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The Kinetics and Mechanisms of the Reactions of Chromium(III) with Pentane-2,4-dione in Aqueous Solution

MICHAEL J. HYNES*, CLARE O'MARA and DERMOT F. KELLY

Chemistry Department, University College, Galway, Ireland

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Abstract

The equilibrium, kinetics and mechanism of the reaction of chromium(III) with pentane-2,4-dione (Hpd) have been investigated in aqueous solution at 55 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. The equilibrium constant ($\log \beta_1$) is 10.08(±0.01) while the p*K* of Hpd is 8.69(±0.01). The kinetics are consistent with a mechanism in which $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(OH)]^{2+}$ react with the enol tautomer of Hpd with rate constants of $1.05(\pm 0.26) \times 10^{-2}$ and $2.78(\pm 0.08) \times 10^{-1}$ dm^3 mol^{-1} s^{-1} respectively. These rate constants are considerably more rapid than those predicted by the Eigen–Wilkins mechanism. These data are compared with literature values.

Introduction

The kinetics and mechanisms of the complex formation reactions of β-diketones with a number of metal ions have been thoroughly investigated [1–10]. However, with the exception of iron(III) most of the metal ions investigated could be classed as 'labile' metal ions. In the majority of these investigations it has been found that the metal species reacts with the protonated enol tautomer of the β-diketone with complex formation rate constants that are considerably less than would be predicted on the basis of the solvent exchange rate and the ion-pair equilibrium constant. A number of possible explanations have been suggested for this. For example, the slow rate of reaction of copper(II) with the enol tautomer of pentane-2,4-dione (Hpd) was explained in terms of a sterically controlled substitution mechanism due to the formation of a six-membered ring [1]. However, such a mechanism predicts that the enolate ion would also react slowly and this was found not to be so. Other workers suggested that due to intramolecular hydrogen bonding the protonated enol tautomer is a poor entering group [2, 3]. However, it was argued that these factors alone would be insufficient to lower the rate constant by the three orders of magnitude observed, and that it was the slow rate of ring closure of the protonated intermediate that caused the slow rates. An inverse correlation was found between the degree of retardation and the hardness of the metal species. This led to the suggestion that the stability of a precursor complex was important in determining the overall rate constant [9].

Although a number of kinetic studies of the complex formation reactions of chromium(III) have recently been reported, none of them have dealt with the reactions of this metal ion with β-diketones [11–19]. Despite the fact that the interpretation of the kinetic data has not always been straightforward, on balance it appears that substitution of hexa-aquachromium(III) takes place via an interchange-associative (I_a) mechanism. The relatively low p*K* of hexa-aquachromium(III) (3.10 at 55 °C) ensures that at pH's below 5 account must be taken of the monohydroxo metal species.

In view of the paucity of kinetic data on the reactions of chromium(III) with β-diketones and the fact that complex formation might take place via an I_a mechanism a study of the reactions of Hpd with this metal ion was undertaken. In order to facilitate the acquisition of the kinetic data it was decided to carry out the kinetic measurements at a temperature of 55 °C. The ionic strength was also carefully controlled.

Experimental

Chromium(III) sulphate (BDH) was used as the source of chromium(III). Stock solutions were standardized by oxidizing the chromium(III) to chromium(VI) using potassium bromate and sulphuric acid. The excess bromine was removed by boiling and the resulting solution was titrated with sodium thiosulphate following the addition of an excess of potassium iodide.

Pentane-2,4-dione (BDH) was freshly distilled prior to use. Stock solutions were standardized by titration with sodium hydroxide. Endpoints were determined using the method of Gran [20].

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*Author to whom correspondence should be addressed.

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The ionic strength of all solutions was adjusted to 0.5 mol dm^{-3} using sodium perchlorate. In order to remove any iron(III) present, stock solutions were adjusted to pH 3 using perchloric acid, following which they were passed over Zerolit 225 cation exchange resin in the sodium form.

UV–Vis spectra were recorded on either Beckman DB-GT or Shimadzu UV260 spectrophotometers. The kinetic data were obtained by following the absorbance increase in the vicinity of 330 nm using a chart recorder attached to the Beckman spectrophotometer. The Hpd concentration used was approximately 1.0×10^{-4} mol dm^{-3}. The pseudo-first-order rate constants were obtained either from plots of $\ln(A_\infty - A_{obs})$ against time or using a curve fitting technique [21]. The experimentally determined absorbance readings at infinity time were in excellent agreement with those calculated using the curve fitting method. All reactions were carried out with the metal ion in pseudo-first-order excess.

pH measurements were made using a Pye Model 290 pH meter equipped with a Pye Ingold E°$_7$ combination electrode. The linearity of the electrode was established using pH 4, 7 and 9 buffers. The electrode was calibrated to read hydrogen ion concentration directly using a series of acid solutions in 0.5 mol dm^{-3} $NaClO_4$. The hydrogen ion concentration in these solutions was determined by titration with standard sodium hydroxide. The endpoints were calculated using the Gran method [22].

The dissociation constant of Hpd was determined by titrating a solution of known concentration at an ionic strength of 0.5 mol dm^{-3} with standard sodium hydroxide. Calculations were carried out using SUPERQUAD [23].

The stability constant for the mono-complex of chromium(III) with Hpd (β_1) was determined by reacting a series of fifteen solutions containing known concentrations of hydrogen ion, Hpd and chromium(III) at 55 °C until no further reaction occurred. The spectra were then recorded in the wavelength range 305–345 nm. The absorbance data were digitized at 5 nm intervals and these together with the reactant concentrations were used as input for SQUAD [24]. The above procedure gave a total of one hundred and thirty five data points.

The keto to enol ratio of Hpd at 55 °C was determined by integrating the terminal CH_3-protons using a JEOL JNM-GX270 spectrometer. This proved much more satisfactory than using the protons on the 3-carbon [25].

The rate of ketonization was determined by adjusting the pH of a solution of Hpd at an ionic strength of 0.5 mol dm^{-3} $NaClO_4$ until appreciable quantities of the enolate ion were present. This solution was then reacted with a range of perchloric acid solutions in the stopped-flow apparatus and the absorbance change was monitored at 295 nm. The observed rate constant which was independent of the acid concentration is equal to the rate of ketonization (k_f) plus the rate of enolization (k_e). Since the keto to enol ratio is equal to k_f/k_e the individual values can be determined. Due to the volatility of bromine it is inconvenient to determine the value of k_e directly.

All measurements were carried out at 55 °C.

Results and Discussion

This study gives a value of 4.04 for the keto/enol ratio of Hpd at 55 °C in aqueous solution at an ionic strength of 0.5 mol dm^{-3} $NaClO_4$. The observed rate constant for the ketonization experiment, 0.615 s^{-1} gives ($k_e + k_f$). Since the ratio k_e/k_f is equal to the enol/keto ratio, the individual values of k_e and k_f are readily calculated to be 0.122 and 0.493 s^{-1} respectively.

TABLE I. Kinetic Data for Reaction of Chromium(III) with Pentane-2,4-dione in Aqueous Solution at 55 °C and Ionic Strength 0.5 mol dm^{-3} $NaClO_4$

10^3 [H$^+$] (mol dm^{-3})	10^3 [M_0] (mol dm^{-3})	$10^5 k_{obs}$ (s^{-1})	$10^5 k_{calc}$ (s^{-1})
0.676	1.92	7.18	6.09
0.676	2.88	9.84	9.04
0.676	3.84	11.65	11.99
0.676	4.80	14.78	14.94
2.14	1.92	3.20	3.35
2.14	3.84	7.23	6.51
2.14	5.76	9.88	9.67
2.14	7.76	12.09	12.96
2.14	9.60	15.64	15.98
6.76	1.92	1.86	1.71
6.76	3.84	3.53	3.18
6.76	5.76	4.93	4.65
6.76	7.76	6.69	6.18
6.76	9.60	7.21	7.59

Table I gives the kinetic data for reaction of chromium(III) with pentane-2,4-dione in aqueous solution at 55 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. The equilibrium and kinetic data may be interpreted with reference to the series of reactions in Scheme 1.

$$HK = HE \qquad (k_e/k_f) \tag{1}$$

$$M^{3+} = M(OH)^{2+} + H^+ \qquad (K_h) \tag{2}$$

$$M^{3+} + HL = ML^{2+} + H^+ \qquad (K_{ML}) \tag{3}$$

$$M^{3+} + HE = ML^{2+} + H^+ \qquad (K_E = k_1/k_{-1}) \tag{4}$$

$$M(OH)^{2+} + HE = ML^{2+} \qquad (k_2/k_{-2}) \tag{5}$$

Scheme 1.

The value of pK_a at 55 °C was found to be 8.69 (±0.01) while the value of K_h was found by extrapolation of the data in ref. 18 to 55 °C to be 7.94×10^{-4}. The ionic strength used was comparable to that used in the present investigation. The value of $\log \beta_1$ calculated by SQUAD was 10.08(±0.01). This results in a value of 24.5 and 123.7 for the equilibrium constants K_{ML} and K_E respectively. K_{ML}, K_E, and K_K are related by eqn. (6)

$$1/K_{ML} = 1/K_E + 1/K_K \qquad (6)$$

where K_E and K_K are the equilibrium constants for reaction of Cr^{3+} with the enol and keto tautomers of Hpd respectively.

In the complex formation reactions of β-diketones investigated to date [1–10] the reactivity toward metal ions has been found to be enolate ion > enol tautomer > keto tautomer. In the present investigation it was assumed that metal complex formation takes place primarily via reaction of the metal species with the enol tautomer of Hpd. In most reactions of Hpd with labile metal ions the keto-enol equilibrium is not maintained during the course of the reaction. However, in the case of chromium(III) complex formation is so slow that the keto-enol equilibrium is maintained during the course of the reaction. Making this assumption and provided that the protolytic reactions are rapid compared to the complex formation reactions, the rate of complex formation is given by eqn. (7) when the metal is in pseudo-first-order excess and the total metal concentration is M_o.

$$k_{obs} = a + b[M_o]/(1 + k_f/k_e) \qquad (7)$$

where $a = k_1[H^+]/K_E + k_2K_h/K_E$ and $b = (k_1[H^+] + k_2K_h)/(K_h + [H^+])$. Fitting the kinetic data to eqn. (7) gives values of k_1 and k_2 equal to $1.05(\pm 0.26) \times 10^{-2}$ and $2.78(\pm 0.08) \times 10^{-1}$ $dm^3\ mol^{-1}\ s^{-1}$ respectively. Equation (7) suggests that a plot of k_{obs} against $[M_o]$ at constant acid concentration should be linear with slope $b(1 + k_f/k_e)$ and intercept a. Figure 1 clearly shows this to be the case. The solid lines in Fig. 1 are derived using the values of k_1 and k_2 obtained above together with the values of metal and hydrogen ion concentration, K_h and K_E. It is apparent that the kinetic data fit the proposed mechanism over the range of hydrogen ion and metal concentration studied. The degree of complex formation is different at the three hydrogen ion concentrations at which the reactions were studied. However, it is also apparent that the intercept of the plot suggested by eqn. (7) is independent of the degree of complex formation. From a consideration of the relevant equilibrium constants it is clear that the term in a involving H^+ is negligible. 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.

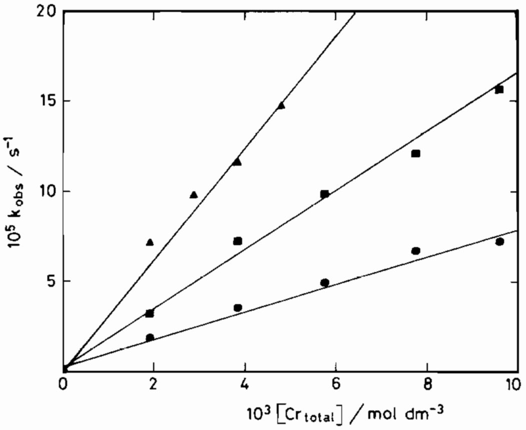

Fig. 1. Plot suggested by eqn. (7) for reaction of chromium(III) with Hpd in aqueous solution at 55 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. $[H^+]$ = ●, 6.76×10^{-3}; ■, 2.14×10^{-3}; ▲, 0.676×10^{-3} mol dm^{-3}.

The alternative formulation of the inverse acid pathway would involve reaction of Cr^{3+} with the enolate ion. If this mechanism is assumed, the rate constant for reaction of Cr^{3+} with the enolate ion is estimated to be 9×10^3 $dm^{-3}\ mol^{-1}\ s^{-1}$. This is clearly much too large and the formulation outlined in Scheme 1 is obviously the correct one.

The results of the present investigation differ considerably from the results obtained by the authors in refs. 11–13, 17 and 18. In all of these investigations, the ligand was present in excess and the reactions were found to be zero order in ligand concentration. Their kinetic results are most reasonably interpreted in terms of a saturated ion-pairing mechanism. The arguments in favour of this are adequately discussed in ref. 18. The present results are similar to the results obtained in refs. 15, 16 and 19 insofar as a dependence on total ligand concentration was found in these investigations while a first order dependence on total metal concentration was found in the present investigation. However the authors in the above-mentioned references did not take account of the presence of $[Cr(H_2O)_5OH]^{2+}$, although at the high acid concentrations used it would have only been a minor species. In all previous investigations, the reactant concentrations were considerably greater than in the present investigation. The lower ligand concentrations could be used due to the relatively large absorbance changes obtained in the region of 330 nm on complexing of Hpd by chromium(III).

For solvent exchange on chromium(III) in aqueous solution $\Delta H^{\ddagger} = 109.7$ kJ mol^{-1} while $\Delta S^{\ddagger} = 1.2$ J $K^{-1}\ mol^{-1}$ [26]. Thus the solvent exchange rate in water at 55 °C is 2.7×10^{-5} s^{-1} at 55 °C. The value of k_1 is considerably larger than this. If complex formation is presumed to take place via the usual ion-pair precursor then k_1 in the mechanism proposed in Scheme 1 would be equal to the product of the outer-sphere association constant and the rate constant for collapse of the ion-pair [27]. The ion pair equilibrium constant for reaction of Cr(III) with the uncharged protonated form of Hpd is approximately 0.3 [28]. Thus k_1 is considerably larger than the rate predicted on the basis of the Eigen–Wilkins mechanism. It is not possible to compare the present results with the results obtained in those investigations in which the kinetics showed no dependence on the concentration of the reagent present in pseudo-first-order excess. However they can be usefully compared with the results obtained for reaction of Cr(III) with acetate [19]. From the data reported in this work the values of K_0 and K_0', the outer sphere association constants for reaction of $[Cr(H_2O)_6]^{3+}$ and $[Cr(H_2O)_5(OH)]^{2+}$ respectively with acetate ion at 55 °C are calculated to be 1.94 and 1.0 mol^{-1} dm^3 respectively. The corresponding values for collapse of the outer sphere complexes are 1.12×10^{-2} and 2.59×10^{-2} s^{-1} respectively. Thus k_1 and k_2 for reaction of hexa-aquochromium(III) and monohydroxopentaaquochromium(III) with acetate ions are estimated to be 2.17×10^{-2} and 2.59×10^{-2} dm^3 mol^{-1} s^{-1} respectively. The value of k_1 is approximately twice that found for Hpd, while the value of k_2 is smaller by a factor of ten. It would appear that k_1 for Hpd is approximately twenty times greater than for malonate [15] or oxalate [16].

In most reactions of β-diketones with metal ions the protolytic reactions can not be treated as 'rapid'. However, in the present work the rate of ionization of Hpd (k_e) is considerably more rapid than the rate of complex formation and the assumption that the protolytic reactions are rapid is valid. This greatly simplifies the interpretation of the kinetic data. It is clear that the rate of formation of the chromium(III)–Hpd complex is considerably more rapid than the rate of solvent exchange on the metal ion. Thus the mechanism must be interchange associative (I_a). It appears that the enolate ion does not participate to any appreciable extent in the complex formation reaction. The labilizing effect of coordinated hydroxide on the metal species is also apparent.

The overall picture regarding the complex formation reactions of chromium(III) is still by no means clear. The reason for the extensive outer-sphere complexation of hexa-aquachromium(III) by some ligands is not immediately evident. In the case of Hpd there is no evidence for the greatly retarded rates of complex formation found in other beta-diketone systems [1–10]. However, the relative inertness of chromium(III) may be the reason for this.

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