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Kinetics and Mechanism of Dissociation of (Acetylacetonato)[*N*-(*o*-carboxyphenyl)iminodiacetato]chromate(III) Ion in Acidic Media

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Acid-catalyzed dissociation of (acetylacetonato) [*N*-(*o*-carboxyphenyl) iminodiacetato]chromate(III) ion has been studied kinetically in aqueous perchloric acid media over a temperature range (60—80 °C). Under these conditions the reaction occurs by two concurrent paths according to the following rate law: Rate$=k_1$[complex]$+k_2$[complex][H$^+$], where k_1 and k_2 are the appropriate rate constants for the spontaneous and acid-catalyzed pathways, respectively Analysis of the rate data corresponding to the rate constants k_1 and k_2 suggests solvent assisted dissociation of the complex and its conjugate acid for the two paths, respectively, and that the opening of the chelate ring is rate determining.

The amino carboxylate ligands have donor groups similar to the more common amino acid residues. Hence the ligand substitution at chromium(III) in amino carboxylate environments have considerable physiological significance. Ogino[1)] and Sykes[2)] have suggested that the addition of a free $-CH_2COOH$, $-CH_2COO^-$, or $-CH_2CH_2OH$ in an associative intramolecular step is responsible for the kinetic lability of $[CrY(H_2O)]^n$ complexes towards the addition of unidentate X^- donor. Guardalabene *et al.*[3)] reported similar pendant group assistance for the acid-catalyzed aquation of the 2,4-pentanedionato chelate ligand (acac$^-$) from [Cr(hedta) (acac)]$^-$ (hedta: hydrogenethylenediamine-*N,N,N′,N′*-tetraacetate) whereas the acid-catalyzed aquation of [Cr(edda)(acac)] (edda: ethylenediamine *N,N*-diacetate) exhibited normal reactivity. In contrast to the extensive study of the acid-catalyzed dissociation of octahedral chromium(III) carboxylato chelates[4—7)], limited data exist for the corresponding *β*-diketonato[3,8,9)] complexes. It is well known[10)] that metal acetylacetone ring possesses quasi-aromatic character which in turn reflects their exceptional stability and relative inertness. A mixed ligand octahedral complex of chromium(III) with carboxymethyl derivative of anthranilic acid (*N*-(*o*-carboxyphenyl)iminodiacetic acid, H_3 atda) as aromatic amino acid and acetylacetone has been described in the literature.[11)] The kinetic studies of dissociation of the title complex appeared to be worthy of investigation for the following reasons:

(a) In order to examine the relative reactivity of aromatic amino acid and acetylacetone as coordinating ligand towards acid solution.

(b) Comparison of kinetic data of acac$^-$ release from Cr(tetradentateaminopolycarboxylate)(acac)$^-$ type complexes with and without pendant group.

Experimental

Materials and Reagents. Diaqua[*N*-(*o*-carboxyphenyl) iminodiacetato]chormium(III) trihydrate, Cr(atda) $(H_2O)_2\cdot 3H_2O$ and potassium (acetylacetonato)[*N*-(*o*-carboxyphenyl) iminodiacetato]chromate(III), K[Cr(atda)(acac)] were prepared following the method described in the literature.[11)] The purity of the sample was checked by elemental analysis.

Found: C, 33.80; N, 3.52; H, 4.67%. Calcd for $[Cr(C_{11}H_8NO_6)(H_2O)_2]\cdot 3H_2O$: C, 33.67; N, 3,57; H. 4.59%. Found: C, 43.70; N, 3.12; H, 3.43%. Calcd for $K[Cr(C_{11}H_8NO_6)(C_5H_7O_2)]$: C, 43.64; N, 3.18; H, 3.41%. The positions and intensities of the d-d bands corresponding to $^4A_{2g}\rightarrow{}^4T_{2g}$ and $^4A_{2g}\rightarrow{}^4T_{1g}$ transitions in a pseudo-octahedral ligand field for both the complexes matched very well with the reported data.[11)] Other chemicals used were of 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 spectrophotometrically using a Varian Superscan 3 and a Toshniwal UV-visible spectrophotometer. Spectral examination of the experimental solutions revealed that under the conditions of acidity employed for the study the metal acetylacetone bond was found to undergo dissociation in preference to aromatic amino acid, atda, leading to diaqua product, $[Cr(atda)(H_2O)_2]$. The enhanced kinetic stability exhibited by aromatic amino acid can be ascribed to the effect of presence of more number of chelate rings in ligated amino acid in comparison to only one six membered (acetylacetonato) metal ring. The course of the aquation reaction in dilute perchloric acid (0.02—0.2 mol dm^{-3}) at an ionic strength 1.0 mol dm^{-3} was followed by observing the decrease in absorbance at 400 nm, where the absorbances of the reacting complex and the product differ appreciably. To follow the reaction a solution containing requisite quantities of perchloric acid and sodium perchlorate (for adjustment of ionic strength to 1.0 mol dm^{-3}) was thermostatted at the experimental temperature. After attainment of thermal equilibrium, the requisite quantity of the complex, K[Cr(atda)(acac)], was added and the solution was thoroughly mixed and diluted to a definite volume with water thermostatted at the experimental temperature. An aliquot was immediately withdrawn from this reaction mixture using a pipette jacketed with ice to quench the reaction and its absorbance was measured at 400 nm. This was repeated at subsequent time intervals. The experimental conditions were so chosen that pseudo-first order rate law was applicable and plots of log $(A_0-A_\infty)/(A_t-A_\infty)$ *versus* time (t) were linear for at least three to four half-lives and passing through the origin with $A_t=A_\infty$ at $10t_{1/2}$. The preliminary spectral observation of the reacting solutions after digesting for at least ten half-lives agreed well with spectra of the corresponding diaqua product, $[Cr(atda)(H_2O)_2]$, indicating the absence of any complication due to reverse anation reaction of aqua complex.

Results and Discussions

Values of k_{obsd} (the first order rate constants) were determined at 50.0±0.1, 60.0±0.1, 70.0±0.1, and

TABLE 1. KINETIC PARAMETERS FOR AQUATION OF (ACETYLACETONATO)[*N*(*o*-CARBOXYPHENYL)-IMINODIACETATO]CHROMATE(III) ION ($\mu = 1.0\ \mathrm{mol\ dm^{-3}}$)

Temp/°C	$k_1/10^{-5}\ \mathrm{s^{-1}}$	$k_2/10^{-4}\ \mathrm{mol^{-1}\ dm^3\ s^{-1}}$
50.0±0.1	1.31±0.1	1.75±0.13
60.0±0.1	3.28±0.18	3.77±0.15
70.0±0.1	8.04±0.15	9.27±0.14
80.0±0.1	16.82±0.28	23.71±0.38
$\Delta H^{*}/\mathrm{kJ\ mol^{-1}}$	80.1±1.6	80.2± 4.1
$\Delta S^{*}/\mathrm{J\ K^{-1}\ mol^{-1}}$	−90.0±4.6	−71.6±11.3
	($\mu = 0.1\ \mathrm{mol\ dm^{-3}}$)	
70.0±0.1	7.98±0.28	8.15±0.43

80.0±0.1 °C, for acid concentration 0.02—0.2 mol dm^{-3} at an ionic strength 1.0 mol dm^{-3} and have been found to vary with acid concentration in a manner which suggests that the dissociation of the title complex proceeds in accordance with the following rate law:

$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][\mathrm{H^+}], \tag{1}$$

where k_1 stands for the first order rate constant for the uncatalyzed and k_2, second order rate constant describing the acid-catalyzed pathways, respectively. Using least squares method k_1 and k_2 values at different temperatures have been determined from the linear plot of k_{obsd} *versus* acid concentration (Fig. 1) and are listed in Table 1 along with the activation parameters ΔH^{*} and ΔS^{*} values evaluated using the Eyring equation. Sequence of changes consistent with the kinetic results are depicted below:

$$[\mathrm{Cr(atda)(acac)}]^- + \mathrm{H_2O} \xrightarrow[\text{slow}]{k_1} [\mathrm{Cr(atda)(\text{-}acac)(H_2O)}]^-$$

$$\Big\downarrow {\scriptstyle +\mathrm{H_2O}}\ \text{rapid}$$

$$[\mathrm{Cr(atda)(H_2O)_2}] + \mathrm{acac^-}$$

$$\mathrm{acac^-} + \mathrm{H^+} \xrightarrow{\text{fast}} \mathrm{acacH}$$

$$[\mathrm{Cr(atda)(acac)}]^+ + \mathrm{H^+} \overset{K}{\rightleftharpoons} \underset{\text{(conjugate acid)}}{[\mathrm{Cr(atda)(acacH^+)}]^-}$$

$$[\mathrm{Cr(atda)(acacH^+)}]^- \xrightarrow[+\mathrm{H_2O}]{k_2'} [\mathrm{Cr(atda)(\text{-}acacH)(H_2O)}]$$

$$\Big\downarrow {\scriptstyle +\mathrm{H_2O}}\ \text{rapid}$$

$$[\mathrm{Cr(atda)(H_2O)_2}] + \mathrm{acacH},$$

where –acac and –acacH stand for the ligand and its protonated form, respectively, functioning as monodentate ligand. The catalytic rate constant k_2 is related to k_2' and K by the relation

$$k_2 = \frac{Kk_2'}{1+K[\mathrm{H^+}]}, \tag{2}$$

under the present experimental conditions $K[\mathrm{H^+}] \ll 1$ as evident from the linearity of the plot of k_{obsd} *versus* [H$^+$] even at highest perchloric acid concentration. Hence Eq. 2 reduces to $k_2 = K\,k_2'$. The activation parameters corresponding to k_2 thus involve both rate constants and equilibrium constants. Guardalabene *et al.*[3] studied the acid-catalyzed aquation of Hacac from [Cr(hedta)(acac)]$^-$ and [Cr(edda)(acac)] complexes. An accelerated rate of about 10^3 relative to [Cr(acac)$_3$] is observed for [Cr(hedta)(acac)]$^-$ complex whereas normal behaviour is found for [Cr(edda) (acac)] system. The pendant group effect for labilizing the release of acetylacetone has been proposed to account for the 10^3 enhancement. In both the cases rupture of Cr–O bond has been proposed to take place in the transition state similar to what has been suggested for the [Cr(acac)$_3$] system.[8] Since the present system under investigation does not possess any pendant carboxylato group, as a result no intramolecular assistance is observed. Similarity in reactivity of the present system with those of [Cr(acac)$_3$] and [Cr(edda) (acac)] thus substantiates the influence of pendant group in enhancement of rate.

The magnitude and sign of the activation parameters corresponding to uncatalyzed and acid-catalyzed paths in the present system is found to be comparable with those reported for [Cr(acac)$_3$]. It is thus logical to conclude that the reactions corresponding to rate constants k_1 and k_2 respectively in the present system proceed by mechanisms identical to those operative in the [Cr(acac)$_3$] system where acid independent step is suggested to involves a simple dissociation of [Cr (atda) (acac)]$^-$ complex, while the acid-catalyzed path involve a dissociation of the conjugate acid formed by protonation in a rapid pre-equilibrium step. Both rate-determining dissociations for uncatalyzed and acid-catalyzed paths in the present system thus involve a one-ended dissociation of a acetylacetonato chelate ring with the simultaneous entry of a molecule of water into the coordination sphere of chromium(III), followed by the rupture of a second Cr–O bond of the unidentate functioning acetylacetone ligand in a much faster process with a simultaneous entry of another molecule of water leading to [Cr(atda) (H$_2$O)$_2$] product. Structural,[12] spectral,[13] and chemical evidence[14] suggests that orbitals of π symmetry are involved in extensive electron delocalization and pseudoaromaticity, within the planar six-membered chelate ring of metal acetylacetonato complex. This special bonding is reflected in its relative kinetic inertness. Cleavage of one of the metal–acetylacetone bond of the chelate ring would destroy the π conjugation thus facilitating the rupture of the second metal–O bond as suggested in the above scheme. The magnitude of the rate constant corresponding to acid-catalyzed path, k_2', can be estimated in the following manner. Linearity of the plots in Fig. 1 indicates $1 \gg K[\mathrm{H^+}]$ at [H$^+$]=0.2 mol dm^{-3}, leading to $K \ll 5$. Thus the value of k_2' is greater than $3.5\times10^{-5}\ \mathrm{s^{-1}}$ at 50.0 °C. In conformity with the proposed scheme, the rate constant corresponding to acid-catalyzed path is observed to be much higher than that of uncatalyzed process (Table 1). This can be ascribed to the fact that the acid-catalyzed path is suggested to involve the protonation of the chelated acetylacetone ligand thereby putting a formal positive charge on ligand oxygen atom .As

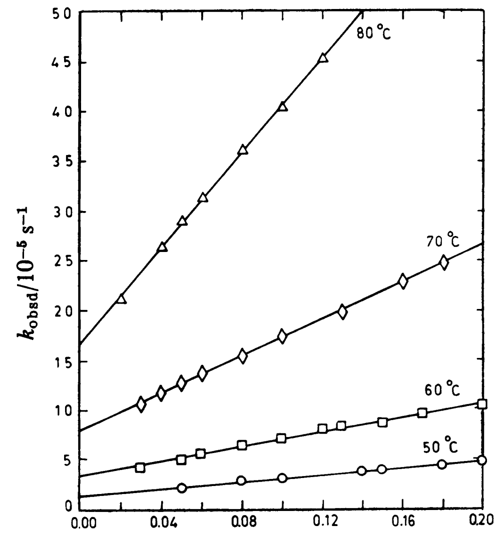
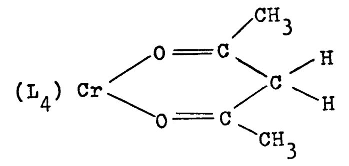
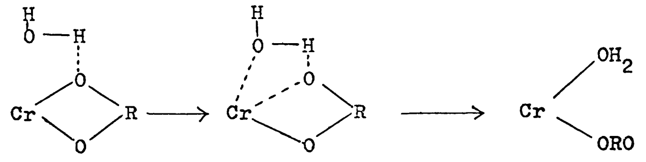


Fig. 1. Effect of acid concentration on k_{obsd} at different temperatures (Complex, 0.002 mol dm^{-3}; μ, 1.0 mol dm^{-3}).

a consequence of strong bonding between oxygen atom of the acetylacetone and H$^+$ ion in the protonated from of the complex (conjugate acid) further weakens the Cr–O bond and thus accounting for a greater lability for the fission of the bond as is indicated by the higher rate for the acid-catalyzed path. A similar trend has been observed in other acetylacetonato complexes of chromium(III).[4,8,9] Alternative pathways for acid catalysis may involve the association of the scavenging proton at the central carbon of the leaving Hacac giving rise to the following structure:



However, the above alternative scheme would leave keto groups as ligands which seems to be less probable.[15] In absence of conclusive evidence the alternative scheme cannot be excluded unambigously. The activation enthalpies corresponding to acid-catalyzed paths for [Cr(acac)$_3$], and [Cr(atda) (acac)]$^-$ are 20.2 kcal mol^{-1} and 19.2 kcal mol^{-1}, respectively. Comparable activation enthalpies clearly suggests that the total cost of bond adjustments is similar in two paths for Cr–O bond rupture. Similarity in activation parameters, ΔH^* and ΔS^* values (Table 1) for spontaneous and acid-catalyzed path seem to suggest that same type of mechanism is operative in the transition state for both the processes. As in the case of [Cr(acac)$_3$] system,[8] the entropy of activation corresponding to k_1 and k_2 in the present system has been found to be highly negative. The high negative ΔS^* values for k_1 and k_2 are compatible with processes in which participation of a molecule of water hydrogen bonded to ligand in the rate-determining step is important,[16] suggesting an assisted dissociative mechanism as depicted below, which also accounts for the low ΔH^* values:



(Transition state)

where ORO stands for acac or acacH as the case may be. As in the case of [Cr(acac)$_3$] system, the entropy of activation, ΔS^* corresponding to uncatalyzed path for the present system is observed to be more negative than that of acid-catalyzed path. The relatively less negative value of ΔS^* for the H$^+$ dependent path is evidently due to the highly negative ΔS^* term for the dissociation of the chromium(III)–ligand bond being partly compensated by the positive ΔS^* term (also contributing to the overall ΔS^* for k_2) expected for the protonation pre-equilibrium, since this will lead to release of water molecules from the solvation spheres of aqueous H$^+$ ion. The effect of ionic strength on the rate of aquation has been studied and the values of k_1 and k_2 evaluated from a plot of k_{obsd} *vs.* [HClO$_4$] are presented in Table 1. Table 1 reveals that under otherwise identical conditions the uncatalyzed rate constant remained unaffected by the variation of ionic strength of the medium in accordance with the proposed mechanism. In contrast to the expected trend the value of k_2 is found to decrease slightly with decrease in ionic strength of the medium the reason of which is not clear at the present moment.

References

1) H. Ogino, T. Watanabe, and N. Tanaka, *Inorg. Chem.*, **14**, 2093 (1975).
2) Y. Sulfab, R. S. Taylor, and A. G. Sykes, *Inorg. Chem.*, **15**, 2388 (1976).
3) J. Guardalabene, S. Gulnac, N. Keder, and R. E. Shepherd, *Inorg. Chem.*, **18**, 22 (1979).
4) K. V. Krishnamurthy and G. M. Harris, *J. Phys. Chem.*, **64**, 346 (1960).
5) D. Banerjea and M. S. Mohan, *J. Inorg. Nucl. Chem.*, **27**, 1643 (1965).
6) D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **29**, 2387 (1967).
7) D. Banerjea and C. Chatterjee, *J. Inorg. Nucl. Chem.*, **30**, 3354 (1968).
8) D. Banerjea, *Z. Anorg. Allg. Chem.*, **359**, 305 (1968).
9) D. Banerjea and S. Sarkar, *J. Indian. Chem. Soc.*, **1**, **635** (1973).
10) J. P. Collman, *Adv. Chem. Ser.*, **37**, 78 (1963).
11) T. Tomita, E. Kyuno, and R. Tsuchiya, *Bull. Chem. Soc. Jpn.*, **42**, 947 (1969).
12) E. C. Lingafelter and R. L. Braun, *J. Am. Chem. Soc.*, **88**, 2951 (1966).
13) a) R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958); b) D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); c) K. Nakamoto, P. L. McCarthy, A. Ruley, and A. E. Martell; *J. Am. Chem. Soc.*, **83**, 1066, 1272

(1961); d) C. K. Jorgensen, *Acta. Chem. Scand.*, **16**, 2406 (1962); e) R. E. Hester and R. A. Plane, *Inorg. Chem.*, **3**, 513 (1964); f) K. DeArmond and L. S. Forster, *Spectrochim. Acta*, **18**, 1393 (1963); g) D. R. Eaton, *J. Am. Chem. Soc.*, **87**, 3097 (1965); h) I. Hanazaki, F. Hanazaki, and S. Nagagura, *J. Chem. Phys.*, **50**, 276 (1969); i) A. M. Fatta and R. L. Lintvedt, *Inorg. Chem.*, **10**, 478 (1971).

14) J. P. Collman. R. A. Moss, H. Maltz, and C. C. Heindel, *J. Am. Chem. Soc.*, **83**, 531 (1961).

15) D. Meisel, K. H. Schmidt, and D. Meyerstein, *Inorg. Chem.*, **18**, 971 (1979).

16) R. E. Powell, *J. Phys. Chem.*, **58**, 528 (1954).