Kinetics and mechanisms of the reaction of chromium(III) and 2,4-hexanedione in aqueous solution

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The kinetics and mechanism of the reaction between Cr(III) and 2,4-hexanedione in aqueous solution have been studied. Complexation occurs by coordination of both oxygen atoms of the ligand to the chromium(III) center, with concomitant loss of a proton yielding 1:1 complex of the type $[Cr(CH_3COCHCOC_2H_5)(H_2O)_4]^{2+}$. When the metal ion is in pseudo first-order excess the concentration dependence of the observed rate constants agrees with a mechanism involving reversible reaction between the enol tautomer of 2,4-hexanedione and the metallic species $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$, with rate constants of 8.0×10^{-4} and 3.5×10^{-2} $dm^3 mol^{-1} s^{-1}$, respectively.

Key words: chromium(III), β-diketones, β-diketonates, kinetics, complexation.

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La cinétique et le mécanisme de la réaction de la 2,4-hexanedione avec le Cr(III) en solution aqueuse ont été étudiés. La complexation se produit par la coordination de tous deux atomes d'oxygène du ligand avec le chrome(III), avec une perte simultanée d'un proton pour produire le complexe 1:1 du type $[Cr(CH_3COCHCOC_2H_5)(H_2O)_4]^{2+}$. Quand l'ion métallique se trouve en pseudo premier-ordre excès, l'influence de la concentration sur la constante de vitesse observée s'accorde avec une mécanisme réversible selon lequel le tautomère énol réactionne avec les espèces $Cr(H_2O)_6^{3+}$ and $Cr(H_2O)_5OH^{2+}$. Les constantes de vitesse qui correspondent à ces réactions ont pour valeur $8,0 \times 10^{-4}$ et $3,5 \times 10^{-2}$ $dm^3 mol^{-1} s^{-1}$, respectivement.

Mots clés : chromo(III), β-dicétones, β-dicétonates, cinétique, complexation.

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Introduction

In recent years a number of papers dealing with the kinetics and mechanisms of the reactions of metal and oxometal ions with β-diketones have appeared in the literature (1–6).

Chromium(III) complexes have been less well studied than the Cu(II), Co(II), Ni(II), or Fe(III) systems which are classified as "labile" metal ions. The particularly interesting feature of chromium(III) chemistry is that the complex-formation reactions from hexaaquachromium(III) or its monohydroxy species are very slow. Substitution at chromium(III) centres has received attention (7) because of the possibility of A (or I_a) (8) associative mechanisms for the d^3 electronic configuration.

We have studied the reaction of chromium(III) with 2,4-hexanedione in the pH region 2.0–3.0 at temperatures typically used for chromium kinetics work (50°C) and ionic strength $I = 0.5$ mol dm^{-3}.

The aim of the present work is the elucidation of the mechanism and the rate of 1:1 complex formation in aqueous solution by measuring the chemical reaction rate using a spectrophotometric method.

Experimental

The solutions of Cr(III) were prepared from Aldrich reagent grade $Cr(NO_3)_3 \cdot 9H_2O$, and they were standardized by oxidizing the chromium(III) to chromium(VI). 2,4-Hexanedione (propionylacetone, PAH) obtained as Kodak reagent grade, was freshly distilled prior to use. Unless otherwise indicated, all materials were of reagent grade (Merck) and were used without further purification. The ionic strength of all solutions was adjusted to 0.5 mol dm^{-3} using $HClO_4$–$NaClO_4$ solutions. Spectra were recorded on a Spectronic 1201 UV-visible spectrophotometer and the kinetic data were obtained by following the absorbance increase in the vicinity of 327 nm using a kinetic programme. pH measurements were made with a Crison 501 pH-meter equipped with an Ingold combined glass-and-reference electrode.

Results

Tautomerization equilibrium

The keto–enol tautomerization equilibrium of 2,4-hexanedione may be represented by reaction [1] where PAH$_k$ and PAH$_e$ represent the keto and enol tautomers, respectively.

$$[1] \qquad PAH_k \underset{k_f}{\overset{k_e}{\rightleftharpoons}} PAH_e$$
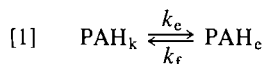
The enolization rates of β-diketones (k_e) are measured by a bromination procedure (2). Usually, the enol tautomer and any enolate ion present react rapidly with bromine added. To maintain equilibrium some of the keto tautomer converts to the enol tautomer which then reacts with bromine; hence the rate of enolization parallels the rate of bromination. Therefore

$$[2] \qquad -d[Br_2]/dt = -d[PAH_k]/dt = k_e[PAH_k]$$

$$[3] \qquad [Br_2] = A/\epsilon \quad \text{and} \quad [PAH_k] = (A/\epsilon + a - b)$$

where A is the optical density at time t due to the absorbance of bromine, ϵ is the molar absorptivity of bromine in a cell of 1 cm path length, a is the total concentration of β-diketone, and b is the total concentration of bromine. Making the appropriate substitution in eqs. [2] and [3], we obtain [4]

$$[4] \qquad -\ln(A/\epsilon + a - b) = k_e t + C$$

where C is a constant.

A plot of the left-hand side of eq. [4] against time gives a straight line of slope k_e, the rate of enolization of the β-diketone.

Since $[PAH] = [PAH_k] + [PAH_e]$, from intercepts obtained in eq. [4] the 2,4-hexanedione enol fraction $y = [PAH_e]/[PAH]$ has been determined equal to 0.16 at 20°C. This result is in agreement with literature values (9, 10).

Stability constant of complex

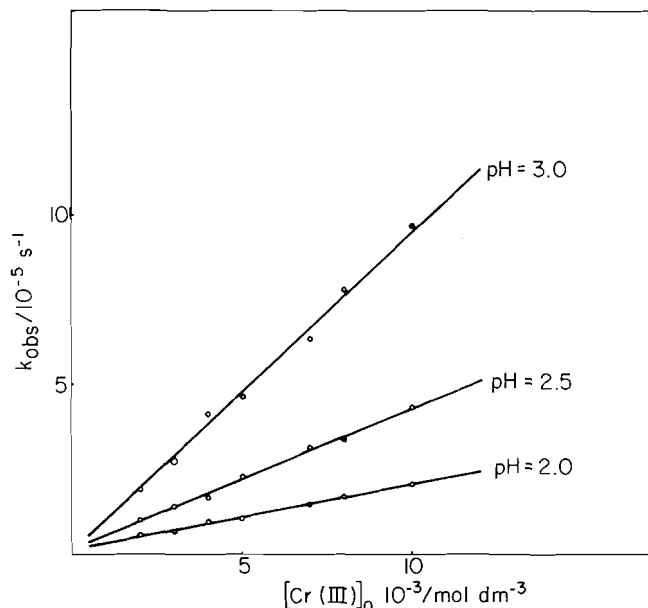The composition of the complex that chromium(III) forms

FIG. 1. k_{obs} as a function of the total concentration of chromium(III) at 50°C and ionic strength 0.5 M (NaClO$_4$). [PAH] = 1.0 × 10^{-4} M.

with 2,4-hexanedione in aqueous solution has been investigated spectrophotometrically using the Job (11) and Yoe–Jones (12) methods. The pH range was low enough to prevent hydrolysis products other than Cr(H$_2$O)$_5$OH^{2+} and the ionic strength was kept at a constant value with HClO$_4$/NaClO$_4$ buffer solutions. The results from both methods agree on a 1:1 stoichiometry (13).

Although the complex ion which will be studied in this work is Cr(H$_2$O)$_4$PA^{2+}, for the sake of simplicity, the solvent molecules will not be written, so the stability constant of CrPA^{2+} complex can be written as,

$$K = \frac{[\text{CrPA}^{2+}]}{[\text{Cr(III)}][\text{PA}^-]}$$

The direct determination of this equilibrium constant is rather complicated because several competing reactions can take place which can affect the extent the complex formation. This is quantitatively expressed by the conditional constants:

[5] $\quad K' = \dfrac{[\text{CrPA}^{2+}]}{[\text{Cr}'][\text{PA}^{-'}]}$

where [Cr'] and [PA$^{-'}$] are the total concentration of chromium and the total concentration of ligand that does not form the complex, respectively (14). The stability constant can be connected with the conditional constant by

[6] $\quad K =$

$$K'\left\{1 + \frac{K_1}{[\text{H}^+]} + \frac{K_2}{[\text{H}^+]^2} + 2\frac{K_3[\text{Cr}^{3+}]}{[\text{H}^+]^2}\right\}\left\{1 + \frac{[\text{H}^+]}{K_I}\right\}$$

where K_1, K_2, and K_3 are the hydrolysis constants of Cr^{3+} to form Cr(OH)$^{2+}$, Cr(OH)$_2^+$, and Cr$_2$(OH)$_2^{4+}$, which are known from the literature (14, 15) amount to 10$^{-4.0}$, 10$^{-9.7}$, and 10$^{-2.4}$, respectively, at 20°C.

The ionization constant of the ligand, K_I = 10$^{-9.40}$ has been determined in our previous paper (16).

K' can be determined from absorption values at the stoichiometric point according to Job's method in the same way as in a previous paper (17). When data range from 1.00 × 10^{-1} to 1.00 × 10^{-3} M acid, K = 9.6 (±0.8) × 10^{10} mol^{-1} dm^3.
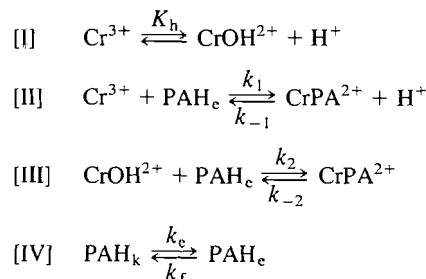
Kinetic measurements

The reaction of Cr(III) with PAH was carried out with the metal ion concentration in excess over the ligand, at the hydrogen ion concentration 0.01–0.001 M. If the complex stability constant value is taken into account, only the propionylacetonatechromium(III) (CrPA^{2+}) ion is formed quantitatively under our experimental conditions. The pseudo first-order rate constants were obtained from plots of ln ($A_\infty - A$) against time, where A_∞ is the complex absorption when the reaction is over.

To study the influence of the Cr(III) concentration on k_{obs}, several series of experiments with constant [PAH], pH, ionic strength, and temperature were performed. It was evaluated by plotting k_{obs} against [Cr(III)], yielding a linear correlation (Fig. 1).

Discussion

Taking into consideration the 2,4-hexanedione tautomeric equilibrium, the mechanism that we have considered is presented in Scheme 1 (coordinated H$_2$O is omitted for clarity), it is consistent with the assumption that the formation of CrPA^{2+} proceeds via two paths, one involving the reaction of Cr^{3+} with the enol tautomer of PAH, (PAH$_e$), and the other involving the reaction of CrOH^{2+} with (PAH$_e$).

[I] $\quad$ Cr^{3+} $\underset{}{\overset{K_h}{\rightleftharpoons}}$ CrOH^{2+} + H$^+$

[II] $\quad$ Cr^{3+} + PAH$_e$ $\underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}}$ CrPA^{2+} + H$^+$

[III] $\quad$ CrOH^{2+} + PAH$_e$ $\underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}}$ CrPA^{2+}

[IV] $\quad$ PAH$_k$ $\underset{k_f}{\overset{k_e}{\rightleftharpoons}}$ PAH$_e$

SCHEME 1

The rate of formation of CrPA^{2+} is then given by

$$\frac{d[\text{CrPA}^{2+}]}{dt} = k_1[\text{Cr}^{3+}][\text{PAH}_e] - k_{-1}[\text{CrPA}^{2+}][\text{H}^+]$$
$$+ k_2[\text{CrOH}^{2+}][\text{PAH}_e] - k_{-2}[\text{CrPA}^{2+}]$$

Substituting the enol fraction y = [PAH$_e$]/[PAH], then

[8] $\quad \dfrac{d[\text{CrPA}^{2+}]}{dt} = -(k_{-1}[\text{H}^+] + k_{-2})[\text{CrPA}^{2+}]$

$$+ \left(k_1 y + \frac{k_2 K_h y}{[\text{H}^+]}\right)[\text{Cr}^{3+}][\text{PAH}]$$

Moreover

$$[\text{CrPA}^{2+}] = [\text{PAH}]_0 - [\text{PAH}]$$

and

$$\frac{d[\text{CrPA}^{2+}]}{dt} = -\frac{d[\text{PAH}]}{dt}$$

Therefore

$$[9] \quad -\frac{d[PAH]}{dt} = -(k_{-1}[H^+] + k_{-2})[PAH]_0$$

$$+ (k_{-1}[H^+] + k_{-2})[PAH]$$

$$+ \left(k_1 y + \frac{k_2 K_h y}{[H^+]}\right)[Cr^{3+}][PAH]$$

Integrating this equation and considering the conditions used in this investigation, we get

$$[10] \quad \ln \frac{[PAH]_0 - [CrPA^{2+}]}{[PAH]_0}$$

$$= -\left\{(k_{-1}[H^+] + k_{-2}) + \left(k_1 y + \frac{k_2 K_h y}{[H^+]}\right)[Cr^{3+}]\right\}t$$

if we consider $[PAH]_0 = [CrPA^{2+}]_\infty$

$$[11] \quad \ln (A_\infty - A) = \ln A_\infty$$

$$- \left\{(k_{-1}[H^+] + k_{-2}) + \left(k_1 y + \frac{k_2 K_h y}{[H^+]}\right)[Cr^{3+}]\right\}t$$

where A and A_∞ are the absorbances of the reaction system at t seconds after the start of the reaction and at equilibrium, respectively. Thus the conditional first-order rate constant obtained by experiment is

$$[12] \quad k_{obs} = (k_{-1}[H^+] + k_{-2}) + \left(k_1 y + \frac{k_2 K_h y}{[H^+]}\right)[Cr^{3+}]$$

Since $[Cr(III)]_0 \gg [PAH]$, it follows that

$$[13] \quad [Cr^{3+}] = \frac{[Cr(III)]_0[H^+]}{[H^+] + K_h}$$

where $[Cr(III)]_0$ is the total concentration of chromium(III), thus

$$[14] \quad k_{obs} = \frac{k_1[H^+]}{K_E} + \frac{k_2 K_h}{K_E}$$

$$+ \left(\frac{k_1[H^+]y + k_2 K_h y}{[H^+] + K_h}\right)[Cr(III)]_0$$

where $K_E = k_1/k_{-1}$.

The value of K_h at 50°C was found to be 3.98×10^{-4} (18) while the value of y was found by extrapolation of the data at 50°C, taking into account ref. 10, to be 0.10.

Equation [14] suggests that a plot of k_{obs} against $[Cr(III)]_0$ at a constant acid concentration should be linear.

Consequently, the values of rate constants k_1 and k_2 were determined from the slopes of Fig. 1 plots by the method of least squares: $k_1 = 8.0(\pm 0.1) \times 10^{-4}$ and $k_2 = 3.5(\pm 0.1) \times 10^{-2}$ dm^3 mol^{-1} s^{-1}, respectively. Due to the relatively small value of the intercept and the resulting uncertainty, the kinetic data can not be reliably used to obtain a value of K_E.

The mechanisms of the complex formation reactions of β-diketones have been widely investigated [1]–[6] and the reactivity toward metal ions has been found to be enolate ion > enol tautomer > keto tautomer. In the present investigation the results show that the reaction of PAH with Cr(III) occurs by a mechanism in which the metal ions $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5OH]^{2+}$ react with the enol form of the β-diketone.

Although the reactions of chromium(III) with 2,4-pentanedione have been thoroughly studied (19–21), and the rate constants can be predicted on the basis of the Eigen–Wilkins

mechanism (22, 23), it is not easy to get clear predictions on Cr(III)–2,4-hexanedione complexation.

The relative inertness of chromium(III) with similar ligands (20, 24), may be the reason for the retarded rates of complex formation, when compared with other β-diketonate systems (1–6). For solvent exchange on chromium(III) in aqueous solution $\Delta H^{\ddagger} = 109.7$ kJ mol^{-1} while $\Delta S^{\ddagger} = 1.2$ J K^{-1} mol^{-1} (25). Thus the solvent exchange rate in water is 1.4×10^{-5} s^{-1} at 50°C. It is clear that the rate of formation of the CrPA^{2+} complex is considerably larger than the rate of solvent exchange on the metal ion. It follows that the mechanism must be interchange associative (I_a) which involves association of the enol tautomer with the hexacoordinated chromium(III) in a rate-determining step to give an intermediate of increased coordination number. High pressure solvent exchange studies in Cr(III) and other non-labile metal ions Co(III), Rh(III), and Ir(III) (26–28) are in accord with an associative interchange for Cr(III), Rh(III), and Ir(III), while a dissociative interchange is indicated for Co(III). It has been suggested that I_a mechanisms are the rule for the 3+ ions, Co(III) being the exception due to its small size.

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