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Equilibrium and kinetic study for the reaction of Trans-$K[Cr(ox)_2(H_2O)_2].3H_2O$ with 4-aminoantipyrine

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Abstract

A new complex of Cr(III) has been prepared. The kinetics and equilibrium study of the substitution reaction for the complex Trans-$K[Cr(ox)_2(H_2O)_2].3H_2O$ {T1}, with 4-aminoantipyrine {AAP}, have been performed in aqueous media at (pH = 4.9, 5.6 and 6.0) (μ=0.4M $NaNO_3$). Activation parameters for the reactions are (Ea_1=1.891 kCal mol^{-1}, $\Delta H^{\ddagger}_1$=89.29 kCal mol^{-1} and $\Delta S^{\ddagger}_1$ = 0.281 Cal. mol^{-1}) and (Ea_2=0.487kCal mol^{-1}, $\Delta H^{\ddagger}_2$ =62.03 kCal mol^{-1} and $\Delta S^{\ddagger}_2$ = -92.8 Cal mol^{-1}). The observed rate constants are in good agreement with substitution reaction of the complex with amino acids(1) and other anions(2).

Introduction

Anti pyrine (2,3-dimethyl-1-phenyl-5-pyrazolone) and it derivatives have a diversity of applications including biological, clinical and pharmacological areas(3). Also, complexation of Chromium(III) with amino acids are of biological importance. Cr(III) complexes present in brewer's yeast and other food called glucose tolerance factor are of outstanding biological activity(4,5). Cr(III) center is well known to be kinetically inert (slow rate) in ligand substitution reactions(6). Despite of this, there have been some few cases in which relatively rapid reaction of Cr(III) complexes has occurred. This character of Cr(III) may be important as a requirement in the achievement of its biological role.(7,8,9)

In previous works we have studied the kinetics of the substitution reaction of {T1} with amino acids in moderately acidic solutions(1). The oxalato groups of the T1 complex are normally resistant against substitution or dissociation(10), so the possible positions for reaction of this complex is on the two aqua groups.

In this work, the kinetic and equilibrium studies of the substitution reaction of T1 with 4-aminoantipyrine {AAP} is performed spectrophotometrically at 560nm.

Experimental

{T1} has been prepared by following (Dawson 1967)(11) procedure. The new complex of T1 with AAP have been prepared by dissolving equimolar amounts of T1 and AAP in distilled water, heated on steam bath for 2 hours and evaporated to dryness. The obtained crystals are then washed several times with alcohol and dried in an oven. Kinetic measurements were performed by dissolving an exact amount of a pre-crushed T1 complex (0.0087 mol/lit) in a thermostat distilled water that contains the ionic strength and mixing with the thermostated AAP solution (0.1 mol/lit) and adjusting the pH to the required value with an acid ($HClO_4$) or a base (NaOH). The solution was then immediately introduced to the reaction vessel, circulated in the system and the absorbance values were recorded with time passing.

Kinetic studies

The rate of reaction was followed at λ_{max} 560 nm with a Jenway 6405 UV-Vis spectrophotometer (with a modified home-made thermostat cell holder), at different temperatures and pHs (μ=0.4M $NaNO_3$). Pseudo first order plots of $\ln(A_\infty - A_t)$ versus time (where A_∞, A_t represents the absorbance at infinite time and at different times passed over the reaction) show two straight crossover lines corresponding to two competitive parallel reactions with observed rate constants k_{obs1} and k_{obs2} which their values are tabulated in table (1) for different pH and temperatures. The effect of hydrogen ion concentration on the observed rate constants k_{obs1} and k_{obs2} is shown in Fig(1) at 40°C, both rates are acid dependent, k_{obs1}

is linearly increase with $1/[H^+]$ and k_{obs2} is linearly decrease with $1/[H^+]$ but in a smaller slop.

The activation energies for the observed rate constants (k_{obs1} & k_{obs2}) for the complexation reaction between T1 and AAP have been determined according to Arrhenius equation: $k = Ae^{-Ea/KT}$ also the enthalpies and entropies of activation have been determined according to Erying equation: $k=(k_bT/h)\ e^{-\Delta S^*/R}.\ e^{-\Delta H^*/RT})$ at pH = 5.6, and the activation parameters are tabulated in Table(2).

These values are in good agreement with that reported by Kallen and Hamm for the anation of {cis-$[Cr(ox)_2(H_2O)_2]^-$} with oxalate ion(2).

Equilibrium Studies:

At the experimental conditions (pH=5.6), the reactant (T1) (pK_{h1} = 7.2 and pK_{h2} =10.5)(12) is expected to be present in diaquo and its conjugated base, (monohydroxy) forms.

$$[Cr(OX)_2(H_2O)_2^-] \xrightleftharpoons{K_{h1}} [Cr(OX)_2(H_2O)(OH)^{2-}] + [H^+] \text{---------} [1]$$

$$K_{h1} = \frac{[Cr(OX)_2(H_2O)(OH)^{2-}][H^+]}{[Cr(OX)_2(H_2O)_2^-]} \text{-----------------------------------} [2]$$

$$AAPH_2^+ \xrightleftharpoons{Ka_1} nAAPH + H^+ \xrightleftharpoons{Ka_2} AAP^- + H^+ \text{----------} [3]$$

pK_{a1} and pK_{a2} for the ligand (AAP) was found experimentally by pH titration method and the results were 4.65 and 9.55 respectively .

The ligation reaction is :-

$$[Cr(OX)_2(H_2O)_2^-] + n\,AAP^- \xrightleftharpoons{Keq} [Cr(OX)_2(AAP)^{2-}] - 2\,H_2O \text{-------------} [4]$$

$$K_{eq} = \frac{[Cr(OX)_2(AAP)^{2-}]}{[Cr(OX)_2(H_2O)_2^-] \times [AAP^-]^n} \text{-------------------------} [5]$$

The ligation of (T1) with (AAP) results in a spectacular increasing of the absorbance at both λ_{max} 560nm and λ_{max} = 410nm, in which the net result is the substitution of both axial H_2O molecules with a bidentate

(AAP) and conversion of the original geometry to Cis-form. So, the equilibrium studies were followed spectrophotometrically at 560nm.

Solutions of (T1) with (AAP) were equilibrated, [T1] =0.002 mol.dm^{-3} and [AAP] = 0.00 to ≤ 0.2 mol.dm^{-3} .

Using mass balance :-

$$[Cr]_T = [Cr(OX)_2(AAP)^{2-}] + [Cr(OX)_2(H_2O)_2^{-}] + [Cr(OX)_2(H_2O)(OH)^{2-}] \text{--------}[6]$$

from eq.[2 and 6]

$$[Cr(OX)_2(H_2O)_2^{-}] = \frac{[Cr]_T - [Cr(OX)_2(AAP)^{2-}]}{\left[1 + \frac{K_{h1}}{[H^+]}\right]} \text{----------------------------------}[7]$$

$$\text{Also :}\quad [AAP]_T = [AAPH^{+}] + [AAPH] + [AAP^{-}] \text{----------------------}[8]$$

$$[AAP^{-}] = \frac{[AAP]_T \,.\, K_{a1} .\, K_{a2}}{\{[H^+]^2 + K_{a1}[H^+] + K_{a1} \,.\, K_{a2}\}} \text{---------------------------}[9]$$

substitute all in eq. [5] :

$$K_{eq} = \frac{[Cr(OX)_2(AAP)]^{2-}\{1 + \frac{K_{h1}}{[H^+]}\}}{[Cr]_T - [Cr(OX)_2(AAP)]^{2-}} \text{ x } \frac{\{[H^{-}]^2 + K_{a1}[H^+] + K_{a1} .\, K_{a2}\}}{K_{a1} .\, K_{a2}} \text{ x } \frac{1}{[AAP]_T^{\,n}} \text{------}[10]$$

$$K_{cond} = K_{eq} \text{ x} \frac{[H^+]}{([H^+] + K_{h1})} \text{ x } \frac{K_{a1} .\, K_{a2}}{\{[H^{-}]^2 + K_{a1}[H^{-}] + K_{a1} .K_{a2}\}} = \frac{[Cr(OX)_2(AAP)]^{2-}}{[Cr]_T - [Cr(OX)_2(AAP)]^{2-}} \text{ x } \frac{1}{[AAP]_T^{\,n}} \text{----}[11]$$

$$K_{cond} = \frac{(A_{obs} - A_o)}{(A_{\&} - A_{obs})} \text{ x } \frac{1}{[AAP]_T^{\,n}} \text{---}[12]$$

Where A_o is the initial absorbance of the reaction mixture, A_{obs} is the equilibrium absorbance for various ratios of the ligand to the reactant, and $A_{\&}$ is the equilibrium absorbance where no appreciable reaction occur and K_{cond} is the experimental (conditional equilibrium constant. Plots of Log $\{(A_{obs} - A_o) / (A_{\&} - A_{obs})\}$ versus log $[AAP]_T$ at different temperatures gives straight lines as shown in Fig. (2) with slops very close to unity (n=1)(1:1 complexation between T1 and AAP), and the intercepts gives $\log K_{cond}$. The values of K_{eq} are calculated from K_{cond} using eq. [12], and the results are tabulated in table (3) .

These results suggest the bidentate ligation of AAP with the T1 complex on carboxyl and the amine groups as shown in Fig .(3).
Gibbs free energy is calculated for the reaction from plotting $\log K_{eq}$ versus 1/T as shown in Fig.(3).

$$\Delta G = 12.785 \text{ kCal.mol}^{-1} .$$

Conclusion

The observed rate constants of substitution of T1 with AAP is relatively labile as compared with other Cr(III) complexes, but it is 5-10 times slower than that reported for substitution of T1 with alanine, glycine and histidine(1), this is maybe due to the associative character of the reaction mechanism and larger size of the ligand AAP. On the other hand, the –ve value of $\Delta S^{\#}$ for k_{obs2} is another indication of the associative mechanism of the reaction. The equilibrium constants for the complexation reaction are nearly identical with the amino acid complexation with T1(1).

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Table:(1) Pseudo first order rate constants k_{obs1} and k_{obs2} for the reaction of T1 with 4-aminoantipyrine

pH	Temp.°C	k_{obs1} (min^{-1})	k_{obs2}(min^{-1})
6.4	40	0.02	0.002
6.4	45	0.023	0.0036
6.4	55	0.05	0.0095
6.0	35	0.0074	0.0015
6.0	40	0.0098	0.0019
6.0	45	0.018	0.0021
6.0	50	0.031	0.0051
5.6	40	0.0083	0.004
5.6	45	0.015	0.0063
5.6	50	0.0256	0.0085
5.6	55	0.0418	0.0128
5	40	0.005	0.005

Table :(2) Activation parameters for the reaction of T1 with 4-aminoantipyrine at pH=5.6 for both (k_{obsl} & k_{obs2}).

Reaction rate		Ea* (kJ/mol)	ΔH* (kJ/mol)	ΔS* (J/mol)
k_{obs1}		1.891	89.29	0.281
k_{obs2}		0.487	62.03	-92.87

Table (3) Equilibrium constants for the reaction of T1 with AAP.

Temp. °C	$\log K_{cond}$	K_{cond}	K_{eq}	$\log K_{eq}$
27	0.4026	2.527	25514.8	4.407
37	0.7678	5.859	59155.12	4.772
44	0.8556	7.171	72404.6	4.86
54	1.1765	15.014	151596.4	5.18

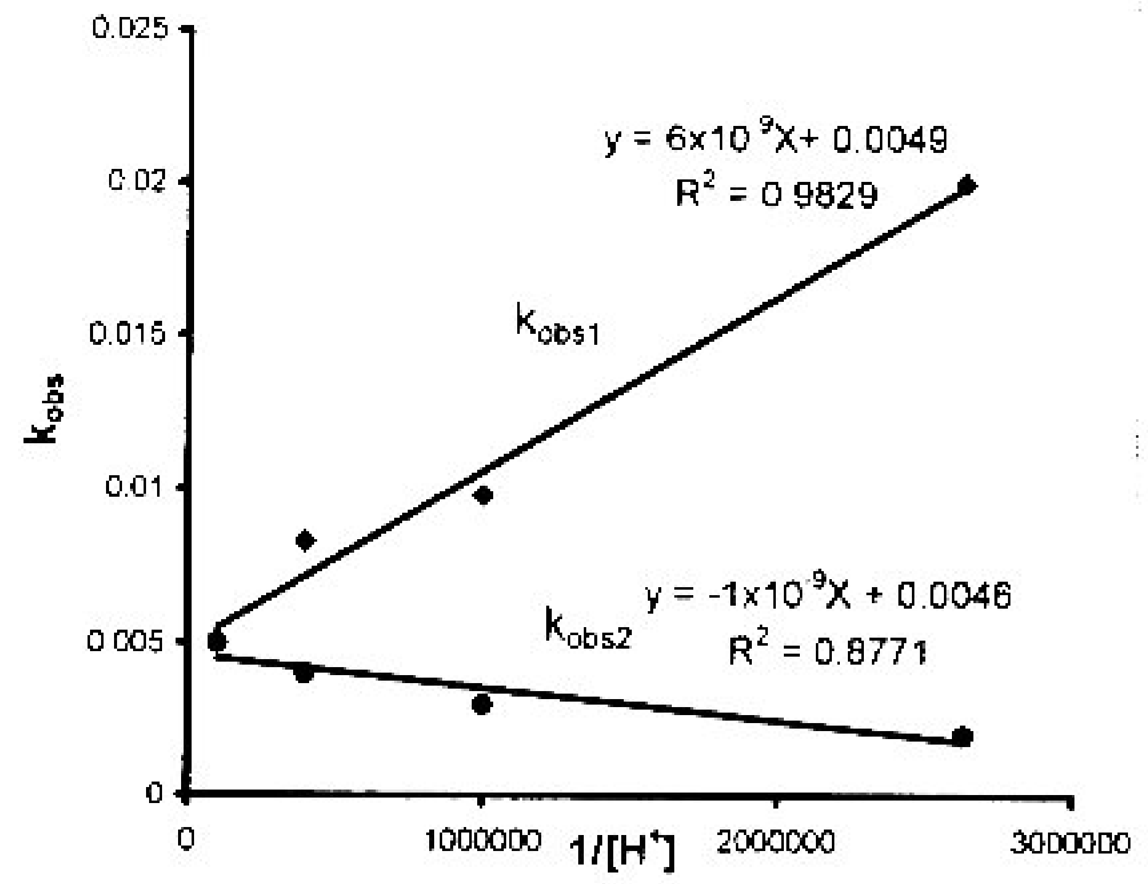

Fig.(1) Effect of hydrogen ion concentration on k_{obs1} and k_{obs2}

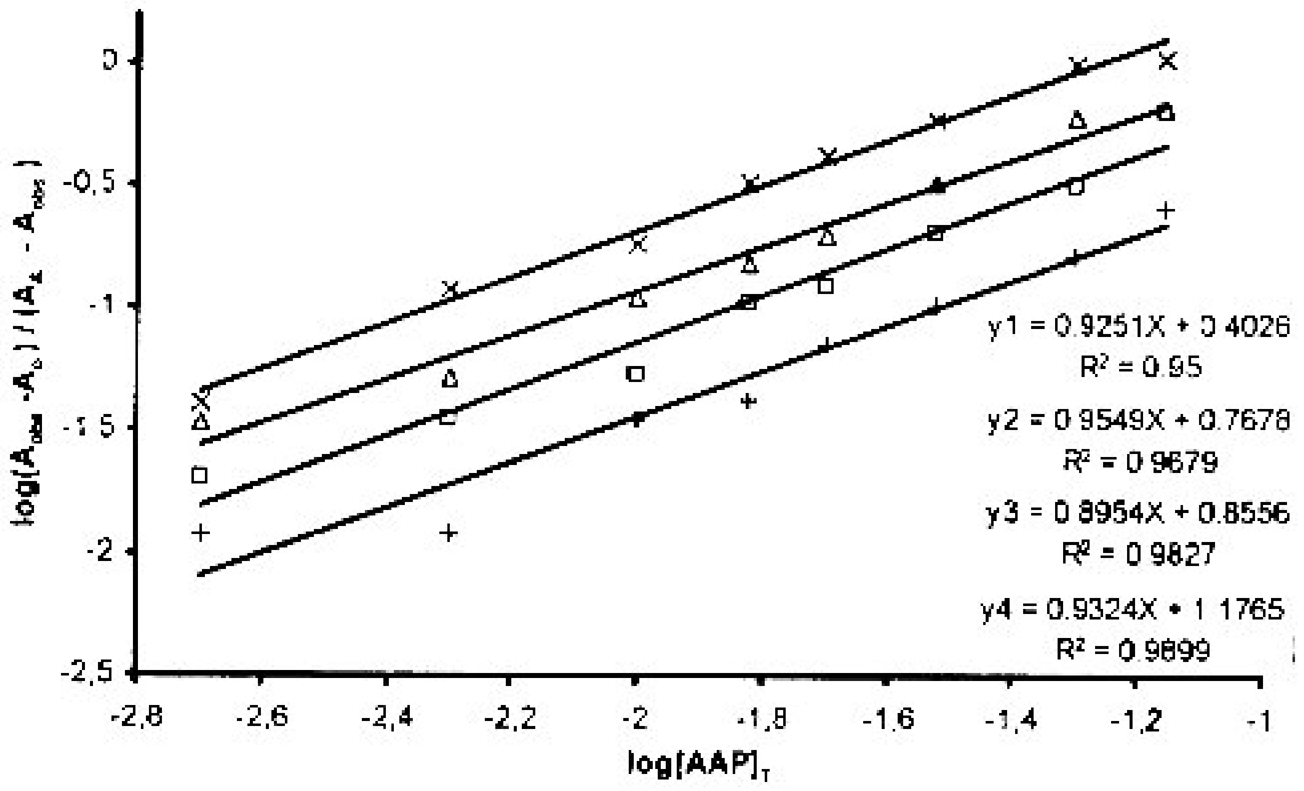

Fig (2) Plots of $\log(A_{obs} - A_o)/(A_\infty - A_{obs})$ versus $\log[AAP]_T$ at temperatures 1= 27°C, 2= 37°C, 3= 44°C and 4= 54°C

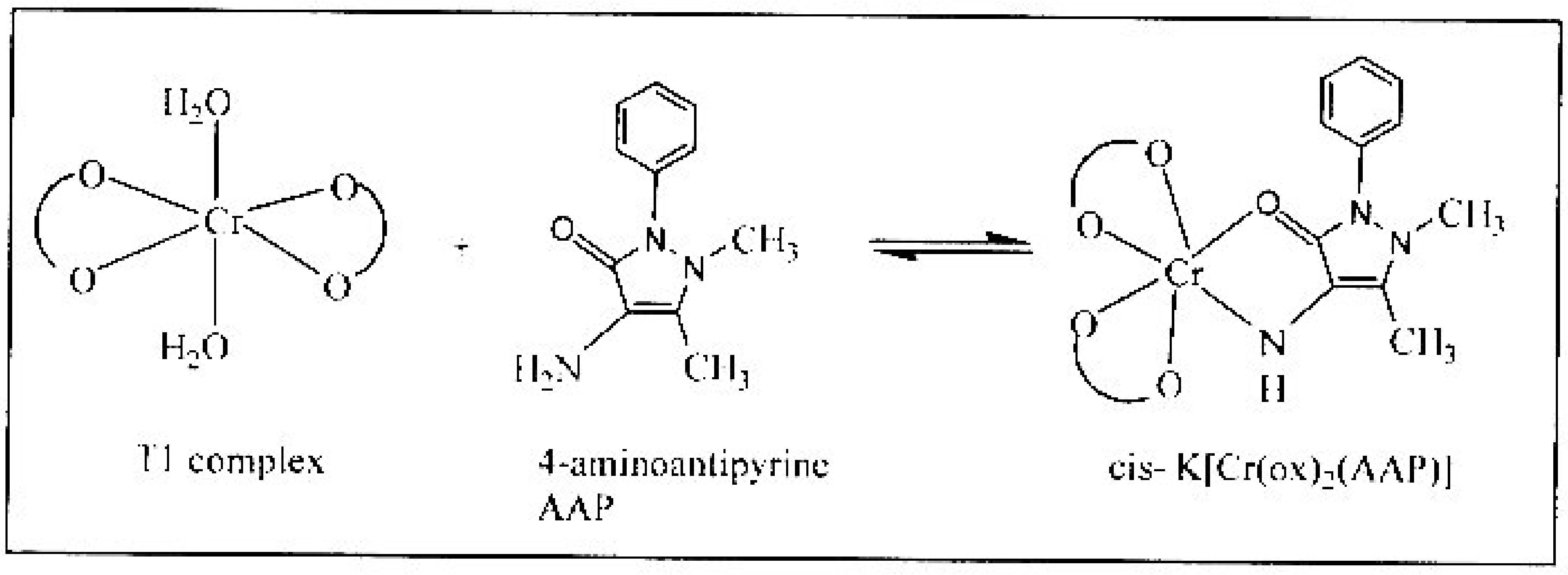

Fig. (3) The reaction of T1 with AAP and formation of cis-K$[Cr(ox)_2(AAP)]$ complex

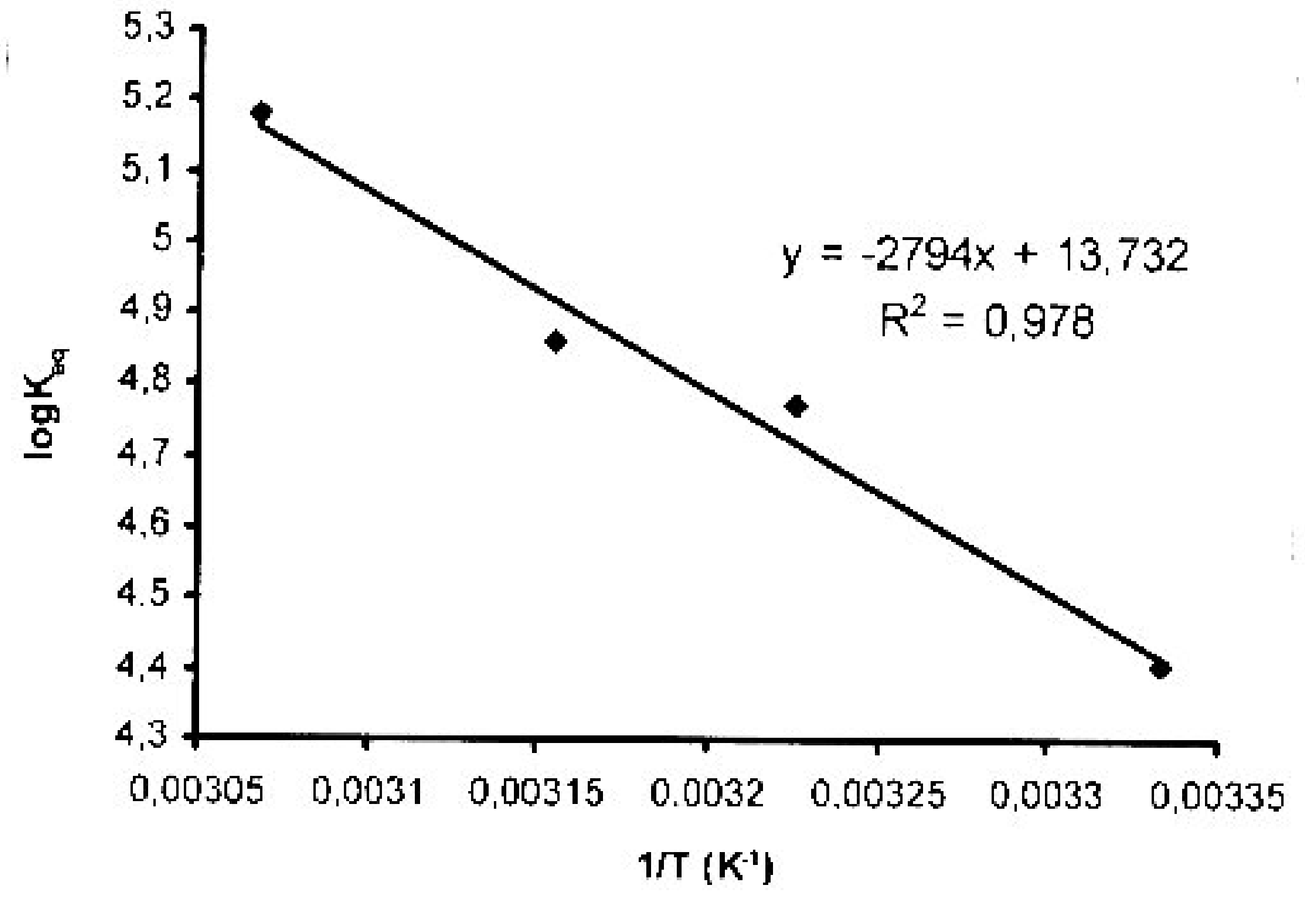

Fig.(4) Plot of $\log K_{eq}$ versus 1/T

دراسة توازنية وحركية تفاعل
Trans –$K[Cr(ox)_2(H_2O)_2].3H_2O$
مع
4-aminoantipyrinc

بختيار كمال عزيز ، كريم جمعة ابراهيم
قسم الكيمياء ، جامعة السليمانية

الخلاصة

تم تحضير معقد جديد للكروم الثلاثي ، وتم دراسة حركية وتوازنية تفاعل الاستبدال للمركب$[Cr(ox)_2(H_2O)_2]$ trans – مع 4-aminoantipyrinc في محيط مائي ذو أس هيدروجيني (pH=4.9,5.6 and 6.0)وقوة أيونية (μ=0.4M $NaNO_3$) ثوابت التنشيط هي (Ea_1=1.891 kCal mol^{-1} , $\Delta H^{\ddagger}$=89.29 kCal mol^{-1} and $\Delta S^{\ddagger}_1$=0.281 Cal. mol^{-1}) (Ea_2 =0.487kCal mol^{-1}, $\Delta H^{\ddagger}_2$=62.03KCal mol^{-1} and $\Delta S^{\ddagger}_2$=-92.8 Cal mol^{-1})

قيم ثوابت السرعة العملية مشابهة لتفاعلات استبدال المقعد المتفاعل مع الأحماض الأمينية (1) او مع الأنيونات (2).