

Kinetics and Mechanism of Acid Catalysed Dissociation of some Octahedral Complexes of Cobalt(III) and Chromium(III)

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Summary

The kinetics of dissociation of glycinepentaamminecobalt(III) and tetraaquomonoacetylacetonatochromium(III) ions in moderately strong perchloric acid media have been investigated spectrophotometrically. From the dependence of the rate on various acidity functions and the observed isokinetic and free energy relationships, both the complexes appear to react by an associative process involving interaction of the conjugate acid form of the substrate complex and H_3O^+ .

Introduction

Investigations carried out earlier⁽¹⁻³⁾ on the acid catalysed dissociation of metal complexes have corroborated the usefulness of an analysis of the rate dependence of such a reaction on acid concentration and different acidity functions in elucidating of the intricate mechanism. In particular, insight on the role of the incoming water molecule in the transition state of the process is obtained. To test the generality of the observation, studies on several other systems are in progress and the results of investigations on the dissociation of the glycinepentaamminecobalt(III) ion into the aquopentaamminecobalt(III) ion and of tetraaquomonoacetylacetonatochromium(III) ion into the hexaaquochromium(III) ion in moderately strong perchloric acid media are reported here.

Results and Discussion

Under the experimental conditions the $[\text{Co}(\text{NH}_3)_5(\text{glyH})]^{3+}$ ion aquates quantitatively to $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$. Thus the visible spectrum of a solution containing $[\text{Co}(\text{NH}_3)_5(\text{glyH})]^{3+}$ (0.002 M) in 1.0–5.0 M HClO_4 at 80° gradually changed with time and finally became identical to that of an aqueous solution of $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ of the same molar concentration⁽⁴⁾ and suffered no significant further change. Similarly, $[\text{Cr}(\text{acac})(\text{OH}_2)_4]^{2+}$ aquates to $[\text{Cr}(\text{OH}_2)_6]^{3+}$ under the experimental conditions, as corroborated by earlier report⁽⁵⁾.

Also under the experimental conditions, the pseudo first order rate constants (k_{obs}) increased for both the complexes in a nonlinear fashion as the HClO_4 concentration increased (see Figure 1). The Zucker-Hammett plots⁽⁶⁾ of $\log k_{\text{obs}}$ vs. $\log [\text{HClO}_4]$, as also the alternative Zucker-Hammett plots⁽⁶⁾ of $\log k_{\text{obs}}$ vs. $-\text{H}_0$ ⁽⁷⁾, are all good straight lines for both the complexes, however the slopes (see Table 1) of these lines are not diagnostic of the mechanism⁽¹⁻³⁾. The plots of $\{\log k_{\text{obs}} + \text{H}_0\}$ vs. $-\log a_{\text{H}_2\text{O}}$ (slope = ω ⁽⁸⁾) as also the plots of $\{\log k_{\text{obs}} + \text{H}_0\}$ vs. $\log \{[\text{HClO}_4] + \text{H}_0\}$ (slope = ϕ ⁽⁹⁾) for both the complexes are good straight lines with correlation coefficients of ca. 0.998. The slopes of these lines, as evaluated by the least squares method (see Table 1), indicates an associative activation for both complexes in the formation of the transition state

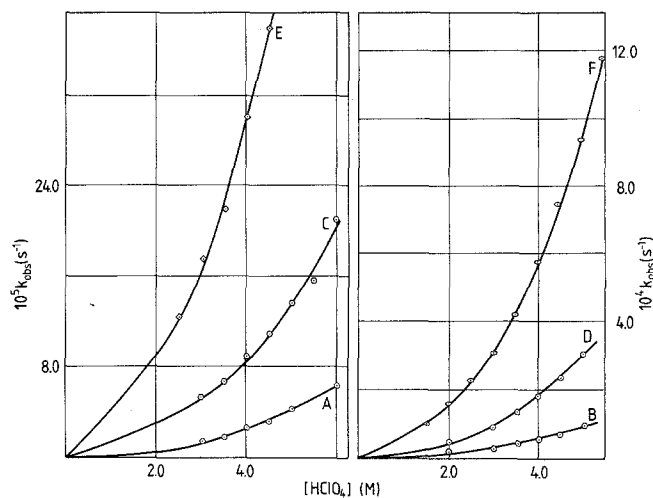


Figure 1. k_{obs} vs. $[\text{HClO}_4]$ plot. (A), (C), (E), for $[\text{Cr}(\text{acac})(\text{OH}_2)_4]^{2+}$ (0.005 M) at 70°, 80°, and 90° respectively; (B), (D), (F), for $[\text{Co}(\text{NH}_3)_5(\text{glyH})]^{3+}$ (0.002 M) at 60°, 70°, and 80° respectively.

involving the conjugate acid form of the complex and H_3O^+ as the interacting species⁽¹⁾.

A plot of $\log k_{\text{obs}}$ for the Co^{III} complex vs. $\log k_{\text{obs}}$ for the Cr^{III} complex at different acid concentrations is linear with a slope of 1.2 (see Figure 2), which suggests the operation of similar mechanism in both the cases.

The activation parameters, ΔH^\ddagger and ΔS^\ddagger , have been evaluated as usual using the Eyring equation in the appropriate form⁽¹⁾ and from k_{obs} values at three different temperatures (60°, 70°, 80° for the Co^{III} complex, and at 70°, 80°, and 90°

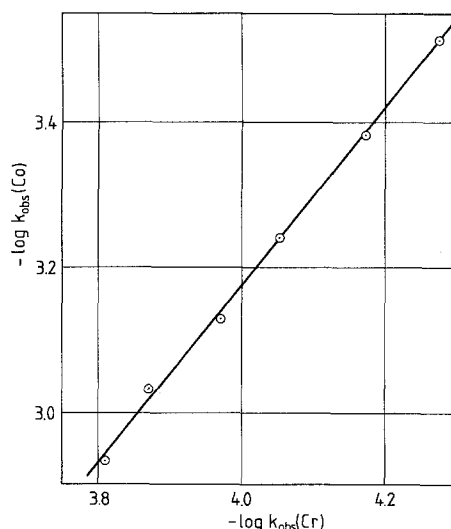


Figure 2. $\log k_{\text{obs}}$ for the Co^{III} complex vs. $\log k_{\text{obs}}$ for the Cr^{III} complex. Temp., 80°; $[\text{HClO}_4]$: (1), 3.0 M; (2), 3.5 M; (3), 4.0 M; (4), 4.5 M; (5), 5.0 M; (6), 5.5 M.

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Table 1. Correlation of the rate constants with different acidity functions

Temp. (°)	Slope of Zucker-Hammett plot ⁽⁶⁾		Slope of the alternative Zucker-Hammett plot ⁽⁶⁾		$\phi^{(8)}$		$\phi^{(9)}$	
	Co ^{III}	Cr ^{III}	Co ^{III}	Cr ^{III}	Co ^{III}	Cr ^{III}	Co ^{III}	Cr ^{III}
60	1.9	—	0.48	—	3.9	—	0.64	—
70	1.9	2.0	0.48	0.45	4.0	3.9	0.65	0.76
80	1.9	2.0	0.47	0.44	3.9	4.1	0.67	0.78
90	—	1.9	—	0.48	—	4.3	—	0.70

for the somewhat slower reacting Cr^{III} complex) under otherwise similar conditions. The average of the least square values for these parameters, evaluated from the k_{obs} values, in different concentrations of HClO₄ (2.0, 3.0, 4.0 or 5.0 M for the Co^{III} complex, and 3.0, 3.5, 4.0 or 4.5 M for the Cr^{III} complex) are given below:

	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{JK}^{-1}\text{mol}^{-1}$
Cr ^{III}	123.7 ± 0.4	13.4 ± 0.4
Co ^{III}	111.2 ± 0.8	-7.9 ± 0.8

In conformity with the conclusion regarding the mechanism of dissociation in the present cases, a linear correlation between ΔH^\ddagger and ΔS^\ddagger values for these two complexes with those for the acid catalysed dissociation of [Cr(acac)₂(OH₂)₂]⁺⁽¹⁰⁾, [Cr(acac)₃]⁽⁵⁾, [Cr(ox)(OH₂)₄]⁺⁽¹⁾ and [Cr(mal)(OH₂)₄]⁺⁽¹⁾, for which similar dissociation mechanisms have been established previously, has been observed (see Figure 3).

It is seen that the ΔH^\ddagger value for [Cr(acac)(OH₂)₄]²⁺ is higher than that for the acid catalysed dissociation of [Cr(acac)₂(OH₂)₂]⁺⁽¹⁰⁾ which in turn is higher than ΔH^\ddagger for [Cr(acac)₃]⁽⁵⁾; this is the kind of general behaviour observed in many systems and is possibly due to an increase in the metal-ligand bond strength with increasing effective positive charge on the complex⁽¹⁰⁾.

Saito *et al.*⁽¹¹⁾ previously studied the reaction of the [Co(NH₃)₅(glyH)]³⁺ complex over a limited and much lower range of HClO₄ concentrations. In general, we find their data to be consistent with ours as regards the acid catalysis; but in the absence of any evidence, these authors were noncommittal as regards the mechanism of the process, whether associative or dissociative. The present studies suggest the operation of an associative mechanism involving attack of the conjugate acid form on the complex by H₃O⁺, which implies that the solvent

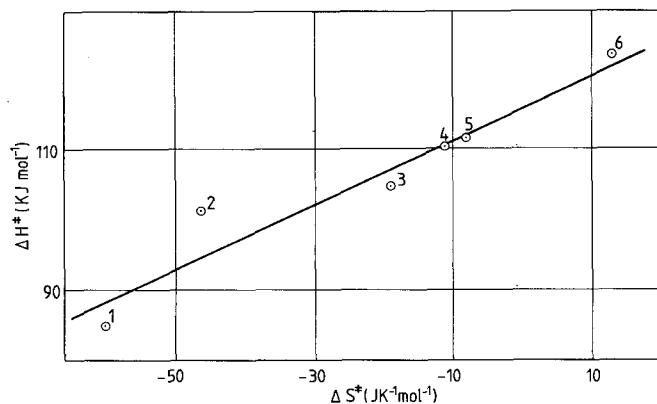


Figure 3. ΔH^\ddagger vs. ΔS^\ddagger plot for the acid catalysed dissociation of (1), Cr(acac)₃; (2), [Cr(ox)(OH₂)₄]⁺; (3), [Cr(mal)(OH₂)₄]⁺; (4), [Cr(acac)₂(OH₂)₂]⁺; (5), [Co(NH₃)₅(glyH)]³⁺; (6), [Cr(acac)(OH₂)₄]²⁺.

in addition to its function as a nucleophile also acts as a proton transfer agent⁽¹⁾.

It is known that dissociation of a metal-carboxylato complex in aqueous solution may involve M–O or C–O bond fission, a point which can only be settled convincingly by making use of tracer studies using labelled oxygen. In fact, for the aquation of [Co(NH₃)₅(OAc)]²⁺ in acidic media such evidence has been furnished in support of Co–O bond fission^(12,13), which has also been inferred by others⁽¹⁴⁾. Similarly, for the aquation of *trans*-[Co(en)₂(OAc)₂]⁺, Co–O bond fission has also logically been postulated⁽¹⁵⁾ since the reaction goes with stereochemical change, a fact which rules out C–O fission. It is therefore likely that aquation of the glycinepentaamminecobalt(III) complex also proceeds by Co–O bond fission. In fact, the dissociation of tris(glycinato)chromium(III) is also reported to take place by Cr–O bond breaking⁽¹⁶⁾. The ΔH^\ddagger value (111.2 kJ mol⁻¹) for the aquation of the [Co(NH₃)₅(glyH)]³⁺ is comparable to that for the aquation of [Co(NH₃)₅(OAc)]²⁺ ($\Delta H^\ddagger = 104.5$ kJ mol⁻¹)⁽¹⁴⁾ and both are much higher than that of the [Co(NH₃)₅(OCO₂)]⁺ ($\Delta H^\ddagger = 71.5$ kJ mol⁻¹)⁽¹⁷⁾ which aquates by the C–O bond fission process.

Much experimental evidence has accumulated in literature that in the majority of cases the ligand replacement reactions of cationic complexes of cobalt(III) involving Co–ligand bond fission occurs by a dissociative mechanism (I_d), while the corresponding reactions of chromium(III) complexes are mostly associative (I_a) in character. Most of the earlier results are well documented in several reports and reviews⁽¹⁸⁻²²⁾. However, departure from these general trends are well-known. Thus, the replacement of S₂O₃²⁻ in [Co(NH₃)₅(S₂O₃)]⁺ by H₂O, NH₃, Cl⁻ and OH⁻ occurs by an associative process^(23,24), and the aquation of *cis*-[Co(en)₂(L)]²⁺ occurs by a dissociative process when L = NH₃, MeNH₂, PhNH₂, *etc.*, but by an associative process when L = pyridine⁽²⁵⁾. Also, the replacement of H₂O in [Cr(NH₃)₅(H₂O)]³⁺ occurs by a dissociative process (I_d)⁽²⁶⁾ in contrast to [Cr(H₂O)₆]³⁺ which reacts associatively (I_a). In the present work an associative mechanism for the aquation of [Co(NH₃)₅(OOCCH₂NH₃)]³⁺ in acid media has been established, while it is believed that [Co(NH₃)₅(OAc)]²⁺ aquates by a dissociative mechanism, the former differing from the latter in having a significant degree of Co^{III}–OH₂ bond formation in the transition state. This is not unlikely since the –NH₃⁺ end group of the O-bonded glycine in the cobalt(III) complex, being electron-withdrawing, is likely to deplete the electron density on the Co^{III} centre sufficiently to facilitate nucleophilic attack thus favouring an associative process. Since the pK_a value of [Co(NH₃)₅(glyH)]³⁺ is known to be *ca.* 8.5⁽²⁷⁾ the complex exists essentially in this form under the experimental conditions with virtually no [Co(NH₃)₅(gly)]²⁺ present. The comparable ΔH^\ddagger values for the aquations of [Co(NH₃)₅(OAc)]²⁺ and [Co(NH₃)₅(OOCH₂NH₃)]³⁺ (*loc. cit.*) are possibly suggestive of an interchange process (I_d and I_a respectively in the two cases) where the Co–O bond fission chiefly contributes to the ΔH^\ddagger term.

Experimental

Materials

Pure glycinepentaamminecobalt(III) perchlorate monohydrate, $[\text{Co}(\text{NH}_3)_5(\text{O}_2\text{CCH}_2\text{NH}_3)](\text{ClO}_4)_3 \cdot \text{H}_2\text{O}$ was synthesised by a known method⁽²⁸⁾ and its purity was checked by its d-d spectrum⁽²⁸⁾ ($\epsilon_{\text{max}}^{500\text{nm}} = 69$). A pure solution of tetraaquomonoacetylacetonatochromium(III) perchlorate, $[\text{Cr}(\text{C}_4\text{H}_7\text{O}_2)(\text{OH}_2)_4](\text{ClO}_4)_2$ was prepared based on the results of the previously reported kinetic studies⁽⁵⁾ on the dissociation of $\text{Cr}(\text{acac})_3$. An aqueous suspension of 0.02 M $\text{Cr}(\text{acac})_3$ in 0.4 M HClO_4 (500 cm³) was digested on a water bath in a stoppered vessel until all the complex dissolved and the absorbance features of the solution (1 cm³ diluted to 10 cm³) closely resembled that reported⁽⁵⁾ for $[\text{Cr}(\text{acac})(\text{OH}_2)_4]^{2+}$. The solution at this stage was cooled, extracted several times with distilled Et₂O to remove free $\text{MeCOCH}_2\text{COME}$ and stored in an amber bottle in a refrigerator. The purity of the solution was checked by analysis. Its chromium content was estimated spectrophotometrically at 372 nm after oxidation to chromate(VI) by alkaline H_2O_2 ⁽²⁹⁾. $\text{MeCOCH}_2\text{COME}$ was estimated volumetrically by Ce^{IV} sulphate⁽³⁰⁾. Found: Cr: $\text{MeCOCH}_2\text{COME} = 1 : 1.02$. The free acid in the solution was estimated by a standard procedure⁽¹⁰⁾ using a strong cation exchange resin (Dowex 50W-X8) in its hydrogen form.

All other chemicals used were of reagent grade.

Methods

Spectral observations indicated that glycinepentaamminecobalt(III) and tetraaquomonoacetylacetonatochromium(III) ions aquate smoothly in moderately strong HClO_4 at conveniently measurable rates into aquopentaamminecobalt(III) ion and hexaaquochromium(III) ion respectively. The rates of these dissociation reactions in a large excess of HClO_4 (1.5–6.0 M) were followed spectrophotometrically by a sample quenching technique at appropriate wavelengths where the absorbance difference between the starting complex and the aquated product is sufficiently large [500 nm for the Co^{III} complex and 560 nm for the Cr^{III} complex]. The pseudo-first-order rate constants (k_{obs}) were evaluated graphically from $-\log(A_t - A_\infty)/(A_0 - A_\infty)$ vs. time (t) plots as usual, using the A_∞ value expected for quantitative formation of the aquated product, viz. $[\text{Co}(\text{NH}_3)_5(\text{OH}_2)]^{3+}$ from $[\text{Co}(\text{NH}_3)_5(\text{glyH})]^{3+}$ and $[\text{Cr}(\text{OH}_2)_6]^{3+}$ from $[\text{Cr}(\text{acac})(\text{OH}_2)_4]^{2+}$. All absorbance measurements were made

using a Carl-Zeiss spectrophotometer (VSU-2P) against water blank using 2 cm quartz cells.

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