

Equilibrium, Kinetic and Mechanistic Studies of Formation of Cis- mono (AA)bis (oxalato) Chromate (III) Complex (where AA is glycine, alanine and histidine)In Monderately Aqueous Acidic Solution.

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Abstract

Equilibrium, kinetic and mechanistic studies for the coordination of some amino acids "AA"; glycine, alanine, and histidine, to Cr (III) center of trans $[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$ {Ti} complex in monderately acidic range of pH=4.8-6.7 ($\mu =0.4\text{M NaNO}_3$) are reported. The equilibrium constants at 25⁰C were found, logKequ.=4.951,5.206and5.128for glycine, alanine, and histidine, ligation reactions respectively. The substitution reaction is kinetically involve two parallel complex reactions, each includes theree different consecutive steps of different species of Cr(III). The reactant, Ti, branches through hyrolysis into, doubly charged anion, conjugated base of trans $[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})\text{OH}]^{2-}$ which interacts with (AAH) to from outer-sphere complex, that is followed by interchange reaction of one molecule H₂O with one end of AA⁻ ion from an active intermediate species of trans- $[\text{Cr}(\text{ox})_2(\text{AA})\text{OH}]^{3-}$ which changes to final product ; cis- $[\text{Cr}(\text{ox})_2(\text{AA})]^{2-}$. While the remaining part of reactant interacts also with zwitter ion (AAH) on other side to form another outer-sphere complex which also undergoes interchange reaction of one molecule H₂O with AA⁻ ion to give two active intermediates species, trans and cis- $[\text{Cr}(\text{ox})_2(\text{AA})\text{H}_2\text{O}]^{2-}$, which later convert to the same product ; cis- $[\text{Cr}(\text{ox})_2(\text{AA})]^{2-}$. The interchange rate constant of trans- $[\text{Cr}(\text{ox})_2(\text{AA})\text{OH}]^{3-}$ formation relatively appears much larger than ($\Delta H^*=8.8\text{kcal/mol}$) that of cis $[\text{Cr}(\text{ox})_2(\text{AA})\text{H}_2\text{O}]^{2-}$ formation ($\Delta H^*=14.0\text{Kcal/mol}$), while the latter rate constant is nearly (5-10) time larger than that of trans- $[\text{Cr}(\text{ox})_2(\text{AA})\text{H}_2\text{O}]^{2-}$ formation

($\Delta H^*18.4\text{Kcal/mole}$). In these complex formation reactions, all species are kinetically substituted at Cr(III) center via interchange associative(I_a) mechanism.

Introduction

Chromium (III) (d³) center is experimentally and theoretically well known to be inert in ligand substitution reactions. This is the reason why substitution at Cr (III) complexes has received great attention, with its analogous to Co (III) complexes. Most of the studies reveal the possibility of an associative A (I_a) mechanism for this d³ – electronic configuration. The majority of these substitution reactions (1,2,3) are following the rate law:

$$k_{obs} = \frac{kK_{os}[L]}{1 + K_{os}[L]} \dots\dots\dots [1]$$

(Where k is an interchange rate constant of ligation reaction, K_{os} is an inner sphere equilibrium constant and L is the substituted ligand at chromium (III) center). However, Basolo and Pearson (4) have suggested a saturated ion-pair (outer-sphere complex) mechanism (for which in eq.1 $k_{obs}=k$) for reasonable explanation of some anomalies of zero order ligand dependent studies (5). We have studied ligation reaction of some amino acids (6,7,8)with $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$ in moderately acid solution in which the Cr(III) conjugated base species is obtained from hydrolysis process was that not ignored under conditions of pH 3.0-3.8 ($\mu=0.4\text{MNaNO}_3$) and excess of amino acid concentration, so we have found that the substitution reactions obey the rate law:

$$K_{obs} = k+k [\text{H}^+]^{-1} \dots\dots\dots [2]$$

In this case the ligation reaction involves two processes one is an associative interchange outer-sphere complex between hexaaquo Cr(III) complex and the amino acid ligand the other is more loosely bond outer-sphere complex of mono hydroxy species with amino acid ligands. So in this pH range and higher, near physiological pH, the active species was assumed to be the mono hydroxy (or dihydroxy) species that cannot be kinetically ignored. Also it was realized that when OH⁻ ion. Also it was realized that when OH⁻ ion is a ligand on Cr(III) center, the ligation reaction was found to be substantially faster than that when a ligand is H₂O (9,10). However labilization of trans

OH⁻ was also observed of imidazole and pyridine at Cr(III) center (10,11). Therefore to understand the lability trans effect of OH⁻ on substitution reaction at Cr(III) center, we selected trans diaquo bis (oxalato) chromate (III) anion to react with some amino acids in moderately aqueous acidic solution (pH 4.8-6.7) and at different temperatures.

Experiment

The chemicals used in this study were all reagent analytical grades, oxalic acid, potassium hydrogen carbonate and potassium dichromate were obtained from Riedel De Haen, Hanover, sodium nitrate, and amino acids; glycine, alanine and histidine were bought from BDH. All are used without further purification. Jenway 66405 UV-Visible spectrophotometer with modified locally thermostat cell holder was used for measuring absorbance and recording absorption electronic spectra. A Buchi chromatographic pump is used to circulate the sample solution from thermostatted reaction vessel to the flow cell. A Philips pH/mv meter (PW9414 type) was used for pH measurements. A circulating thermostatted bath (LKB Bromma 2209 multitemp.) was used to control temperature to ± 0.1 °C. Trans-K₂[Cr(C₂O₄)₂(H₂O)₂]. 3H₂O {Ti} has been prepared by the following Dawson procedure (12). Kinetic and thermodynamic studies were performed by mixing thermostatted solutions of amino acids and Cr(III), and adjusting the pH to the required values of pHs with NaOH (or HNO₃). The thermostatted mixture was circulated through the flow cell in the thermostatted block of spectrophotometer at the same temperature, than the absorbance change (A_{obs}) was recorded with time.

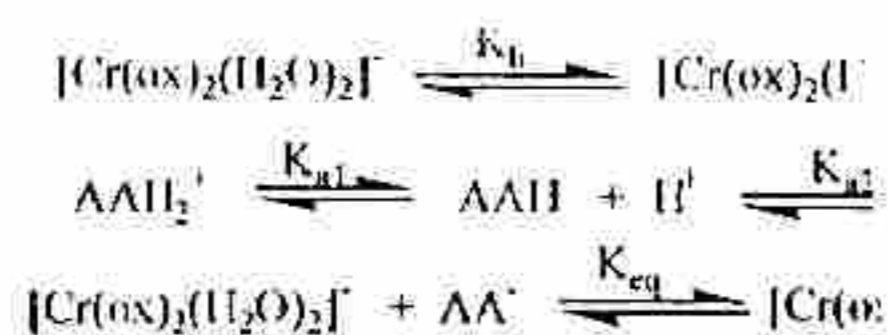
Results and Discussion

Under our experimental conditions, with respect to pH range 4.8-6.7 ($\mu = 0.4$ M NaNO₃), and in the presence of large excess of amino acid (AA), the Ti complex undergoes a series of reactions, in which the net result is the replacement of both axial (H₂O) molecules with a bidentate amino acid AA(N,O), and conversion of original geometry to cis-form. This product, cis-mono (AA) bis (oxalato) chromate (III) complex, is in equilibrium with its reactants. The overall reaction is accompanied by visible electronic absorbance change and this change

allows equilibrium and kinetic substitution studies to be performed at different temperatures and pHs.

(1) Equilibrium studies

The values of acid – hydrolysis constants of $[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$ are, $\text{pK}_{\text{h1}} = 7.2$ and $\text{pK}_{\text{h2}} = 10.5$ (13), which indicate that reactants are expected to be essentially present in diaquo and its conjugated base, monoquo monohydroxy Cr(III), species under experimental conditions of moderately acidic solution. These values were used to calculate the [diaquo] and [monoquo monohydroxy] present in solution at various temperatures and pHs. Also the concentrations of mainly existence species of the incoming ligand in solution as zwitter ion (AAH) and anion AA^- are obtained from acid hydrolysis constants of amino acids (for glycine $\text{pK}_{\text{a1}} = 2.35$, $\text{pK}_{\text{a2}} = 9.6$) for alanine $\text{pK}_{\text{a2}} = 9.69$, for histidine $\text{pK}_{\text{a2}} = 9.2$ (14). These species all are shown in the following equilibrium reactions:



Solutions of Cr(III) complex with amino acids AA were equilibrated $[\text{Cr}(\text{III})] = 0.004 \text{ mol.dm}^{-3}$ and $[\text{AA}]_{\text{T}} \leq 0.35 \text{ mol.dm}^{-3}$. The final electronic spectra was characterized by two peaks $\lambda_{\text{max}} = 550 \text{ nm}$ ($\epsilon_{\text{max}} = 112$) and for 405 nm ($\epsilon_{\text{max}} = 120$) and the red pink reactant $\text{trans-}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$, {TII}, shows also two peaks at $\lambda_{\text{max}} = 565 \text{ nm}$ ($\epsilon_{\text{max}} = 32$) and $\lambda_{\text{max}} = 416 \text{ nm}$ ($\epsilon_{\text{max}} = 34.4$) respectively (13). This increasing in absorbance with slight change in positions of the bands are correspond to NO_2 chromophore formation (15). Kallen and Hamm (16) have previously reported the inverse absorption change for aquation reaction of $[\text{Cr}(\text{ox})_2(\text{glyO})]^{2-}$ ion to $\text{cis-}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$. So depending on the changing of electronic absorbance (A_{obs}), using Beer's law, the mass balance, $[\text{Cr}_{\text{T}} - \text{product}] = [\text{diaquo Cr}] + [\text{monoquo monohydroxy Cr}]$, $[\text{AA}]_{\text{T}} = [\text{AA H}_2] + [\text{AA H}] + [\text{AA}]^-$ and the definition of the species involved in the complexation reactions above, the conditional equilibrium constant (K_{cond}) were calculated for different amino acids using equations 6 and 7.

$$K_{cond} = \frac{[Product]}{[Cr_T - product] \{ [AA]_T \}^n} \dots\dots\dots [6]$$

$$\text{Log}(A_{obs} - A_o) / (A_o - A_{obs}) = \log K_{cond} = n \log [AA]_T \dots\dots\dots [7]$$

(A_{obs}, is the equilibrium absorbance for various molar ratios of amino acids (AA) to [Cr(ox)₂(H₂O)₂], A_a is the equilibrium absorbance where no appreciable reaction occur, A_o is initial absorbance of mixture).

In all three amino acid reactins a straight line is obtained when the log(A_{obs}-A_o)/(A_a-A_{obs}) versus log [AA]_T is plotted at different temperatures (Fig.1), the straight lines have slops very close to unity indicates only 1:1 legation complexation was occur and from the intercepts of the plots, the values of K_{cond} were calculated and then converted to real equilibrium constants (K_{eq}) using relative eq (10).

The obtained values are tabulated in Table (1). These values are in areasonable agreement with those reported for bidentate complexation of anion species (13).

$$K_{equ} = \frac{[Cr(ox)_2(AA)]^{2-}}{[Cr(ox)_2(H_2O)_2]^- [AA]^-} \text{ (according to reaction 5 above) } \dots [8]$$

$$K_{equ} = \frac{[Product]}{[Cr_T - product] \{ 1 + K_h / [H^+] \}} \left\{ \frac{\{ [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2} \}}{K_{a1}K_{a2}} \right\} \frac{1}{[AA]_T} \dots\dots [9]$$

$$K_{equ} \times \{ [H^+] / [H^+] + K_h \} \left\{ \frac{K_{a1}K_{a2}}{\{ [H^+]^2 + K_{a1}[H^+] + K_{a1}K_{a2} \}} \right\} = K_{cond} \dots [10]$$

-Kinetic studies

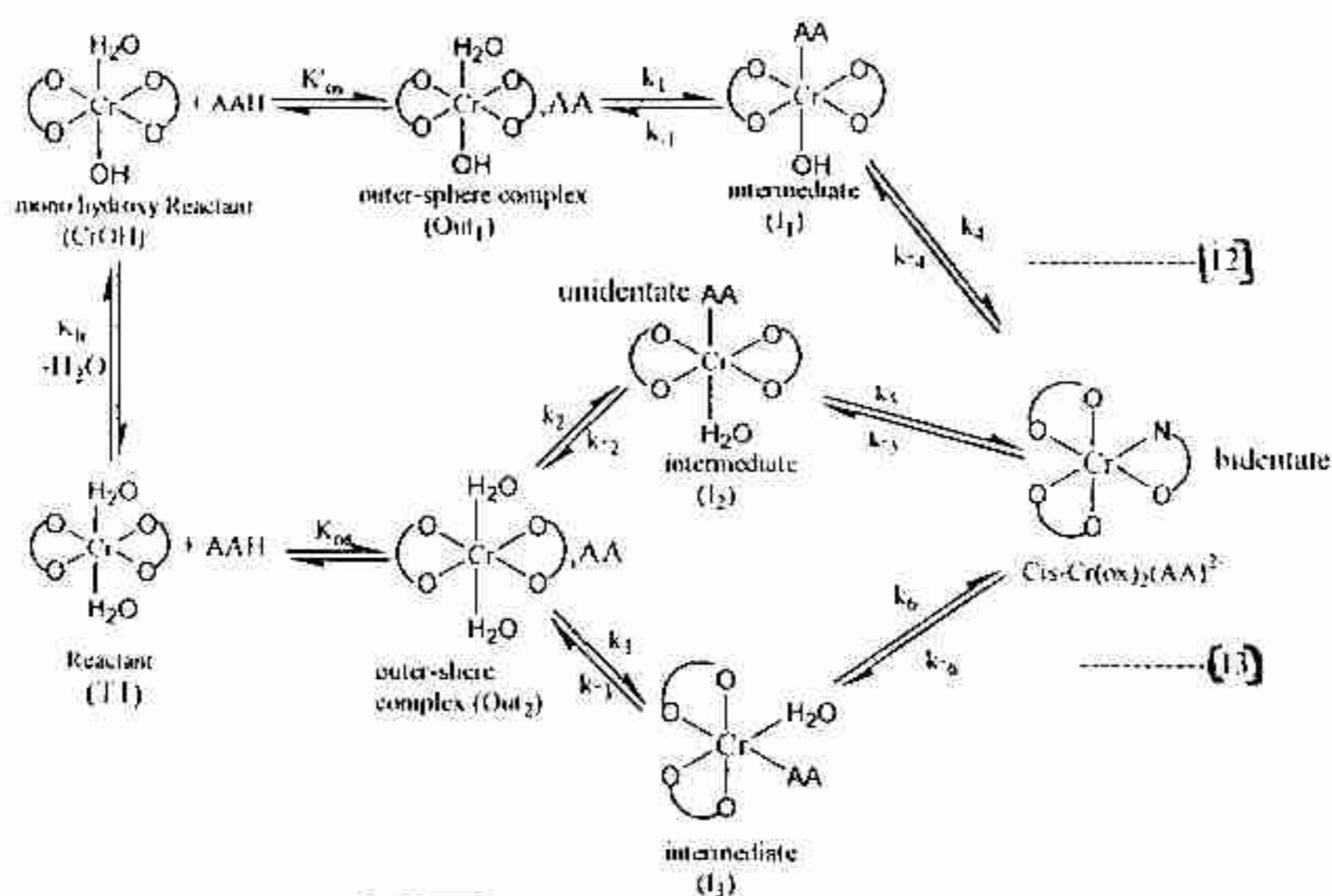
The reaction was followed kinetically at λ_{max}=550 nm, for different temperatures and pHs (μ=0.4M NaNO₃), the plots of log (A_{obs}-A_o) versus time were found in all cases of amino acids to contain two straight crossover lines correspond to two competitive parallel pseudo first order reactions with k_{obs1} and k_{obs2}. Table-2shows some of the observed pseudo first order rate constants (k_{obs1} and k_{obs2})for the reaction of the reactant complex with alanine at diffrents tempratuers and pH. The most important observation are that (k_{obs1}) is fast and acid dependent rate constant and obeys the following equation:-

$$K_{obs1} = k + k'[H]^{-1} \dots \dots \dots [11]$$

The k_{obs2} is also acid independent rate constant

The above equation shows that the rate constant k_{obs1} is composed of acid independent rate constant (k) and an acid dependent rate constant (k'). Therefore, the three kinetically important rates of substitution reactions are found in ligation reactions and all in competitive with the rapid $trans \leftrightarrow cis$ isomerization of reaction of $[Cr(ox)_2(H_2O)_2]^-$ ion in presence of active ligands in aqueous solution.

The following scheme was suggested as a mechanism for substitution of both axial water molecules with AA anion in moderately acidic solution:



The Scheme. (K_{os} , K_{os} are outer sphere associative constants and I_1, I_2, I_3 are intermediates species)

The above mechanism includes three different pathways for product formation, in which each pathway involves three steps of sequent reaction; the formation of outer sphere complex, interchange H_2O molecule and relatively fast chelation (ring closure) reaction. Here the starting complex of trans-bis (oxalato) diaquo Cr(III) ion branches into a relatively active monohydroxy bis (oxalato) monoquo Cr(III) ion, which interacts with AAH (Zwitter ion) in solution to an outer

sphere complex, that is followed by are a rate determinant step (k_1) of interchange one (H_2O) molecule with one end AA^- ion to an intermediate species of trans monohydroxy mono (AA) bis (oxalate) $Cr(III)$ ion (I_1). While, the remain part undergoes interaction with AAH in solution to form another outer sphere complex formation, that is also followed by two relatively slow rate steps (k_2 and k_3) of interchange one H_2O molecule with one end of AA ion to form two different species of cis- and trans intermediates (I_2 and I_3 respectively) of monoquo mono (AA) bis (oxalato) $Cr(III)$ ions. However, there is a possibility that all intermediates (I_2 and I_3) with the internal bidentate ligand $AA(N,O)$ later undergo fast chelation rates (via k_4, k_5 and k_6) to produce final product. The product and all intermediates are in equilibration with the reactants via very slow hydrolysis reactions, that is the reverse of anation reaction. Therefore, on the basis of the reasonable assumption that chelating rates of steps k_4, k_5 and $k_6 \gg k_1, k_2$ and k_3 (steady state conditions), the rate equation of reaction can be expressed as in the followed equations 14, 15 and the mass balance in equation 16, which gives the initial total chromium (III) $[Cr_T]$ as in equation 17.

The rate of the product formation via reactions 12, which includes both relative fast rates of intermediates species trans- I_1 , and cis- I_2 :

$$Rate_1 = k_4[trans-Cr(ox)_2(AA)OH] + k_5[trans-Cr(ox)_2(AA)H_2O] - k_4[Cis-Cr(ox)_2(AA)] - k_4[Cr_{trans}-Cr(ox)_2(AA)] \dots\dots\dots [14]$$

The rate of the product formation via reaction I_3 , which includes only intermediate species trans- I_3 :

$$Rate_2 = k_6[cis-Cr(ox)_2(AA)H_2O] - k_6[cis-Cr(ox)_2(AA)] \dots\dots\dots [15]$$

$$[Cr_T] = [trans-Cr(ox)_2(H_2O)_2] + [trans-Cr(ox)_2(H_2O)OH] + [trans-Cr(ox)_2(H_2O)_2, AAH] + [trans-Cr(ox)_2(H_2O)OH, AAH] + [trans-I_1] + [cis-I_2] + [trans-I_3] \dots\dots\dots [16]$$

$$[trans-Cr(ox)_2(H_2O)_2] = [Cr_T][H^+] / k_{os}[AAH] \dots\dots\dots [17]$$

Substituting $K_h, K_{a1}, K_{a2}, K'_{os}$ and K_{os} , concentrations of all intermediates (from steady state condition) and concentration of reactant trans bis(oxalato) diaquo $Cr(III)$ in above equations 14, 15, the result gives the following expressions for both experimental observed rates k_{obs1} and k_{obs2} as:

$$K_{obs1} = \frac{K_1 K_h K'_{os}}{K_{os}} \frac{1}{[H^+]} + K_2 \dots\dots\dots [18]$$

$$K_{obs2} = K_3 \dots\dots\dots [19]$$

So this mechanism is in consistent with our experimental observation that the acid dependent rate constant k_{obs1} isadequately described by equation 18 (correspond to $K_1 K_h K'_{os}/ K_{os} = k'$ and $k_2 = k$ of the equations 2 and 11), where k_{obs1} is linearly related with inverse of hydrogen ion concentration in solution. The real acid independent rate constant rate k_2 for interchange reaction of cis- I_2 formation obtained form intercept of equation 11 and the slope gives $K_1 K_h K'_{os}/ K_{os}$. The last equation 19 in which k_{obs2} is equal to rate constant k_3 value for interchange reaction of the trans- I_3 intermediate formation. Table-2 shows the values of $(k_1 k'_{os}/ k_{os})$, k_2 and k_3 with calculated activation parameters.

The enthalpy of activations ΔH^\ddagger values for internal interchange of AA⁻ in outer-sphere trans-[Cr(ox)(H₂O),AAH] complex to trans- I_3 intermediates species are 19.8, 15.7 and 19.1 kCal/mole for glycine, alanine and histidine respectively. These values are lower than that for water solvent exchange reaction 26.6 Kcal/mole(17), this result and (-ve) values of ΔS^\ddagger for all above amino acids reactions suggest the association character for the interchange reactions. This result is very close to that previously recorded by Kallen (16) for anation of cis-[Cr(ox)₂(H₂O)₂]⁻ with bidentate oxalate in acid solution ($\Delta H^\ddagger = 9.8$ kCal/mole).

As might be expected that OH⁻ labilizes the interchange reaction by trans labilizing effect. The ΔH^\ddagger (or Ea) values for conjugated base Cr(III) species in all amino acids are much lower than that of trans- I_3 and cis- I_2 intermediates formation reactions. While ¹⁸O exchange and racemization reactions in several studies of coordinated oxalate ligand have been reported to show on end ring opening character (18,19,20). So it is fairly acceptable that the outer-sphere complex formation (as sagged in the above scheme), between reactants [Cr(ox)₂(H₂O)₂]⁻, [Cr(ox)₂(H₂O)OH]⁻² and the incoming (AAH) are formed, once opening one-end oxalate ring occur in these complexes. The attack may occur on the opposite to -ve free charged open end of oxalate ring, since similar charges repel each other, that results AA substitutions and gives trans form of I_3 intermediate species, that is followed by fast chelating process to final cis-product. ΔH^\ddagger for this intermediate formation is in the range of 19.8-22.6 Kcal/ mol as were reported for substitution one water molecule by oxalate in

$[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^-$ (15). However, the attack on the empty position at Cr(III) is not excluded as ring moving occur, which gives a cis-form of I_2 as another intermediate species, but with relatively higher rate constant and slightly lower energy of activation, in all amino acids substitution reactions (see Table-2). As almost expected from the labilizing trans-effect and the -ve charge repulsion of OH^- ligand with AA^- ion, the attack also possible only in the vicinity of vacant position of oxlato and this gives trans form of I_1 . The high observed $k_1(K'_{\text{os}}/K_{\text{os}})$ values are consistent with trans- effect (21) of conjugated base reaction (CrOH). However the composites nature of the rate constant $k_1 = (\text{slope}) K_{\text{os}}/K_{\text{h}} K'_{\text{os}}$ makes to calculate k_1 values are difficult as the values of K_{os} and K'_{os} are unknown (both K'_{os} and K_{os} are expected in low rang values). The low value of ΔH^\ddagger is consistent with that the lability and kinetically trans-effect of OH^- decreases the value of activation energy by 2-6 K cal/mol.

So, in conclusion the above results are consistent with associative interchange substitution mechanism (I_a) in which the attached ligand on Cr(III) center of anion such as OH^- , $\text{C}_2\text{O}_4^{2-}$ (ox) may have effect in labilizing the rate and determine the operative mechanism for anion complex formation of chromate (III) complex.

References

1. Langford, C.H. and Gray, H. (1965). "Ligand substitution processes" W.A. Benjamin, New York, Ch. 1 and 3.
2. Barrett, J.; O'Brien, P. and Penderosa De Jesus, J. (1985). *Polyhedron*, 4:(1), (1-14).
3. Burgess, J. (1978). *Metal ion solution*, Ellis Horwood, Chichester Ch 12.
4. Basolo, F. and Pearson, R. G. (1967). *Mechanism of inorganic reaction*, 2nd ed., Wiley, New York, p-124-150.
5. Hamm, R. E. ; Johnson, R. L. ; Perkins, R. H. and Davis, R. E. (1958). *J. Am. Chem. Soc.*, 80,4469.
6. Abdullah, M. A.; Barrett, J. and O'Brien, P. (1984). *J. Am. Chem. Soc.* Dalton Trans.
7. Abdullah, M. A.; Barrett, J. and O'Brien, P. (1985). *Inorg. Chem Acta*, 96.
8. Abdullah, M. A.; Barrett, J. and O'Brien, P. (1985). *J. Chem. Soc. Dalton Trans.* 2085-2089.

9. Casula, M.; Illuminati, G. and Ortaggi, G. (1972). *Inorg. Chem.* 11:(5), 1062.
10. Ashley, K. R. and Trent, *Inorg. I.* (1989). *Chim. Acta*, 163,159.
11. Ashley, K.K. and Leipoldt, J. G. (1981). *Inorg. Chem.*, 20, 2326.
12. Dawson, B. E. (1967). "Practical Inorganic Chemistry", Methuen and Co. Ltd, London, 2nd ed., p-214.
13. Krishnamurty, K. V. and Harris, G. M. (1961). *Chemical reviews*, 61:(1), published by A. Chem. Soc.
14. Voet, D. and Voet, J. G. (1990). *Biochemistry*, John Wiley & Sons. New York.
15. a- Nicholas, D.(1978) "Complexes and First Row Transition Element" Methuen London,86.
b- Banejea, D. and Chaudhuari, S.D. (1968). *J. Inorg. Nucl.Chem.*,30,871.
16. Kallen, T. W. and Hamm, R. E.(1979). *Inorg. Chem.*, 18:(8).
17. Plane, R. and Taube, H. (1952). *J. Phys. Chem.*
18. Thomas, W.; Kallen, and Randall, E. Hamm,(1979). *Inorg. Chem.*, 18: (8),2157.
19. Hamm, R. E. (1953). *J. Am. Chem. Soc.* 75, 609.
- 20.(a) Hamm, R. E. ; Kollreck, R.; Welch, G. L. and Perkins, R. M.(1961). *J. Am. Chem. Soc.* 13, 340.
(b) Bromhead, J. A. (1965) *J. Inorg. Nucl. Chem.* 27, 2049.
(c) Welch, G. L. and Hamm, R. E. (1963). *Inorg. Chem.*,2,295.
(d) Grant, D.M. and Hamm, R.E. (1956) *J. Am.Chem. Soc.*78, 3006.
21. Benjamin Coe, J. and Glen Wright, S.J. (2000). *coordination chemistry reviews*, 203 :(1), 5 – 80.

Table (1) Equilibrium Constant of Reaction of trans-[Cr(OX)₂(AA)]²⁻ Formation (where AA = glycinate, alaninate, and histidinate)

T °C	Log Kequ for [Cr(ox) ₂ (glyO)] ²⁻	T °C	Log Kequ for [Cr(ox) ₂ (AlanO)] ²⁻	T °C	Log Kequ for [Cr(ox) ₂ (HistO)] ²⁻
25	4.95	25	5.21	25	5.13
35	4.99	32	5.29	32	5.20
45	5.02	40	5.35	40	5.33
50	5.09	50	5.44	50	5.35

Table(2) Pseudo first-order rate constants (k_{obs1} and k_{obs2}) for the reaction of trans-Cr(ox)₂(H₂O)₂ with alanine.

Temp. °C	pH	$k_{obs1} \text{ min}^{-1}$	$k_{obs2} \text{ min}^{-1}$
30	4.8	0.0293	0.0026
37.5	4.8	0.0512	0.0062
40	4.8	0.0632	0.0069
43.5	4.8	0.0691	0.0113
50	4.8	0.1303	0.039
56	4.8	0.155	0.0506
30	5.6	0.0473	0.0066
35	5.6	0.0636	0.0076
40	5.6	0.0841	0.0124
45	5.6	0.1223	0.0191
50	5.6	0.1679	0.0293
55	5.6	0.1909	0.0444
30	5.9	0.0543	0.0032
35	5.9	0.0728	0.0062
40	5.9	0.1023	0.0115
45	5.9	0.1613	0.0203
50	5.9	0.200	0.0225

Table (2) The derived rate constant values for For glycine reaction K_1 (k_{os}/k_{os}), K_2 and K_3 and calculated activation parameters for glycinereaction mamino acid glycine, alanine, and histidine reactions with Tl complex

T °C	$k_1 (k_{os}/k_{os}) \times 10^2 \text{ sec}^{-1}$	E_a (kCal/mol)= 9.97	$k_2 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 16.25	$K_3 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 20.4
30	3.50	ΔH^\ddagger (Kcal/mol)= 9.93	3.98	ΔH^\ddagger (Kcal/mol)= 15.60	0.93	ΔH^\ddagger (Kcal/mol)= 19.8
35	4.42		5.48		2.13	
40	5.18		11.40		2.38	
45	7.18		13.30		5.27	
50	9.92		2.60		8.37	
		ΔS^\ddagger (Cal/mol)= -34.47			ΔS^\ddagger (Cal/mol)= -22.5	ΔS^\ddagger (Cal/mol)= -10.9

For Alanine reaction

T °C	$K_1 (K'_{in}/K_{os}) \times 10^2 \text{ sec}^{-1}$	E_a (kCal/mol)= 9.24	$k_2 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 12.77	$k_3 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 15.77
30	2.36	ΔH^\ddagger (Kcal/mol)= 8.62	4.92	ΔH^\ddagger (Kca/mot)= 12.15	1.10	ΔH^\ddagger (Kcal/mol)= 15.184
35	2.50		2.50		1.27	
40	2.67		2.67		2.07	
45	4.42		4.42		3.18	
50	5.48		5.48		4.88	
55	6.90	6.90	6.90	7.40		
		ΔS^\ddagger (Cal/mol)= -37.85			ΔS^\ddagger (Cal/mol)= -33.5	ΔS^\ddagger (Cal/mol)= -27.0

For Alanine reaction

T °C	$k_1 (K'_{in}/K_{os}) \times 10^2 \text{ sec}^{-1}$	E_a (kCal/mol)= 7.3	$k_2 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 12.75	$k_3 \times 10^4 \text{ sec}^{-1}$	E_a (kCal/mol)= 19.1
30	0.68	ΔH^\ddagger (Kcal/mol)= 6.67	4.30	ΔH^\ddagger (Kca/mot)= 12.1	0.28	ΔH^\ddagger (Kcal/mol)= 15.5
35	0.84		6.30		0.52	
40	1.01		10.00		0.77	
45	1.11		12.33		1.40	
50	1.53		15.6		2.00	
		ΔS^\ddagger (Cal/mol)= 46.5			ΔS^\ddagger (Cal/mol)= -33.94	ΔS^\ddagger (Cal/mol)= -18.33

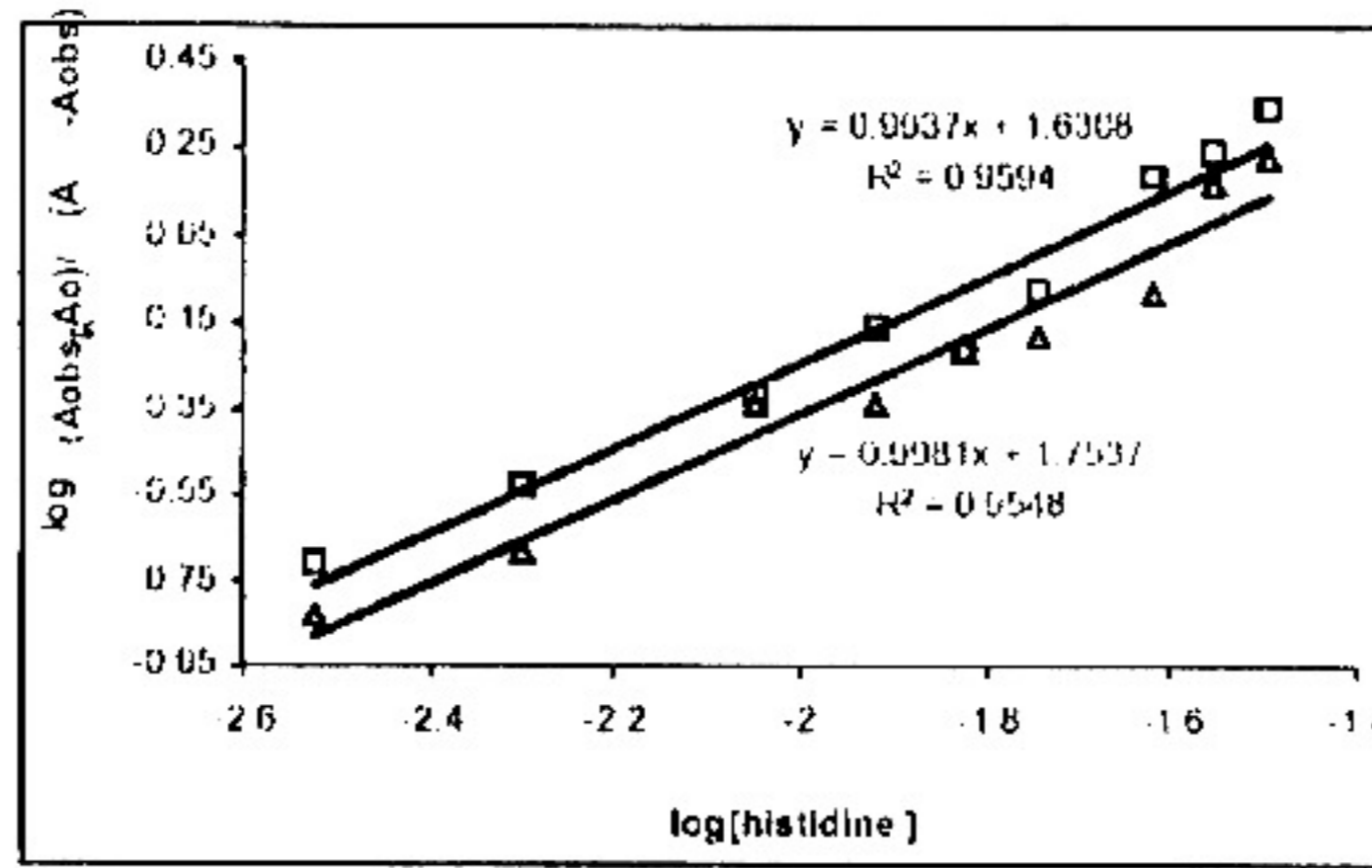


Fig (1) Plots of the $\log (A_{obs} - A_0) / (A_a - A_{obs})$ versus $\log [\text{histidine}]_T$ at temperatures 30°C (Δ), 50°C (\square).

دراسة توازنية وحركية وميكانيكية تكوين المعقد -Cis
mono (AA)bis (oxalate) chromate (III) (حيث
AA هي الكلايسين الالنين والهستيدين) في وسط حامضي
ضعيف

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الخلاصة

تم دراسة توازنية وحركية وميكانيكية التفاعل للأحماض الامينية (AA)، الكلايسين، الالنين و الهستيدين مع معقد الكروم(3+) $trans-[Cr(ox)_2(H_2O)_2]^-$ في محيط حامضي ذو اس هيدروجيني (4,8 - 6,7) وقوة ايونية (0,4 مولارنترات الصوديوم) وفي درجات حرارية مختلفة. ثابت الاتزان في (25 درجة مئوية) $(\log K_{eq})$ تساوي 4,951 و 5,206 و 5,128 لتفاعل الاحماض الامينية (كلايسين، النين و الهستيدين مع $trans-[Cr(ox)_2(H_2O)_2]^-$ على التوالي.

وقد تم دراسة حركية تكوين هذه المعقدات، ان حركية تفاعل ايون المعقد المتفاعل -trans- $[Cr(ox)_2(H_2O)_2]^-$ مع الاحماض الامينية المذكورة سابقا تتضمن تفاعلين متوازيين معقدتين، حيث تشمل كلا من هذين التفاعلين ثلاث خطوات متعاقبة مختلفة لمكونات مختلفة للكروم الثلاثي.

ان ايون المعقد المتفاعل $trans-[Cr(ox)_2(H_2O)_2]^-$ تتفرع ضمن خطوة التحلل المائي الى الايون السالب الثنائي (القاعدة المرافقة) $trans-[Cr(ox)_2(H_2O)(OH)]^{2-}$ الذي يتفاعل مع ايون الزويتزر AHH لتكوين معقد المجال الخارجي (outer-spher) والذي يليه استبدال جزيئة واحدة من الماء بايون AA لتكوين المركب الوسطي الفعال -trans- $[Cr(ox)_2(AA)(OH)]^{3-}$ الذي يتحول بدوره الى النتائج الأخير، وهو -Cis- $[Cr(ox)_2(AA)]^{2-}$.

أما الجزء المتبقي من المعقد المتفاعل، يتفاعل أيضا مع AHH من جهة أخرى لتكوين معقد مجال خارجي آخر، الذي يلية أيضا استبدال جزيئة واحدة من ماء بأيون AA^- لتكون مركبين وسطين من (Cis) و (Trans) للمركب $trans-[Cr(ox)_2(AA)H_2O]^{2-}$ والذي يتحولان أيضا الى الناتج الأخير $Cis-[Cr(ox)_2(AA)H_2O]^{2-}$.
أن الخطوات المهمة حركيا في هذا النظام هي خطوات تكوين المركبات الوسطية (Csi) و (Trans)، بينما الناتج الأخير يكون في حالة أتران مع المعقد المتفاعل في المحلول. أن ثابت سرعة الأستبدال لتكوين المركب الوسطي- $trans-[Cr(ox)_2(AA)(OH)]^{3-}$ يكون نسبيا أكبر بكثير (أنثالبي التنشيط تساوي 8 و8 كيلوكالوري. مول⁻¹) من ثابت سرعة تكوين $Cis-[Cr(ox)_2(AA)(H_2O)]^{2-}$ (أنثالبي التنشيط تساوي 14 كيلوكالوري. مول⁻¹) بينما ثابت السرعة لتكوين $Cis-[Cr(ox)_2(AA)(H_2O)]^{2-}$ أكبر بمقدار (5-10) مرة من ثابت السرعة لتكوين $trans-[Cr(ox)_2(AA)(H_2O)]^{2-}$ (أنثالبي التنشيط تساوي 18,4 كيلوكالوري. مول⁻¹).
أن ميكانيكية كل التفاعلات الأستبدال الموجودة في هذا النظام لتكوين المعقد الناتج تكون من نوع التبادل الترافقي (associative interchange).