metal due to decarboxylation and synchronous cleavage of the C-C bond in the complexes.

Effect of variation temperature of α -Thio acid the reaction has been carried out at six different temperatures keeping [BPBC] = 10^{-3} mol dm⁻³ Thio Acid = 1.00×10^{-2} mol dm⁻³ (table 2). Absorbance decrease while reaction time of BPBC with alpha thio acid. The rate constants were calculated by the integrated rate equation. The graph of logarithm of absorbance versus time was linear and the rate constants calculated from the slope of the graph.

Temperature increases rate also increased. The rate of the reaction as followed pseudo first order kinetics. The rate of cationic micelles much more the anionic micelles and neutral micelles.

Table 1:Stoichiometric Data for BPBC oxidation of Co (III) bound and unbound α -Thio acids in presence of Triton-X 100 (TRITON) at 328K

$$[HClO_4] = 1.00 \times 10^{-1} \text{ mol dm}^{-3} [TRITON] = 1.00 \times 10^{-2} \text{ mol dm}^{-3} \text{ Temperature} = 328K$$

10^2 [Compound]	10^2 [BPBC] _{Initial}	10^2 [BPBC] _{Final}	$\Delta 10^2$ [BPBC]	[Compound]: Δ [BPBC]
Thio Lactic acid				
1.0	10.0	9.25	0.75	1.00 : 0.75
2.0	10.0	8.52	1.48	1.00 : 0.74
3.0	20.0	17.75	2.25	1.00 : 0.75
Thio Glycolic acid				
1.0	10.0	9.27	0.73	1.00 : 0.73
2.0	10.0	8.56	1.44	1.00 : 0.72
3.0	20.0	17.87	2.13	1.00 : 0.71
Thio Malic acid				
1.0	10.0	9.26	0.74	1.00 : 0.74
2.0	10.0	8.55	1.45	1.00 : 0.72
3.0	20.0	17.80	2.20	1.00 : 0.73
Co^{III} Thio Lactato				
1.0	10.0	9.62	0.38	1.00 : 0.38
2.0	10.0	9.26	0.74	1.00 : 0.37
3.0	20.0	18.89	1.11	1.00 : 0.37
Co^{III} Thio Glycolato				
1.0	10.0	9.64	0.36	1.00 : 0.36
2.0	10.0	9.30	0.70	1.00 : 0.35
3.0	20.0	18.98	1.02	1.00 : 0.34
Co^{III} Thio Malato				
1.0	10.0	9.66	0.34	1.00 : 0.36
2.0	10.0	9.24	0.76	1.00 : 0.33
3.0	20.0	18.94	1.06	1.00 : 0.35

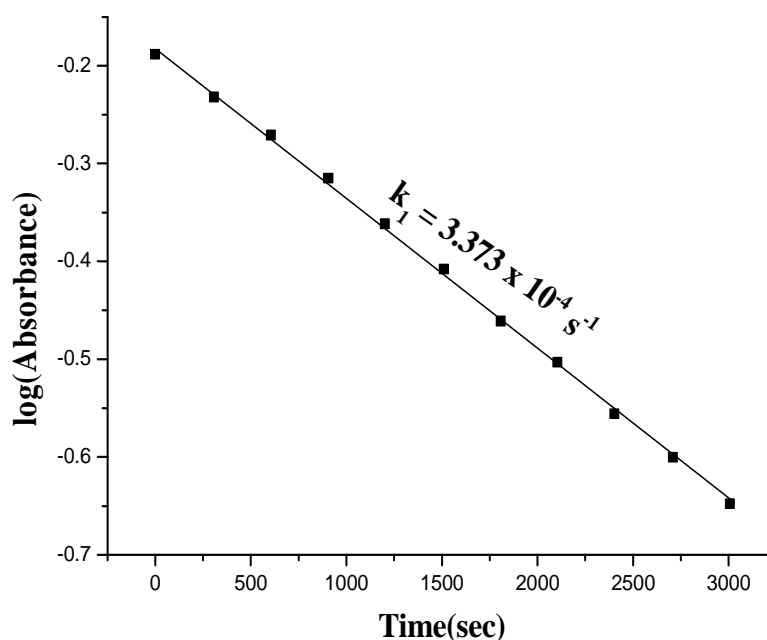


Fig.1: First Order Dependence Plot

Table-3 shows effect of variation temperature of alpha thio acid. α - thio glycolic acid α - thio malic acid and α - thio lactic acid increase the temperature increase rate of the reaction and different the micelles. The rate of the micelles increase CTAB compare than other micelles respectively. The graph of the temperature versus log of absorbance got the straight line. The rate of the reaction of α -Thio acid with micelles is more than the α -Thio acid of without micelles.

Table 2: Rate data on the oxidation alpha thio acid by 2, 2'- bipyridinium bromo chromate (BPBC)

$[BPBC] = 10^{-3} \text{ mol dm}^{-3}$ $[HClO_4] = 0.1 \text{ mol dm}^{-3}$ Temperature = 328K
 α -Thio Glycolic Acid = $1.00 \times 10^{-2} \text{ mol dm}^{-3}$ $[CTAB] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$

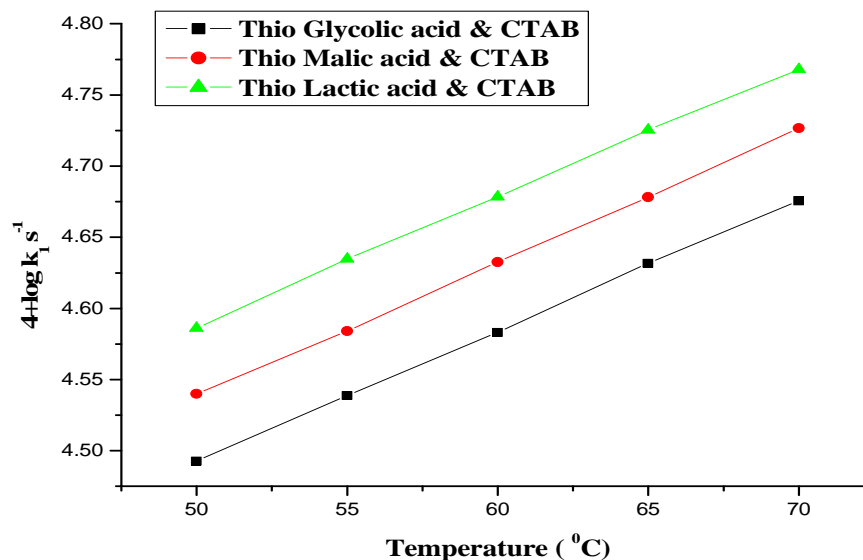
Time(s)	log(Absorbance)	$10^4 k_1 (\text{s}^{-1})$
0	-0.18842	0.00
308	-0.23210	3.265
606	-0.27084	3.131
906	-0.31515	3.221
1202	-0.36151	3.316
1510	-0.40782	3.346
1807	-0.46092	3.472
2105	-0.50307	3.442
2403	-0.55596	3.522
2709	-0.60033	3.501
3008	-0.64782	3.517

Table 3: Effect of Temperature of the α - Thio acid

$[BPBC] = 10^{-3} \text{ mol dm}^{-3}$ $[HClO_4] = 0.1 \text{ mol dm}^{-3}$ $[Micelles] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}$

Temp(K)	$10^4 k_1 (\text{s}^{-1})$								
	NaLS	TRITON	CTAB	NaLS	TRITON	CTAB	NaLS	TRITON	CTAB
	Thio Glycolic acid			Thio Malic acid			Thio Lactic acid		
323	2.341	2.543	3.109	2.666	3.179	3.467	3.265	3.670	3.856
328	2.600	2.840	3.458	2.966	3.534	3.837	3.623	4.050	4.312
333	2.897	3.171	3.830	3.315	3.899	4.290	4.029	4.499	4.768
338	3.227	3.549	4.283	3.685	4.333	4.765	4.425	4.964	5.314
343	3.568	3.954	4.739	4.122	4.816	5.329	4.875	5.504	5.860

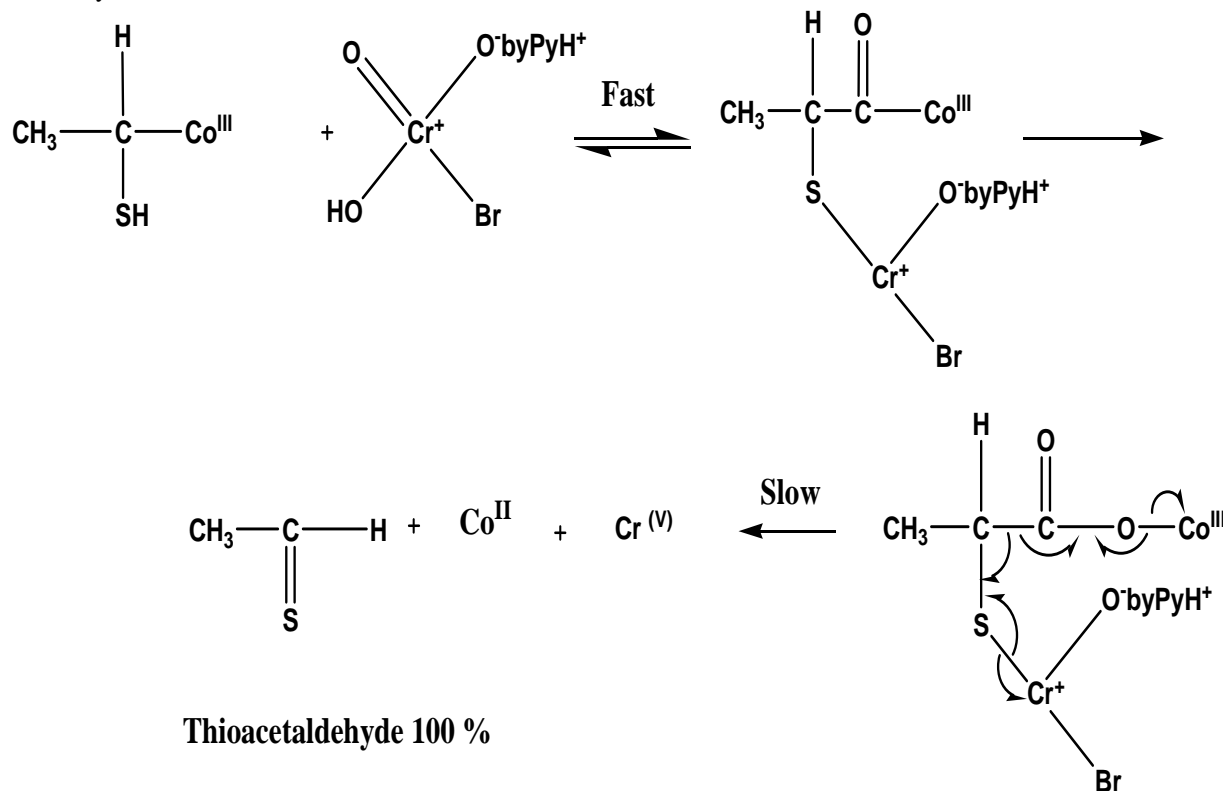
Figure.2 shows the effect of six varies Temperature of the oxidation of thio acids by BPBC in the presence of surfactant CTAB. The first order plots of $\log k_1$ versus Temperature were linear and when the Temperature increases rate of the reaction was increases.

**Fig 2: Dependence of rate on $[\alpha$ -Thio acid]**

The effect of varying substrate concentration of the BPBC oxidation of α - thio acid with and without micelles at 328 K. The concentration of the substrates, α - thio glycolic acid α - thio malic acid and α - thio lactic acid were varied in the range of 0.5×10^{-2} to $2.5 \times 10^{-2} \text{ mol dm}^{-3}$ at 328K and keeping all other reactant concentrations were constant and the rates were measured. The rate constants were calculated by the integrated rate equation. The change the α -thio acid concentration without micelles rate of the reaction increase and with the micelles rate of the reaction increase compare than the without micelles. CTAB rate is more than the TRITON, 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 and their complexes. The rate of oxidation increased progressively with increasing the substrate concentration of α -thio acids and their complexes.

Mechanistic Aspects

The oxidation of α -Thio acids and their complexes by BPBC 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 BPBC to give a stronger oxidant and electrophile. The formation of a protonated Cr (VI) species has been postulated earlier. The kinetic and absence of keto acids as a product leads to a mechanism involving one electron transfer from Cr(VI) with C-C cleavage. It was confirmed by product analysis, that formation of 2, 4-dinitro phenyl hydrazone. Hence, synchronous C-C fission and one electron transfer in to Co (III) centre. Mechanism explain reduction of Co (III) centre to Co (II) and chromium (VI) in to chromium (V) is a rate determine step. Finally the product of Thio acetaldehyde formed.



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 328K. The rate of reaction increases with increasing substrate concentration, Perchloric acid concentration, Temperature and surfactants concentration. Mechanism explains the synchronous C-C bond fission and oneelectron transfer to cobalt (III) centre. 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, Thio lactic acid, and Thio Malic acid and Co (III) complexes of Thio lactate, Thio Malato and Thio glycolato. The observed reaction rate is Thio Lactic acid>Thio Malic acid> Thio Glycolic acid.

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.

REFERENCES

- [1] K.B. Wilberg, "oxidation in organic Chemistry" Part -A" 69 Academic Press, New York, **1965**.
- [2] S.Anbuselvi, C.Chellaram, S.Jonesh, L. Jayanthi, Edward J.K.P., *Journal of Medical Sciences*,**2009**, 9(5), 240-244.
- [3] G.Cainelli and G.Cardillo, "Chromium Oxidation in Organic Chemistry" 5 Springer – Verlag, Perling Heidelberg **1984**.
- [4] Arumugam, S., Ramareddy, S., *Journal of Electrical Engineering*,**2012**, 12(2), 71-76.

- [5] E.J. Covey and J.W.Suggs, *Tetrahedron Lett.*, **1975**, 2647
- [6] S. Rathore, P. K. Sharma and K. K. Banerji, *J. Chem. Res.* **1994**,(S) 298(M) 1636.
- [7] S.Rathore, P. K. Sharma and K. K. Banerji, *Indian J. Chem.* **1995**, B34702.
- [8] K. Loonkar, P K Sharma and K. K. Banerji, *J. Chem. Res.* **1997**, (S) 242(M) 1663.
- [9] K.Loonkar, P. K. Sharma and K. K. Banerji, *J. Chem. Res.* **1998**, (S) 66(M) 0457.
- [10] R. R. F. Fan and E. S. Gould, *Inorg. Chem.*, **1974**, 13, 2636.
- [11] A .Thangaraj and R. Gopalan, *J. Indian Chem.Soc.*, **1996**, **67**, 453.
- [12] J .Long, J. J. Auborn and F. M. J. Eyring, *Colloid, Interface Sci.*, **1973**, 41, 457.
- [13] J .Yasunaga, K Takeda and S. Harada, *J. Colloid, Interface, Sci.*, **1973**, 42, 457.
- [14] N.K. Mohantly and P. K. Nanda, *Indian J. Chem.*, **1982**, 21 A, 522.
- [15] A G Dash R K Nanda and P Mohanti, *Indian, J. Chem.*, **1984**, 23 A, 162
- [16] A .Thaminum Ansari, *International Journal of ChemTech Research*, **2009**, 1(2), 308-313.
- [17] M.Vellaisamy and M.Sharmila, *Journal of Chemical and Pharmaceutical Research*, **2013**, 5(4), 29-32.
- [18] P. Rajkumar and K. Subramani, *J. Chem. Pharm. Res.*, **2012**, Vol 4, No.7, pp3759-3764.
- [19] S.Udhayavani, and K.Subramani, *J.Current Chem Pharm. Sc.*, **2012**, 2(2), 92-99.
- [20] K. G. Sekar, and G. Manikandan, *Der Chemica Sinica*, **2013**, 4(1), 100-104.
- [21] A.Pandurangan and V. Murugesan, "*React.kinet.catal.Lett*, **1995**, Vol.54, No.1, 173-180.
- [22] S.Sheik Mansoor, V.Saleem Malik, K.Aswin, K.Logaiya, A.M.Hussain, *Arabian Journals of Chemistry*, **2012**, 1319- 6103.