

The Kinetics of the Hydrolysis of Trans-K[Cr(ox)₂(H₂O)₂].3H₂O



Mohamad Ali Abdullah and Bakhtyar Kamal Aziz

Department of Chemistry, University of Sulaimani, Sulaimani,
Kurdistan Region / Iraq

Abstract

In the present work, the kinetics of the hydrolysis of the complex Trans-K[Cr(ox)₂(H₂O)₂].3H₂O have been studied in aqueous media at (pH = 4.7, 5.1, 5.6 and 6.3) ($\mu=0.4$ NaNO₃). The hydrolysis rate was found to be acid dependent and show a linear increase with $[H^+]^{-1}$. The activation parameters for the reactions are ($E_{a1}=45.77$ kJ mol⁻¹, $\Delta H^{\ddagger}_1=43.15$ kJ mol⁻¹ and $\Delta S^{\ddagger}_1=-240$ J mol⁻¹) and ($E_{a2}=81.21$ kJ mol⁻¹, $\Delta H^{\ddagger}_2=78.59$ kJ mol⁻¹ and $\Delta S^{\ddagger}_2=-13.82$ J mol⁻¹). The observed rate constants are in good agreement with that reported by Kallen and Hamm for the anation of {Cis-[Cr(ox)₂(H₂O)₂]}.

Keywords: Cr (III) complex, kinetic lability, hydrolysis.

Introduction

Studies of the biochemistry of none of the other transition metals have been as problematic as those of chromium. The biologically important form of chromium is the trivalent, Cr³⁺. The coordination chemistry of this ion is part of the problem[1].

Chromium (III) (d³) center is well known to be kinetically inert in ligand substitution reactions[2]. This is the reason why substitution at Cr(III) complexes have received great attention, with its similarity Co(III) complexes. 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.[3-5]

The complexes of Cr(III) are susceptible to hydrolysis and formation of poly-nuclear complexes by oligation[6]. The oxalato groups of the [Cr(ox)₂(H₂O)₂]⁻ complex are normally resistant against

substitution or dissociation[7], so the possible positions for reaction of this complex is on the two aqua groups.

We have studied the kinetics of the hydrolysis of trans-K[Cr(ox)₂(H₂O)₂].3H₂O in moderately acidic solutions, also the pH effect on the rate of hydrolysis have been determined.

Experimental

Trans-K[Cr(ox)₂(H₂O)₂].3H₂O has been prepared by following (Dawson 1967) procedure[9]. Kinetic measurements were performed by dissolving an exact amount of a pre-crushed Trans-K [Cr(ox)₂(H₂O)₂].3H₂O complex (0.0087 mol/lit) in a thermostat distilled water that contains the ionic strength and adjusting the pH to the required value with an acid (HNO₃) 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

Spectrophotometric rate determinations were followed at λ_{max} 550 nm with a Jenway 6405 UV-Vis spectrophotometer (with a modified home-made thermostat cell holder), at different temperatures and pHs ($\mu=0.4$ NaNO₃) (a typical plot is shown in Fig.1).

The plots of $\log (A_{obs}-A_t)$ versus time is linear (Fig. 2).

The observed rate constants are tabulated in table (1) for different temperatures and pHs with constant ionic strength (0.4M KNO₃), which are in a good agreement with those values that were obtained by Kallen and Hamm for the anation of Cis-[Cr(ox)₂(H₂O)₂][8].

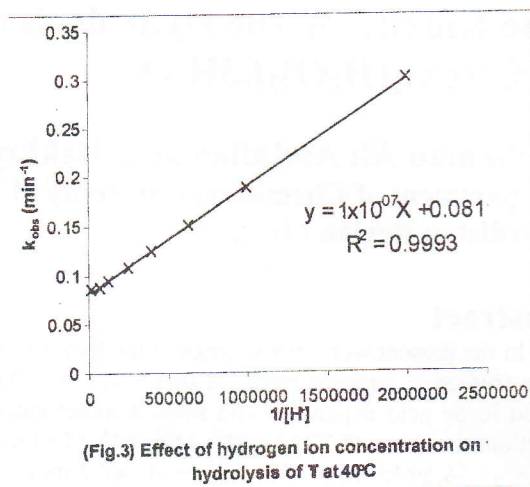
The observed rate constant (k_{obs}) is pH dependent, a typical plot of (k_{obs}) versus $[H^+]^{-1}$ at 40°C is shown in fig (3).

The variation of the observed rate constant (k_{obs}) with hydrogen ion concentration for the hydrolysis at 40°C are illustrated in table (2). The hydrolysis rate (k_{obs}) is found to be acid dependence and show a linear increase with $[H^+]^{-1}$, which is expressed by the following equation:-

$$k_{obs} = k_1 [H^+]^{-1} + k_2 \text{ -----(1) [9,10]}$$

Table (1) The observed rate constants for the hydrolysis of trans-[Cr(ox)₂(H₂O)₂]⁻ for different temperatures at different pHs ($\mu = 0.4$)

Temp. °C	$k_{obs} (\text{min}^{-1}) \times 10^3$ at			
	pH=4.7	pH=5.1	pH=5.6	pH=6.3
30	38.6	41.3	55.3	174.7
34	59	-	074.1	-
35	-	73.8	-	198.4
40	103	112.34	-	-
41	-	-	141.9	316.4
45	158.8	177	203	423.5
48	-	-	309.6	-
50	257.7	280.6	-	0.575.9
55	399.4	-	458	779



(Fig.3) Effect of hydrogen ion concentration on hydrolysis of T at 40°C

Table(2) Variation of k_{obs} with hydrogen ion concentration.

pH	$[H^+]^{-1}$	k_{obs}
4.05	11220	0.0922
4.25	17783	0.087
4.85	70795	0.0873
5.1	125893	0.0953
5.4	251189	0.1073
5.6	398107	0.124
5.8	630957	0.1503
6.0	1000000	0.1894
6.3	1995262	0.3016

The above equation(1) shows that the observed rate constant k_{obs1} is composed of two path mechanism, acid dependent rate constant (k_1) and acid independent rate constant (k_2), which have the values of (0.0811 and 1×10^{-7}) respectively at 40°C .

The values of both (k_1 & k_2) have been calculated from the slop and the intercepts of the plots of ($1/[H^+]$) vs (k_{obs}) at different temperatures (table 3).

The k_1 results represent a rate of water exchange with water molecule in solvent, that is very low rate. However, k_2 path is greater by many folder of magnitude is resemble the rate of hydrolysis of water substitution reaction as shown in scheme (1). The activation energies for both paths

(k_1 & k_2) for the hydrolysis of the complex have been determined using Arrhenius equation:- $k = A e^{-E_a/RT}$. Also, enthalpies and entropies of

activation have been calculated using Eyring equation :- $k = (k_b T/h) e^{\Delta S^*/R} \cdot e^{-\Delta H^*/RT}$. The activation parameters are tabulated in table(4).

Table (3) Values of the calculated rate constants (k_1 & k_2) at different temperatures.

Temp. °C	k_1 (min^{-1}) (slope)	k_2 (min^{-1}) (intercept)
30	7×10^{-8}	0.0317
35	7.5×10^{-8}	0.0614
40	1×10^{-7}	0.0811
45	1.5×10^{-7}	0.154
50	2×10^{-7}	0.2511
55	2.5×10^{-7}	0.3854

Scheme (1): Schematic diagram explaining the suggested mechanism of the hydrolysis of $\text{trans-Cr(ox)}_2(\text{H}_2\text{O})_2^-$.

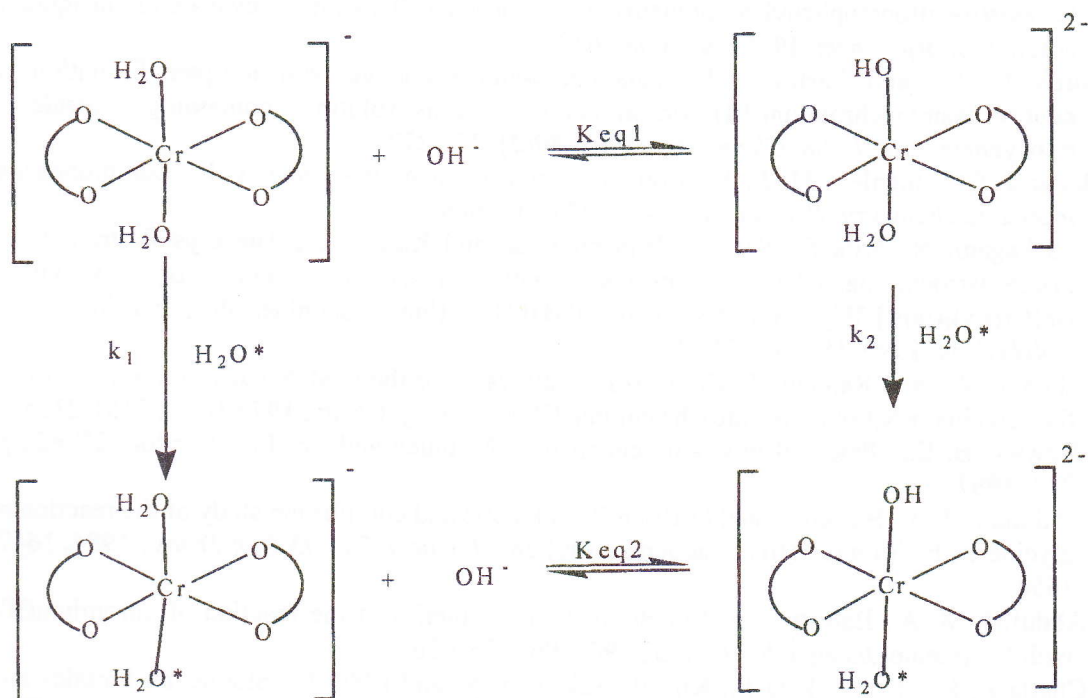


Table (4) Activation parameters for the hydrolysis of Trans- $\text{K}[\text{Cr(ox)}_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ for both (k_1 & k_2).

Reaction rate	E_a^* (KJ/mol)	ΔH^* (KJ/mol)	ΔS^* (J/mol)
Path 1	45.77 ± 3.89	43.15 ± 3.89	-240.6 ± 11.63
Path 2	81.21 ± 2.03	78.59 ± 2.03	-13.82 ± 4.52

Conclusions

The above values are in a good agreement with that reported by Kallen and Hamm for the anation of {Cis-[Cr(ox)₂(H₂O)₂]} with oxalate ion. Some other anation reactions of Cr(III) complexes have nearly the same values of activation parameters. For example anation of cis-equatorial-[Cr(S-pdtra)(Him)]⁰, were [S-pdtra = (S)-propylenediaminetriacetate][12], and the

acid hydrolysis of Trans-K[Cr(ox)₂(py)₃COOEt]₂ in aqueous media[13].

Therefore, we conclude two reactions of starting compounds present in solution at a pHs range (4 - 7) and selecting appropriate experimental condition is important in dealing with the complex as starting reaction species for the synthesis of other substituted complexes.

References

1. John B. V., The bioinorganic chemistry of chromium(III), *Polyhedron*, **2001**, 20, 1-26.
2. Cotton F. A. and Wilkinson G., Advanced inorganic chemistry, comprehensive text, *John Wiley and sons*, New York, **1972**, 4th edn., 727-730.
3. Fleischer E. B. and Krishnamurthy M., Substitutionally labile chromium(III), *J. Am. Chem. Soc.* **1971**, 93, 3784-3786.
4. Ashley K., Leipoldt J., and Joshi V., Kinetic and equilibrium study of the reaction of (meso-tetrakis(p-sulfonatophenyl)porphinato) diaquochromate(III) with thiocyanate ion in aqueous solution, *Inorg. Chem.* **1980**, 19, 1608-1612
5. Duffy N. V., and Earley J. E., Anation, water exchange, and ion-pair formation of aquopentaamminechromium(III) ion in acidic aqueous solutions containing chloride or thiocyanate ions, *J. Am. Chem. Soc.*, **1967**, 89(2), 272-277.
6. Bailar J. C., Emenleus H. J., Sir Ronald N. and Troman-Dickenson A. F., Comprehensive inorganic chemistry, *Pergamon press.*, **1973**, 664-688.
7. Sakagami N., Kita E., Kita P., Winsniewska, and Kaizaki S., The crystal structure of bis(oxalato)chromate(III) complexes with histamine and B₆ Vitamine: Na[Cr(ox)₂(hm)].3H₂O and Na[Cr(ox)₂(PM)].H₂O (hm, histamine; PM, pyridoxamine), *Polyhedron*, **1999**, 18, 2001-2007.
8. Kallen T. W., and Randall H., Competitive pathways for the oxalate substitution reaction of the (glycinato-N,O)bis(oxalato)chromium(III) ion, *Inorg. Chem.*, **1979**, 18(8), 2151-2155.
9. Dawson B. E., "Practical inorganic chemistry", Methuen and Co. Ltd, London, 2nd ed., p-214, **1967**.
10. Abdullah M. A., Barrett J., and O'Brien P., A kinetic and equilibrium study of the reaction of glycine with chromium(III) in aqueous solution., *J. Chem. Soc. Dalton Trans.*, **1984**, 1647-1650.
11. Abdullah M. A., Barrett J., and O'Brien P., The kinetics of the reaction of chromium(III) with L-cysteine, *Inorg. Chimi. Acta.*, **1985**, 96, L35-L36.
12. Chatla J., Kaizaki S., Kita E., Kita P., Sakagami N. and Eldik R., Studies on kinetics and mechanism of imidazole substitution from cis-equatorial-[Cr(S-pdtra)(Him)]⁰ complex in acidic and alkaline aqueous solutions [S-pdtra = (S)-propylenediaminetriacetate], *J. Chem. Soc., Dalton Trans.*, **1999**, 91-95.
13. Yormah T. B. R., Fode D. V. A. and Kormoh M. K., Kinetics of the hydrolysis of Potassium trans- dioxalato bis(ethylnicotinate)chromium(III), *AJST*, **2002**, 3(1), 108-112.

كائىنېتېكى ئاۋەشېيۈنەۋەي $\text{trans-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$

محمد علي عبدالله، بهختيار كمال عزيز

كولېجى زانست / زانكۆي سۇلەيمانى / ھەرئىمى كوردستان - عىراق

پوختە

ئەم توۋرۇنەۋەيەدا كائىنېتېكى ئاۋەشېيۈنەۋەي ناۋۇزى $\text{trans-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ پىشكۇرا ئە ئاۋەندى ناۋى دا (تۋانى ھایدروژىنى ۴، ۵، ۶، ۷، ۸، ۹، ۱۰، ۱۱، ۱۲) ۋە (ھىزى ئايۋنى ۰، ۴ مولار NaNO_3). خىرايى شى بوۋنەۋەكە بەندە ئەسەر ترشېتى ئاۋەندەكە ۋە خىرايىبەكە بە رېكى زىاد دەكات ئەگەن $[\text{H}^+]^{-1}$. جىگىرە چالاككە رەكەنى ئەم كارلىكە برىتىن ئە ($E_{a2} = 81.21$ ۋە ($E_a = 45.77 \text{ kJ mol}^{-1}$, $\Delta H^\ddagger = 43.15 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -240 \text{ J mol}^{-1}$) جىگىرە كەنى خىرايى كارلىكە كانى دەستمان ($\Delta H^\ddagger_2 = 78.59 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger_2 = -13.82 \text{ J mol}^{-1}$). جىگىرە كەنى خىرايى كارلىكە كەنى دەستمان ۋە Hamm ۋە Kallen دەستمان كەۋتۈە بۇ كارلىكى جىگىرەنەۋەي $[\text{Cis-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^{-1}$.

دراسة حركية التحلل المائي للمعقد $\text{Trans-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$

محمد علي عبدالله، بهختيار كمال عزيز

كلية العلوم / جامعة السليمانية / اقليم كوردستان - العراق

الخلاصة

تم دراسة حركية تحلل المعقد $\text{Trans-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ في الوسط المائي ذو الأس الهيدروجيني (۷، ۸، ۹، ۱۰، ۱۱، ۱۲) و ذو قوة أيونية ($\mu = 0.4 \text{ NaNO}_3$). وجد بان سرعة التحلل تعتمد الأس الهيدروجيني و تزداد السرعة بشكل خطي مع $[\text{H}^+]^{-1}$. ثوابت التنشيط للتفاعل هي ($E_{a2} = 81.21$ كيلو جول.مول⁻¹ و ($E_{a1} = 45.77$ كيلو جول.مول⁻¹ و $\Delta H^\ddagger_1 = 43.15$ كيلو جول.مول⁻¹ و $\Delta S^\ddagger_1 = -240$ جول.مول⁻¹) و ($E_{a2} = 81.21$ كيلو جول.مول⁻¹ و $\Delta H^\ddagger_2 = 78.59$ كيلو جول.مول⁻¹ و $\Delta S^\ddagger_2 = -13.82$ جول.مول⁻¹). ثوابت السرعة المستحصلة عمليا تتناسب مع القيم المستحصلة عليها من قبل (كالن و هام) لتفاعلات التعويض بالانيونات للمعقد $\{\text{Cis-K}[\text{Cr}(\text{ox})_2(\text{H}_2\text{O})_2]^{-1}\}$.