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Research Article

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A Kinetic Study of 2-Amino-4-(Methyl-Thio) Butanoic Acid By Quinaldinium Fluorochromate In Selected Hydrophilic Solvent Medium

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Abstract: A Major role in oxidation kinetics is to determine the reaction mechanism that comprise chemical reaction. In the present paper we derived rate law for reaction mechanism and to recognized the order of reaction, give rate equation, calculate the rate constant. Identify the product of this oxidation reaction.The chemical oxidation of 2-Amino-4-methyl thio-butanoic acid by Quinaldinium Fluorochromate was studied in 50-50 (v/v) selected hydrophilic solvent medium at 308 Kelvin. The reaction is acid catalysed and exhibits first order dependence with respect to oxidant, substrate, and fractional order respect to H+ ion concentrations. Chemical oxidation kinetics is the study of the rate of chemical reaction.the factors Manganesh sulphate, Acrylonitrile, Sodium perchlorate that affect these rates (or) not, and draw of ln K_{obs}/T *verses* 1/T energy diagram to find the activation energy. Addition of sodium perchlorate slightly decreases the rate of reaction. However, Acrylonitrile is not induced by the polymerization reaction, showing that there is no free radical route. Added Mn^{2+} increases with slightly increase rate in the reaction medium. 2-Amino-4-(MethylThio)-Butanoic acid by Quinaldinium Fluorochromate has not been reported. Hence, the investigation of oxidation of 2-Amino-4-Methyl Thio-Butanoic acid by QNFC in selected hydrophilic solvent medium and the corresponding mechanistic aspects are discussed in this research paper. A systematic kinetic work carried out to explore the physical characterization of the reactance. The characterstic effects like Substrate, Oxidant, Perchloric acid, Solvent, Sodium perchlorate, Acrylonitrile, Manganes sulphate and Influence Temperature it clearly shows effect on that reaction path. The process was carried out at four different temperatures to determine the activation conditions. The measured kinetic findings ΔH# and ΔS# are derived from the value.

Keywords: Chromium VI, Organic substrate, Oxidation, Product, Mechanism, solvent.

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1. INTRODUCTION

The kinetics deal with change in concentrations of the components system with the passage of time and the results are summarized in the form of rate expressions. The investigation of reaction kinetics in chemical reactions is the most important in deciding the reaction mechanisms.Oxidation Process a subject major importance to many chemists and elucidation mechanism is undoubtedly most the fascinating problems in the mind of chemists. Chromium compounds have been proved to be versatile oxidation reagents almost all the organic functional groups[1-4]. Amino acids are susceptible to oxidation by various forms of reactive oxygen species and the oxidation reaction may proceed through one or two electron transfers depending on the nature of the oxidant[5-6]. However, studies show that when an oxidation sensitive sulphide is located in a bio molecule such as methionine residue in a peptide or protein, the Redox reaction is affected by amino and carboxyl groups present in close proximity to sulphide function[7-9].Chromium VI reagents with polymer support have also been produced. These reagents have the benefit of being simplifying work procedure. Recently. The oxidant Quinaldinium fluorochromate [10-16] is used this work.Most of the biological reaction pathway and their mechanisms are very complex in nature. understanding the mechanistic aspects is the current interest in many fields. Quinaldinium fluorochromate Cr VI Oxidising agent. it is an efficient, economical and selective oxidant for many organic substrates.To explore the possibility find out certain selective substrates using QNFC as an oxidant,the present work is initiated and carried out. the main objectives of the present investigations to examine the uncatalytic behavior oxidation of 2-Amino-4-Methyl Thio Butanoic Acid by QNFC in hydrophilic solvent medium.

2. EXPERIMENTAL METHODS AND MATERIALS

2.1 Preparation of Substrate

Met oxidation to MEt- sulphoxide MtO has a function to based on the potential reversion by the enzyme MSR[17]. The study on the oxidation by Cr VI has been extensively studied, but no attempt the reactivity of like QNFC[18]. In the present investigation of 2-amino-4-(methyl thio)-butanoic acid by Quinaldinium fluorochromate[19].The corresponding 2-amino-4-methyl thio-butanoic acid (2-A-4-(MT)-BA) was prepared a described by Dupuisetal[20].

2.2 Other chemicals

Quinaldinium Fluorochromate (QNFC) was synthesized as per the literature[21]. All other chemicals used in this experiment are all of AR grade samples.

2.3 Product analysis and stoichiometry

Product analysis was done by get the reaction path containing 2-amino-4-methyl thio butanoic acid (0.01 mol), $HClO_4$ (2 M), QNFC (0.01 mol) was dissolved in hydrophilic solvent (20mL) and subjected it to stand for 2 h at308 K. There after 10 mL of Na_2CO_3 was added and the solution was stirred vigorously, the followed by drop wise addition of C_6H_5Cl solution with precipitation was completed. The precipitate was identified as 2-amino-4-(methylthio)butanoic acid sulfoxide (m.p.183°C) as 2-amino-4-methyl thio butanoic acid sulfoxide (2-A-4-(MT)-BAS). The estimation of unreacted QNFC indicated that 1mol of substrate consumed one mol of QNFC.

2.4 Kinetic Measurements

All the kinetic reactions were examined under pseudo-first order conditions, keeping [substrate] >> [QNFC] in a solvent system of 50% (v/v) hydrophilic solvent medium at 33°C (308 Kelvin) unless otherwise mentioned and course work the followed by Iodometrically.

3. RESULTS AND DISCUSSION

3.1 Effect of variation of concentration [QNFC]

The reactions were conducted with varying concentrations of QNFC and keeping all other reactant concentrations constant and rate constants were calculated (shown in Table.1). unit order dependence on QNFC was evidenced from the linear plots of log titre versus time[21-22].

Table 1. Effect of variation of concentration oxidant

10^3 [QNFC] (moldm-3)	$10^4 k_{obs}$ (s^{-1})
0.75	3.35
1.00	3.43
1.25	3.65
1.50	3.83
1.75	3.95
2.00	3.98

3.2 Effect of variation of concentration [2-amino-4-(methylthio) butanoic acid]

The reactions were investigated with varying concentration of 2-amino-4-(methylthio)butanoic acid and keeping all other reactant concentrations constant and rate constant values were given in Table .2. A plot of log k_{obs}versus log [2-amino-4-(methylthio)butanoic acid] is straight line a slope = 1.10, r = 0.998, sd = 0.010 in the rate of reaction. These results show that unit(first) order dependence with respect to [2-amino-4-(methylthio)butanoic acid] uncatalyzed reaction[20-22].

Table 2. Effect of variation of concentration substrate	
10^3 [2-Amino-4-(methylthio)-butanoic acid] (mol dm^{-3})	$10^4k_{obs}(s^{-1})$
05.00	1.93
07.50	2.67
10.00	3.43
12.50	3.96
15.00	4.67
17.50	4.96
20.00	5.46
22.05	6.09
25.00	6.85

3.3 Effect of variation of concentration [$HClO_4$]

The reactions with varying concentration of $HClO_4$ and keeping all other reactant concentrations were constant. with the increase in the concentration of perchloric acid, the rate constants also increased (shown in Table.3). The plot of log k_{obs} versus log [H^+] shows that fractional order dependence is observed (slope = 0.288; r = 0.996; sd = 0.010) in this reaction[23].

Table. 3. Effect of variation of concentration perchloric acid	
10^3 [$HClO_4$](mol dm^{-3})	$10^4k_{obs}(s^{-1})$
02.5	2.51
05.0	3.43
10.0	4.15
15.0	4.66
20.0	4.67
25.0	5.29

3.4 Effect of variation of concentration AcOH-H_2O(% v/v)

The reaction was conducted with different solvent composition of hydrophilic solvent mixture and keeping all other reactant concentrations constant and the corresponding rate constants were given in Table.4. This suggests that an ion-dipole interaction may be involved in the mechanistic pathway. A plot of log k_{obs} versus1/D is linear with a positive slope in these reactions[24].

Table .4. Effect of solvent composition	
AcOH-H_2O (% v/v)	10^4k_{obs} (s^{-1})
30-70	1.87
35-65	2.61
40-60	3.67
45-55	4.13
50-50	5.75
55-45	6.86
60-40	7.22
65-35	8.89
70-30	9.31

3.5 Effect of added [$NaClO_4$], [acrylonitrile] and [$MnSO_4$] on the rate of reaction

The rate data was measured with different concentration of $NaClO_4$ and keeping all other reactant concentrations constant. With increase in the concentration of $NaClO_4$, rate constants slightly decrease, Due to reaction was occurs may be between an ion and a neutral molecule[6]. Added acrylonitrile rules out the possibility of radical pathway mechanism[25]. Added Mn^{2+}increases with Slightly increase the rate of reaction[5]. Which is shown in the Table.5.

[2-A-4-(MT)-BA] = 10.0×10^{-3} mol dm^{-3},
[QNFC] = 1.0×10^{-3} mol dm^{-3}

Solvent = 50-50 (% v/v) AcOH-H_2O,
[$HClO_4$] =5.00×10^{-3} mol dm^{-3},
Temperature = 308 K,

Table 5.Rate data for the Effect of added [$NaClO_4$], [Acrylonitrile]and[$MnSO_4$]

10^4 [$NaClO_4$] (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^4 [Acrylonitrile] (mol dm^{-3})	10^4k_{obs} (s^{-1})	10^4 [$MnSO_4$] (mol dm^{-3})	10^4k_{obs} (s^{-1})
0.00	3.43	0.00	3.43	0.00	3.43
0.50	2.24	0.50	3.38	0.50	3.56
0.75	2.46	0.75	3.36	0.75	3.68
1.00	2.68	1.00	3.40	1.00	3.86

3.6 Rate dependence on different oxidants

The reactions were carried with various oxidizing agents viz., BIFC, QNFC, PFC and NDC and keeping all other reactant concentrations constant, the measured rate constant values were shown in Table 6. The observed results show that both BIFC and QNFC show higher oxidizing Efficiency[10-16]

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Table 6. Rate constants of 2-amino-4-(methylthio)butanoic acid with various chromium (VI) reagents

Oxidant	10^3 [Oxidant](mol dm^{-3})	10^4k_{obs}(s^{-1})
QNFC	1.00	3.43
BIFC	1.00	3.32
PFC	1.00	3.22
NDC	1.00	2.83

3.7 Effect of temperature (K)

The reactions were carried out at four different temperatures *viz.,* 303, 308, 313 and 318 K and keeping all other reactant concentrations constant and the rate constants were calculated shown in Table.7. The thermodynamic parameters were determined by the Eyring's plot of ln k_{obs}/T versus 1/T are given in below fig.1.The oxidation reaction has been conducted at four different temperatures and the Activation parameters were calculated[26]. For uncatalyzed reaction $\Delta H^{\#}$ = 35.22 kJ $mol^{-1}$and $\Delta S^{\#}$ =-201.80 J K^{-1} mol^{-1}.

Table 7. Effect of temperature on reaction rates

Temperature (K)	10^4k_{obs} (s^{-1})
303	2.50
308	3.43
313	4.22
318	5.06

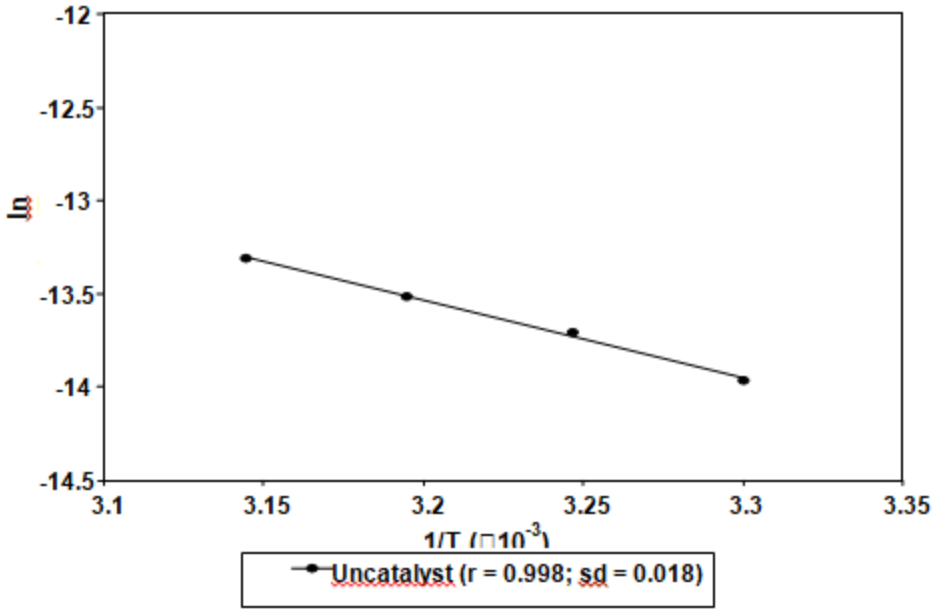

Fig.1. Plot of ln k_{obs}/T *versus* 1/T

3.8 Mechanism and rate law

3.8.1 Uncatalyzed Oxidation of 2-amino-4-(Methylthio)-Butanoic Acid by QNFC[28]

Kinetic results From the following mechanism has been proposed. The effective oxidizing species $HCrO_4^-$ protonates[27] to give H_2CrO_4 in the equilibrium step. Further H_2CrO_4 react with 2-amino-4-(methylthio)butanoic acid[19] to given complex C_1, then this C_1 dissociate to yield a complex[17] C_2. The complex C_2 dissociate a product in the fast and rate determining step[18-19].

$$HCrO_4^- + H^+ \overset{K_1}{\rightleftharpoons} H_2CrO_4$$

$$H_2CrO_4 + [2\text{-A-4-(MT)-BA}] \overset{K_2}{\rightleftharpoons} \text{Complex } (C_1)$$

$$\text{Complex } (C_1) \xrightarrow[\text{slow}]{k_3} \text{2-A-4-(MT)-BAS}(C_2) + \text{Chromium (IV)}$$

$$\text{Complex } (C_2) \xrightarrow{\text{fast}} \text{Product}$$

The mechanism proposed characterized with the following Rate law =

$$\frac{-\,d[Cr(VI)]}{dt} = \frac{K_1K_2k_3[2\text{-amino-4-(methylthio)utanoic acid}][Cr(VI)][H^+]}{\{1+K_1[H^+]\}}$$

4. CONCLUSION

Our study implies,at 308 K, the reaction is carried out in a hydrophilic solvent medium, yielding the following results. It has been reported that [Cr(VI)], [2- amino-4-(methylthio)butanoic acid], and the fractional order [H+] have unit 1order dependence. The rate of the reaction increases as the percentage of hydrophilic solvent increases. Due to added salt, reaction rate was slowed by salt, while the rate of the reaction is unaffected by acrylonitrile. The notion of a free radical route mechanism has been ruled out. With the addition of Mn^{2+}, the amount of Mn^{2+} in the body increases. Added Salt decreases the rate of the reaction and acrylonitrile has no effect on the reaction rate, ruling out the possibility of free radical pathway mechanism. Added Mn^{2+}increases with Slightly increase the reaction rate in the reaction. The oxidation reaction has been conducted at four different temperatures and the activation parameters were calculated. The reaction is characterized by low enthalpy and negative entropy of activation values are $\Delta H^{\#}$ =35.22 kJ mol^{-1} and $\Delta S^{\#}$ = -201.80 J K^{-1} $mol.^{-1}$

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6. AUTHORS' CONTRIBUTION STATEMENT

Both Authors contributed equally in collection of references, interpretation of data a conceptualizing of the whole investigation processes.

7. APPLICATION

The oxidation process most chemical research and industrial applications. Determine the chemical kinetics is the vital everyday cycle that is called human life significantly depending upon chemical essential in different forms.

8. CONFLICT OF INTEREST

Conflict of interest declared none.

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