KINETICS AND MECHANISM OF OXIDATION OF SOME A-AMINO ACIDS BY CHROMIC ACID IN PRESENCE OF CHLORO SUBSTITUTEDACETIC ACIDS

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Abstract — Organic chemistry has its own significance in chemical reactions, the biochemistry also deals with this part of organic relation, kinetics and mechanics of various chemical reaction are done to analyze the thermodynamic effect for its kinetics, due to this energy of new chemical reaction is determined, thus from these chemical reactions toxicity and irritation from chemical is reduced and a new mechanism is created which is eco-friendly for environment, In our analysis alpha amino (L-alanine) is used for oxidation and the reaction is done with different concentrations of chromic substituted acetic acid to determine it kinetics effect thus energy of solution is also determined by its thermodynamic stability as the reaction is mixed with different concentrations of chromic acid with alpha amino acid the oxidation process takes place thus its kinetics and mechanics of solution increases with increased thermodynamic stability, hence ionic stability is also analyzed in this analysis.

Keywords— Alpha amino (L-alanine), chromic substituted acetic acid, chromic acid, acetaldehyde, oxidation, harmetten.

I INTRODUCTION

"Kinetic" originates from Greek "kinetikos" that, in flip, originates from Greek "kinetos' which means that "shifting". In general, the word "kinetics" is used in physical and life sciences to represent the dependence of something on time. Thermodynamics tells us which path a response will cross (e.g. At room temperature and widespread strain, carbon is strong in a shape of graphite). Kinetics can inform us how quick it's going to get there e.g. A diamond takes a long time, even centuries to convert to graphite. Such studies are critical in offering vital proof as to the mechanisms of chemical tactics. Macroscopic kinetics describes the department of kinetics, which ends relate to the conduct of a totally big organization of molecules in thermal equilibrium. Microscopic kinetics is to investigate the molecules in properly-described states, if you want to offer information approximately the dynamic of both reactive and un reactive collisions. (Crossed molecular beams). Chemical kinetics is the have a look at of the charges of chemical reactions. If a reaction is able to taking place, we want to understand how far the reaction will proceed, and how rapid it will manifest. Consider reactions: the rusting of an iron nail and the combustion of propane. Both reactions will occur, and both will occur to crowning glory. The rusting will take years to finish, but propane will combust in an on the spot. Furthermore, the nail will rust faster whilst it's moist, and slower in the presence of less oxygen. Obviously, there are elements that affect the rates of chemical reactions. The study of these factors and rates is chemical kinetics. Consider this generic chemical reaction.

II RATE OF REACTION

Consider a typical chemical reaction:

$$a\,A + b\,B \longrightarrow c\,C + d\,D$$

The lowercase letters (a, b, c, and d) represents stoichiometric coefficient, while the capital letters represent the reactants (A and B) and the products (C and D). According to IUPAC's Gold Book definition the reaction fee r for a chemical response going on in a closed gadget under isochoric situations, without a build-up of response intermediates, is described as: The rate of a response is usually high quality. A terrible signal is gift to signify the reactant concentration is reducing. The IUPAC recommends that the unit of time have to constantly be the second one. In this type of case the price of response differs from the rate of growth of awareness of a product P by means of a steady component (the reciprocal of its stoichiometric quantity) and for a reactant A by way of minus the reciprocal of the stoichiometric number. Reaction price generally has the devices of mol $L{-}1$ $s{-}1$. It is vital to undergo in thoughts that the preceding definition is simplest valid for a single response, in a closed device of consistent extent. This most usually implicit assumption must be stated explicitly, otherwise the definition is incorrect: If water is added to a pot containing salty water, the concentration of salt decreases, although there is no chemical reaction.

III FACTORS INFLUENCING RATE OF REACTION

The nature of the reaction: Some reactions are naturally faster than others. The number of reacting species,their physical state the debris that form solids circulate a whole lot more slowly than the ones of gases or the ones in solution, the complexity of the response and different factors can significantly influence the fee of a response.

Concentration: Reaction rate increases with concentration, as described by the rate law and explained by collision theory. As reactant concentration increases, the frequency of collision increases.

Pressure: The rate of gaseous reactions increases with pressure, which is, in fact, equivalent to an increase in concentration of the gas. The reaction rate increases in the direction where there are fewer moles of gas and decreases in the reverse direction. For condensed-phase reactions, the pressure dependence is weak.

Order: The order of the reaction controls how the reactant concentration (or pressure) affects reaction rate.

Temperature: Usually conducting a reaction at a higher temperature delivers more energy into the system and increases the reaction rate by causing more collisions between particles, as explained by collision theory. However, the main reason that temperature increases the rate of reaction is that more of the colliding particles will have the necessary activation energy resulting in more successful collisions (when bonds are formed between reactants) [1]. The influence of temperature is described by the Arrhenius equation. As a rule of thumb, reaction rates for many

reactions double for every 10 degrees Celsius increase in temperature,[1] though the effect of temperature may be very much larger or smaller than this. For example, coal burns in a fireplace in the presence of oxygen, but it does not when it is stored at room temperature. The reaction is spontaneous at low and high temperatures but at room temperature its rate is so slow that it is negligible. The increase in temperature, as created by a match, allows the reaction to start and then it heats itself, because it is exothermic. That is valid for many other fuels, such as methane, butane, and hydrogen. Reaction rates can be independent of temperature (non-Arrhenius) or decrease with increasing temperature (anti- Arrhenius). Reactions without an activation barrier (e.g., some radical reactions), tend to have anti Arrhenius temperature dependence: the rate constant decreases with increasing temperature.

Solvent: Many reactions take place in solution and the properties of the solvent affect the reaction rate. The ionic strength also has an effect on reaction rate.

Electromagnetic radiation and intensity of light: Electromagnetic radiation is a form of energy. As such, It could speed up the fee or even make a reaction spontaneous because it offers the debris of the reactants with more energy. This electricity is in one way or any other saved inside the reacting debris (it can ruin bonds, sell molecules to electronically or vibrationally excited states) growing intermediate species that react without problems. As the intensity of light will increase, the debris take in greater energy and therefore the charge of response will increase. For instance, while methane reacts with chlorine in the dark, the reaction price is very sluggish. It can be speed up when the mixture is put under diffused light. In bright sunlight, the reaction is explosive.

A catalyst: The presence of a catalyst increases the reaction rate (in both the forward and reverse reactions) by providing an alternative pathway with lower activation energy. For example, platinum catalyzes the combustion of hydrogen with oxygen at room temperature.

Isotopes: The kinetic isotope effect consists in a different reaction rate for the same molecule if it has different isotopes, usually hydrogen isotopes, because of the mass difference between hydrogen and deuterium.

Surface Area: In reactions on surfaces, which take place for example during heterogeneous catalysis, the rate of reaction increases as the surface area does. That is because more particles of the solid are exposed and can be hit by reactant molecules.

Stirring: Stirring can have a strong effect on the rate of reaction for heterogeneous reactions.

All the factors that affect a reaction rate, except for concentration and reaction order, are taken into account in the rate equation of the reaction.

IV THEORIES OF CHEMICAL KINETICS

The stepwise explanation of a chemical reaction is called as its mechanism. The individual steps which taking place are generally called elementary processes. There are different theories which explain the mechanism of chemical reaction. The most common theories include collision theory and activated complex theory. In this section, a brief discussion of these two theories is given.
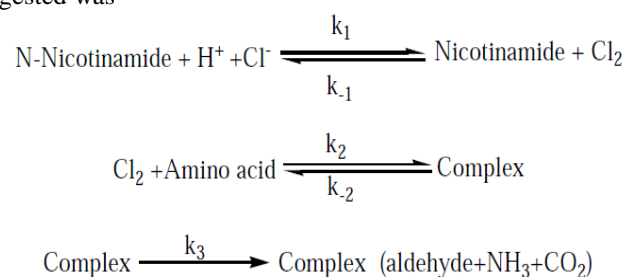
Collision theory: - This theory is primarily formulated for bimolecular reactions. The reacting particles approach to every different to a sufficiently close distance. It assumes that collision among pair of molecules can lead to a response. Further, it's far count on that a response will continually arise if the preliminary relative pace Vo of the two molecules equal or exceed a restrict Vm and if, for a given velocity Vo, their Centre of mass approach within a distance, R, much less than or same to a restriction Rm. The relative motion of the molecule is influenced by a spherically symmetric intermolecular potential V(R). The rate constant k for bimolecular reaction is calculated in two steps. First, consider all collisions with same initial velocity Vo (where Vo>Vm). The rate at

which the projection A hit their target B is equal to the volume per time VoSr, multiplied by the projectile A (Vo), i.e. concentration Vo Sr A (Vo). The reaction rate is Vo Sr A (Vo), multiplied by the number of targets per unit volume NB (Vo)

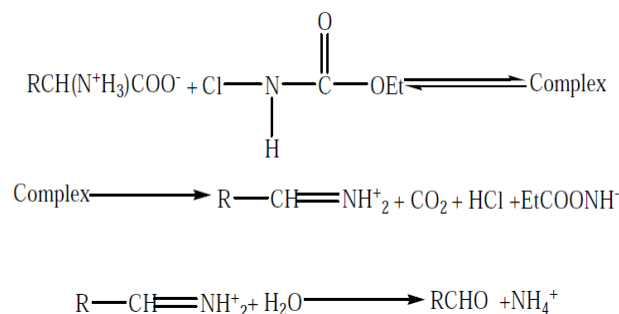$$r (Vo) = (Vo\ Sr\ N)\ A (Vo)\ B(Vo)$$
$$= k\ A (Vo)\ B (Vo)$$

Where k is the rate constant and N is Avogadro's number. Although this is a useful expression for the interpretation of specialized experiments where the relative translation velocity of reactant is selected, in the usual macroscopic reacting system a variety of relative speeds Vo are present. Hence this theory predicts an empirically acceptable form for the rate constant. It is not possible to compare theoretical and experimental activation energies because collision theory does not predict a value for the theoretical equation. In the solution state, a molecule interacts with its nearest neighbors. These nearest neighbors form a cage around the molecule. The cage creates a potential well within which the molecule can move back and forth.

Oxidizing agents:- The species which oxidizes other species give up oxygen or electronegative atom which accept hydrogen or any other electropositive element which gain electron are called oxidizing agents. There are massive numbers of compounds which can be used as oxidizing marketers in natural chemistry. Classification of these compounds is complex and hard. Although the oxidation of medicinal drugs, inside the present observe is carried out with the aid of potassium permanganate, it is necessary to have a investigate the different oxidizing retailers available. The N-halo compounds are widely used as oxidizing agents for example, N-chloronicotinamide which can be prepared by passing a slow stream of chlorine in the solution of nicotinamide in HCl. It is white precipitate with M.P. 220oC [2]. Kinetics of oxidation of alpha amino acids by N-Chloronicotinamide in aqueous acetic acid medium in presence of hydrochloric acid has been investigated by Vivekanandan and Nimbi [3]. They reported first order oxidation with respect to [oxidant] and [HCl]. The rate of reaction depend on solvent, it increases with decrease in dielectric constant. They proposed that reaction takes place because of molecular chlorine, which act as strong oxidizing agent. The mechanism of reaction suggested was

$$N\text{-Nicotinamide} + H^+ + Cl^- \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{Nicotinamide} + Cl_2$$

$$Cl_2 + \text{Amino acid} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{Complex}$$

$$\text{Complex} \overset{k_3}{\longrightarrow} \text{Complex (aldehyde} + NH_3 + CO_2)$$

The other N-halo compounds are N-Bromophthalimide [4], N-Bromoacetamide [5], and N-Chorobenzamide [6]. The oxidation of alpha amino acids by ethyl N- Chlorocarbamate (ECC) in aqueous acetic acid leads to the formation of the corresponding aldehydes [7]. The reaction is first order with respect to ECC. It was observed that reaction rate increases with an increase in the polarity of the medium. The reaction was susceptible to the both polar and sterric effects of the substituents. The mechanism proposed is

$$RCH(N^+H_3)COO^- + Cl-N(H)-\overset{\overset{\displaystyle O}{\|}}{C}-OEt \rightleftharpoons \text{Complex}$$

$$\text{Complex} \longrightarrow R-CH=NH^+_2 + CO_2 + HCl + EtCOONH^-$$

$$R-CH=NH^+_2 + H_2O \longrightarrow RCHO + NH_4^+$$

The N halo amine has diverse nature of its ability to furnish halonium cations, hypo species, an N anion which acts as both bases and nucleophile.These compounds contain positive halogen and are mild oxidants [8]. The various compounds of which oxidation kinetics was investigated in the literature include. N-Chloronicotinamide which is reported to oxidized cyclohexanol [9]. N- Bromosuccinimide oxidation [10] of L-arginine in aqueous acidic medium is first order in [NBS], fractional order in [L-arginine] and of inverse fractional order in [H+]. The suggested mechanism was
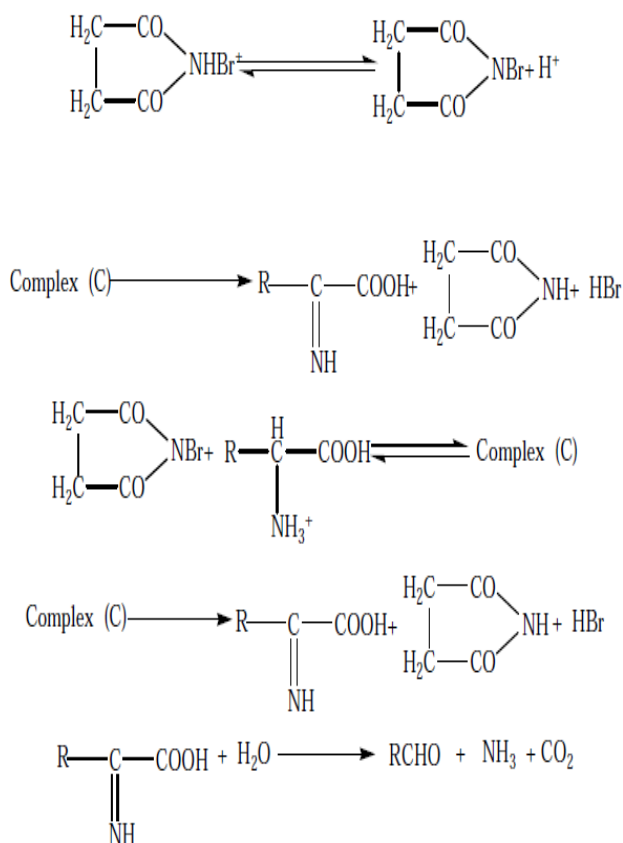
V LITERATURE REVIEW

Although, a variety of compounds can be oxidised by chromic acid, Dash et al.7 used chromic acid as an oximetric titrant. The oxidation of malonic acid by using acid dichromate in aqueous acetic acid medium has been found to be first order with recognize to each oxidant and substrate related to complex formation between them. The acid dependence indicates first order in (sulphuric acid) and past molar acid concentrations, the order was found to be more than 3.0. The participation of both HCrO4 - and Cr2O7 2- has been inferred.

Kinetics of chromic acid oxidation of substituted mandelic acids was followed by Sundaram and Venkata Subramaniyan1 in acetic acid - water. The effect of various substituents and the structural influences has been analysed, with the help of Hammett equation. Venkataraman and Brahamaji Rao2 followed the oxidation kinetics of formic acid by chromic acid, at different molar concentrations of sulphuric acid, ranging from 1 to 5.5. The facts have been examined in the mild of Bunnett's standards of response mechanism. A tentative mechanism regarding each SN1 and SN2 reaction at decrease pH was proposed.

The same kinetics when followed by Obula Reddy and Brahamaji Rao3 in moderately high concentrations of phosphoric acid (1.0 to 7.0 M), A reported price enhancement was located. There changed into a linear proportionality among the prices and the concentrations of formic acid. This observation can be employed for the analytical determination of even small quantity of formic acid. Sen Gupta et al.4 made an extensive kinetic study on the oxidation of α-hydroxy isobutyric dl-α-phenyl acetic acid and citric acids. The kinetic results do not indicate the formation of the intermediate

compound between Cr (VI) and the substrates. The reactions also do no longer proceed via free radicals. A mechanism based at the formation of carbonium ion inside the slow fee determining step has been suggested. Singh Dhakaray and Ghosh5 followed the acid catalysed oxidation of mandelic acid in the pH range, 1.90-3.30. Bivalent manganese accelerates the rate of the reaction. The probable mechanisms for Mn2+ catalysed and uncatalysed reactions were discussed.

Paul and Pradhan6 proposed a novel mechanism (Scheme 1.1) for the oxidative decarboxylation of mandelic acid based on a study of deuterium labelling, solvent isotope effect.
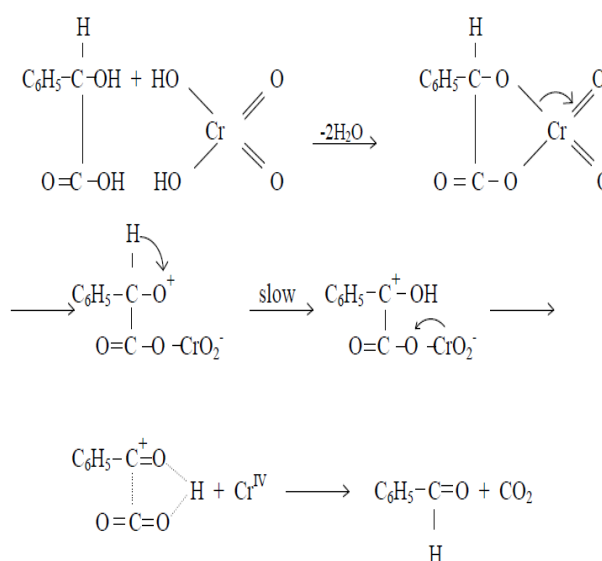
The mechanism shown is proposed for decarboxylation in which a cyclic anhydride is fashioned first. It then breaks up accompanied by way of the hydride ion transfer from Alpha-carbon to the adjacent electron-poor oxygen. This is likely because the nice fee at the Alpha-carbon atom can be stabilized via the Alpha-electron cloud of the benzene ring.

Valachha and Dakwale7 at Low concentrations of the substrate, the order of the response become pseudo-zero and one with recognize to oxidant. At high concentrations of the substrate, the respective orders have been located to be one and two. The product of oxidation was formaldehyde. Influence of temperature, solvent, acids and added salts of Mn (II) and Cr (III) has been studied. Singh et al.8 has reported the result of the process of oxidation of some hydroxy acids by Cr (VI).

Radhakrishna moorthy and Pande9 made an extensive kinetic study of Os (VIII) catalysed chromic acid oxidation of maleic, fumaric, acrylic and cinnamic acids in aqueous and in aqueous acetic acid media, in the presence of perchloric acid. Maleic acid and cinnamic acids exhibit zero order dependence in oxidant at lower concentration of oxidant and first order dependence at higher concentration of oxidant. Acrylic acid showed zero order dependence in oxidant in the total range of [oxidant] studied, while fractional order dependence in oxidant was noted in the case of fumaric acid. The order in substrate was unity in all the case of study.

The effect of acidity become marginal and the rate reduced slowly with the increase of percentage of acetic acid. Chromic acid oxidation of fragrant acetals (got from benzaldehyde and aliphatic alcohols) studied by Nambi et al.10 in aqueous acetic acid, yielded the corresponding esters as the main products. A total second order kinetics, first order each in [acetal] and [Cr (VI)] was observed correlation analysis of the rate data, elimination of proton in the rate determining step were the prominent points of this study.

Kinetics of chromic acid oxidation of dimethyl malonate by Oswal11 in acetic acid - water solutions of H2SO4 - H3PO4, in the presence and in the absence of Mn (II) ions, was studied at constant ionic strength. A welldefined induction period, marked catalysed activity of Mn (II) species and the thermodynamic portions of

uncatalysed reaction had been considered to propose a possible mechanism concerning loose radicals.

A mechanism involving the formation of an iminoxy radical in the rate determining step was proposed during the kinetics of oxidation of some para- substituted acetophenone oximes by Cr (VI). Oxidative hydrolysis of the reaction showed a first order rate dependence on the substrate concentration but inverse dependence on the concentration of Cr (VI). The ion-dipole type of this reaction was favoured by electron donating substituents with a reaction constant δ = -0.7. Several substituted N-methyl-2, 6-diphenyl piperidin-4-ones12 were subjected to oxidation by aqueous acidic CrO3, to investigate the effect of 3-alkyl substituent on this reaction. Increase of rate with increase of [H+], solvent composition and ionic strength (due to the addition of Na2SO4) was observed. A suitable mechanism involving a rate determining formation of chromate ester between CrO3 and piperidone was discussed in detail.

Kinetics of oxidation of aliphatic acetals13 (prepared from aliphatic aldehydes, aliphatic alcohols, halogen substituted alcohols and aromatic alcohols) by chromic acid in acetic acid medium showed first order each in oxidant and acetal the corresponding ester was the main product. Substituent effect, activation parameters and salt impact suggested that the removal of a proton from the complex species involving the acetal and chromium, will be the fee determining step.

It was shown that the oxidation of dipentyl and diphenyl sulphoxides followed with Cr (VI) in sulphuric acid medium involved an electron transfer from the sulphoxide to Cr (VI) and HCrO3 - in the rate determining step. A cation radical rapidly attacking the Cr-O bond gave rise to a complex, undergoing subsequent hydrolysis to yield the corresponding sulphone, camphor when subjected to Cr (VI) oxidation25 showed total second order kinetics, the condition of constant acidity. Addition of Mn (II) and Co (II) ions retarded the rate while ethylene diamine facilitated the same. A suitable mechanism has been proposed.

Kinetics of oxidation of diethyl tartarate26 by chromic acid was found to be first order each with respect to Cr (VI), ester and H+ ion. The product of oxidation was ethyl glyoxalate. The results of the overall second order kinetics of oxidation of some aliphatic aldehydes by chromic acid were discussed in the light of the theories of Amis and Laidler14.

Electron releasing substituents enhanced the rate of oxidation of parasubstituted toluenes by CrO3 in acetic acid - water mixtures at [HCrO4 -] 0.1 to 1.0 M. Radical intermediates were formulated to propose a suitable mechanism, to compute the δ value and to explain the importance of acidity function OH, rather than H+.

Ramanathan and Varadarajan15 studied the kinetics of oxidation of benzoin by chromic acid. The price changed into proportional to the first strength of attention of each of benzoin and Cr (VI). The authors stated that the charge determining enolization envisaged in different instances of similar have a look at isn't constant with their results.

5.1 Pyridinium Bromochromate (PBC)

Narayanan and Balasubramaniyan16 have found PBC as an efficient oxidant for alcohols as well as a brominating agent for aromatic compounds.

5.2 Pyridinium Chlorochromate (PCC)

Banerji et al.17 studied the kinetics of oxidation of thioglycollic acid, thiolactic acid and thiomalic acid by PCC. The reaction is first order with respect to [PCC] and Michaelis-Menten types of kinetics were observed with respect to all the [thioacids]. The rate turned into no longer tormented by the addition of acrylonitrile indicates the absence of the free radical mechanism. From the effects, a suitable mechanism turned into proposed as follows.
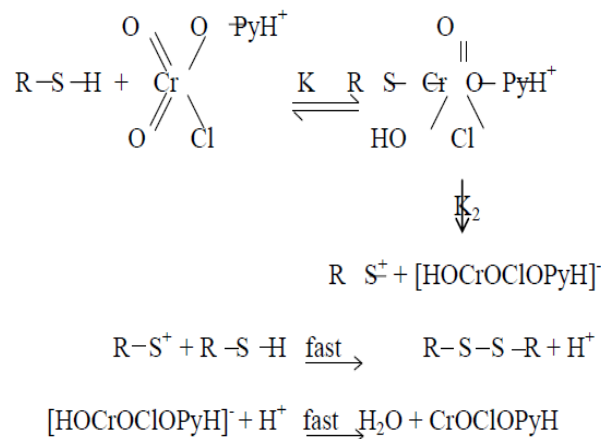
5.3 Bipyridinium Chlorochromate (BPCC)

Kabilan et al.25 have determined the effect of ring size on the rate of oxidation of cyclanols by BPCC in acetonitrile medium.

5.4 Quinoxalinium Dichromate [(C8H6N2 +H2) Cr2O7 2-]

Quinoxalinium dichromate (QxDC)63 can be easily prepared in good yield (78%) by addition of quinoxaline to a solution of chromium trioxide in water in a molar ratio of 1:1. QxDC is a yellow, non-hygroscopic and stable solid compound which can be stored in the darkness for months without losing its activity. The structure of the product turned into confirmed by using elemental analysis and its IR spectrum. In order to envision the performance of the reagent as an oxidant, it become tested on a big selection of substrates in dichloromethane at room temperature. Moreover, it's far solid and may be stored for long durations with out a lot loss in its interest and hence seems to be a totally beneficial reagent in synthetic natural chemistry.

Oxidation of some primary and secondary alcohols by quinoxalinium dichromate was studied by Degirmenbasi26. In this study, oxidants were carried out in dichloromethane with a substrate to oxidant ratio of 1:1.5 at room temperature. The products of the reactions were corresponding aldehydes and ketones, Recognized through assessment of their bodily and spectroscopic facts with those of actual samples inside the presence of anhydrous acetic acid as catalyst.

Ozgun27 studied the oxidation of substituted benzyl alcohols by quinoxalinium dichromate. A kinetic study quinoxalinium dichromate oxidizes benzyl alcohol and substituted benzyl alcohols smoothly in dimethyl sulfoxide and in the presence of acid to the corresponding aldehydes. The reaction has unit dependence on each of the alcohol, QxDC and acid concentration. Electron-releasing substituents accelerate the reaction, whereas electron-withdrawing groups retard the reaction and the rate data obey Hammett's relationship. The evaluation of the dependence of the kinetic isotope impact on temperature indicated that the reaction entails a symmetrical cyclic transition kingdom. The fees of oxidation were decided at special temperature and the activation parameters were evaluated. A appropriate mechanism is proposed.

5.5 S-Phenylmercaptoacetic Acids

Oxidation of S-phenylmercaptoacetic acid is interesting in the fact that it can undergo a Pummerer type of rearrangement followed by the cleavage of the molecule leading to the products thiophenol and glyoxalic acid 65-74. The rearrangement takes vicinity due to the instability of the intermediate, α-sulfinyl acetic acid in acetic medium. Similarly α-sulfinyl ketones and β-disulfoxides also are unstable in acidic situations The instability of sulfoxide within the presence of acid varying from dilute mineral acids via dry hydrogen halides to mercuric chloride has been stated in advance75 -79.

Generally oxidation of natural sulphides via numerous oxidizing reagents ends in both sulfoxide or sulfone relying on the response conditions. However the oxidation of S-phenylmercaptoacetic acid differs from that of alkyl or aryl sulphides because of the presence of an active methylene organization adjacent to the sulfur atom. Though, the made of oxidation is phenyl sulfinyl acetic acid, the instability of the equal results in the rearrangement in presence of acids.

Kabilan et al.28 studied the oxidation of S-phenylmercaptoacetic acid and phenoxy acetic acid by pyridinium dichromate. The reaction for phenylmercaptoacetic acid is carried out in presence of oxalic acid, it acts as a catalyst and also a co-substrate. The reaction for phenylmercaptoacetic acid is carried out in presence of perchloric acid. Both the reactions have been observed to be acid catalysed one. The order with recognize to PDC is one. The reaction follows a Michaelis-Menten sort of kinetics with admire to substrate.

A plausible mechanism which is applicable to both the oxidation reaction has been proposed. In aqueous acetic acid medium the effective oxidizing species of a chromium (VI) reagent is reported to the HCrO4 - ion. Initially, the HCrO4 - ions form a complex with the substrate in an equilibrium step which is followed by the dissociation of the complex in presence of H+ ions in a slow and rate determining step.

Oxidation cleavage of S-phenylmercaptoacetic acids by pyridinium chlorochromate – kinetic and correlation analysis done by Kabilan et al29. Oxidation of 24 S-arylmercapto acetic acid by pyridinium chlorochromate have been studied in acid medium. The fee records of meta- and parasubstituted acids had been correlated nicely with σI, σR zero values and the metacompounds correlate properly with F, R values. Further, the ortho- substituted acids show an awesome correlation with triparametric equation related to Taft's σI and σR zero and Charton's steric parameter γ. There is no tremendous steric contribution to the full ortho substituent effect.

VI SCOPE OF THE WORK

[1] In recent years, kinetics and mechanism of oxidation reactions of chromic acid for a number of substrates have been fairly well studied.

[2] The interesting point in the chromic acid oxidation is the mechanism of oxidation varies with the nature of the chromium species and the solvent used. Chromic substituted acetic acid is one among the oxidant and due to its synthetic and selective oxidant nature.

[3] It has been proposed to investigate the kinetic and mechanistic aspects of oxidation reaction of Chromic substituted acetic acid. Study of the oxidation of alpha amino acid (l-alanine) by various oxidants is reported in literature. There seems to be no report on the oxidation of alpha amino acid (l-alanine) by Chromic substituted acetic acid.

[4] It is proposed to investigate the kinetics and mechanism of oxidation of alpha amino acid (l-alanine) in presence of chromic acid with a view to understand about the substituent effect and possible mechanism for the reaction.

VII EXPERIMENTAL PROCEDURE

7.1 Preparation of Acetaldehyde (Ethanal) α – amino acid

This solution was prepared by the partial oxidation of ethanol in an exothermic reaction. This system commonly is performed over a silver catalyst at about 500–650 °C, The reaction is carried out at 90–95 °C, and the acetaldehyde formed is separated from water and mercury and cooled to 25–30 °C.

$$CH3CH2OH + 1/2\ O2 \rightarrow CH3CHO + H2O$$
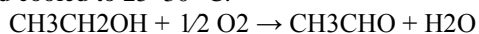
Preparation of DL- Lacto nitrile (2-Hydroxypropanenitrile) α – amino acid: Lactonitrile is obtained by reacting hydrogen cyanide with acetaldehyde.

acet-aldehyde   DL-lacto-nitrile

7.2 Preparation of 5-methyl hydantoin (Imidazolidine-2,4-dione) α – amino acid:

In a 600-ml. beaker are mixed 85 g. (1 mole) of acetone cyanohydrin and 150 g. (1.31 moles) of freshly powdered ammonium carbonate. The combination is warmed on a steam bath, preferably in a hood , and stirred with a thermometer. Gentle action starts offevolved around 50° and maintains during approximately 3 hours at sixty eight–eighty°. To entire the reaction and to decompose extra ammonium carbonate, the temperature is finally raised to 90° and maintained at this point until the liquid mixture is quiescent (30 minutes). The residue is colorless or pale yellow and solidifies on cooling. It is dissolved in 100 ml. of hot water, digested with Norit, and filtered rapidly through a heated filter. The filtrate is evaporated on a hot plate until crystals appear at the surface of the liquid, which is then chilled in an ice bath. The white crystals are filtered with suction; the filter cake is pressed and sucked dry and then washed twice with small portions (5–7 ml.) of ether, each portion being well incorporated with the crystals and then drawn through with suction**.
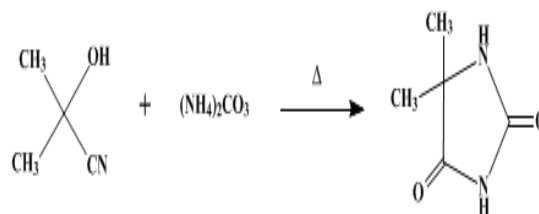

7.3 Preparation of DL alanine

To a cooled solution of 4.45 g. of DL-alanine in 30cc. of 20% sodium hydroxide solution was added 7.73g. of phenyl acetyl chloride drop wise during the period of one hour. The solution was allowed to stand overnight. The cooled solution was acidified with hydrochloric acid. The precipitate turned into eliminated with the aid of filtration, dried and extracted with ether. The residue became two times recrysllized from water to provide five-6 g. Of phenyl acetyl DL-alanine.

7.4 Preparation of L – alanine (2-Aminopropanoic acid) α – amino acid:

120 gm. of dry, Finely powdered kidncy were thoroughly mixed with six hundred cc. Of water. Water turned into delivered to approximately 3200 cc. And the cloth turned into stirred at 3540' fol half-hour. The coarse precipitate became eliminated via filtering thru pleasant cheese-material. The cloudy answer remaining turned into quick exceeded thru a Sharples fantastic centrifuge, whereby an almost clear answer turned into obtained. If facilities permit, centrifuging the entire suspension at 2000 to 2500 R.P.M. may be substituted for the filtration and super centrifugation. The extraction of the kidney powder must be completed to this point within 1% hours. The enzyme solution thus obtained was immediately added to a solution of 72 gm. of dl-alanine in 40 cc. of N SaOH and 760 cc. of Water, and oxygen turned into bubbled through the answer from a sintered glass plate with very energetic stirring. The stirring and oxygenation were continued for a period of 5 hours, during

which the temperature was maintained at 3540". The total oxygen uptake, which may be measured with a closed system, should be 4600 cc. The reaction should be complete in 3 to 5 hours. The solution was treated with 40 cc. of N HCl, heated to boiling to coagulate the dissolved protein material, and filtered. The clear filtrate was concentrated in uacuo to 600 to 900 cc. Sufficient 20 to 25 per cent aqueous trichloro acetic acid was added to bring the concentration of the entire solution to 2.5 per cent. The slight precipitate became eliminated with the aid of vacuum filtration thru coarse paper and a skinny layer of Filter Gel, 100 cc. of concentrated HCl were added, and the solution was evaporated to dryness in vacuo. The evaporation was repeated two times with the addition of small portions of water to remove excess HCl and then three times with the addition of small portions of alcohol. The precipitate remaining was extracted with 200 cc. of hot absolute alcohol. The residue (predominantly NH&l and NaCl) was re extracted with 100 cc. of 95 per cent alcohol. To the combined filtrates were added 67 cc. of aniline with stirring. The material was cooled to about 20' during 3 to 1 hour and filtered with suction. The brown precipitate as a consequence acquired changed into suspended in 100 cc. of warm alcohol, filtered, and washed on the filter with 50 cc. of ether. 33 to 40 gm. of crude I-alanine were thus obtained. [a]"d = +9-12" (3 per cent in HCl). This cloth includes a considerable amount of an inactive substance. The alanine was recrystallized from three components of boiling water by addition of nine components of alcohol. In the recrystallization any fabric that is insoluble in 3 parts of boiling water is not alanine and may safely be discarded. Yield, 22 gm., [(Y):~ = f14.5'; amino N, 15.5 per cent; calculated for CsHiOzN, 15.7 per cent. After one more recrystallization the rotation was [o!]E5 = + 14.5O.
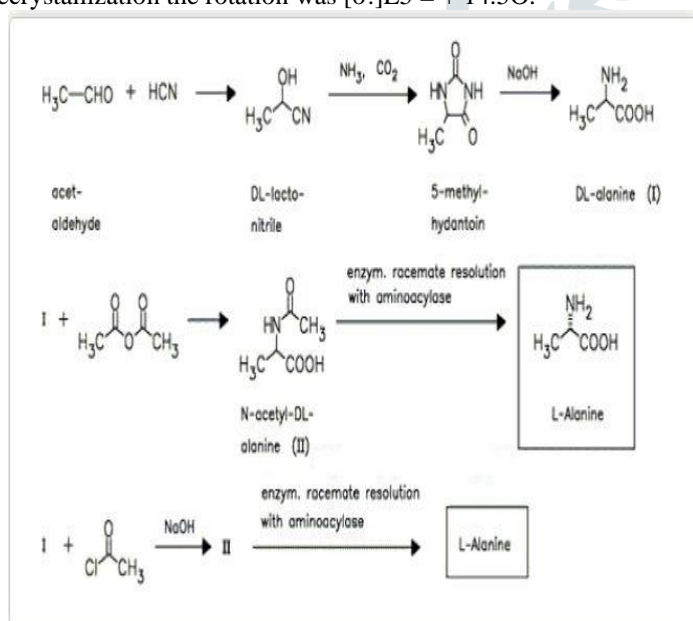

7.5 Preparation of chromic acid (Dihydroxidodioxidochromium):

To prepare a chromic acid wash mix 20 g of Sodium or Potassium Chromate with sufficient distilled H_2O to make a paste of the chromate salt. Add 300mL of concentrated Sulfuric Acid. Make larger amounts by increasing the proportions. Use the aggregate until it turns green in color. Soak heavily soiled items. The duration of time depends on how soiled the object is. For heavily soiled objects it could be important to let soak in a single day.

7.6 Preparation of Substituted Acetic Acid:

The process of this chemical reaction where diethyl malonate or another ester of malonic acid is alkylated at the carbon alpha (directly adjacent) to both carbonyl groups, and then converted to a substituted acetic acid.
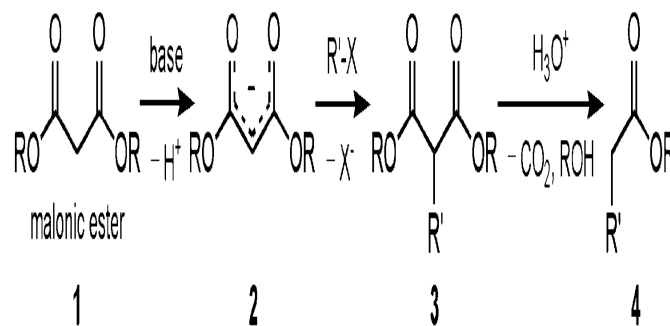
7.7 Kinetic Measurements for the Oxidation of some amino Acid by Chromic Acid

Solutions of l- alanin alpha amino acid in substituted acetic acid and other reagent like chromic acid solutions in doubly distilled water were prepared. In all the reactions pseudo-first order conditions were maintained. The kinetic measurements were made using spectrophotometer (ELICO SL 207 MINI SPEC) λ max = 470 nm as follows. All the solutions have been kept in a thermostat constant temperature for 1/2 an hour for each run. The temperature was controlled using Raagaa thermostat to an accuracy of ± 0.1°C. Then the response turned into began by means of adding a acknowledged quantity of acetic acid dichromate into the reaction flask. Immediately, 1 ml of aliquot (approximate) was transferred in to the quartz cuvette, which had already been kept and thermostated in the instrument. The reactions had been observed through determining the awareness of the unreacted substituted acetic acid dichromate for known intervals of time.

7.8 Non-Kinetic Study

The kinetics of reaction was to establish the stoichiometry of the reaction and identify any side reactions. The stoichiometry of the reaction [QxDC]: [α – amino acid] was determined by taking excess of [QxDC] over [α – amino acid] and allowing the reaction to go for completion. After enough duration of time, all of the substrate has completely reacted to chloro substituted acetic acid leaving at the back of the unreacted chloro substituted acetic acid. The unreacted chloro substituted acetic acid was estimated iodometrically. The estimation of unreacted chloro substituted acetic acid showed that one mole of substrate consumed by one mole of oxidant. The stoichiometry between α – amino acid acid and QxDC was found to be 1:1.

VIII RESULT AND DISSCUSSION
8.1 Kinetics and Mechanism of Oxidation of some α – amino acid by Chromic acid in presence of chloro substituted acetic acid

The kinetics of oxidation of some α – amino acid with chloro substituted acetic acid solvent system was carried out under psuedo-first order conditions. The effects are mentioned inside the following pages.

8.2 Effect of varying the [QxDC]

The reaction was investigated with varying concentrations of chloro substituted acetic acid at constant α – amino acid (l-alanin) and acetic acid concentrations. The response turned into determined to be first order with respect to QxDC as evidenced by the linear plot of log absorbance *versus* time (Fig 5.1) and also from the constancy of the pseudo-first order rate constants. The price or response reduced with increase the concentration of chloro substituted acetic acid. Because in that condition the whole chromic acid become inside the shape of acid chromate wherein is the effective oxidant.

[PMA] = $5.00 \times 10\text{-}2$ mol dm$^-$ AcOH-H2O = 50:50 (%)
[H+] = $3.50 \times 10\text{-}1$ mol dm^{-3} Temperature = 313 K

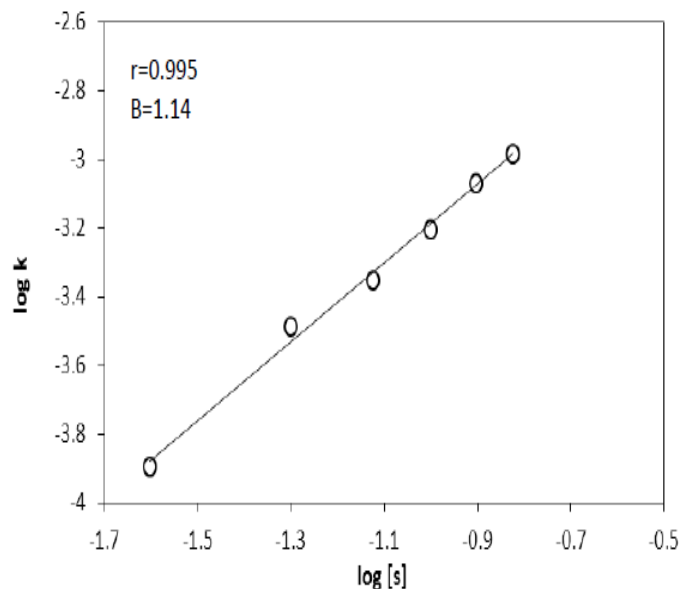| $[Q_xDC]\ 10^3\ mol\ dm^{-3}$	$k_1\ 10^4\ s^{-1}$
1.5	3.99
2	3.26
2.5	2.35
3	1.97
3.5	1.62

Log absorbance versus time

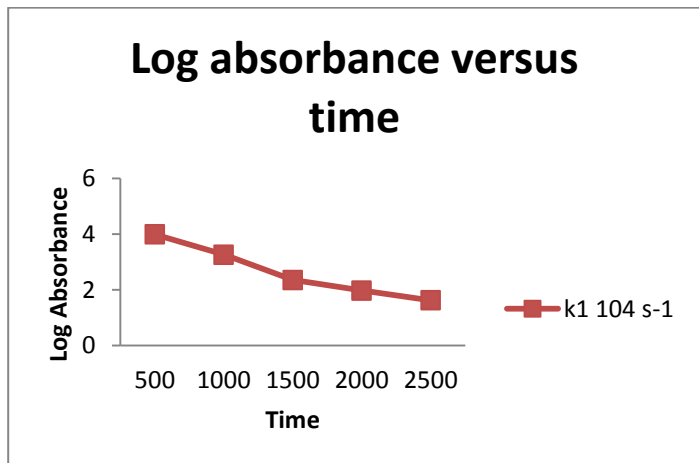

Fig 8.2 Plot of log k *versus* log [substrate]

8.4 Effect of varying hydrogen ion concentration

$[HClO4]\ 10^1\ mol\ dm^{-3}$	$k_1\ 10^4\ s^{-1}$
3.5	3.26
7	1.98
10.5	1.46
14	0.98
17.5	0.78
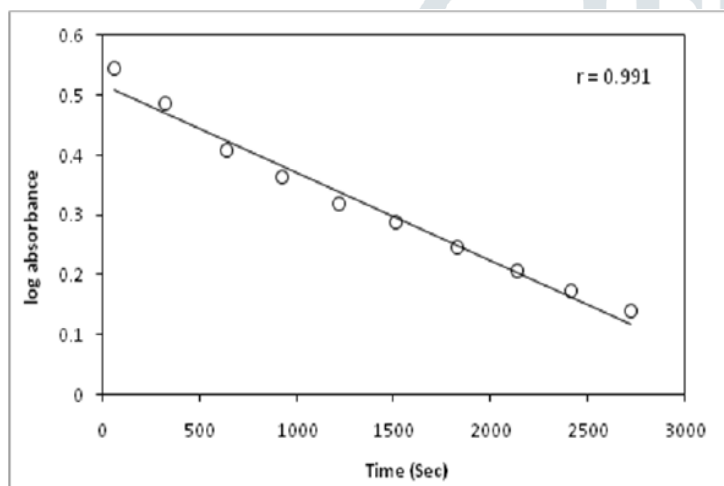
Fig 8.1 Plot of log absorbance versus time

K versus 1/[H*]
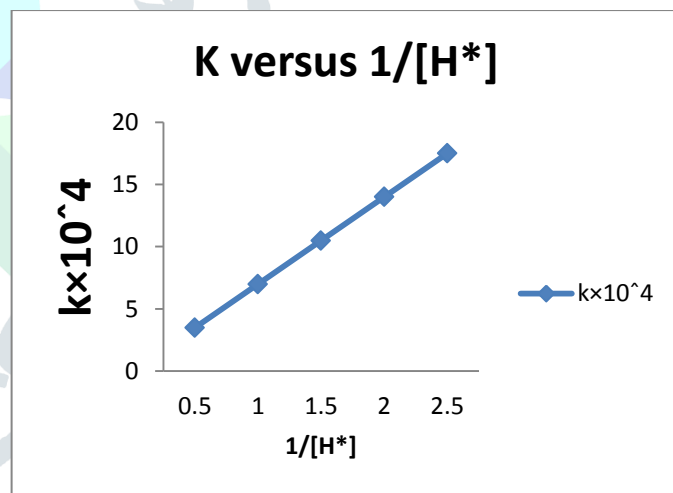
$[PMA]\ 10^2\ mol\ dm^{-3}$	$k_1\ 10^4\ s^{-1}$	$k2 = k1/[s]\ 10\ mol^{-1}\ dm^3\ s^{-1}$
2.5	1.27	0.05
5	3.26	0.06
7.5	4.42	0.06
10	6.42	0.06
12.5	8.52	0.07
15	10.38	0.07

8.3 Effect of varying the [PMA]

log K versus log S

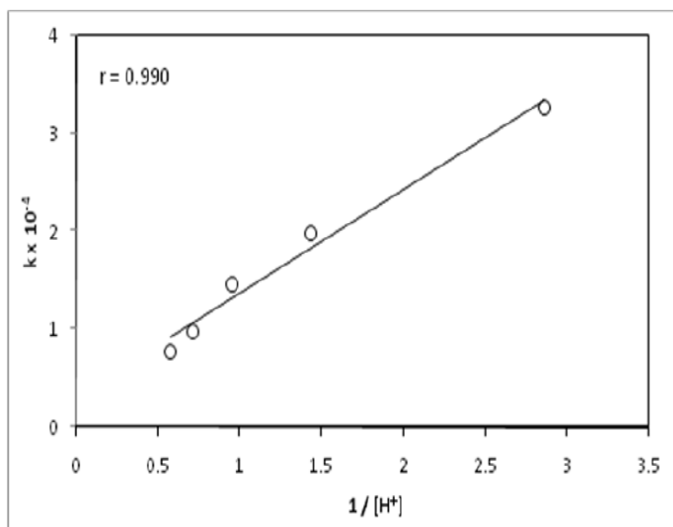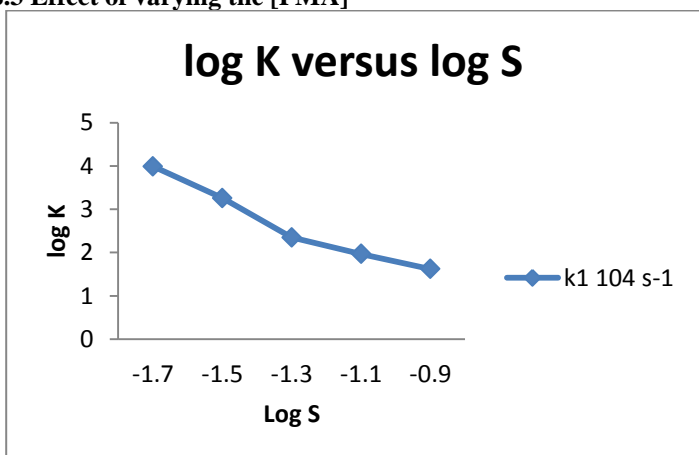

Fig 8.3 Plot of k versus 1 / [H+]

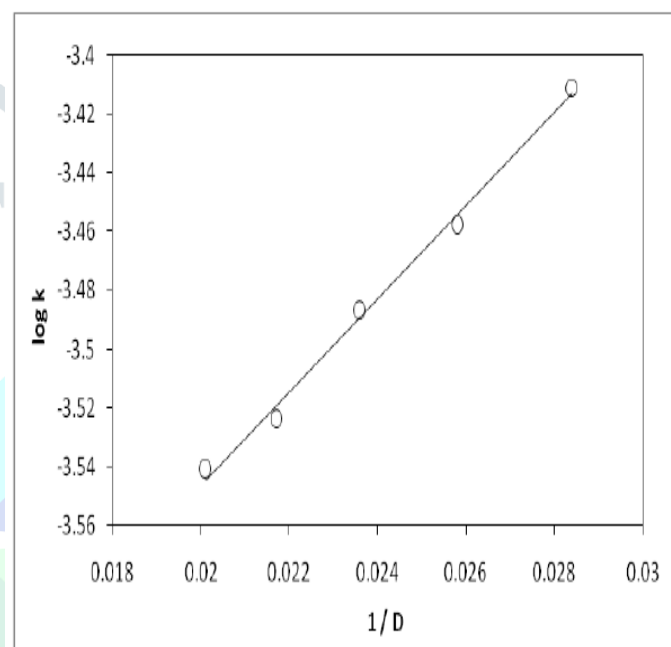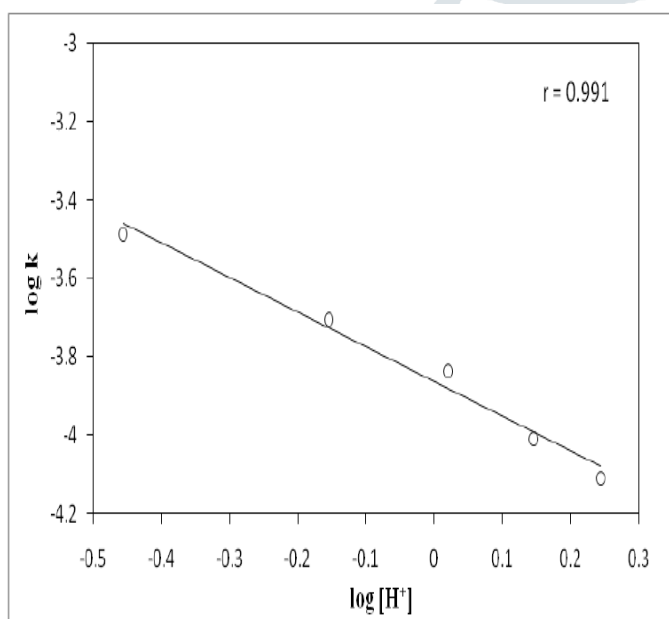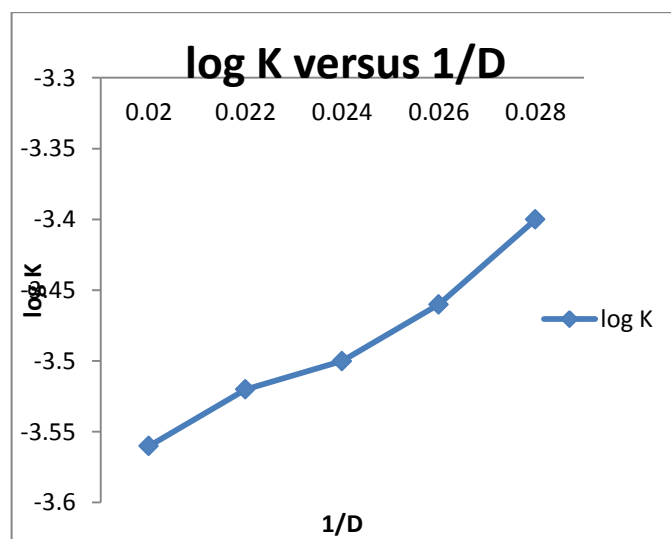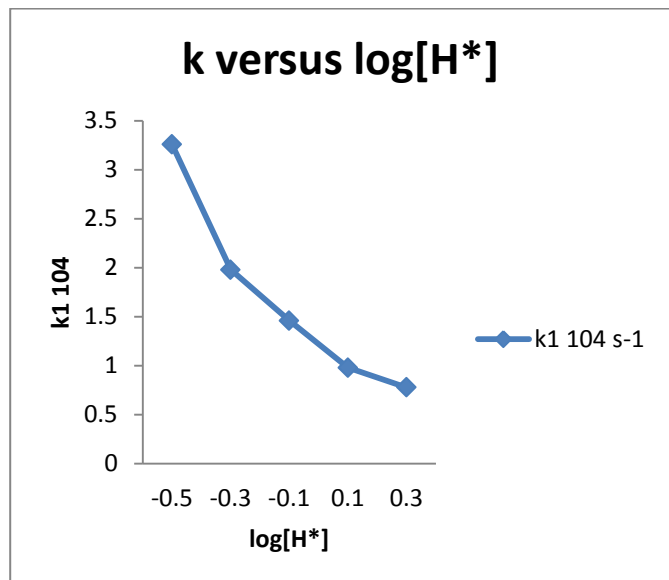## 8.5 Effect of varying the ionic strength

k versus log[H*]

log K versus 1/D

Fig 8.4 Plot of log k versus log [H+]

Fig 8.5 Plot of log k versus 1 / D

8.6 Effect of varying the ionic strength

[NaClO4] 10^2 mol dm^{-3}	k^1 10^4 s^{-1}
0	3.26
0.05	3.24
10.10	3.18
15.15	3.22
20.20	3.16

8.7 Effect of varying solvent composition

AcOH-H2O% (v/v)	D	k_1 10^4 s^{-1}
40-60	49.6	2.87
45-55	45.99	2.99
50-50	42.37	3.26
55-45	38.75	3.48
60-40	35.14	3.88

IX CONCLUSION AND SUMMARY

1. The rate of oxidation of l-alanine (α – amino acid) acid with substituted acetic acid under pseudo-first order conditions has been studied at 313 K. The reaction shows first order dependence with respect to oxidant and substrate.

2. The reaction follows inverse first order kinetics with respect to H+. Increase in ionic strength has no effect on the reaction rate and decrease in the dielectric constant of the medium increases the reaction rate.

3. There is no possibility of free radical mechanism since there is no polymerization of acrylonitrile. Increase in the concentration of chromic acid retards the reaction rate which confirms the two electrons transfer involved in the mechanism.

4. Based on the experimental observations a suitable mechanism has been proposed and rate law has been derived.

5. The products of the oxidation reaction are found to be corresponding sulfoxides.

6. The effect of chromic acid with substituted acetic acid in α – amino acid (l-alanine) on the reaction rate has been studied at four different temperatures viz., 303 K, 313 K, 323 K and 333 K and the thermodynamic parameters are calculated using Eyring‟s equation.

7. The plot of ΔH# versus ΔS# does not vary linearly, no iso kinetic relationship is observed. An excellent correlation is obtained (r = 0.999) when log k(313 K) versus log k(303 K) values are plotted. This indicates that all the substituents follow a common mechanism.

8. 8.The rate increases with decrease in the dielectric constant of the medium and increase in ionic strength has no effect on the reaction rate.

9. There is no appreciable change when acrylonitrile is added to the reaction mixture indicating the absence of free radical mechanism.

10. The rate of the reaction decreases with increase in the concentration of chromic acid suggesting that the two electron transfer involved in the reaction.

11. A suitable mechanism has been proposed on the basis of experimental facts and a suitable rate law is derived.

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