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Kinetics of formation and dissociation of the ternary complex ion (pentane-2,4-dionato)(nitrilotriacetato)chromate(III) in aqueous media

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Abstract—Synthesis of solid $[Cr(nta)(H_2O)_2]$ **1**, kinetics and equilibrium of its reaction with pentane-2,4-dione (Hpd) to form $[Cr(nta)(pd)]^-$ **2** (H_3nta is nitrilotriacetic acid), aquation of **2** into **1**, and some related reactions have been described. Parallel proton-independent and inverse proton-dependent paths lead from **1** to **2**. The $[H^+]^{-1}$ path arises from metal assisted deprotonation of HE, the enol form of Hpd. Aquation of **2** into **1** involves $[Cr(Hnta)(pd)(H_2O)]^+$ **2H** (Hnta is tridentate nta) in addition to **2**. The nta complex **1** is considerably more labile and a weaker acid than $[Cr(H_2O)_6]^{3+}$. © 1997 Elsevier Science Ltd

Keywords: kinetics; chromium(III); nitrilotriacetic acid; pentane-2,4-dione; formation; aquation.

Kinetics and mechanism of reactions of β-diketones with metal ions, including Cr^{III} have been well studied [1–5]. But no papers have considered the possibility of metal-assisted deprotonation of pentane-2,4-dione (Hpd). The complex, $[Cr(nta)(H_2O)_2]$ **1** is a weak acid. Hence, protic equilibria of Hpd may be identified in its reactions with **1**.

EXPERIMENTAL

The complex **1** was prepared by digesting at 80°C an aqueous suspension of $Cr(OH)_3$ with H_3nta in 1 : 1 molar proportion. After 5 h the mixture (15 cm^3) was mixed with equal volume of MeOH and stored for 7 days at 4°C. It was then filtered, concentrated to 5 cm^3 and stored at 4°C. Blue–violet crystals separated over 48 h. Yield, 20% of the theoretical. (Found: C, 26.2; H, 3.9; N, 5.2; Cr, 18.8; $C_6H_{10}NCrO_8$ requires C, 26.1; H, 3.65; N, 5.1; Cr, 18.8%.) $\varepsilon = 99.5$ and 93.0 $mol^{-1}\ dm^3\ cm^{-1}$ at 405 and 556 nm, respectively (pH, 1.5–2.5).

The pure solid $NH_4[Cr(nta)(pd)]\cdot H_2O$ was prepared according to the method of Uehara *et al.* [6]. The chromium content of the sample was determined spectrophotometrically [7] and indicated 99.9% purity. $\varepsilon = 215$ and 97.7 $mol^{-1}\ dm^3\ cm^{-1}$ at 385 and 555 nm, respectively in close agreement with those reported [8]. Pentane-2,4-dione (BDH) was freshly distilled before use. All other chemicals used were of reagent grade. A Shimadzu (UV-240) spectrophotometer equipped with a thermostatted cell housing (±0.1°C) was used for kinetic and spectral measurements. The first-order rate constants, k_f and k_d for the formation and aquation reactions, respectively were evaluated from the usual first-order plots. The kinetics were followed at 385 nm.

All the pH values were measured on an Orion (Model 710 A) pH-meter, equipped with a calibrated micro glass combination electrode (9802 BN). The proton dissociation constants pK_{a1} and pK_{a2} for the two co-ordinated water molecules in **1** were determined by pH-metric titration of a mixture of 2.0 mmol dm^{-3} complex and 0.01 mol dm^{-3} $HClO_4$ against a standard NaOH. The data were processed using the program PKAS [9].

Equilibrium constant K_1 [eq. (1)] and K_{1H} [eq. (2)] were determined spectrophotometrically using eqs (3) and (4), respectively. In these equations Hnta is tridentate nta with one open carboxylate arm, c_M and

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c_{Hpd} are the total analytical concentrations of $\mathrm{Cr^{III}}$ and pentane-2,4-dione, respectively; $\Delta\varepsilon = (\varepsilon_2 - \varepsilon_1)$ at 385 nm, and $\varepsilon_e = A_e/c_M$, where A_e is the equilibrium absorbance of a mixture of **1** and **1H** in $[\mathrm{H^+}] \geqslant 0.1$ mol dm^{-3}; ε_1 and ε_2 are molar absorption coefficients of **1** and **2** respectively.

$$\underset{\mathbf{1}}{[\mathrm{Cr(nta)(H_2O)_2}]} + \mathrm{Hpd} \overset{K_1}{\rightleftharpoons} \underset{\mathbf{2}}{[\mathrm{Cr(nta)(pd)}]^-} + \mathrm{H^+} + 2\mathrm{H_2O} \quad (1)$$

$$\underset{\mathbf{1}}{[\mathrm{Cr(nta)(H_2O)_2}]} + \mathrm{H^+} + \mathrm{H_2O} \overset{K_{1\mathrm{H}}}{\rightleftharpoons} \underset{\mathbf{1H}}{[\mathrm{Cr(Hnta)(H_2O)_3}]^+} \quad (2)$$

$$c_M/(A_e - A_o) = [\mathrm{H^+}]/K_1 c_{\mathrm{Hpd}}\Delta\varepsilon + 1/\Delta\varepsilon \quad (3)$$

$$(\varepsilon_1 - \varepsilon_e)/[\mathrm{H^+}] = \varepsilon_e K_{1\mathrm{H}} - \varepsilon_{1\mathrm{H}} K_{1\mathrm{H}} \quad (4)$$

All straight line equations were analysed by standard linear least-squares regression program and the reported error limits on kinetic and equilibrium parameters are standard deviations [10]. Our experimental data were collected at $I = 1.0$ mol dm^{-3} ($\mathrm{NaClO_4}$) unless stated otherwise.

RESULTS AND DISCUSSION

There have been several preparations of the complex **1** in solution [11–14] but none isolated the solid. Barton *et al.* [13] had a solid dmf compound $[\mathrm{Cr(nta)(H_2O)_2}]\cdot 0.5\mathrm{dmf}$, but its electronic spectra are sufficiently different from those of **1** observed by us and by the earlier workers [11,12,15]. It probably contained co-ordinated dmf.

Equilibrium studies

The acid dissociation constants K_{a1} and K_{a2} are defined by eqs (5) and (6).

$$\underset{\mathbf{1}}{[\mathrm{Cr(nta)(H_2O)_2}]} \overset{K_{a1}}{\rightleftharpoons} \underset{\mathbf{1h}}{[\mathrm{Cr(nta)(H_2O)(OH)}]^-} + \mathrm{H^+} \quad (5)$$

$$\underset{\mathbf{1h}}{[\mathrm{Cr(nta)(H_2O)(OH)}]^-} \overset{K_{a2}}{\rightleftharpoons} [\mathrm{Cr(nta)(OH)_2}]^{2-} + \mathrm{H^+} \quad (6)$$

The measured $\mathrm{p}K_{a1}$ and $\mathrm{p}K_{a2}$ values are given below:

T(°C)	30.0	40.0	50.0
$\mathrm{p}K_{a1}$	5.78 ± 0.11	5.53 ± 0.13	5.29 ± 0.12
$\mathrm{p}K_{a2}$	8.33 ± 0.14	8.00 ± 0.16	7.70 ± 0.18

They compare well with the $\mathrm{p}K_{a1}$ (5.87) and $\mathrm{p}K_{a2}$ (8.74) reported by Irving and Al-Jarrah [15] at 22 ± 0.5°C and $I = 0.1$ mol dm^{-3} ($\mathrm{KNO_3}$). The values show that the nta complexes **1** and **1h** are weaker acids compared to $\mathrm{Cr^{3+}_{aq}}$ and $\mathrm{Cr(OH)^{2+}_{aq}}$, respectively. This is a likely consequence of the strong σ-donor ability of nta, which partially neutralises the Lewis acidity of $\mathrm{Cr^{III}}$.

Excellent straight lines ($r \geqslant 0.99$) were obtained corresponding to eqs (3) and (4) and yielded at 50°C, $K_1 = 1.35 \pm 0.05$, $K_{1\mathrm{H}} = 1.81 \pm 0.06$; and $\Delta\varepsilon = 152$ (known value, 148), $\varepsilon_{1\mathrm{H}} = 93.5$ dm^3 mol^{-1} cm^{-1} at 385 nm. The value $\varepsilon_{1\mathrm{H}}$ is lower than ε_1 (99.5 dm^3 mol^{-1} cm^{-1}) as expected for the more symmetric structure of the complex **1H** [16].

Using standard relations [2] and known equilibrium data [2,3] K_1 at 50°C was apportioned into K_K (1.66) and K_E (7.3), the equilibrium constants of the reaction of **1** with the keto and the enol form [17] of Hpd, respectively. The higher K_E value (123.7 at 55°C) [3] for the reaction of HE with $\mathrm{Cr^{3+}_{aq}}$ demonstrates again the markedly low Lewis acidity of $\mathrm{Cr^{III}}$, bound to nta.

Kinetics

The formation of **2** from **1** in the presence of a large excess of Hpd, follows simple first-order kinetics at least up to 90% reaction. Aquation reaction of **2** in the presence of large excess of $[\mathrm{H^+}]$ (0.05–0.25 mol dm^{-3}) also follows simple first-order kinetics until near completion. Plots of k_f against c_{Hpd} ($c_{\mathrm{Hpd}} = [\mathrm{Hpd}] + [\mathrm{pd^-}]$) at a given pH are excellent straight lines with zero intercept. This and spectral observations on formation and aquation reactions suggest that they proceed to completion and they do not interfere with each other. Plot of k_f *vs* $1/[\mathrm{H^+}]$ at a fixed c_{Hpd} are excellent straight lines ($r > 0.99$) with finite intercept (Fig. 1) and indicate parallel proton-independent and inverse proton-dependent paths.

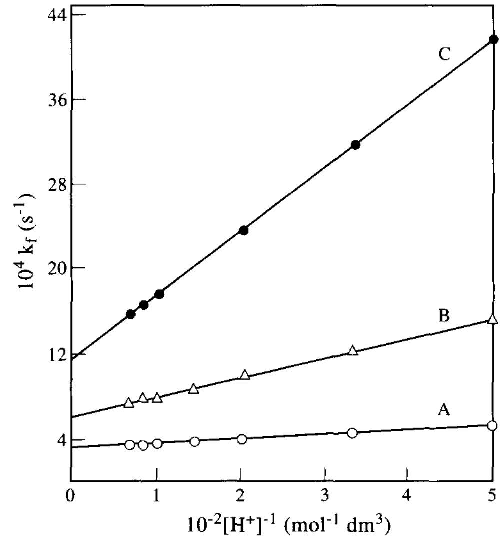

Fig. 1. Observed acid dependence of formation rate constants (k_f) at 40.0°C (A), 50.0°C (B) and 60.0°C; $I = 1.0$ mol dm^{-3}.

Under the experimental conditions of pH, [**1h**] is very small. Moreover, its kinetic activity is at most 8 times more than that of **1** [12,18,19]. Also, [E^-] is too small to be kinetically significant. Therefore the observed $[H^+]^{-1}$-dependence of k_f can arise only from a pre-equilibrium deprotonation of HE, assisted by the Cr^{III} centre. The k_d values exhibit a complex dependence on [H^+] [eq. (7), Fig. 2].

$$k_d(1+A[H^+])/[H^+] = a_1+a_2[H^+] \qquad (7)$$

The observed kinetic dependence may be explained by the equilibrium and rate steps shown in Scheme 1. It ignores HK but considers reactions of **1**, **1H** and **2H**. The species **1H** is known in solution [12,16] and since **1H** is known, **2H** is very likely.

Scheme 1.

$$\begin{tikzcd} \underset{\mathbf{1}}{ML+HE} \arrow[r, "K_1", shift left=0.5ex] & ML(HE) \arrow[l, shift left=0.5ex] \arrow[r, "K_2", shift left=0.5ex] \arrow[d, "k_1"', shift right=0.5ex] & ML(-E)+H^+ \arrow[l, shift left=0.5ex] \arrow[d, "k_2"', shift right=0.5ex] \\ & ML(=E)+H^+ \arrow[u, "k_{-1}"', shift right=0.5ex] & ML(=E) \arrow[u, "k_{-2}"', shift right=0.5ex] \end{tikzcd} \qquad (8)$$

$$ML+H^+ \overset{K_{1H}}{\rightleftharpoons} \underset{\mathbf{1H}}{M(HL)} \qquad (9)$$

$$M(HL)+HE \overset{K_3}{\rightleftharpoons}$$

$$\begin{tikzcd} M(HL)(HE) \arrow[r, "K_4", shift left=0.5ex] \arrow[d, "k_3"', shift right=0.5ex] & M(HL)(-E)+H^+ \arrow[l, shift left=0.5ex] \arrow[d, "k_4"', shift right=0.5ex] \\ M(HL)(=E)+H^+ \arrow[u, "k_{-3}"', shift right=0.5ex] & M(HL)(=E) \arrow[u, "k_{-4}"', shift right=0.5ex] \end{tikzcd} \qquad (10)$$

$$ML+HE \overset{K_E}{\rightleftharpoons} \underset{\mathbf{2}}{ML(=E)+H^+}; \qquad K_E = k_2K_1K_2/k_{-2} \qquad (11)$$

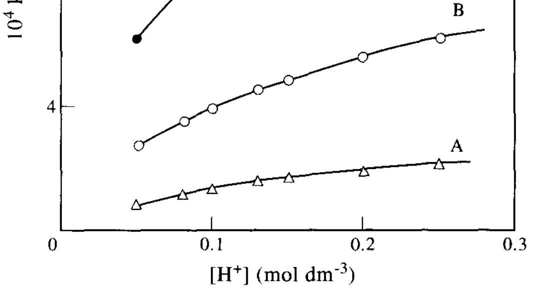

Fig. 2. Observed acid dependence of dissociation rate constant (k_d) at 40.0°C (A), 50.0°C (B) and 60.0°C; I = 1.0 mol dm^{-3}.

$$M(HL)+HE \overset{K}{\rightleftharpoons} \underset{\mathbf{2H}}{M(HL)(=E)+H^+};$$

$$K = K_EK_{2H}/K_{1H} \qquad (12)$$

$$ML(=E)+H^+ \overset{K_{2H}}{\rightleftharpoons} M(HL)(=E) \qquad (13)$$

In this scheme, ML is $[Cr(nta)(H_2O_2)_2]$, M(HL) is $[Cr(Hnta)(H_2O)_3]^+$, ML(=E) is $[Cr(nta)(pd)]^-$ and M(HL)(=E) is $[Cr(Hnta)(pd)(H_2O)]$, '−E' is half-bonded enol; '=E' is chelated enol. From Scheme 1 one can derive eq. (14) for the formation and eq. (15) for the aquation reaction:

$$k_f(1+K_{HK})(c_{Hpd})^{-1} = k_1K_1K_{HK} + k_4K_3K_4K_{1H}K_{HK} + k_2K_1K_2K_{HK}/[H^+] + k_3K_3K_{1H}K_{HK}[H^+] \qquad (14)$$

$$k_d(1+K_{2H}[H^+])/[H^+] = k_{-2}/[H^+] + (k_{-1}+k_{-4}K_{2H}) + k_{-3}K_{2H}[H^+] \qquad (15)$$

Plots of left hand side of eq. (14) against $1/[H^+]$ were excellent straight lines with finite intercepts. Clearly the k_3 path is insignificant due to the absence of M(HL) under the weakly acidic conditions for formation reaction. From the intercept and slope of such plots we evaluated $(k_1K_1+k_4K_3K_4K_{1H})$ $K_{HK} = (7.69 \pm 0.53) \times 10^{-3}$ mol^{-1} dm^{-3} s^{-1} and $k_2K_1K_2K_{HK} = (2.17 \pm 0.18) \times 10^{-5}$ s^{-1} at 50°C. The corresponding $\Delta H^{\neq}$ values are 58 ± 4 and 111 ± 7 kJ mol^{-1}; $\Delta S^{\neq}$ values are -107 ± 7 and 6.8 ± 0.5 J K^{-1} mol^{-1}.

Equation (15) is the same as the empirical eq. (7), provided $A = K_{2H}$; $a_1 = (k_{-1}+k_{-4}K_{2H})$; $a_2 = k_{-3}K_{2H}$, and k_{-2} is negligible. The values for the constants at 50°C are A = 20 dm^3 mol^{-1}, a_1 = 0.01 dm^3 mol^{-1} s^{-1} and a_2 = 0.021 dm^6 mol^{-2} s^{-1}. $\Delta H^{\neq}$ values (kJ mol^{-1}) for a_1 is 85 ± 6, for a_2, 67 ± 5; $\Delta S^{\neq}$ (J K^{-1} mol^{-1}) for a_1 is -22 ± 2 and for a_2 is -71 ± 4.

From the relation, $K_E = k_2K_1K_2/k_{-2}$ and known K_E (7.3) one can evaluate $k_{-2} \sim 10^{-6}$, an actually negligible value as assumed in comparing eq. (7) with (15). Again the measured K_{1H} (1.8) and K_{2H} (20) values and the relation $K = K_EK_{2H}/K_{1H}$ may be used to evaluate $K = 81.1$ at 50°C. It is higher than K_E probably because the Cr^{III} centre in **1H** is more electropositive than it is in **1**.

The activation parameters correspond to composite constants and detailed interpretation may not be rewarding. However, the negative or weakly positive $\Delta S^{\neq}$ along with moderate values for $\Delta H^{\neq}$ are typical for chromium(III) substitutions with solvent assisted associative mechanism.

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