



**Kinetic reactions of amino acids with chromium (III)
complexes-A case study**

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Abstract:

The research work on the kinetics of substitution reactions between amino acids and Chromium (III) complexes are not dynamically studied by researchers. These substitution reactions are feasible to study in aqueous medium under in acid and alkaline conditions. So an opportunity is there in the research for the study of kinetic reactions with different Chromium (III) complexes by using amino acids as ligands, also good prospect is there in the preparation of complexes with Chromium (III) and different amino acids and studies of their kinetics, spectral properties as well as speciation. In this review paper, important points are related to Chromium (III) and amino acids are discussed and relevant research papers are reviewed related to the kinetics of substitution of different Chromium (III) complexes with different ligands (as amino acids) and briefly presented the reaction mechanisms.

INTRODUCTION

1. Introduction about Chromium (III)

At low concentrations chromium is favorable to plant species and higher concentrations of chromium in the same plants being toxic were proven by Ochiai. (1) The biological role and bioinorganic chemistry of Chromium (III) is not studied well due to Chromium (III) complexes are substitution inert and redox in active. In the context of substitution processes that the aqueous chemistry of Chromium (III) assumes considerable importance and +3 states is the most stable

oxidation state of chromium. Chromium (III) ions are not toxic but Chromium (VI) is both toxic and carcinogenic. Chromium forms stable green Chromium (III) ion and a great opportunity is there in the investigations of aqueous solutions of Chromium (III) with ligands to form numerous Chromium (III) complexes and also the central ion like Chromium (III) governing the kinetic stability of the complex. Many octahedral complexes of Chromium (III) are well known exists in both solution and solid-state. Because of kinetic inertness of Chromium (III) complexes, these types of species may continue for extensive time even underneath conditions where they are thermodynamically unsteady. The stability of the complexes varies with the ligand and traditionally sluggish reactions of Chromium (III) are most typical for ligands with oxygen donors or chelated nitrogen. The aqueous chemistry of chromium (III) is not so comprehensively studied, the slow rates of substitution of Chromium (III) is a familiar phenomenon. The substitution reaction of Chromium (III) can be broadly classified as hydrolysis and ligand substitution reactions. Hydrolysis reactions can be performed in both acidic and basic media and most of the reported kinetic investigations of Chromium (III) complexes are acid hydrolysis (aquation) reactions. Aquation studies of Chromium (III) complexes can generally be extended to lower acid concentrations because base hydrolysis is a less significant reaction in acid solution. For Chromium (III) complexes under base hydrolysis, a dissociative mechanism was operative for Chromium (III) amine complexes, Chromium (III) would be less able to accept electrons donated by the amide ligand in the conjugate base intermediate. Ligand substitution reactions are classified as based on the denticity of the participating ligand in the substitution process and prime part of these reactions are known as anation reactions involving an anion as a ligand. Ligand substitution reactions are studied extensively. The study encompasses very fast to slow reaction and involves in both transition and non-transition elements of coordination compounds. The bulk of the effort to date has been devoted to the reaction of non-labile complexes because they slow enough to be accessible to kinetic techniques.

2. Importance of Chromium (III) in kinetics

Different Chromium (III) substrates are easily forms a complex with ligands. The kinetics of substitution reactions with Chromium (III) and different ligands are easily handling without any interference. These kinetic reactions are slow and carried at room temperature, even at high temperatures also favorable without any deviations in the nature of substrate of Chromium (III).

Chromium (III) with ligand complexes gives valuable information through spectral studies in the formation of species. Once the product has developed in these reactions it does not alter under any circumstances, so identification of the product species is accurate. In the kinetic studies the nature of substrate of chromium (III) is not altered under the addition of ligand, varying of pH, ionic strength and temperature and also does not change in ethanol or methanol medium. So much kinetic substitution reactions were done by researchers with different chromium (III) substrates and EDTA, CDTA and different ligands. Based on these favorable conditions of chromium (III) are taken into account by many researchers are studied the kinetic reactions with amino acids.

3. Introduction about amino acids

Amino acids are belongs to organic molecules and these are represents mainly significant component of biological composition and body chemistry. There are about 30 different amino acid building blocks that can be linked together in different lengths (chains) and different combinations. These may be formed either structures of parallel chain or globular ranging from a combination of two amino acids to a large protein molecule like nucleohistone which has a molecular weight of 21, 00,000. Amino acids are easily recognized by the existence of groups of an amino (-NH₂) and an acidic carboxyl (-COOH). The remains of the molecule being changeable, the amino group (-NH₂) is the fundamental segment of the molecule and it is able to react with both inorganic and organic acids to form salts, amides while the acid proton is capable of reacting with bases. These are classified under various heads, based on their functional groups and biosynthesis. During the process of absorption, synthesis or catabolism, increase in concentration of amino acids occur in vivo, called temporary pool and is used for metabolic process. (2)

All naturally occurring amino acids with a few exceptions have a spatial structural arrangement or configuration known as the L-configuration. Almost all amino acids have optically active carbon atoms, except for the simplest amino acid and glycine. Certain bacteria and molds contain amino acids of the D-configuration. If the amino group (-NH₂) and a carboxyl group (-COO-) are attached to the same carbon atom, the amino acid is known as alpha-amino acid. The untiring efforts of biochemists, pharmaceutical scientists and chemists reveal the nature and responsibility of metal ions in the living systems. Nearly 99% of the metal ions are present in trace quantities in

the human body are of alkali and alkaline earth metals and these hydrated cations are take part in an important responsibility in maintaining the necessary osmotic pressure in triggering mechanisms of biological reactions.

Amino acid be present as a neutral species and exist as an ion pair at a pH of 6.05 (iso electric), is also known as zwitter ions and it possesses an extremely high electric moment and is highly soluble in water. Aqueous solutions of amino acids at neutral pH, the carboxylic and amino acid groups are having a property of de-protonated and protonated resultant is an amino acids are exists as zwitter ions. Various metal ions with amino acids are to form stable 5 member chelates through the moieties of chelation of nitrogen and oxygen (carboxylate and amine). In the side chain some amino acids containing extra metal binding site due to this these amino acids are to be form metal complexes.

Walter Mertz reviewed (3) the research work from 1959 to 1980 on Chromium, he found researchers have identified that Chromium (III) is as an important element, as per the in vitro and in vivo studies Chromium (III) was interaction with insulin and action identified as the insulin sensitive cell membrane. (4-8) Mertz (3) has revealed that a low molecular Chromium (III) complex known as Glucose Tolerance Factor (GFT) potentiates insulin activity. He isolated a complex of Chromium (III) containing nicotinic acid, glycine, glutamic acid and cysteine from brewer's yeast. According to him this complex (of unknown structure) illustrates notable in vitro action, potentiating the action of insulin in glucose oxidation by Chromium deficient at a dipose tissue.

In this review paper mainly focused on the kinetics and substitution reactions of different substrates of Chromium (III) with amino acids are only presented here. The reason for chosen the review study is under simple experimental conditions through reactions of aquation and anation, the Chromium (III) forms a beautiful colored complexes with amino acids as ligands. Formations of complexes are easily due to the rupture of chromium water bond and in that place the entry of amino acid as in the form of zwitter ion. Much research work on the kinetics of substitution reactions with amino acids as ligands are not take place, so an opportunity is there in the research

for the study of kinetic reactions with different Chromium (III) substrates by using amino acids as ligands.

4. Review studies on Chromium (III) with amino acids

Many researchers are studied the anation reactions of Hexa aquo Chromium (III) and hydroxo penta aquo Chromium (III) with different ligands. (9-12) Substitution reactions of oxalato complexes of metals, structure, stability and lability of coordination compounds/complexes are reviewed by Krishna Murthy and Haris (23), but partial research work was available (24) in the research region of kinetics of oxalate complexes with mono dentate ligands. (25-29) Kinetic reaction between hexa aqua Chromium (III) and glycine was studied by Banerjea and Dutta chaudhari (13) and they proposed (SN²IP) mechanism. In this reaction the authors are identified that formation of bond by amino acid of glycine take place, at the same time breaking the chromium water bond (Cr-OH₂) and also found ion pair formation constant (K_{IP}), which may be very high due to purely electrostatic considerations and probably hydrogen bonding. For this reaction the authors are proposed the rate determining step (slow, k) equation as $\text{Cr}(\text{H}_2\text{O})_6^{3+} + \text{G}^- \rightarrow \text{Cr}(\text{H}_2\text{O})_5\text{G}^{2+} + \text{H}_2\text{O}$ and this reaction undergoes involve extremely pre equilibrium for formation of an ion pair of the type $[\text{Cr}(\text{H}_2\text{O})_6^{3+} \text{G}^-]$ of the species from the reactants.

Khan and Kabir-ud-Din (30) reinvestigated the anation of hexa aquo Chromium (III) by glycine reaction, suggested that an associative interchange (I_a) mechanism. Based on the observed K_{IP} values, discarded an opportunity of ion-pairing of the zwitter ions with hydroxyl species of Cr (H₂O)₆³⁺. The proposed rate equation for this anation reaction is $k_{\text{obs}} = k_{\text{an}}K_{\text{IP}} [\text{Glycine}]_{\text{T}} / [\text{H}^+] + K_{\text{a}} + K_{\text{IP}}K_{\text{a}}[\text{Glycine}]_{\text{T}}$. Anation of mono (oxalato) tetra aqua Chromium (III) with glycine in the pH range of 3.00 -5.90 at temperatures in between 28 to 40° C was studied by Subrahmanyam and Ananta Ramam. (31) As per experimental results they revealed that anation process proceed two in steps, one is glycine dependent path (I_a mechanism) and the other one is glycine independent path with D mechanism. The breaking of chromium water bond (Cr-OH₂) is a governing factor in this kinetic reaction between Cr (NH₃)₅H₂O³⁺ and glycine and a dissociative mechanism was observed by Ramasami et al. (32) The proposed kinetic reaction for this reaction is: $\text{Cr}(\text{NH}_3)_5 \text{H}_2\text{O}^{3+} + ^+\text{NH}_3\text{CH}_2\text{CO}_2^- \rightarrow \text{Cr}(\text{NH}_3)_5 (\text{O}_2\text{CCH}_2\text{NH}_3)^{3+} + \text{H}_2\text{O}$



Finally the rate law can be proposed as $k_{\text{obsd}} = k_{\text{an}}K_{\text{IP}}K_{\text{a}} [\text{Gly}]_{\text{T}} / [\text{H}^+] K_{\text{a}} + K_{\text{IP}}K_{\text{a}}[\text{Gly}]_{\text{T}}$

Complexes of $[\text{Cr}(\text{gly})_3]$ and $[\text{Cr}(\text{gly})_2(\text{OH})_2]$ (here gly- ligand of glycinato) are prepared and their (33) products are identified through acid-catalyzed equation by Kita et.al. This aquation of $[\text{Cr}(\text{gly})_3]$ and $[\text{Cr}(\text{gly})_2(\text{OH})_2]$ direct to the formation of inert product, $[\text{Cr}(\text{gly})_2(\text{H}_2\text{O})_2]^+$ in a two stages process. Based on experimental results pseudo-first order rate constants, which are dependencies on $[\text{H}^+]$ are obtained. As per the results the rate law of this reaction as $k_{\text{obsH}} = k_0 + k_1k_{\text{p1}}[\text{H}^+]$ (k_0 and k_1 are the rate constants and K_{p1} is the protonated constant. The authors are understood that a mechanism was proposed as the development of reactive intermediate as a result of proton addition to coordinated carboxylate group of the bidentate ligand and also identified as one end bond glycine liberation.

Subbarao et al. studied (34) the kinetics of substitution reaction of [Cis bis oxalato di aquo chromate(III), $\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2^-$] with amino acids (AA) [AA = glycine, DL-alanine, and DL-phenyl alanine] in acid medium follows spectro photometrically and found that formed a complex with maroon-colored containing the wavelength maxima at 406 and 550 nm respectively. Molar extinction coefficients of this complex at these nanometers are well a concurrence with reported (35) work for glycine oxalate complex of Chromium (III) $[\text{Cr}(\text{OX})_2(\text{gly})_2^-]$. It be a sign of that the two water molecules in cis - bis oxalato di aquo chromate (III) are replaced by glycine and the molecules of oxalate are in whole. Hence they do not involve in the substitution reaction representing that under the experimental settings aquation does not take part. In addition to that the authors are identified that this reaction does not precede at pH 3.00 even in the longer period (i.e. even more than week days) which supports the groups of oxalate in the complex are unbroken, so aquation was not carried out or formed the glycinato complex. The same kind of analogous products are seen in the remaining amino acids of DL-alanine and DL-Phenyl alanine. Under the kinetic experimental studies, the rate constants are estimated and the authors are suggested that the substitution reaction proceeded through amino acid dependent and independent paths. It was point out that this substitution reaction takes place through associative (I_{a}) and dissociative mechanism in the amino acid-dependent and independent paths respectively. The following is the rate law of this substitution reaction as:

Rate = $k' [\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2^-] [\text{AA}] + k'' [\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2^-]$, here AA represents glycine / alanine and /phenyl alanine and $k' = Kk_1 / [\text{H}_3\text{O}^+]$ $k'' = k_2$

Subbarao et al. (36) studied substitution reaction of $[\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2^-]$ with amino acids (AA) [AA = glycine, DL-alanine, and DL-phenylalanine] in alkaline medium by spectrophotometrically. The authors are observed that at pH 8.50 substrate and amino acids are [AA] formed identical product complexes with an absorption maximum at 398 and 540 nm. The researchers carried out the kinetic studies for these three amino acids under suitable experimental conditions, the rate constants are estimated at different temperatures (30, 35 and 40 °C) under varying the ligand concentrations, pH and substrate. Based on the experimental results that the authors suggested that this substitution reaction proceeds through two steps, one is amino acid-dependent path (through I_a mechanism) and the further one is the amino acid independent path it indicates dissociative mechanism is leading. The proposed rate law for the reaction as follows: Rate = $Kk_1 [\text{Cr}(\text{OX})_2(\text{H}_2\text{O})(\text{OH})^{2-}] [\text{OH}^-] [\text{AA}^-] + k_2 [\text{Cr}(\text{OX})_2(\text{H}_2\text{O})_2(\text{OH})_2^-]$. Here, AA^- represents glycine / alanine /phenyl alanine.

Mitra and De (37) studied the anation of cis-di aquo-bis oxalato chromium (III) ion by DL-alanine in different ethanol water mixture in between the pH of 3.80 – 7.30. In this anation reaction the rate of the reactions were estimated in three unlike compositions of ethanol – water mixtures that and they observed that rate of anation was higher in each solvent medium when compared to water exchange reaction. Further they noticed that making of bond and breaking of bond are significant in this reaction. Based on the obtained experimental results and activation parameters the associative path is between the substrate ion and –ve end of the zwitter ion. According to reaction mechanism the proposed rate law as $k_{\text{obs}} = k' + k''K_1[\text{H}^+]^{-1}$ [k' and k'' are the represents of rate constants of diaquo and hydroxo complexes. The above mentioned type of results is also observed in the anation reaction between phenyl alanine with cis-di aquo-bis oxalato chromium (III) ion by Mitra and De. (38)

Substitution reaction of cis-bis oxalate di aquo Chromate (III) and L-Dopa is studied (39) in aqueous medium in temperature between 35° C to 50° C at pH range of 3.50 to 6.00 with varying the concentration of amino acid. The substrate and L-Dopa forms 1:1 metal ligand product

complex, it was confirmed through spectral studies (shift takes place from wavelength 472 to 413 nm). This kinetic reaction was followed varying of pH, ligand and temperature. As per the experimental results the reaction proceed through an outer sphere relationship between cis-[Cr(C₂O₄)₂(H₂O)₂] and L-Dopa followed by chelation. A detailed and elaborated mechanism was given by authors and the following is the rate law of this substitution reaction. Rate = k_{obs} [Chromium (III) complex]_T

Here k_{obs} = k_{an} K_{OS} K₁. [H₄ L⁺]_T / {[H⁺] + K₁} + K_{OS}K₁ [H₄ L⁺]_T. Here K_{OS} is outer sphere formation constant.

Subba Rao et al. (40) studied the kinetic reaction of [Cr(mal)₂(H₂O)₂]⁻{cis-bis (malonato) di aquo chromate (III)} with amino acids [AA] {AA = glycine, DL-alanine, and DL-phenylalanine} in an acid medium. This reaction was studied at different concentration of amino acids [AA], temperature, pH and substrate of Cr(mal)₂(H₂O)₂⁻. As per spectral studies the authors are identified that a bathochromic shift was noticed in the peak at longer wavelength (566 nm) with an increase in molar extinction coefficient from 50.75 to 54.0 M⁻¹ cm⁻¹ while the peak at 417 nm that is at shorter wavelength it is not altered but molar extinction coefficient increases from 41.50 to 46.0 M⁻¹ cm⁻¹ with increasing pH. From the spectral studies it clearly indicates that formation of hydroxyl species is slow, but sure the formation of the type of the species is Cr(mal)₂(OH)(H₂O)₂²⁻ under experimental pH range. Based on the results authors are concluded that in this reaction an associative interchange (I_a) and dissociative mechanism proceeds through amino acid-dependent and independent paths respectively under the experimental conditions. As per the results and mechanism the following is the rate law. Rate = k' [Cr(mal)₂(H₂O)₂]⁻ [AA] + k'' [Cr(OX)₂(H₂O)₂]⁻, here AA represents glycine / alanine /phenyl alanine and k' = Kk₁ / [H₃O⁺] and k'' = k₂

Subba Rao et al. Studied (41) the substitution reaction of amino acids [AA] {AA glycine, DL-alanine, and DL-phenyl alanine} with [Cr(mal)₂(H₂O)₂]⁻ {cis-bis (malonato) di aquo chromate (III)} in alkaline medium. This reaction was carried out varying of the concentrations of ligands as amino acids {AA}, pH, temperature and substrate for kinetic studies. Under spectral studies up to pH of 6.00 the substrate solution retains in the purple color and further than this pH the solution is changed to diverse gloominess of color of green was observed. They also identified

that under the pH conditions of 7.55 to 11.80, the spectra of $[\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2]^-$ gives a peak at shorter wavelength (415 nm) show evidence of a small hypsochromic shift and the peak at longer wavelength (566 nm) exhibits a bathochromic shift. Further they noticed that at shorter wavelength the molar extinction coefficient increases with increasing pH up to 10.45 and beyond this pH the extinction coefficient value decreases. In addition to identification was at longer wavelength the molar extinction coefficient decreases with increasing pH. Based on experimental results the authors are proposed that the substitution reaction proceeds through amino acid-dependent (I_a mechanism) and independent path (a dissociative mechanism), showing that the elevated reactivity of single-ended malonate $[\text{Cr}(\text{mal})(-\text{mal})(\text{OH})_2(\text{H}_2\text{O})_3]^-$ complex. The following is the rate law :Rate = $k_1 [\text{Cr}(\text{mal})_2(\text{H}_2\text{O})(\text{OH})_2]^- [\text{OH}^-] [\text{AA}^-] + k_2 [\text{Cr}(\text{mal})_2(\text{H}_2\text{O})_2(\text{OH})_2]^-$, here AA^- represents glycine / alanine /phenyl alanine. By varying conditions of concentration of H^+ , ligand, ionic strength and temperature an anation reaction between aqua penta amine chromium (III) with DL-alanine was studied by Khan and Kabir-ud-Din. (42) Before the anation reaction an ion pair formation was observed between the zwitter ion form of alanine and $[\text{Cr}(\text{NH}_3)_5 \text{H}_2\text{O}]^{3+}$.As per the data, suggested that a mechanism intermediate between the types of associative and dissociative interchange. Proposed rate law of this reaction as $k_{\text{obs}} = k_{\text{an}} K_{\text{IP}} K_{\text{a}} [\text{alanine}]_{\text{T}} / [\text{H}^+] + K_{\text{IP}} K_{\text{a}}[\text{alanine}]_{\text{T}}$

Hydroxypentaaquochromium (III) and DL-alanine substitution reaction was followed through kinetic studies in the pH range of 4.50 to 5.40 by Niogy and De. (43) In this reaction ion pair formation was recognized in between the pH range of 4.50 to 5.40.As per the results obtained from kinetic studies they proposed an outer sphere association mechanism between the reacting species followed by both bond breaking and building are equally significant. They also noticed that under aquo ligand in hydroxo penta aquo chromim (III) by alanine is to a great extent faster due to the hydroxyl ion the complex leads to an easy way in the rupture of Chromium (III) – OH_2 bond. Based on the results Niogy and De (43) proposed rate law as $k_{\text{obs}} = k_{\text{KE}}[\text{alanine}] / 1 + K_{\text{E}}[\text{alanine}]$.

Niogy and De (44) studied the anation reaction of hydroxo penta aquo chromium (III) ion $\{[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}\}$ by DL phenylalanine was studied through spectro photometrically. Ion pair formation was observed in between the pH range of 3.50 to 4.50. This reaction was studied by

varying the concentrations of substrate, pH, ligand, ionic strength and temperature under suitable experimental conditions. Based on the results an outer sphere association involved in between the hydroxo penta aquo chromium (III) and zwitter ionic form of phenylalanine followed by associative interchange process. The following is the rate law proposed Niogy and De [35] as:

$$\text{Rate} = k K_E [\text{Cr}(\text{H}_2\text{O})_5 \text{OH}]^{2+}_{\text{Total}} [\text{PheH}] / 1 + K_E [\text{PheH}]$$

Khan et al. studied (45) the kinetic investigation between hexa aquo chromium (III) $[\text{Cr}(\text{H}_2\text{O})_6^{3+}]$ and Serine in aqueous acidic media and the composition of the metal-ligand complex was found to be 1:3 under the pH conditions of 2.90 to 3.85 and the reacting species are type cation H_2L^+ and zwitter ion HL. The rates of the reaction was studied with varying of the ionic strength 0.2 to 1.0 mol dm^{-3} , observed that in this reaction the rate is not dependent on ionic strength. It clearly indicates that no involvement of either L^- or H_2L^+ as in the form of reactive species in this anation reaction. According to experimental results involvement of zwitter ion with ion pair equilibrium and slowly entering the ligand in place of water and it leads to an interchange (I_a) mechanism in this anation reaction. Based on the mechanism the rate law was proposed by authors for this reaction as: $k_{\text{obs}} = k_{\text{an}} K_a K_{\text{IP}} [\text{Serine}]_{\text{T}} / [\text{H}^+] + K_a + K_a K_{\text{IP}} [\text{Serine}]_{\text{T}}$.

Khan and Kabir-ud-din (46) was studied the kinetic reaction between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with valine under maintaining ionic strength and observed a 1:2 composition of Cr (III)-valine complex. Also observed when the concentration of ligand increases, then the rate constants increases but not nearly indirect proportions. In addition to they found at lower $[\text{H}^+]$ deviations are more pronounced, so it indicates between the reactants an ion pair equilibrium was established. Based on the obtained results they proposed an associative interchange mechanism and which is further evidenced by the low enthalpy of activation and by the iso kinetic relationship for the contact of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ through a variety of mono amino carboxylic acid ligands. Based on the mechanism in this reaction the proposed rate law as $k_{\text{obs}} = K_1 k_{\text{an}} K_{\text{IP}} [\text{Valine}]_{\text{T}} / [\text{H}^+] + K_1 K_{\text{IP}} [\text{Valine}]_{\text{T}}$. Kabir-ud-din et.al examined (47) kinetic reaction involving hexa aquo chromium(III) and amino acid of L-leucine in ethanol-water mixture medium under selective experimental conditions. In this reaction they observed as per the experimental results $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ follows an associative interchange mechanism and whereas $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ a dissociative path.

Kabir-ud-din et.al studied (48) the kinetic reaction between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and asparagine as a function of pH in ethanol-water mixtures (0-30%). As per the results anation of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ has an associative mechanism whereas $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ has an dissociative mechanism was observed (43) and based on the reaction mechanism following rate law has proposed. $k_{\text{obs}} = (k_{\text{an}} k_{\text{a}} K_{\text{IP}} [\text{H}^+] + k'_{\text{an}} k_{\text{a}} k'_{\text{a}} K'_{\text{IP}}) [\text{Asparagine}]_{\text{total}} / ([\text{H}^+]^2 + [\text{H}^+]k_{\text{a}} + [\text{H}^+]k'_{\text{a}} + k_{\text{a}} k'_{\text{a}}) + (k_{\text{a}} K_{\text{IP}} [\text{H}^+] + k_{\text{a}} k'_{\text{a}} K'_{\text{IP}}) [\text{Asparagine total}]$. Here the anation rate constants k_{an} and k'_{an} are respectively for hexa aquo chromium (III) [$\text{Cr}(\text{H}_2\text{O})_6^{3+}$] and hydroxo penta aquo chromium (III) [$\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$]. K_{IP} and K'_{IP} are respective ion pair formation constants; k_{a} and k'_{a} are the acid concentration constant of protonated asparagine and acid dissociation constant of hexa aquo chromium (III) respectively.

De and De (49) are investigated a kinetic reaction between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and glutamic acid, a 1:2 metal-ligand complex formation was observed. They observed that the rate of reaction increased with the increase of pH(2.00 - 4.50) and the effect is considerable at a higher range of pH. At pH of nearly 4.50, $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ presents mainly as $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ and ligand as an anion only, therefore the rate levels off above pH of 4.50. In this reaction by increasing the ligand of glutamic acid concentration simultaneously the rate of the reaction increases but rate of this reaction reaches to restrictive value at an elevated concentration of glutamic acid.

Kabir-ud-din et al. (50) Studied the substitution reaction of $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with glutamine in presence of changing the concentrations of substrate, ligand, ionic strength, % of ethyl alcohol and temperature. A 1:2 Chromium (III) and glutamine complex was observed and an absorption maximum was noticed at 560 nm for this complex. For this reaction the authors have proposed an associative interchange path for hexa aquo chromium (III) and whereas that of $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ follows a dissociative interchange path. According to mechanism the following rate law has proposed by authors. $k_{\text{obs}} = (k_1 K_{\text{A}} K_{\text{OS1}} [\text{H}^+] + k_2 K_{\text{a}} K_{\text{h}} K_{\text{OS2}}) [\text{glutamine}]_{\text{T}} / \{[\text{H}^+]^2 + [\text{H}^+] K_{\text{a}} + [\text{H}^+] K_{\text{h}} + K_{\text{a}} K_{\text{h}} + (K_{\text{a}} K_{\text{OS1}} [\text{H}^+] + K_{\text{a}} K_{\text{h}} K_{\text{OS2}}) [\text{glutamine}]_{\text{T}}\}$

Kabir – ud-din and Jilani Khan investigated (51) the kinetic reaction with $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ with an amino acid of L-arginine at 550 nm, pseudo first order rate constants were obtained under the varying the concentrations of ligand, H^+ , percentage of ethyl alcohol and temperature. Based on the experimental results the authors are proposed an I_{a} mechanism for the anation of hexa aquo

chromium (III) and dissociative mechanism (I_d) for $\text{Cr}(\text{H}_2\text{O})_5\text{OH}^{2+}$ by ligand L-arginine. According to experimental results the following rate law has assumed.

$$k_{\text{obs}} = \{k_1 K_a K_{\text{OS}1} [\text{H}^+] + k_2 K_a K_h + K_{\text{OS}2}\} [\text{Arginine}]_{\text{T}} / \{ [\text{H}^+]^2 + [\text{H}^+] K_a + [\text{H}^+] K_h + K_a K_h + (K_a K_{\text{OS}1} [\text{H}^+] + K_a K_h K_{\text{OS}2}) [\text{Arginine}]_{\text{T}} \}$$

A kinetic reaction (52) between Hexa aquo chromium (III) $[\text{Cr}(\text{H}_2\text{O})_6^{3+}]$ and L-lysine was studied in the acid medium and found 1:2 stoichiometry complex by Job's method. The pseudo-first-order rate constants are obtained with increasing the concentration of lysine, acidity, temperature (35 to 50° C), and percentage of ethyl alcohol. They proposed that I_a path was followed in reaction of hexa aquo chromium(III) whereas that of $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ follows an I_d path mechanism. Based on the experimental results and proposed mechanism the authors are recommended the following rate law for this reaction.

$$k_{\text{obs}} = \{(k_1 K_a K_{\text{OS}1} [\text{H}^+] + k_2 K_a K_h + K_{\text{OS}2}) [\text{Lysine}]_{\text{T}}\} / \{ [\text{H}^+]^2 + [\text{H}^+] K_a + [\text{H}^+] K_h + K_a K_h + (K_a K_{\text{OS}1} [\text{H}^+] + K_a K_h K_{\text{OS}2}) [\text{Lysine}]_{\text{T}} \}$$

Kabir-ud-din et al studied (53) the substitution reaction between $\text{Cr}(\text{H}_2\text{O})_6^{3+}$ and L-cysteine. L-cysteine has three coordinating centers (N, O, and S). As the concentration of cysteine increases, the observed rate constant increases but not nearly in direct proportions and appears to reach a limiting value at a higher concentration of ligand indicating the existence of an ion pair equilibrium between the reactants. For this reaction, an ion pair interchange mechanism is observed. Further, a slight increase in the observed rate constant with raise in ionic concentration indicates a simple elimination of a coordinated water molecule from the ion pair.

Kabir-ud-din and Jilanikhan studied [54] a kinetic reaction between $\text{Cr}(\text{H}_2\text{O})_6$ and L-Proline in acidic medium and form a purple complex 1:1 shows absorption maxima at 420 nm and 570 nm. The rate of the reaction increases with an increase in the concentration of Chromium (III), proline, percentage of ethyl alcohol, ionic strength, and temperature but decreases with an increase in $[\text{H}^+]$. At higher concentration of ligand at different temperatures the rate appears to reach a limiting value and it shows the formation of an outer sphere association complex between the reactive species.

Shahid et al. studied (55) the kinetic reaction of hexa aquo chromium (III) with DL-Tryptophan, they found that formation of 1:3 complex and this reaction study was followed in between the pH of 2.75 to 3.75. Chelation is not favored in this reaction, but the ligand tryptophan combine with chromium(III) only during carboxylate oxygen. As per the proposed mechanism in inner coordination sphere by entry of one molecule of tryptophan zwitter ions takes place and the corresponding type of complexes $[\text{Cr}(\text{H}_2\text{O})_5(\text{HA})]^{3+} / [\text{Cr}(\text{H}_2\text{O})_4(\text{OH})(\text{HA})^{2+}]$ are formed. The authors are suggested that associative (I_a) and dissociative (I_d) interchange mechanisms for the anation of hexa aquo chromium (III) and penta aquo chromium (III). Based on the proposed mechanism the following is the rate law for this anation reaction as $k_{\text{obs}} = (k_1 K_a K_{\text{OS1}} [\text{H}^+] + k_2 K_a K_h K_{\text{OS2}}) [\text{trp}]_{\text{T}} / \{ [\text{H}^+]^2 + [\text{H}^+] K_a + [\text{H}^+] K_h + K_a K_h + (K_a K_{\text{OS1}} [\text{H}^+] + K_a K_h K_{\text{OS2}}) [\text{tpt}]_{\text{T}} \}$. Substitution of aqua ligands of $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ ion by DI-methionine was studied in a water-ethanol medium by Mitra Mustofy et.al. (56) As per the experimental results the 1:2 and 1:3 of metal and ligand product complexes showed the same spectra with an absorption maximum at 400 and 540 nm. This reaction rate was studied under varying the concentrations of metal, ligand, pH, ionic strength and temperature. The important observation was made by authors according to elemental analyses they identified that soluble maroon-colored crystalline product having the composition of $[\text{Cr}(\text{Methio})_2(\text{H}_2\text{O})(\text{OH})]$. The IR spectra of the this product indicated that simple OH stretching vibration or OH in water or both are involved and also identified during complexation the carboxyl group undertake participation. They also identified that according to IR spectra absence of O-H and presence of M-O bending bands respectively at 1280cm^{-1} and at 950cm^{-1} . Further observation was made by authors, the presence of C-S bending in ligand and substrate complex at 1150cm^{-1} indicating that sulfur atom not functioning as a donor center. The experimental results revealed that associative interchange mechanism was leading and the following rate law was proposed by authors as $k_{\text{obs}} = k_a K_E [\text{Methio.H}] / 1 + K_E [\text{Methio.H}]$.

Anation of aquo chromium (III) studied by Khan et al (57) with Methionine by varying the concentration of methionine, pH, ionic strength and temperature through spectrophotometry. The outcomes are in good agreement with the species formation of substrate and ligand in accordance with mechanism. The authors are proposed an I_a and I_d mechanism paths k_1 (metal ion) and k_2 hydroxo penta aquo chromium (III) routes respectively. According to mechanism the following

is the rate law: $k_{\text{obs}} = (k_1 K_a K_{\text{OS1}} [\text{H}^+] + k_2 K_a K_h K_{\text{OS2}}) [\text{Methionine}]_{\text{T}} / \{ [\text{H}^+]^2 + [\text{H}^+] K_a + [\text{H}^+] K_h + K_a K_h + (K_a K_{\text{OS1}} [\text{H}^+] + K_a K_h K_{\text{OS2}}) [\text{Methionine}]_{\text{T}} \}$

A kinetic reaction with $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ and amino acid of L-aspartic acid was done by Niogy and De (58), they observed that a purple colored product of metal complex was developed and maximum absorption was noticed at 390 nm and 520 nm. They noticed that this reaction was extremely slow at lower pH values (less than 3.30) and found that this reaction was feasible in a good manner in between the pH of 3.30 to 5.40. Increasing the aspartic acid concentration the rate is increased, but at a high concentration of ligand in this reaction limiting rate is reached, it indicated that ion-pair formation was completed through the negative end of ligand anion. Under experimental conditions, they concluded that associative interchange mechanism for this reaction. Based on the scheme of mechanism for this reaction, the suggested rate law as: $k_{\text{obs}} = k K_E [\text{AsPH}^{1-}] / 1 + K_E [\text{AsPH}^{1-}]$ [k and K_E are rate constant and ion pair equilibrium constant respectively].

Chatterjee and De studied (59) the kinetic reaction between $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ and DL-valine in pH range of 4.50 to 5.20 under at temperatures between 40 - 50° C. Through Job's method a maroon-colored 1: 2 metal - ligand composition of the product was confirmed and also it was identified by the ion exchange process. They noticed that by enhancing the electron density on the metal ion then the entry of ligand (valine) molecule in the inner coordination sphere labializes the water molecule. In this reaction run the formation of ion-pair through outer sphere association leads through an associative interchange path.

Mitra Mustofy and De (60) studied the substitution reaction of $\text{Cr}(\text{H}_2\text{O})_5(\text{OH})^{2+}$ with the amino acid of histidine in the water-ethanol medium under varying experimental conditions. The reaction engage an outer sphere association between the hydroxo penta aquo chromium(III) and histidine species followed by the process of an associative interchange where both bond breaking and making are uniformly significant. The rate of law involving the ion-pair formation has been established. In this reaction for conclusion of mechanism the authors are followed variation of the dielectric constant of the medium used as a tool. The proposed rate law as $k_{\text{obs}} = k_a K_E [\text{Hist.H}] / 1 + K_E [\text{Hist.H}]$.

Kabir-ud-din et al. Investigated (61) the kinetic reaction between hexa aquo chromium (III) and L-Histidine, the reaction followed the first order concerning chromium (III). The Job's dependence on the concentration of ligand at temperature was non-linear and reached a limiting value at a higher concentration of histidine ligand. Therefore it indicates an outer sphere association between the reactant species of hexa aquo chromium (III) and L-Histidine.

Guindy et al. (62) studied the kinetic reactions of Chromium (III) with amino acids such as L-glutamic acid and DL-Lysine by spectro photometrically at wavelength maxima of 550 nm. They observed that these amino acids formed 1:3 complex [chromium with L-glutamic acid / DL-Lysine] and found to be followed first order rate reaction with substrate and ligands of glutamic and lysine. They also observed that increasing H^+ concentration in these kinetic studies retarded the reaction rate. Complete experimental conditions along with suitable mechanisms were given in their research paper. According to the experimental results due to entering of one molecule of amino acid (AA) in to the Chromium (III) substrate in inner coordinate sphere to form $[Cr(H_2O)_5HA]^{+3}$ and $[Cr(H_2O)_4(OH)(HA)]^{+2}$ and due to increase of electron density on chromium (III) the remaining water ligands are in a position of labilizing in easy way. The rate constants and activation parameters of different amino acids with $Cr(H_2O)_6^{3+}$ complexes are given and compared their study with available literature to support their proposed mechanism. Based on the recommended mechanism the following is the rate law: $k_{obs} = (k_1.K_1 + k_2 .K_2.K_h. [H^+]^{-1}).[HA] / (1 + K_h. [H^+]^{-1}) + (k_1 .K_2.K_h. [H^+]^{-1}).[HA]$

Kinetic studies of chromium (III) with DL-leucine in aqueous acidic medium was studied by Guindy et al (63) and they observed that 1:2 complex was formed between Chromium (III) and DL-leucine under experimental conditions through spectro photometric studies at the maximum wavelength at 540 nm. This reaction was followed by first-order kinetics and also observed that increasing hydrogen ion concentration; they noticed that decreasing the reaction rate under experimental conditions. The following is the rate law for suggested mechanism of this reaction as : $k_{obs} = (k_1 K_{OS1} + k_2 K_{OS2} K_h [H^+]^{-1}) [HA] / (1+ K_h [H^+]^{-1}) + (K_{OS1} + K_{OS2} K_h [H^+]^{-1}) [HA]$
An amino acid of alanine with chromium (III) forms a complex in aqueous medium and this kinetic reaction was investigated by Khan and Kabir-Ud-Din (64). This reaction was studied by spectro phtometrically at 540 nm and followed at 45, 50, and 55° C in between the pH of 3.30 -

4.40 with potassium nitrate to maintain the ionic strength of the reaction. A 1:3 metal complex with alanine was established and it was authenticated by Job's method. Under experimental conditions, they observed that pseudo-first-order rate constant with suitable mechanism was proposed for this substitution reaction. Based on the well established mechanism for this reaction by the researchers and finally a rate law was suggested as follows. $k_{obs} = (k_{an} K_{IP} K_a [H^+] + k'_{an} K'_{IP} K'_a K_a [Alanine]_T) / [H^+]^2 + [H^+] K_a + [H^+] K'_a + K_a K'_a + (K_{IP} K_a [H^+] K'_{IP} K'_a K_a [Alanine]_T$

Aqueous Chromium (III) with either L-glutamic acid or sodium hydrogen glutamate follows kinetic reaction at pH 2.46 -5.87 and due to accumulation and posterior decay of an intermediate in non-negligible concentration the products of reaction showed acceleration-declaration periods are identified by Benito. (65) As per the results, the reaction showed two rate constants, one is associated with the appearance and the other one is the decay of long-lived intermediate. They also observed increased hydrogen l-glutamate(k_1) or hydroxide ions(k_2) concentration consequence both the rate constants are increased but when the addition potassium nitrate resulted in opposite effects on first-rate constants which is decrease and the second rate constant(k_2) increase. Based on the experimental results showed that breaking of bond of chromium(III) and water bond, which is the rate determining step for the reaction.

Benito and Millan (66) are studied the reaction between amino acid of L- Histidine and Chromium (III) substitution reaction in an aqueous medium in presence of acid conditions(pH of 3.60 – 5.79) by spectrophotometer at 530 nm. In this reaction the mechanism is divided into three parts, two parts divided for long lived intermediates. These are concerned in series of elementary reactions and are accountable to their rate determining steps. The authors are observed that in spectral studies, the spectrum of the first intermediate rather close to the inorganic reactant, while the spectrum of the second long-lived intermediate was in between the reactant and product, in the final reactant revealed the co-existence of at least two complexes. The proposed mechanism with three rate-determining steps (slow) is in which the breakage of a Chromium (III) water bond and ligand histidine can coordinate in that place. Based on the experimental results and sequential reaction mechanism of this reaction, the following are the three observed rate constants are obtained.

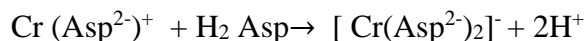
$$k_1 = K_I k_{II} k_{IV} [YH^+] / (k_{III} + k_{IV} [YH^+] [H^+])$$

$$k_2 = K_V k_{VI} k_{VIII} [YH^+] / (k_{VII} + k_{VIII} [YH^+] [H^+])$$

$$k_3 = K_{IX} k_X k_{XII} [YH^+] / (k_{XI} + k_{XII} [YH^+] [H^+])$$

Chromium (III) aqua complexes with L-Alanine kinetic reaction was studied by Beneto and cereza (67) in the pH range of 3.55 – 5.61 by pursue through spectrophotometer. In this reaction the orders of the l-alanine are found to be fractional and also observed that increases the rate with rising pH was due to development of the Chromium (III) aqua bonds encouraged by hydroxo ligands. According to experimental data formation of Chromium (III) complex by amino acid of L alanine proceeds through two elementary sequence reactions for explanation about mechanism of this. In the first step long lived intermediate has formed from the reactants and in the second step direct to formation of products from intermediate. A detailed elaborative mechanism was given by authors and also found breakage of Chromium (III) - water bond in this reaction, just similar to other many complex reactions with Chromium (III) and amino acids.

Dei et al (68) studied the kinetic reaction between L-ascorbic acid and aquo chromium (III) in between the pH range and temperatures of 3.50 to 6.00 and 25 to 50° C with varying the concentrations of ligand, ionic strength and percentage of methyl alcohol. A 1:2 metal ligand complex was established and found that the ligand binding takes place through phenolic oxygen with chromium (III). A detailed mechanism was given and the following is the rate law for this reaction. $k_{obs} = (k_1 K_{a1} K_{OS1} [H^+] + k_2 K_{a1} K_h K_{OS2} [H_2A]_T) / [H^+]^2 + [H^+] K_{a1} + [H^+] K_h + K_{a1} K_h + (K_{a1} K_{OS1} [H^+] + K_{a1} K_h K_{OS2}) [H_2A]_T$. A list of Chromium (III) complexes (69) with amino acids are reported and analytical results data are related to percentages of carbon, hydrogen, and nitrogen of these complexes and also absorption maxima of cis and tris of these complexes are given in detail, which is helpful to researchers in their studies for checking and confirmation for their study results. Chromium (III) and Aspartic acid in solution to form a complex and this reaction was studied (70) potentiometrically by Hamada et.al. Within a wide pH range of 3.50 to 10.50 at 25° C with 0.1M sodium nitrate as ionic strength was maintained in the experimental studies. As per the spectral studies a good binding was observed between Cr³⁺ and Aspartic acid. The formed species in this reaction are identified as one to one complex [Cr – ASP], bis complex [Cr(ASP)₂] and bis - mono- protonated complex [Cr(ASP)₂H]. The following equation represents the product species present in the solution in this research work.



Anation reaction of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ by L-Phenylalanine studied (71) spectrophotometrically with varying the concentrations of substrate, L-phenylalanine, pH, ionic strength, percentage of ethanol at different temperatures. A 1:2 metal and ligand complex was established. Kinetic studies are performed with varying concentration and found first order rate constants. In addition to very important information was given as comparison of anation rate constants at 35° C of hexa aquo chromium (III) and hydroxo penta aquo chromium (III) with different amino acids in this research paper. Based on the kinetics results they proposed that I_a path for $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ and I_d path for $[\text{Cr}(\text{H}_2\text{O})_5\text{OH}]^{2+}$ respectively with detailed mechanism along with rate law equation.

5. Complexes of chromium with amino acids and it kinetic studies

Hexa aquo chromium (III), hydroxo penta aquo chromium (III), cis-bis (oxalato) di aquo chromate (III), cis-bis (malonato) di aquo chromate (III), Mono (oxalato) tetra aquo chromium (III), aqua penta amine chromium (III), tris (oxalato) chromate (III), tris (malonato) chromate (III) and Mono (malonato) tetra aqua chromium (III) etc. complexes are available. Only a lot of research work was done on kinetics of substitutions reactions of Hexa aquo chromium(III) with glycine, alanine, serine, valine, L-leucine, L-aspartic acid, asparagine, glutamic acid, glutamine, L-arginine, L-lysine, L-cysteine, L-proline, DL-tryptophan and L-histidine etc. and a few papers are published with hydroxo penta aquochromium (III). Hence a lot of possibility is there for studying of kinetic reactions with different chromium (III) complexes and amino acids to researchers.

6. Applications

It is a well known to all; the study of the reaction rates constitutes the discipline of kinetics and kinetic investigations are leading to establish the mechanism of reaction under favorable experimental conditions. Kinetics finds application in the most effective use of procedure for development of situation in organic synthesis, in analytical reactions and in manufacturing of chemical industry. An additional practical use is for the estimation and control of the stability of

the products such as pharmaceutical dosage forms, food, paint and metals. Apart from the following may be applicable to amino acid studies.

7. Conclusions

Limited research work was reported on that the kinetics of substitution reactions with different chromium (III) complexes and amino acids. So a remarkable possibility is there to the researchers who wish to want to do their research in the kinetic studies with amino acids as ligands with different chromium (III) complexes.

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