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Kinetics of oxidation of Thiomalic acid by Quinaldinium fluorochromate

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ABSTRACT

The kinetics of oxidation of thiomalic acid by quinaldinium fluorochromate(QnFC) has been studied in non - aqueous medium. The oxidation kinetics was followed photoelectric colorimetrically in the temperature range of $30^{\circ}C$ - $60^{\circ}C$. The reaction shows unit order dependence each with respect to substrate and oxidant. The reaction is catalyzed by hydrogen ions. The hydrogen ion dependence takes in the form $k_{obs} = a + b [H^+]$. The reaction rate decreases with increasing the concentration of Mn^{2+} ions. The reaction does not induce the polymerization of acrylonitrile. A plausible mechanism has been proposed in the formation of a thio ester and its decomposition which occurs in the slow step.

Keywords: Kinetics, Oxidation, Thiomalic acid, Quinaldinium fluorochromate.

INTRODUCTION

Recently a variety of new Cr(VI) complexes have been developed to study the selective oxidation of organic compounds [1-7]. Quinaldinium fluorochromate has been used as a mild and stable oxidizing agent in synthetic organic chemistry [8]. The structure of the quinaldinium fluorochromate is given below



Quinaldinium Fluorochromate

A thiomalic acid or mercaptosuccinic acid (TMA) is a dicarboxylic acid containing a thiol functional group. It is suggested by the presence of SH group instead of an OH group on malic acid. Salts and esters are known as thiomalates. Thiomalic acid forms the backbone of the pesticide. Thiomalic acid structure as shown below,

The oxidation of thioacids by pyridinium fluorochromate [9] and 2,2' bipyridinium chlorochromate [10] has been reported. Mostly thioacids are used in convergent synthesis of peptides and proteins [11]. On treatment with suitable nucleophile provide very facile access to thioacids [12,13]. Literature survey to study of the kinetics of oxidation of thiomalic acid by quinaldinium fluorochromate has not been reported. In the present study, the kinetics of oxidation of thiomalic acid by quinaldinium fluorochromate in non – aqueous medium and the mechanism has also been discussed.



Thiomalic acid or Mercaptosuccinic acid

MATERIALS AND METHODS

The thiomalic acid (Aldrich) was used as such. The solutions of the thiomalic acid was freshly prepared in dimethyl sulphoxide and standardized by titrating it against a standard solution of iodine. Quinaldinium fluorochromate was prepared by the reported method [8] and its purity was checked by an iodometric method. The solvents were purified by usual methods [14]. *p- Toluene- sulphonic acid* was used as a source of hydrogen ions and all other chemicals were used in AR grade.

Stoichiometry

The stoichiometry of the reaction was determined by performing the experiments under nitrogen at 333 K, under the conditions of $[QnFC]_0 > [Thiomalic acid]_0$, at varying concentration of acid. The disappearance of Cr(VI) was monitored until a constancy in the absorbance values was attained. The $[QnFC]_{\infty}$ was estimated. A stoichiometric ratio $\Delta[QnFC] / \Delta[Thiomalic acid]$ was obtained, The reaction exhibited as 1:2 stoichiometry. which confirmed to the overall equation.

 $CH_{2}COOHCHCOOH-S-H_{+}O_{2}CrFOQnH \longrightarrow CH_{2}COOHCHCOOH-S-S-CHCOOHCH_{2}COOH_{+}H_{2}O_{+}CrOFO-QnH --- (1)$

Kinetic measurements

The reaction was followed under pseudo-first order conditions by keeping the thiomalic acid concentration in excess over that of quinaldinium fluorochromate. All the reactions were carried out in flasks blackened from the outside to prevent any photochemical reactions and were followed up to Ca 80% conversion by monitoring the decrease in the [QnFC] at 470 nm on the photoelectric colorimeter. The rate constants were obtained from the slope of the plot of log absorbance *versus* time by the linear least square method. The results were reproducible within $\pm 3\%$. The second order rate constants were evaluated from the relation $k_2 = k_{obs}/[reductant]$.

RESULTS AND DISCUSSION

Kinetic dependence

The reaction was found to be first order with respect to the oxidant as evidenced by a good linearity in the plot of log [QnFC] *versus* time (Figure. 1). The pseudo - first order rate constants were found to be independent of the initial concentration of the quinaldinium fluorochromate. At constant [QnFC], the rate constants were increased with the increase in the concentration of substrate. A plot of log k_1 *versus* log [TMA] gave a straight line with a slope of unity (Figure. 2). This was further well demonstrated by the constancy of the second-order rate constant $k_2 = k_1$ /[substrate] (**Table - 1**).

$[QnFC] 10^3$	$[TMA] 10^3$	$k_{obs} 10^4$	$k_2 = k_1 / [s]$
mol dm ⁻³	mol dm ⁻³	s^{-1}	$(1 \text{ mol}^{-1} \text{s}^{-1})$
2.50	7.50	7.82	
3.00	7.50	7.83	
3.50	7.50	7.83	
4.00	7.50	7.81	
4.50	7.50	7.83	
3.00	5.00	5.07	1.01
3.00	7.50	7.83	1.04
3.00	10.00	10.49	1.05
3.00	12.50	13.18	1.05
3.00	15.00	15.87	1.06

Table -1 Rate constant for the oxidation of thiomalic acid and Quinaldinium Fluorochromate at 313 K







Figure. 2 Plot of log k1 versus log [TMA]

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Effect of acidity

The effect of acidity was studied by varying the concentration of *p*- toluene sulphonic acid and the rate constants were found to increase with the increase in the concentration of *p*- toluene sulphonic acid (**Table - 2**). The plot of log k versus log $[H^+]$ gave a straight line with the slope of 1.38 indicating that the reaction is acid catalyzed one. The hydrogen ion dependence takes in the form of $k_{obs} = a + b [H^+]$. The values of a and b, for thiomalic acid (TMA), are $7.67 \times 10^{-1} \text{ s}^{-1}$ and $13.60 \times 10^{-1} \text{ mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$, respectively (r =0.999).

Table -2Effect of Hydrogen ion concentration on the oxidation of thiomalic acid by Quinaldinium fluorochromate $[QnFC]=3.00 \times 10^{-3} mol dm^{-3}$ Temperature=313 K

[QnFC] =	$3.00 \times 10^{-3} \text{ mol } dm^{-3}$	Temperatu
	$[TMA] = 7.50 \times 10^{-3}$	mol dm ⁻³
	[TsOH] 10 ³ mol dm ⁻³	$k_{obs} 10^4 s^{-1}$
	1.25	7.83
	2.50	15.84
	3.75	25.11
	5.00	33.88
	6.25	43.65

Effect of varying solvent composition

The reaction was carried out at five different percentages of DMSO-DMF mixtures while all other factors are constant. The reaction is facilitated by the medium of low dielectric constant (ϵ) and it was decreased by the addition of DMF (**Table - 3**). The plot of log k₁ versus inverse the dielectric constant gave a straight line with the positive slope(Figure. 3). It indicates that the involvement of ion-dipole interaction in the reaction [15-17] and in the presence of acid, the rate determining step involved a protonated Cr(VI) species [18].





Figure. 3 Plot of log k₁ versus D⁻¹

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Induced polymerization of acrylonitrile

The oxidation of thiomalic acid by quinaldinium fluorochromate, in an atmosphere of nitrogen, is failed to induce the polymerization of acrylonitrile [19, 20]. Further, the addition of acrylonitrile does not affect the rate. It indicates that a one electron oxidation giving rise to free radicals, is unlikely in the present reaction.

Effect of varying Manganous sulphate

The reaction rate decreases with increasing the concentration of Mn^{2+} ions , confirming the involvement of two electron process in this reaction [21] (**Table – 4**).

[QnFC] = 3.0	$10^{-3} \text{ mol } dm^{-3}$	[TsOH]	$= 1.25 \times 10^{-3} mol dm^{-3}$
[TMA] = 7.50	$0 \times 10^{-3} \text{ mol } dm^{-3}$	Temper	rature = 313 K
	[MnSO ₄] mol dm ⁻³	$k_1 \ 10^4 \ s^{-1}$	
	0.00	7.83	
	0.50	6.61	
	1.00	6.35	
	1.50	6.17	
	2.00	6.03]

Table - 4 Effect of varying Manganous sulphate

Effect of varying Temperature

The rates of oxidation of thiomalic acid was determined at four different temperatures and it was observed that the rate increased with an increase in temperature (**Table - 5**). From the linear plots of log k_1 against the reciprocal of temperature (Figure. 4), the activation energy (Ea) was calculated. The entropy of activation ($\Delta S^{\#}$), the enthalpy of activation ($\Delta H^{\#}$), and the free energy of activation ($\Delta G^{\#}$) were calculated using the Eyring's equation respectively [22 - 24].

 $(\Delta H^{\#}) = 29.92 \ k \ J \ mol^{-1}$ $(\Delta S^{\#}) = 168.94 \ J \ K^{-1} mol^{-1}$ $(\Delta G^{\#}) = 81.72 \ k \ J \ mol^{-1} \ at \ 313 \ K$ $Ea = 32.52 \ k \ J \ mol^{-1} \ at \ 313 \ K.$



[TMA]=7.5×10 ⁻	³ mol dm ⁻³
Temperature K	$k_1 \ 10^4 \ s^{-1}$
303	4.96
313	7.83
323	10.93
333	16.14



Figure. 4 Plot of ln k₂/ T versus 1/T

Mechanism and rate law

The lack of any radical scavenger such as acrylonitrile on the reaction rate and the failure to induce the polymerization of acrylonitrile, point against the operation of a one electron oxidation giving rise to free radicals. The observed solvent effect supports a transition state, which is more polar than the reactant state. Therefore, a mechanism involving transfer of a direct hydride ion from S-H group to quinaldinium fluorochromate is suggested in **Scheme 1**.

$CH_2COOHCHCOOH - S - H$	[+	OCrOFOQnH	$\frac{k_1}{slow}$	CH ₂ COOHCHCOOH	[— S	+ +	[HOCrOFOQnH]
$CH_2COOHCHCOOH - S^+$	+ CH ₂ CC	оонснсоон-s- н	$\frac{k_2}{fast}$ CH ₂	соонснсоон—s-	- s –	СНСООНС	$CH_2COOH + H^+$
[HOCrOFOQnH]-	+	H ⁺	$\frac{k_3}{fast}$	H ₂ O	+	CrOFOQ	н

Rate Law

The above mechanism leads to the following rate law:

Rate = k_1 [QnFC] [TMA]

Bimolecular reactions usually exhibits negative entropy of activation .As the activated complex is formed the reactant lose their freedom to move independently. Further as, the charge separation takes place in the transition state, the charged ends get solvated by solvent molecules. This results in immobilization of large number solvent molecules results in unfavourable entropy.

CONCLUSION

The oxidation of thiomalic acid by quinaldinium fluorochromate in non - aqueous medium leads to the formation of complex and finally gives the products. The reaction follows simple order kinetics. The mechanism proposed for this oxidation reaction is in accordance with the observed kinetic facts.

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