Kinetics and mechanistic studies of the dissociation of anthranilic-diacetato-2,2′-dipyridyl chromium (III) dihydrated in acidic media

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Abstract : Acid catalysed dissociation of anthranilic-diacetato-2,2′-dipyridyl chromium (III) dihydrated [Cr(atda)(dipyridyl)] hydrate has been studied kinetically in aqueous perchloric media over a temperature range 50-70º C, under these experimental conditions, the reaction occurs by acid assisted path only. According to the rate law: Rate = k_H^+ [Complex][H^+], where k_H^+ is the rate constant for acid assisted path. Analysis of the rate data corresponding to k_H^+ path suggests that the reaction is first order in [$HClO_4$] for the title complex and the chelate ring in 2,2′-dipyridyl complex suffers one ended dissociation accompanied by protonation of the released end of the basic ligand which leads to a faster rupture of the remaining metal ligand bond leading to the complex loss of the ligand.

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Introduction

Not much data is available on the mechanistic studies of the acid catalysed dissociation of chromium (III) complexes containing acetyl acetone, 2,2′-dipyridyl and 1:10 phenanthroline as the chelating ligands. It is well known that metal acetylacetone ring possess quasi aromatic character which in turn reflects the exceptional stability and relative inertness [1]. It is found that the chelating in metal acetylacetone, 2,2′-dipyridyl and 1:10 phenanthroline under go many reactions typical of aromatic systems. The hydrogen at the central position in these chelate rings can be substituted by a variety of electrophilic reagents [2]. Halogenation [3-5], nitration [6-9] and other reactions [10-11] take place without rupture of chelate ring.

Shephard et al. [12] reported the acid catalyzed dissociation of coordinated acetyl acetone (acac) from mixed ligand chromium-chelate Cr (edda) acac, where edda is ethylene diamine diaacetic acid. The presence of uncoordinated pendant carboxylatye arm in the former complex has been found to accelerate the rate of release of coordinate acac by a factor of 10^3 compared with the usually observed Cr $(acac)_3$ [13]. However, a normal rate of release of acetylacetone is observed from Cr(edda)(acac).

Balzani et al. [11] studied the kinetics of dissociation of 2-2′-dipyridyl from tris,2-2′-dipyridyl chromium (III) chelate. The dissociation is shown to be base catalyzed. They further suggested that four mechanisms are consistent with the observed kinetic data, dissociative (D), associative (A), Gillard's General mechanism (GGM) and ion-pair mechanism (I. P.).

To examine the relative reactivity of aromatic amino acids and dipyridyl in coordinating sphere towards acid solution, it seemed worth while to study the dissociation of [Cr(atda)(dipyridyl)] $2H_2O$ complex using acid medium.

Experimental studies

Material and reagent

Anthranilic diacetatodiaquo chromium (III) tri-hydrate i.e. [Cr(atda)(H$_2$O)$_2$] $3H_2O$ and anthranilic diacetato, 2,2′-dipyridyl chromium (III) dihydrated i.e. [Cr(atda)(dipy)] $2H_2O$ were prepared following the method described in the literature [15]. The purity of the samples were checked by elemental analysis. Found: C, 33.80; N, 3.52; H, 4.67 %. Calculated for [Cr(atda)(H$_2$O)] $3H_2O$: C, 33.6; N, 3.57; H, 4.57%. Found: C, 51.17; N, 8.40; H, 4.21%. Calculated for [Cr(C$_{11}$H$_8$NO$_6$)(C$_{10}$H$_8$N$_2$)]2H$_2$O: C, 51.01; N, 8.5; H, 4.05%

The d-d spectrum ($\lambda_{max.} = 520$ nm, $\varepsilon_m = 67.8$, $\lambda_{max.} = 391$ nm, $\varepsilon_m = 142.0$) matched with the reported data.

The chemicals used were reagent grade purity or prepared in the pure state by suitable methods. Sodium perchlorate was used to adjust the ionic strength of the medium.

Kinetic measurements

The aquation rates were monitored spectro-photo-metrically using Shimadzu UV-visible spectrophotometer. Spectral examination of the experimental solution revealed that under

the conditions of acidity employed for the study, the metal – dipyridyl bond was found to undergo dissociation in preference to aromatic amino acid, atda leading to the formation of diaquo product, i.e. [Cr(atda)(H$_2$O)$_2$]. Presence of liberated dipyridyl as a result of aquation was confirmed by its characteristic spectrum in the UV- region as well as its reaction with Fe^{2+} ion. The enhanced kinetic stability exhibited by aromatic amino acid can be explained due to the presence of more number of chelate rings offered by the ligated amino-acid in comparison to only one five membered chelate ring offered by dipyridyl. The stability of the diaquo complex under experimental conditions was revealed from the fact that the absorption spectra of the diaquo complex in 0.02 to 0.2 M HClO$_4$ at 70° C remained unchanged even after several hours. The above findings prove that liberation of dipyridyl during aquation is not complicated by the decomposition of diaquo-species. The course of the aquation reaction in dilute perchloric acid (0.02 to 0.20 M) at an ionic strength of 1.0 M was followed by observing decrease in absorbance at 391 nm, where the molar extinction coefficient of the reacting and product complex differ appreciably using a sample quenching technique [15]. The absorbance of the solutions at the end of the reactions were found to be in agreement with those of the solutions containing isolated diaquo (i.e. [Cr(atda)(H$_2$O)$_2$] 3H$_2$O) complex and dipyridyl (monoprotoated) ion. This indicated the absence of reverse anation reaction. Under the experimental conditions pseudo first order rate constants; K$_{obs.}$ For each experiment were evaluated from $\log \dfrac{A_0 - A_\infty}{A_t - A_\infty}$ versus time (t) plots, using for A$_\infty$, the calculated values of the absorbance corresponding to complete transformation of the reacting complex to the product complex.

Results and discussion

The values of $k_{obs.}$ (pseudo first order rate constants) were determined at 50.0 ± 0.1, 60.0 ± 0.1 and 70.0 ± 0.1 °C for acid concentration 0.02 to 0.2 M at an ionic strength of 1.0 M (Table 1). The pseudo first order rate constants ($k_{obs.}$) increase linearly with increasing acid concentration. The results obtained show that for the acid-concentration (perchloric acid) range, the replacement of dipyridyl ligand from the coordination sphere of [Cr(atda)(dipy)] by di-aquo follow pseudo first order kinetics.

$$[\text{Cr(atda)(dipy)}] \xrightarrow[H^+, H_2O]{k_{Obs.}} [\text{Cr(atda)}(H_2O)_2] + \text{Hdipy}^+$$
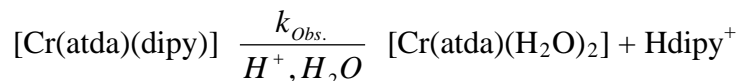
The results show that the reaction is first order in [HClO$_4$] for the title complex, since the straight lines in all cases with in experimental error pass through origin. There is no detectable acid independent dissociation reaction. The second order rate k_{H^+} determined from the slopes of the straight lines at different temperatures, together with enthalpy and entropy of activation are given in Table 1.

On the basis of the experimental results, the mechanism shown in Figure 1 is suggested. The rates are dependent on acid concentration. This is due to the fact that the chelate ring in 2,2′-dipyridyl complex may suffer one ended dissociation accompanied by protonation of the released end of the basic ligand which leads to a faster rupture of the remaining metal- ligand bond leading to complete loss of the ligand.

On the basis of above scheme and using both steady state treatment on the concentration of the coordinated intermediate and the assumptions that $k_2 [H^+] \langle\langle k_{-1}$ at low acid concentration used for the present investigation.

The expression,

$$k_{obs.} = \frac{k_1 k_2 [H^+]}{k_{-1} + k_2 [H^+]}$$

reduced to our experimental form, given by,

$$k_{obs.} = \frac{k_1 k_2 [H^+]}{k_{-1}} \approx k_{H+} [H^+]$$

$$\text{Where, } k_{H+} = \frac{k_1 k_2}{k_{-1}}$$

The mechanism shown in Figure 1 suggests a very general kind of behavior that is possible for bi or multi- dentate ligands. If such a ligand is removed by a dissociative mechanism, it is very likely that this occurs by steps, such a step would usually be easily reversible because the coordinated atom remains in the vicinity of the vacated spot in the metal atom coordination space. It can be prevented from reversing by either an electrophile groups (e.g. H^+) reacting with the exposed metal atom. The overall dissociation would than be accelerated.

A dissociative mechanism will thus be subjected to both base and acid catalysis [16]. Acid catalysis was experimentally found for $Ni(dipy)_3^{2+}$ [17], $Fe(dipy)_3^{2+}$ [17] and $[Cr(en)_2OX]^+$ ions involving chromium-nitrogen bond rupture, where as base- hydrolysis also involving chromium nitrogen bond rupture was observed for $Ni(dipy)_3^{3+}$ [11,17]

Davies et al. [17] suggested from their investigation on the aquation of $[Cr(en)_2(OX)]^+$ ion, chromium-nitrogen bond rupture is facilitated at low acid concentration range (i.e. 0.10 to 1.0 M) and chromium-oxygen bond breaking is facilitated at higher acid concentration range.

The activation parameters $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the present system (Table 2) are similar to other systems where metal-nitrogen bond breaking is involved. On the basis of similarity in activation parameters, it is concluded that the reaction proceeds by essentially a dissociative mechanism in which rupture of metal nitrogen bond is primarily important in the transition state.

The effect of ionic strength on the rate of dissociation of dipyridyl from [Cr(atda)(dipy)] complex was examined and it was found that observed rate constant ($k_{obs.}$) does not change with the change in ionic strength from 1.0 M to 0.1 M at 70° C as shown in Figure 2.

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Table 1. Rate data aquation of anthranilic diaceto, 2,2′-dipyridyl chromium (III) complex {[Complex] = 1x 10^{-3} M and $\lambda_{max.}$ = 391 nm }

[HClO$_4$] M	Ionic strength (μ) = 1.0 M, 10^5 k$_{obs.}$ sec-1			Ionic strength (μ) = 0.1 M, 10^5 k$_{obs.}$ sec-1
	50 ± 0.1 (°C)	60 ± 0.1 (°C)	70 ± 0.1 (°C)	70 ± 0.1 (°C)
0.02			1.04	1.01
0.03			1.52	1.5
0.04	0.34	0.70	2.23	2.21
0.05	0.38	1.02	2.82	2.77
0.06	0.41	1.18	3.22	3.2
0.08	0.43	1.34	4.38	4.36
0.10	0.64	1.78	5.89	5.85
0.12	0.73	2.07	7.10	
0.16	0.98	2.67	9.21	
0.18	1.05	3.33	10.17	
0.20	1.13	3.56	11.13	

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Table 2. Kinetic parameters for aquation of anthranilic diaceto, 2,2′-dipyridyl chromium (III) complex

Temperature (°C)	k_{H_+} ($M^{-1}sec^{-1}$)
50.0 ± 0.1	6.0×10^{-5}
60.0 ± 0.1	18.0×10^{-5}
70.0 ± 0.1	55.71×10^{-5}

$\Delta H^{\neq} = 23.76 \pm 0.5$ (Kcal/mol)

$\Delta S^{\neq} = -4.86 \pm 0.06$ (cal/deg. mol)

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Figure Captions:

Figure 1. Mechanism for dissociation of anthranilic-diacetato-2,2′-dipyridyl chromium (III) dehydrated.

Figure 2. Kinetic plots for the acid catalysed aquation of anthranilic-diacetato-2,2′-dipyridyl chromium (III) complex at 50 ± 0.1 (°C) (Series 1), 60 ± 0.1 (°C) (Series 2) and 70 ± 0.1 (°C) (Series 3) with ionic strength = 1.0M while 70 ± 0.1 (°C) (Series 4) with ionic strength = 0.1 M.
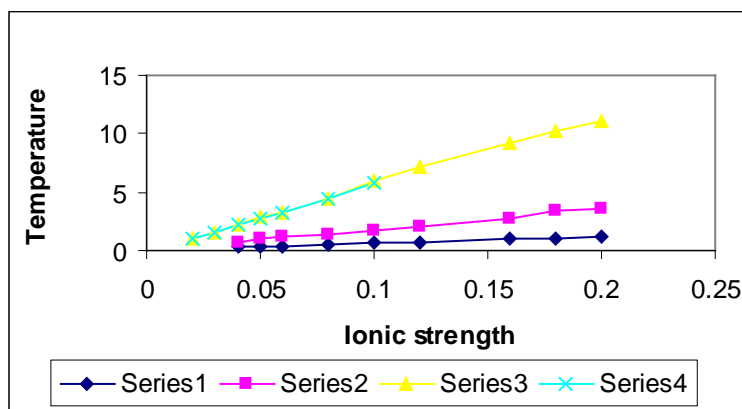

Figure 1

Figure 2