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Kinetics of monochelation of aqueous chromium(III) by methyl 2-oxocyclopentanecarboxylate

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ABSTRACT: From a study of the complexation of methyl 2-oxocyclopentanecarboxylate with Cr(III) in aqueous solution, thermodynamic and kinetic parameters were obtained. The equilibrium constant of the monocomplex was determined spectrophotometrically. The kinetic processes of monochelation were investigated spectrophotometrically in aqueous solution at 50 °C and ionic strength 0.5 mol dm^{-3} $NaClO_4$. The mechanism proposed to account for the kinetic data involves a double reversible pathway where both Cr^{3+} and $Cr(OH)^{2+}$ react with the enol tautomer of the ligand. Some comparative analyses with the homologous 2-acetylcyclopentanonechromium(III) were made. Copyright © 2000 John Wiley & Sons, Ltd.

KEYWORDS: methyl 2-oxocyclopentanecarboxylate; chromium; kinetics; complexation; chelation

INTRODUCTION

Reagents containing multiple functionalities are very important both for their diverse mechanistic behaviour and in organic synthesis since they can be versatile and effective species for the efficient construction of complex structures from relatively simple starting materials.

One important example of such reagents is represented by β-keto esters, which undergo multicoupling reactions with electrophilic and nucleophilic sites and have proved to be valuable tools in the synthesis of a wide variety of molecular systems.[1]

Alkyl esters of 2-oxocycloalkanecarboxylic acids are receiving considerable attention, not only from the viewpoints of synthesis,2–5 reactivity[6–8] and spectroscopic behaviour,[9] but also because of their pharmacological and therapeutic properties, which make them useful lead compounds for the development of safer antiepileptic drugs[10] or derivatives with anti-inflammatory effects.[11]

Furthermore, they exhibit the phenomenon of keto–enol tautomerism and are able to form complex compounds similar to those of β-diketones. In fact, β-keto esters behave as bidentate ligands, forming coordination compounds with metal ions such as Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and La(III), Ce(III) and Pr(III).[12,13]

These complexes usually contain coordinated water molecules, thus completing a distorted octahedral coordination around the metallic site. The immediate environment of the metal in these complexes is very similar to that existing in their acetylacetonate compounds, e.g. $Co^{II}(acac)_2(H_2O_2)$, which is known to exist in near-octahedral coordination.[14]

In order to study the chelation abilities of keto esters in aqueous solutions, chromium(III) has been used as a metal centre for the first time. Chromium(III), which has a low-spin configuration (d^3) and consequently may be classified as a non-labile metal ion, is fairly stable in acidic aqueous solution.

Addition of base to a solution of $[Cr(H_2O)_6]^{3+}$ produces multiproduct equilibria that depend on $[Cr(III)]:[OH^-]$ ratios, temperature, pH and time. The hydrolytic polymerization of Cr(III) is not complicated by redox processes, and structural assignments can readily be made by relying on the almost exclusive and constant octahedral coordination at chromium(III) centres. The nature of the 'second hydration shell' has been probed with a variety of techniques including spectroscopy, x-ray diffraction and neutron diffraction.[15] Surprisingly consistent results have been obtained, with $n = 13 \pm 1$ in $[Cr(H_2O)_6]^{3+}(H_2O)_n$ and a Cr—O distance of 4.02 Å for the water molecules in the second hydration shell.

The oligomerization process[16–18] that takes place when $[Cr(H_2O)_6]^{3+}$ solutions are aged may be avoided by

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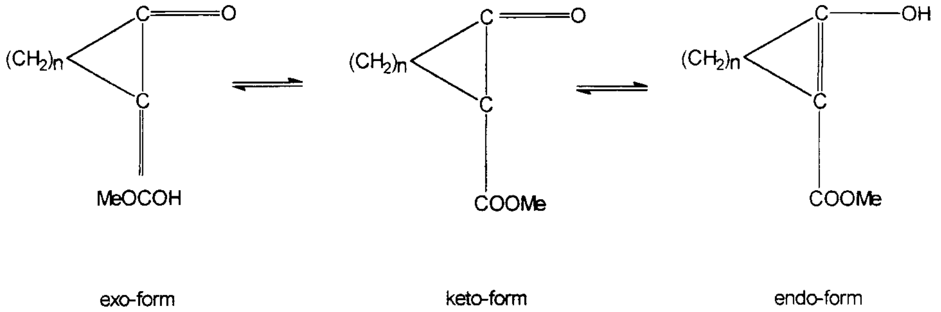

Figure 1. Keto and enol forms of the methyl 2-oxocycloalkanecarboxylate

working in acidic solutions. Arising from this, kinetic studies of chromium complexation reactions must be carried out under relatively acidic conditions and low chromium concentrations.

As part of our continuing interest in complexation reactions[19–21] in aqueous solutions, we now report a kinetic study of the complexation of a bidentate ligand with multiple functionality. To our knowledge, this is the first reported kinetic work in which a complex of stoichiometry 1:1 between an alkyl ester of 2-oxocycloalkanecarboxylic acid and chromium(III) in aqueous solution has been studied.

EXPERIMENTAL

Reagent-grade methyl 2-oxocyclopentanecarboxylate, (HMCP, H being the enolic hydrogen atom) (Aldrich) was freshly distilled under reduced pressure. Stock solutions were standardized by titration with standard sodium hydroxide.

A large excess of the methanol over the keto ester concentration ($[CH_3OH] = 20[HMCP]$) was always present in aqueous solution. In order to verify the ligand stability, sequential UV–visible overlapping spectra at different times following dissolution were registered. After the mixture time (and up to 1200 min) no further change was observed in 30 min interval spectra, indicating that the system had reached equilibrium in the aqueous solution referred to.

Solutions of Cr(III) were prepared from reagent-grade $Cr(NO_3)_3{\cdot}9H_2O$ (Aldrich) and were standardized by oxidizing the chromium(III) to chromium(VI) with potassium bromate.

The source of hydrogen ions was perchloric acid (Merck), and the ionic strength of reactant solutions was 0.5 mol dm^{-3}, adjusted using $NaClO_4{\cdot}H_2O$ (Merck).

Standard buffer solutions were obtained from borax, $Na_2HPO_4{\cdot}H_2O$ and NaOH (Aldrich). Unless indicated, otherwise all materials were of analytical-reagent grade, and were used without further purification.

pH measurements were made using a Crison 2002 pH meter calibrated to read hydrogen ion concentration directly by titrating solutions of perchloric acid with standard sodium hydroxide solutions. End-points were determined using the method of Johansson.[22]

UV–visible spectra were recorded on a Hitachi U-3000 spectrophotometer. A Spectronic 1201 UV–visible spectrophotometer which includes a kinetic resident programme was used to follow the kinetic runs. The standard cell length was 1 cm.

^1H and ^{13}C NMR spectra were recorded on Bruker AC-300 and ARX-300 instruments at 300 and 75 MHz, respectively, in D_2O–CD_3OD; chemical shifts are given in ppm relative to tetramethylsilane (TMS) as internal standard.

Since the inertness of chromium(III) gives rise to extremely slow ligand-substitution processes, experiments were carried out at $50 \pm 0.1\,°C$, a temperature typically used for chromium kinetic studies. The chelate compound stoichiometry and related thermodynamic parameters (stability constant, equilibrium constant) were determined when equilibrium was reached. To achieve this, the reaction mixture was kept in a thermostated oven for at least 48 h depending on the reagent concentrations utilized.

RESULTS AND DISCUSSION

It is well known that 1,3-dicarbonyl compounds are characteristically an equilibrium mixture of tautomers in solution. In general, alkyl α-ketocycloalkanelcarboxylates easily undergo keto–enol tautomerism (Fig. 1). The extent of enolization has been found to depend upon solvent and temperature. On the basis of bromine titrations and UV and ^1H NMR studies, Rhoads[23] concluded that amongst the ethyl esters of the C_5–C_{10} 2-oxocycloalkanecarboxylic acids, the even-membered systems exhibit 60–80% enol content while the odd-membered series exist as enols to a much lower extent, the lowest value of $\sim$11% being observed for the cyclopentane derivative (the terminology C_5, C_6, C_7, ..., C_{10} in the current discussion refers to the ring size of the cycloalkane derivatives). On the other hand, Sterk[24] found that the C_5 keto ester mentioned above exists exclusively in the keto form in DMSO or nitrobenzene in the 20–120 °C temperature range, while the correspond-

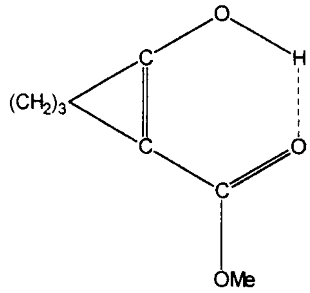

Figure 2. Quasi-aromatic structure of *endo*-enol form of methyl 2-oxocyclopentanecarboxylate

ing C_6 analogue showed an enol content of 80–50% in the same temperature range.

Kallury *et al.*,[25] on the basis of the mass-analysed ion kinetic energy (MIKE) spectrum of the molecular ion $[C_7H_{10}O_3]^{+\cdot}$, concluded that methyl 2-oxocyclopentanecarboxylate exists solely in the keto form in the gas phase. The results of Morizur *et al.*[26] on the enol content determined by photoelectron spectroscopy contradict the above conclusion. They found that, between 150 and 250 °C, methyl 2-oxocyclopentanecarboxylate exhibits 20–25% of the enol form.

Comparative studies using Fourier transform IR and ^{13}C NMR spectroscopy concluded that methyl 2-oxocyclopentanecarboxylate exists solely in the keto[27] form in the pure liquid and in $CDCl_3$ solution phase. On the other hand, the enol forms are present in all phases in C_6, C_7 and C_8 cycloalkane derivatives.

Further studies utilizing NMR spectroscopy provided a detailed molecular picture of the keto–enol tautomerism where only the quasi-aromatic structure of the *endo*-enol form of methyl 2-oxocyclopentanecarboxylate is considered present in the equilibrium[28,29] (Fig. 2).

The composition of the tautomeric mixture in polar solvents is usually unknown. The extent of enolization is expected to diminish in aqueous solution, as in the case of β-diketones and acyclic β-keto esters. In fact, in low-polarity solvents, the percentage of the less polar enolic form increases. Conversely, polar solvents displace the equilibrium towards the polar diketo form.[9] This can be explained by the solvation of the carbonyl groups by the polar solvent molecules, which increases the stability of the keto forms, and this is found to be true in the case of methyl 2-oxocyclopentanecarboxylate. In fact, our analysis of the ^1H and ^{13}C NMR spectra indicated that the keto tautomer of methyl 2-oxocyclopentanecarboxylate ($HMCP_k$) was present in D_2O–CD_3OD aqueous solution at 25 °C, while the enol tautomer ($HMCP_e$) was undetected, indicating less than 5% of enol form in the medium.

The keto–enol interconversion in this ligand was also investigated in aqueous solutions by using a spectrophotometric method to measure the rate at which bromine reacts. Bromine first reacts very rapidly with any enol

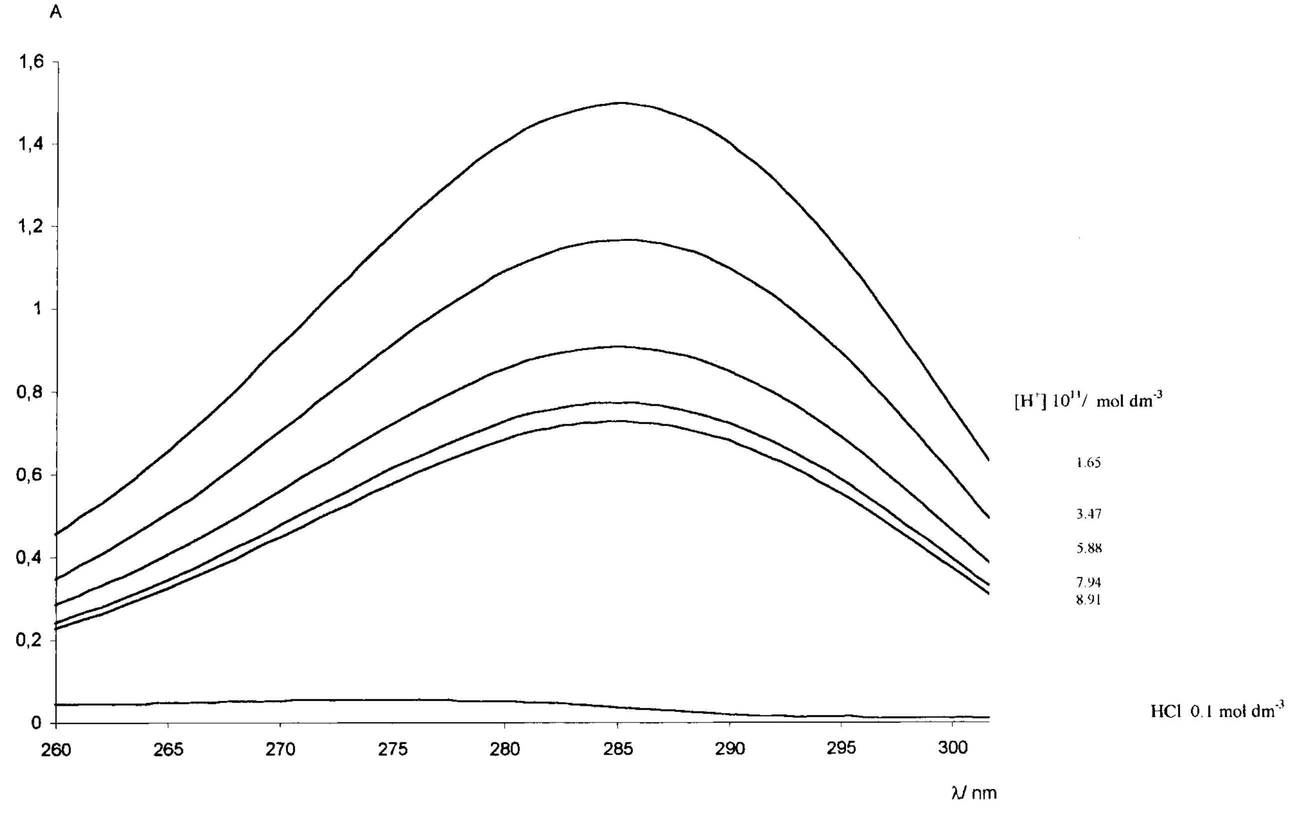

Figure 3. Methyl 2-oxocycloalkanecarboxylate UV keto–enolate absorption bands as a function of medium acidity. $[HMCP] = 2.5 \times 10^{-4}$ mol dm^{-3}

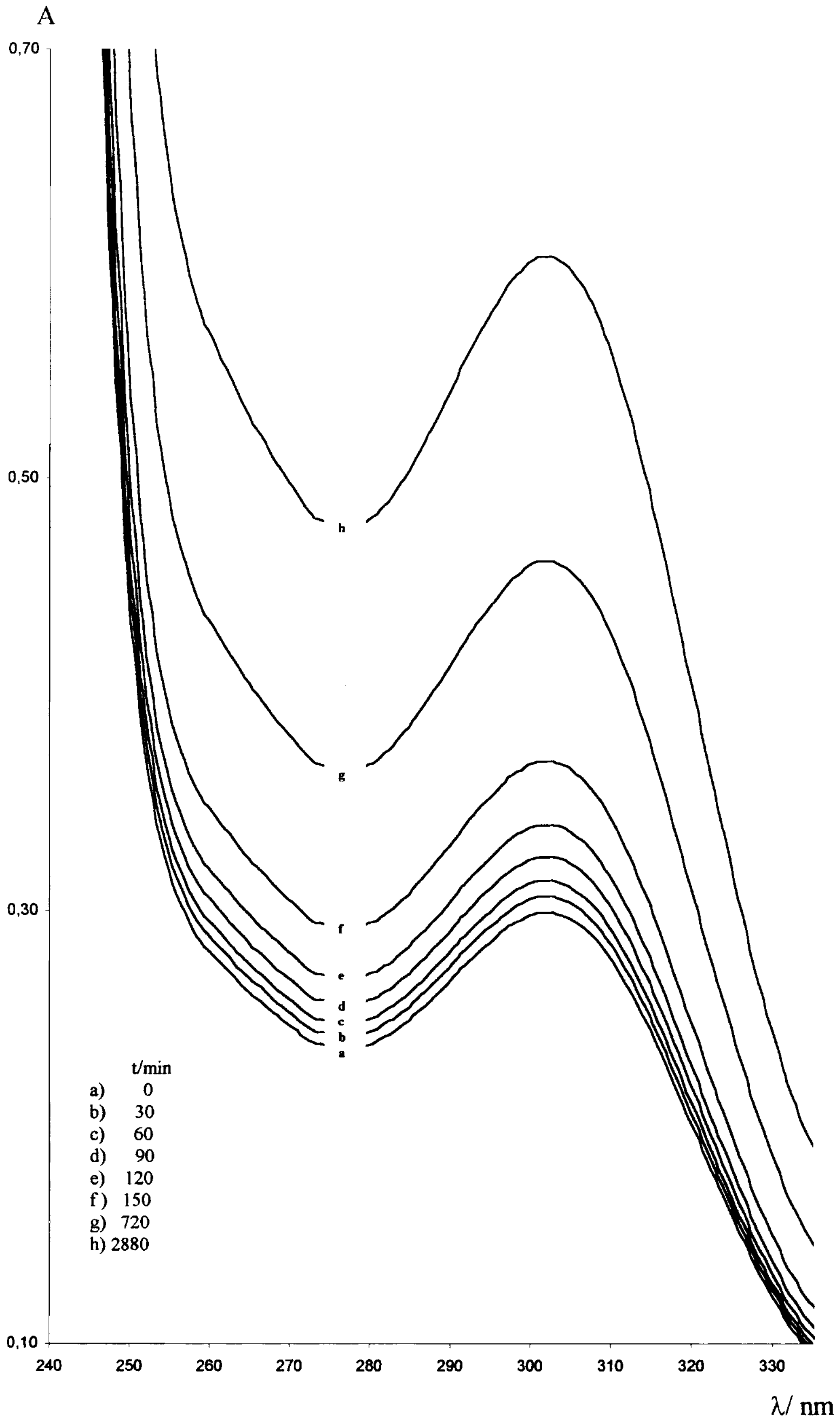

Figure 4. Spectra of monochelate complex scanned after different standing times indicated on the curves. [HMCP] = 1.0×10^{-4} mol dm^{-3}, [Cr^{3+}] = 1.5×10^{-2} mol dm^{-3} and [H^+] = 1.0×10^{-2} mol dm^{-3}

already present in solution. Thereafter, the bromination rate is governed by the rate of enol formation.

The procedure for the kinetic measurements was the same as in our previous paper.[30] The ligand concentrations in the cell, $[\mathrm{HMCP}]_0$, ranged from 2.2×10^{-3} to 3.3×10^{-3} mol dm^{-3}, whereas the bromine concentrations, $[\mathrm{Br}_2]_0$, ranged from 2.0×10^{-3} to 3.0×10^{-3} mol dm^{-3}.

Since $[\mathrm{HMCP}] = [\mathrm{HMCP_k}] + [\mathrm{HMCP_e}]$, and considering a first-order bromination equation,[30] the intercept values obtained in plots of $-\ln\{A/(\varepsilon 1) + [\mathrm{HMCP}]_0 - [\mathrm{Br}_2]_0\}$ versus time allow the determination of the enol fraction $y = [\mathrm{HMCP_e}]/[\mathrm{HMCP}]$. The term in the braces brackets corresponds to the keto tautomer concentration, where A is the absorption due to bromine at any time t at the observation wavelength (452 nm); ε is the absorption coefficient of bromine at 452 nm ($\epsilon = 103$) and ℓ is the pathlength (1 cm). Each of the bromine solutions contained 10^{-3} mol dm^{-3} NaBr in order to suppress hydrolysis of bromine. Changes in absorption at 452 nm were recorded at 1 s intervals. Thus, at 50 °C, the enolization rate constant was found to be $k_e = 8.3 \times 10^{-3}$ s^{-1} and $y = 0.04$.

As ligands of this class usually undergo hydrolysis in alkaline solution, it was thought desirable to determine their ionization constant through a spectrophotometric method such as parallel straight lines method,[31] allowing comparisons to be made between different deprotonation degrees of the ligand without using high concentrations of alkaline solutions. In fact β-keto esters in solution show maxima in the region of 270–300 nm associated with the $\pi \rightarrow \pi^*$ transition. The UV spectra (Fig. 3) show the change is the intensity of the characteristic absorption bands for the keto form of the ligand in several buffer solutions in the range $(\mathrm{p}K - 1) < \mathrm{pH} < (\mathrm{p}K + 1)$; the concentration of ligand used was 2.5×10^{-4} mol dm^{-3}. The wavelengths were selected at regular intervals around the absorption maximum of the ligand (285, 287, 289, 291 and 293 nm). A family of parallel straight lines was obtained and from their slopes the pK values for each wavelength could be determined. The average pK of the ligand at 25 °C was 10.3 ± 0.1, which agrees fairly well with the value determined by a kinetic method.[32]

The complex stoichimetry was characterized spectrophotometrically according to the method of continuous variations introduced by Job,[33] by keeping the total concentration ([Cr(III)] + [HMCP]) equal to 1.0×10^{-3} mol dm^{-3}, and also by the Yoe and Jones method[34] (in this case the total chromium concentration was 5.0×10^{-4} mol dm^{-3}, and the [HMCP] concentration was varied up to 2.0×10^{-3} mol dm^{-3}). The pH range (1.0×10^{-3}–1.0×10^{-2} mol dm^{-3}) was low enough to prevent the formation of hydrolysis products other than $\mathrm{Cr(H_2O)_5OH^{2+}}$ and the ionic strength was kept at 0.5 mol dm^{-3}. The results obtained from the above methods are in good agreement with each other, and they indicate a 1:1 stoichiometry. Finally, a COMIC plot was used. COMIC is a computer program[35] which can calculate the equilibrium concentrations of each entity (both free and complexed species) in a multicomponent system of metal ions and ligands.

The overall equilibrium of complex formation, which may be expressed as

$$K_{\mathrm{ML}} = [\mathrm{Cr(MCP)^{2+}}][\mathrm{H^+}]/[\mathrm{Cr^{3+}}][\mathrm{HMCP}] \qquad (1)$$

was obtained spectrophotometrically. The range of hydrogen-ion concentrations was high enough to prevent high degrees of chromium(III) hydrolysis/polymerization. The solutions contained such excess of metal ion that only the 1:1 complex was formed.

It should be taken into account that

$$[\mathrm{HMCP}] = [\mathrm{HMCP}]_0 - [\mathrm{Cr(MCP)^{2+}}] \qquad (2)$$

and

$$[\mathrm{Cr(MCP)^{2+}}] = A/\varepsilon \qquad (3)$$

where A is the metal complex absorption and ε is the metal complex absorption coefficient. Hence, the absorption change, at a fixed wavelength where the monochelated complex absorbs strongly, is a function of the equilibrium constant and the metal, ligand and proton concentrations used:

$$[\mathrm{HMCP}]_0/A = [\mathrm{H^+}]/([\mathrm{Cr^{3+}}]\varepsilon K_{\mathrm{ML}}) + 1/\varepsilon \qquad (4)$$

From an appropriate analysis of the data, using a correlation of the ratio $[\mathrm{HMCP}]_0/A$ vs the ratio $[\mathrm{H^+}]/[\mathrm{Cr^{3+}}]$, K_{ML} can be readily determined. Several series of solutions were prepared in which the Cr(III) concentration ranged from 2.0×10^{-3} to 8.0×10^{-3} mol dm^{-3}, $[\mathrm{H^+}] = 1.0 \times 10^{-2}$ mol dm^{-3} and $[\mathrm{HMCP}]_0 = 2.0 \times 10^{-4}$ mol dm^{-3}. Measurements were monitored by recording absorbance changes at 302 nm. At 0.5 mol dm^{-3} ionic strength a value of 0.39 ± 0.01 was obtained for K_{ML}. The results show that K_{ML} may be considered to be approximately constant over a wide range of temperatures (20–60 °C).

The kinetic analysis of the complexation process was carried out by following changes in the absorbance of bands originating from the appearance of the monochelated species. (Fig. 4). The reaction of complex formation was carried out with the metal ion concentration in great excess over the ligand to ensure pseudo-first-order conditions. First-order rate constants were obtained by fitting absorbance data to the general first-order kinetic equation. Each observed rate constant, k_{obs}, subsequently used for further calculation, is the average of at least three determinations. The standard deviation in individual runs was usually less than 2%.

Several series of experiments were carried out to study

Table 1. Kinetic data for reaction of chromium(III) with HMCP in aqueous solution at 50 °C and ionic strength 0.5 mol dm^{-3} with [HMCP] = 2.0 × 10^{-4} mol dm^{-3}[a]

$[Cr(III)] \times 10^2$ (mol dm^{-3})	$[H^+] \times 10^3$ (mol dm^{-3})	$k_{obs} \times 10^6$ (s^{-1})	$k_{cal} \times 10^6$ (s^{-1})	$(k_{obs} - k_{cal})/k_{obs} \times 10^2$
1.00	2.00	11.6	11.5	0.86
1.00	4.00	8.93	8.65	3.14
1.00	6.00	7.45	7.71	−3.49
1.00	8.00	7.32	7.33	−0.14
1.00	10.0	7.10	7.17	−0.99
1.20	2.00	12.9	12.9	0.00
1.20	4.00	9.31	9.46	−1.61
1.20	6.00	7.89	8.30	−5.20
1.20	8.00	7.45	7.79	−4.56
1.20	10.0	7.21	7.56	−4.85
1.50	2.00	14.5	15.0	−3.45
1.50	4.00	9.96	10.7	−7.43
1.50	6.00	8.60	9.17	−6.63
1.50	8.00	7.90	8.49	−7.47
1.50	10.0	7.85	8.14	−4.36
2.00	2.00	17.6	18.6	−5.68
2.00	4.00	13.6	12.7	6.62
2.00	6.00	11.3	10.6	6.19
2.00	8.00	10.5	9.64	8.19
2.00	10.0	9.85	9.12	7.41
2.40	2.00	22.4	21.4	4.46
2.40	4.00	15.5	14.3	7.74
2.40	6.00	12.3	11.8	4.07
2.40	8.00	10.1	10.6	−4.95
2.40	10.0	9.71	9.90	−1.96

[a] $k_1 = 1.57 \times 10^{-3}$ mol^{-1} dm^3 s^{-1}; $k_2 = 1.58\ 10^{-1}$ mol^{-1} dm^3 s^{-1}; RSS = 4.64.

the influence of the metal and proton concentrations on the observed rate constants, while the ligand concentration, ionic strength and temperature remained constant (Table 1).

Depending on the ligand and the pH of the reactant solutions, the reactive ligand species can be either or both of the protonated tautomers and/or the enolate ion. Since these reactions were carried out in acidic medium where the pH is considerably less than the pK of the ligand, the fraction of the ligand present as the enolate ion is very small, and need not be considered. The mechanisms of the complex formation reactions of β-dicarbonylic ligands have been widely investigated[36,,19] and the reactivity of the enol tautomer toward metal ions has been found to be greater than that towards the keto tautomer. In the case of HMCP, the greater reactivity should correspond to the above-mentioned *endo*-enol form.

Although the majority of chromium(III) substitution reactions are carried out under sufficiently acidic conditions for the monohydroxy species to be ignored, in the range of hydrogen ion concentration 2.0 × 10^{-3}–1.0 × 10^{-2} mol dm^{-3} the conjugate base, $Cr(H_2O)_5OH^{2+}$, is in equilibrium with the hexaaqua ion, offering an alternative pathway for complexation, which must be accounted for. The final product is invariably the metal–enolate complex irrespective of which metallic species predominates. This process, obviously, involves the loss of a proton from the ligand (Scheme 1), where coordinated water molecules have been omitted for clarity.

$$\mathrm{HMCP_e} + \mathrm{Cr^{3+}} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{Cr(MCP)^{2+}} + \mathrm{H^+}$$

$$\mathrm{HMCP_e} + \mathrm{Cr(OH)^{2+}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cr(MCP)^{2+}} + \mathrm{H_2O}$$

Scheme 1.

In Scheme 1, k_1 and k_2 are the rate constants for reaction of the enol tautomer with the hexahydrated and hydrolysed metallic species, respectively, and k_{-1} and k_{-2} are the rate constants for complex dissociation.

The $Cr(MCP)^{2+}$ formation rate can be expressed as

$$\begin{aligned}\frac{\mathrm{d}\ [\mathrm{Cr(MCP)}]}{\mathrm{d}t} &= k_1[\mathrm{Cr^{3+}}][\mathrm{HMCP_e}] \\ &\quad - k_{-1}[\mathrm{Cr(MCP)^{2+}}][\mathrm{H^+}] \\ &\quad + k_2[\mathrm{Cr(OH)^{2+}}][\mathrm{HMCP_e}] \\ &\quad - k_{-2}[\mathrm{Cr(MCP)^{2+}}] \qquad (5)\end{aligned}$$

since [HMCP] = [HMCP$_k$] + [HMCP$_e$] and [HMCP$_e$] = y[HMCP], and in addition d[$Cr(MCP)^{2+}$]/dt =

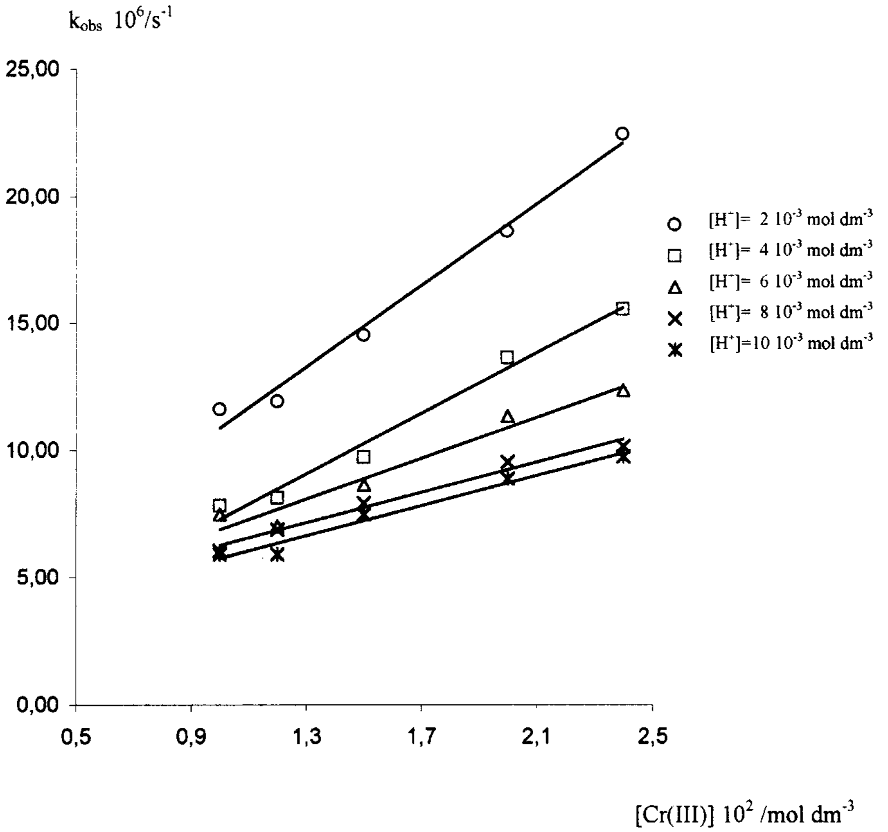

Figure 5. Observed rate constant as a function of the total concentration of chromium(III) at 50 °C and ionic strength 0.5 mol dm^{-3}. [HMCP] = 2.0 × 10^{-4} mol dm^{-3}

$-$d[HMCP]/dt, then

$$-\frac{\mathrm{d[HMCP]}}{\mathrm{d}t} = (k_{-1}[\mathrm{H}^+] + k_{-2})[\mathrm{HMCP}]_0 + (k_{-1}[\mathrm{H}^+] + k_{-2})[\mathrm{HMCP}] + \left(k_1 y + \frac{k_2 K_\mathrm{h} y}{[\mathrm{H}^+]}\right)[\mathrm{Cr}^{3+}][\mathrm{HMCP}] \quad (6)$$

where K_h is the hydrolysis constant of Cr^{3+} to form $\mathrm{Cr(OH)}^{2+}$, which at 50 °C was found[37] to be 3.98 × 10^{-4}.

Integrating Eqn. (6) and taking into account that since $[\mathrm{Cr(III)}]_0 = [\mathrm{Cr}^{3+}] + [\mathrm{Cr(OH)}^{2+}]$, the concentrations of $[\mathrm{Cr}^{3+}]$ and $[\mathrm{Cr(OH)}^{2+}]$ can be connected with the whole metal concentration throughout the hydrolysis constant k_h, and

$$[\mathrm{Cr(OH)}^{2+}] = [\mathrm{Cr(III)}_0]/(1 + [\mathrm{H}^+]/K_\mathrm{h}) \quad (7)$$

$$[\mathrm{Cr}^{3+}] = [\mathrm{Cr(III)}_0]/(1 + K_\mathrm{h}/[\mathrm{H}^+]) \quad (8)$$

$$k_{-1} = yk_1/K_\mathrm{ML} \quad (9)$$

$$k_{-2} = yk_2K_\mathrm{h}/K_\mathrm{ML} \quad (10)$$

the pseudo-first-order rate constant derived may be expressed as

$$k_\mathrm{obs} = \left[\frac{1}{K_\mathrm{ML}} + \frac{[\mathrm{Cr(III)}]_0}{[\mathrm{H}^+] + K_\mathrm{h}}\right] y(k_1[\mathrm{H}^+] + k_2K_\mathrm{h}) \quad (11)$$

Equation (11) indicates that the k_obs values are independent of the initial concentration of HMCP, as was found experimentally. The observed rate constant represented in Eqn. (11) now contains only two unknown parameters, k_1 and k_2. In order to obtain these, the equilibrium and kinetic data obtained were fitted to the above-mentioned equations. Using a NAG Fortran Library routine, values of k_1 and k_2 were determined at 50 °C (Table 1). The agreement between k_obs and k_calc values is satisfactory over the range of ligand and hydrogen ion concentrations studied, as can be seen in Table 1. The ‘goodness of fit’ as denoted by the corrected residual sum of squares (RSS) clearly demonstrates that the data are well described by Scheme 1.

One aim in this work was to determine whether a keto ester chromium monochelate structurally analogous to the homologous 2-acetylcyclopentanonechromium(III) has a similar kinetic behaviour.

It is noteworthy that the ester and amide groups are hardly enolized, in conformity with their low tendency towards nucleophilic addition reactions involving the carbonyl group. The failure of malonic ester to enolize[9] and the increasing degree of enolization with increasing electron-accepting capacity of the substituents are consistent with this view.[38,39] It is interesting that the extent of the enol contribution to the structure of HMCP is less than that of any other of the alkyl 2-oxocycloalkanecarboxylates mentioned, which is presumably related to the low electron-accepting capacity of the substituent. Furthermore, the enol content, in terms of the exclusively present *endo*-enol form in HMCP, is less than that of its homologous 2-acetylcyclopentanone and the rate of enolization is also two orders of magnitude slower. It is noteworthy also that even though the stability constant of methyl 2-oxocyclopentanecarboxylatechromium(III) is much lower than that of 2-acetylcyclopentanonechromium(III) ($K_{ML} = 14.2$), the reaction rate throughout the hydrolysed species is much higher for the keto ester complexation. On the other hand, kinetic results are inverted for the hexahydrated species pathways.

The reaction rates of both pathways are considerably larger than would be predicted on the basis of the outer-sphere association constant and the rates of solvent exchange (k_s). In this case, the overall water exchange rate constant, k_s, will therefore be the sum of contributions from the two reaction paths available at equilibrium, the water exchange on the hexaaqua species with rate constant k_0 and on its hydrolysed form with rate constant k_{OH}. Thus, a two-term rate equation of the type

$$k_s = k_0 + \mathrm{k}_{OH} K_h [H^+]^{-1} \tag{12}$$

has to be considered.[40] By interpolation of the data points in Ref. 40, the values of k_0 and k_{OH} obtained in our particular conditions are 7.7×10^{-5} s^{-1} and 6.6×10^{-3} s^{-1}, respectively. From these data the value of k_s at 50 °C and $[H^+] = 2.0 \times 10^{-3}$ is calculated to be 1.3×10^{-3} s^{-1}, implying that, in Eqn. (12), the term which involves the rate coefficient for exchange of an aqua ligand on $Cr(H_2O)_5OH^{2+}$ is the predominant one.

Taking into account that the reaction is first order, and the nature of the initial and final products, the tentative mechanism depicted in Scheme 1 can be assumed. The observed linear dependence between k_{obs} and chromium concentration, which may be presented as in Eqn. (13), may be justified from the data in Table 1. Accordingly, for a series of kinetic runs where $[H^+]$ is constant, a plot of k_{obs} against $[Cr(III)]_0$ according to Eqn. (13) should be a straight line (Fig. 5).

$$k_{obs} = f([H^+]) + g([H^+])[Cr(III)]_0 \tag{13}$$

This was verified in all cases with excellent correlation coefficients. The k_1 and k_2 values obtained from the slopes agree fairly well with those obtained from the overall fitting, as was expected.

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