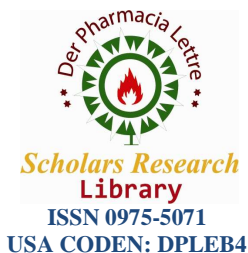




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Kinetics and mechanism of oxidation of 4-oxo-4-phenyl butanoic acid by benzimidazolium fluorochromate in presence of 1,10-phenanthroline catalyst in acetic acid-water medium

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ABSTRACT

The catalytic activity of 1, 10-phenanthroline (phen) in benzimidazolium fluorochromate (BIFC) oxidation of 4-oxo-4-phenyl butanoic acid (4-oxo acid) has been studied in 50% acetic acid – 50 % water medium. The oxidation leads to the formation of benzoic acid. The reaction is first order each in [BIFC], [4-oxo acid] and [H⁺]. The reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. Various thermodynamic parameters have been determined at different acetic acid-water composition. A suitable mechanism has been proposed.

Keywords: 4-oxo acid; kinetics; benzimidazolium fluorochromate; 1,10-phenanthroline

INTRODUCTION

Hexavalent chromium compounds are important, very powerful oxidizing agents suitable for organic synthesis [1,2]. A number of new Cr(VI) containing compounds like tripropylammonium fluorochromate [3], benzyltriethylammonium chlorochromate [4], quinoxalinium dichromate [5], tributylammonium chlorochromate [6] and tetraethylammonium chlorochromate [7] have been used to study the kinetics and mechanism of various organic compounds.

Benzimidazolium fluorochromate is also one such oxidant developed recently [8,9]. It is a more efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. Among the different chelating agents [10-13] that promote Cr(VI) oxidation of different types of organic substrate, picolinic acid, 2,2'-bipyridine, and 1,10-phenanthroline are quite important [14-17].

Extensive studies on the mechanism of oxidation of 4-oxo acids by different oxidants have been the subject of study by various workers [18-21]. As part of our continuing investigations on the oxidation of organic substrates by BIFC [22, 23], this paper reports the kinetic features of the oxidation of 4-oxo-4-phenyl butanoic acid by BIFC in the presence of 1,10-phenanthroline. Mechanistic aspects are also discussed.

MATERIALS AND METHODS

Materials

Benzimidazole and chromium trioxide were obtained from Fluka (Buchs, Switzerland). Acetic acid was purified by standard method and the fraction distilling at 118 °C was collected. Perchloric acid is used as the source of hydrogen ion.

Preparation of benzimidazolium fluorochromate

Benzimidazolium fluorochromate has been prepared from benzimidazole, 40% hydrofluoric acid and chromium trioxide in the molar ratio 1:1.3:1 at 0 °C as reported in the literature [8].

Preparation of 4-oxo-4-phenyl butanic acid

The 4-oxo-4-phenyl butanic acid is synthesized by the Friedel-Craft's reaction between succinic anhydride and benzene in the presence of anhydrous aluminium chloride [18].

Kinetic measurements

The pseudo – first-order conditions were attained by maintaining a large excess (x 15 or more) of 4-oxo acid over BIFC. The solvent was 50% acetic acid – 50% water (v/v), unless specified otherwise. The reactions were followed, at constant temperatures (± 0.01 K), by monitoring the decrease in [BIFC] spectrophotometrically at 364 nm using UV-Vis spectrophotometer, Shimadzu UV-1800 model. The pseudo-first-order rate constant k_{obs} , was evaluated from the linear ($r = 0.990$ to 0.999) plots of $\log [BIFC]$ against time for up to 80% reaction. The second order rate constant k_2 , was obtained from the relation $k_2 = k_{obs} / [4\text{-Oxo acid}]$.

RESULTS AND DISCUSSION

Product study was made under mineral acid catalysed condition in 4-oxo-4-phenyl butanic acid. The product was obtained which had melting point of 121 °C. The product was dissolved in benzene and a careful TLC analysis was done with benzoic acid and 4-oxo-4-phenyl butanoic acid as references. Only one spot corresponding to benzoic acid was obtained. The stoichiometric studies for the oxidation of 4-oxo acid by BIFC were carried out with oxidant in excess. The stoichiometric studies showed that 1 mol of BIFC reacts with 1 mol of 4-oxo-4-phenyl butanic acid. Kinetic study for the f oxidation of 4-oxo-4-phenyl butanoic acid by BIFC has been conducted in 50% acetic acid – 50 % water medium at 303 K in the presence of 1,10-Phenanthroline under pseudo-first order conditions and the results obtained were discussed here.

Effect of varying the concentrtration of 1,10-phenanthroline

The concentration of 1,10-phenanthroline is varied in the range of 0.0×10^{-3} to 8.0×10^{-3} mol dm⁻¹ at constant [BIFC], [4-Oxo acid] and [H⁺] at 303 K and the rates were measured (Table 1). We observed that the rate increases linearly with increasing 1,10-phenanthroline concentration.

Order of the reaction

The reactions are first order with respect to BIFC as evidenced by a linear plot of $\log [BIFC]$ against time. The pseudo first-order rate constants do not depend on the initial concentration of BIFC (Table 1). This further confirms first-order dependence of rate on oxidant concentration. Reaction rates increase linearly with increase in the concentrations of the 4-Oxo acid (Table 1). A plot of $\log k_{obs}$ vs $\log [4\text{-Oxo acid}]$ is linear with a slope = 1.001, indicating that the order with respect to 4-Oxo acid is also one (Figure 1).

The acid catalysed nature of this oxidation is confirmed by an increase in the rate on the addition of H⁺. Perchloric acid has been used as a source of H⁺ in reaction medium. The plot of $\log k_{obs}$ versus $\log [H^+]$ is a straight line with the slope of 1.0003 (Figure 2). Therefore, order with respect to H⁺ is one. BIFC may become protonated in the presence of acid and the protonated BIFC may function as an effective oxidant.

The acid-catalysis may well be attributed to a protonation of BIFC to give a stronger oxidant and electrophile.



The formation of a protonated Cr(VI) species has earlier been postulated in the reactions of structurally similar PFC [24].

Effect of acrylonitrile and MnSO₄

The reaction did not promote polymerization of acrylonitrile indicating the absence of free radicals (Table – 1). However, the addition of Mn(II) (0.003 mol dm⁻³), in the form of MnSO₄ retards the rate of oxidation (Table – 1). This indicates the involvement of Cr(IV) intermediate in the oxidation of 4-oxo acid by Cr(VI) reagent and confirms the two electron transfer process in the reaction. Mn(II) ion reduces Cr(IV) formed to Cr(III). In the absence of Mn(II) ion, formed Cr(IV) reduces Cr(VI) to Cr(V) and the oxidation of 4-oxo acid by Cr(V) is fast [25]. The decrease in the rate of Cr(VI) reduction on the addition of Mn(II) has been attributed to the removal of Cr(IV) by reaction with Mn(II) [26].

Effect of solvent polarity on reaction rate

The oxidation of 4-oxo-4-phenyl butanoic acid in the presence of oxalic acid has been studied in the binary mixture of acetic acid and water as the solvent medium. For the oxidation of 4-oxo-4-phenyl butanoic acid, the reaction rate increased remarkably with the increase in the proportion of acetic acid in the solvent medium. These results are presented in Table 2 and Figure 3.

Amis (1967) holds the view that in an ion–dipole reaction involving a positive ionic reactant, the rate would decrease with increasing dielectric constant of the medium and if the reactant were to be a negatively charged ion, the rate would increase with the increasing dielectric constant. In this case there is a possibility of a positive ionic reactant, as the rate decreases with the increasing dielectric constant of the medium [27]. Due to the polar nature of the solvent, transition state is stabilized, *i.e.*, the polar solvent molecules surround the transition state and result in less disproportion.

Table - 1 Rate constants for the oxidation of 4-oxo-4-phenyl butanoic acid by BIFC in aqueous acetic acid medium in the presence of 1,10-Phenanthroline at 303 K^{a,b}

10 ³ [BIFC] (mol dm ⁻³)	10 ³ [4-oxo] (mol dm ⁻³)	[H ⁺] (mol dm ⁻³)	10 ³ [Phen] (mol dm ⁻³)	10 ⁴ k _t (s ⁻¹)
1.2	2.0	0.18	0.0	16.22
1.2	2.0	0.18	2.0	22.92
1.2	2.0	0.18	4.0	29.12
1.2	2.0	0.18	6.0	34.84
1.2	2.0	0.18	8.0	42.70
0.8	2.0	0.18	6.0	34.79
1.6	2.0	0.18	6.0	34.88
2.0	2.0	0.18	6.0	34.90
2.4	2.0	0.18	6.0	34.76
1.2	1.0	0.18	6.0	20.24
1.2	1.5	0.18	6.0	30.64
1.2	2.5	0.18	6.0	51.30
1.2	3.0	0.18	6.0	62.00
1.2	2.0	0.10	6.0	20.66
1.2	2.0	0.14	6.0	30.76
1.2	2.0	0.22	6.0	51.42
1.2	2.0	0.26	6.0	61.80
1.2	2.0	0.18	6.0	34.77 ^c
1.2	2.0	0.18	6.0	31.88 ^d

^aAs determined by a spectrophotometric technique following the disappearance of oxidant
10²[4-Oxo acid] = 2.0 mol dm⁻³; 10³[BIFC] = 1.2 mol dm⁻³; [H⁺] = 0.18 mol dm⁻³

Solvent composition : 50% Acetic acid – 50% Water (v / v)

^bEstimated from pseudo-first order plots over 80% reaction

^cContained 0.001 mol dm⁻³ acrylonitrile.

^dIn the presence of 0.003 mol dm⁻³ Mn(II).

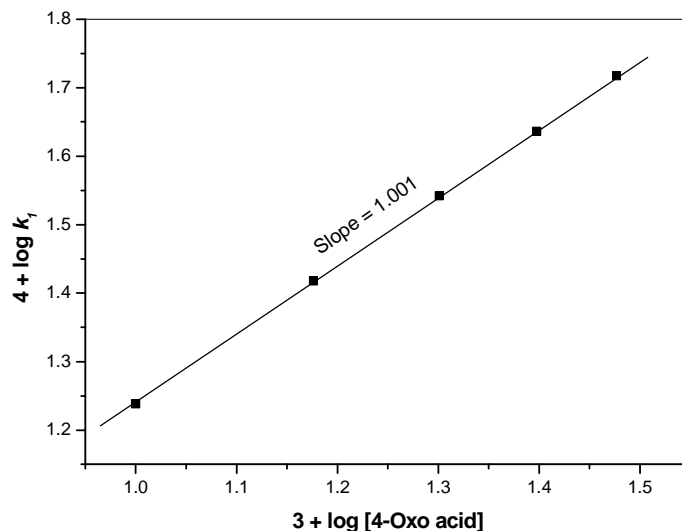


Figure 1 Showing order plot of 4-oxo acid for the oxidation of 4-oxo acid by BIFC in the presence of 1,10-phenanthroline

In the present study, the significant rate enhancement with the lowering of dielectric constant of the solvent medium may be attributed to the enolisation of the keto acid group in the 4-oxo-4-phenyl butanoic acid. The enolisation of the keto group of the oxo acid is facilitated by the increase in percentage of acetic acid in the solvent medium and this may also favors the rate enhancement.

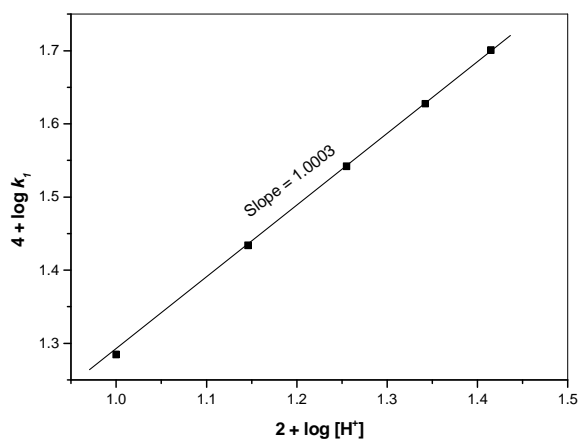


Figure 2 Showing order plot of perchloric acid for the oxidation of 4-oxo acid by BIFC in the presence of 1,10-phenanthroline

Table – 2 Pseudo-first order rate constants for the oxidation of 4-oxo-4-phenyl butanoic acid by BIFC at various percentage of acetic acid-water medium in the presence of 1,10-Phenanthroline at various temperatures

% AcOH - H ₂ O (v/v)	Dielectric constant	10 ⁴ k _f (s ⁻¹)			
		298 K	303 K	308 K	313 K
30-70	72.0	20.10	28.06	39.10	55.96
40-60	63.3	22.42	30.16	43.16	60.40
50-50	56.0	25.04	34.84	48.44	65.10
60-40	45.5	30.00	42.40	56.60	76.00
70-30	38.5	36.08	49.44	66.40	88.66

$$10^2 [4\text{-oxo}] = 2.0 \text{ mol dm}^{-3}; 10^3 [\text{BIFC}] = 1.2 \text{ mol dm}^{-3}; 10^3 [\text{Phen}] = 6.0 \text{ mol dm}^{-3}; 10 [\text{H}^+] = 1.8 \text{ mol dm}^{-3}$$

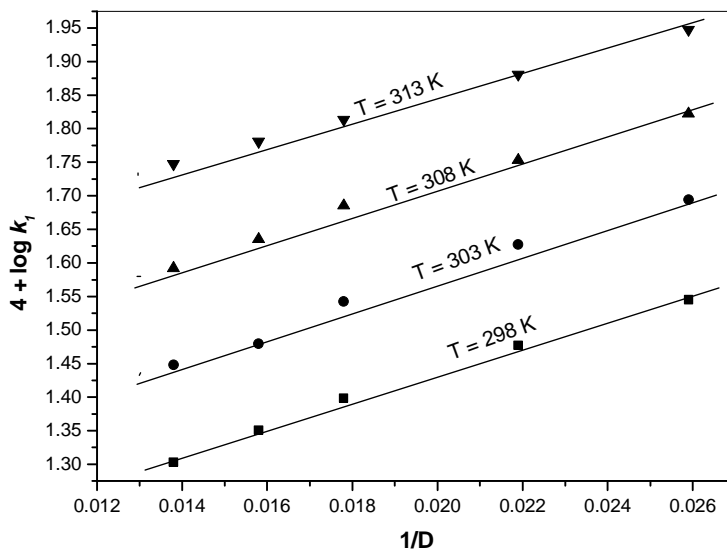


Figure 3 Plot of $1/D$ against $\log k_t$ showing effect of solvent polarity at various temperatures in the presence of 1,10-phenanthroline

Rate of enolisation by bromination method

It has been reported earlier in the case of oxidation of keto compounds that the oxidation proceeds *via* enolisation of the keto compounds. The rate of enolisation of keto compound is faster than the rate of oxidation. The reactive species of the substrate may be determined by enolisation, which is an acid as well as base catalysed reaction and proceeds by a concerted or push-pull mechanism. The rate of enolisation was determined by bromination method for the system under investigation.

The order of bromination reaction with respect to the 4-oxo-4-phenyl butanoic acid, bromine and H^+ has been determined. These data indicate that the bromination of the 4-oxo-4-phenyl butanoic acid is first order each with respect to the substrate and H^+ ion but zero order with respect to bromine.

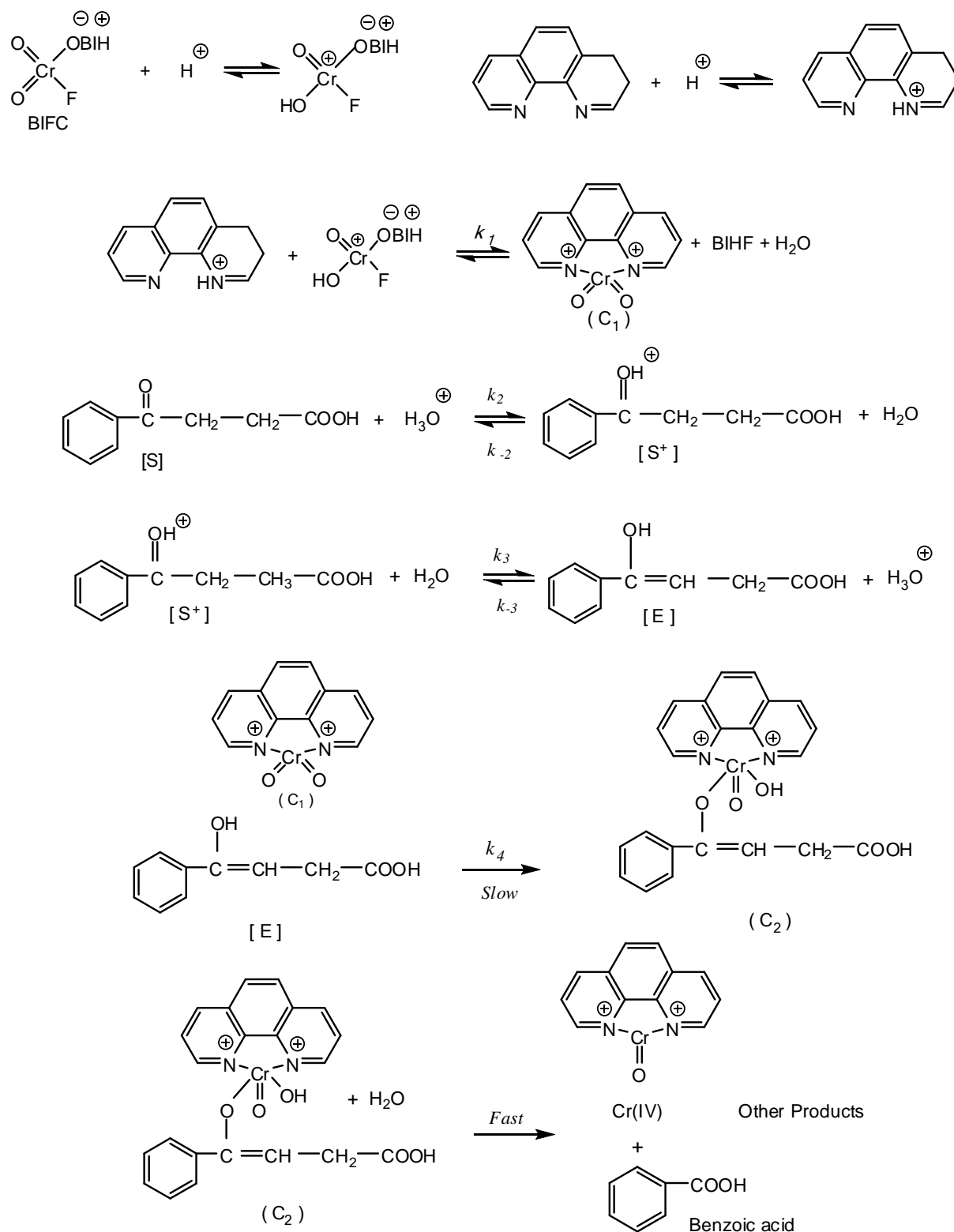
Thermodynamic parameters

The kinetics of oxidation of 4-oxo acid in the presence of 1,10-phenanthroline is studied at four different temperatures *viz.*, 298, 303, 308 and 313 K at various percentage of acetic acid-water medium. The second order rate constants were calculated (Table 3). The Arrhenius plot of $\log k_2$ versus $1/T$ is found to be linear. The enthalpy of activation, entropy of activation and free energy of activation were calculated from k_2 at 298, 303, 308 and 313 K using the Eyring relationship by the method of least square and presented in Table 3.

Table – 3 Second order rate constants and activation parameters for the oxidation of 4-oxo-4-phenyl butanoic acid by BIFC at various percentage of acetic acid-water medium in the presence of 1,10-Phenanthroline

% AcOH - H ₂ O (v/v)	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)				E_a (kJ mol ⁻¹)	$-\Delta S^\ddagger$ (J K ⁻¹ mol ⁻¹)	ΔH^\ddagger (kJ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹) (at 303 K)
	298 K	303 K	308 K	313 K				
30-70	10.05	14.03	19.55	27.98	52.84	094.94±3.0	50.54±1.0	79.30±1.9
40-60	11.21	15.08	21.58	30.20	51.70	098.39±3.3	48.32±1.1	78.63±2.1
50-50	12.52	17.42	24.22	32.55	49.78	103.94±0.6	47.10±0.2	78.59±0.4
60-40	15.00	21.20	28.30	38.00	47.86	108.34±2.4	45.38±0.8	78.20±1.5
70-30	17.54	24.72	33.20	44.33	48.48	106.43±3.0	44.80±1.0	77.05±1.9

$$10^2 [4\text{-oxo}] = 2.0 \text{ mol dm}^{-3}; 10^3 [\text{BIFC}] = 1.2 \text{ mol dm}^{-3}; 10^3 [\text{Phen}] = 6.0 \text{ mol dm}^{-3}; 10 [H^+] = 1.8 \text{ mol dm}^{-3}$$



Scheme 1 Mechanism of oxidation of 4-Oxo acid by BIFC in the presence of 1, 10-phenanthroline

Mechanism of oxidation

A probable mechanism for the oxidation of 4-oxo-4-phenyl butanoic acid in the presence of 1,10-phenanthroline by BIFC has been proposed based on the experimental results and in analogy with the oxidation of oxo compounds with the other oxidants. The results obtained in the kinetic study are briefly summarized below: The reaction is first order each with respect to the 4-oxo-4-phenyl butanoic acid, BIFC and H^+ ion. The linear increase in the reaction rate with the increase in $[H^+]$ ion is attributed to the formation of protonated BIFC *i.e.*, $BIFCH^+$ and to the enolisation of the 4-oxo-4-phenyl butanoic acid. The formation of $BIFCH^+$ ion and the enolisation of the 4-oxo-4-phenyl butanoic acid is facilitated at lower dielectric constant of the medium. The rate of enolisation is found to be greater than the rate of oxidation. The course of oxidation does not involve any free radical intermediate.

It is believed that the catalytic activity of complexing agent such as 1,10-phenanthroline depends on their ability to stabilize intermediate chromium valence states [28]. 1,10-Phenanthroline readily form complex (C_1) with Cr(VI). In the next step, the complex reacts with the substrate to form a ternary complex (C_2). This ternary complex (C_2) undergoes redox decomposition by two electron transfer within the cyclic transition state in a rate-determining step involving simultaneous rupture of C–C and C–H bonds to give a benzoic acid and the Cr(IV)-Phen complexes. Considering these facts and findings a suitable mechanism has been proposed for the oxidation (Scheme–1).

CONCLUSION

The Cr(VI)-phen complex is believed to be the probable electrophile in the catalyzed oxidation. The kinetics of oxidation of 4-oxo-4-phenyl butanoic acid has been investigated in aqueous acetic acid medium by spectrophotometrically at 303 K in the presence of 1,10-phenanthroline. The addition of Mn(II), in the form of $MnSO_4$ retards the rate of oxidation indicating the involvement of Cr(IV) intermediate. The Arrhenius plot of $\log k_2$ versus $1/T$ is found to be linear. Using the Eyring relationship the enthalpy of activation, entropy of activation and free energy of activation were calculated. The lowering of dielectric constant of reaction medium increases the reaction rate significantly.

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