Reactions of Metal Ions with Triketones. Part 2.† Kinetics and Mechanisms of the Reactions of Nickel(II) and Cobalt(II) with Heptane-2,4,6-trione in Methanol–Water (70:30 v/v)

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The kinetics and mechanisms of the reactions of nickel(II) and cobalt(II) with heptane-2,4,6-trione (H_2hpto) to form the 1:1 and 2:2 complexes have been studied in methanol–water (70:30 v/v) at 25 °C and an ionic strength of 0.5 mol dm^{-3} ($NaClO_4$). The rate constants of the mono complex formation with H_2hpto (k_{HL}) and with Hhpto$^-$ (k_L) have been determined. For Ni^{2+}, $k_{HL} = 180$, $k_L = 4.88 \times 10^4$ dm^3 mol^{-1} s^{-1}, while for Co^{2+} $k_{HL} = 476$, and $k_L = 1.36 \times 10^6$ dm^3 mol^{-1} s^{-1}. The conversion of the 1:1 to the 2:2 complex takes place *via* a two-stage mechanism. The rate constants for Ni^{2+} are 6.1 and 0.21 s^{-1} while for Co^{2+} they are 24.6 and 0.026 s^{-1}.

It has been shown that when heptane-2,4,6-trione (H_2hpto) is reacted with Ni^{II} or Co^{II} it may act as a bidentate or tridentate ligand depending on the experimental conditions.[1,2] In the former case, mononuclear complexes are formed while in the latter case dinuclear 2:2 complexes are formed. The π-system of the dianion, with the consequent preference for a planar configuration, apparently precludes tridentate co-ordination to a single metal ion. To date most of the investigations of metal complexes of heptane-2,4,6-trione have been concerned with the solid-state structures and magnetic properties.[3] We have recently shown that in methanol–water (70:30 v/v) mononuclear complex formation takes place at relatively high concentrations of hydrogen ion, while at lower concentrations of H^+, conversion to the 2:2 complex takes place.[4] The equilibrium constants for these reactions have been determined also. To date the kinetics and mechanisms of these reactions have not been reported.

β-Diketones undergo slow proton-transfer reactions and the kinetics of their complex-formation reactions are considerably modified as a result of this. It has recently been shown that the pseudo-equilibrium of acid dissociation may fail during complex formation reactions and that in such instances, kinetic measurements may lead to erroneous rate constants for the rate of complex formation.[5,6] This study was undertaken in order to elucidate the kinetics and mechanisms of the complex formation and dissociation reactions of nickel(II) and cobalt(II) with heptane-2,4,6-trione.

Experimental

Stock solutions of nickel(II) and cobalt(II) were prepared from their nitrates (BDH). These solutions were standardised by titration with ethylenediaminetetra-acetate (edta). Heptane-2,4,6-trione was prepared according to the method of Bethel and Maitland,[7] and was purified by distillation under reduced pressure. Freshly distilled material was used for the kinetic runs. Stock solutions of the ligand were standardised by titration with standard sodium hydroxide and the end-point was determined using an iterative computer program based on the method of Gran.[8]

Methanol was purified by distillation from magnesium and iodine. All solutions were prepared using distilled water which had been boiled out for 15 min. Methanol–water solutions (70:30 v/v) were prepared by adding water (300 cm^3) to a 1 000-cm^3 volumetric flask and diluting to the mark with distilled methanol. The mole fraction of methanol in this solution is 0.508. Sodium perchlorate, purified as previously described,[9] was used to adjust the ionic strength of all solutions to 0.5 mol dm^{-3}. Readings of pH were measured using a Pye model 290 pH meter and a Pye Ingold E_7^0 combination electrode. The KCl solution in the electrode compartment was replaced by 3 mol dm^{-3} NaCl; pH readings were converted to $[H^+]$ as described by Agrawal.[10] Solutions of perchloric acid and sodium hydroxide were used to adjust the pH.

Cacodylic acid [$Me_2As(O)OH$], *N*-(2-hydroxyethyl)-piperazine-*N'*-ethane-2-sulphonic acid (hepes), 2,6-dimethyl-pyridine-3-sulphonic acid, acetic acid–sodium acetate, and $HCl–HN(CH_2CH_2OH)_2$ were used to control the pH during the kinetic measurements. Rate constants were measured using an Applied Photophysics stopped-flow device interfaced to a BBC microcomputer *via* a Datalab DL901 transient recorder. Pseudo-first-order rate constants could be determined from plots of ln $(A - A_\infty)$ against time or from Guggenheim plots. Up to 160 points were used in the calculations (due to the shortage of RAM in the BBC microcomputer every fifth point from the transient recorder was used). In each case calculated absorbance values at each point were calculated from the experimentally determined values of the amplitude and rate constant. They were then compared graphically with the raw data and a magnified plot of the residuals was displayed. Using this method the quality of the kinetic data could be rapidly evaluated. In the case of the conversion of the 1:1 to the 2:2 complexes where two reactions steps were observed, the rate constants were evaluated using an exponential stripping program written for the BBC microcomputer. The method is based on those described by Wagner.[11]

The kinetics of the ionization of the ligand were investigated using a pH-jump technique. A slightly acidic solution of 5×10^{-4} mol dm^{-3} H_2hpto was mixed in the stopped-flow apparatus with a series of $HCl–HN(CH_2CH_2OH)_2$ buffers of the same ionic strength having pH values in the range 8.5—10.5.

The kinetics of formation of the 1:1 complexes of both Co^{II} and Ni^{II} were measured under pseudo-first-order conditions with the metal in excess. In both instances the reactions were monitored by observing the absorbance increase at 350 nm. The Ni^{II} reactions were measured in the pH range 3—7 while the Co^{II} reactions were measured in the pH range 5—6. Reactions with Co^{II} were limited to this pH range as at the lower pH's there is little complex formation and above pH 6, formation of the 2:2 complex takes place. In the case of measurements carried out at

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† Part 1 is ref. 4.

Table 1. Observed rate constants for the reaction of Ni^{2+} and Co^{2+} with heptane-2,4,6-trione in methanol–water (70:30 v/v), at 25 °C and $I = 0.5$ mol dm^{-3} ($NaClO_4$)*

M	10^3[M]/ mol dm^{-3}	[H^+]/ mol dm^{-3}	$k_{obs.}$/s^{-1}	$k_{calc.}$/s^{-1}
Ni^{2+}	1.13	1.36×10^{-7}	2.67	2.37
	2.25	1.36×10^{-7}	5.01	4.74
	3.37	1.36×10^{-7}	6.97	7.10
	4.50	1.36×10^{-7}	9.20	9.49
	5.60	1.36×10^{-7}	12.0	11.8
	1.13	1.36×10^{-6}	0.35	0.42
	2.25	1.36×10^{-6}	0.73	0.84
	3.37	1.36×10^{-6}	1.10	1.26
	4.50	1.36×10^{-6}	1.50	1.68
	5.60	1.36×10^{-6}	1.91	2.09
	13.50	1.36×10^{-3}	3.09	3.05
	20.20	1.36×10^{-3}	4.30	4.26
	27.20	1.36×10^{-3}	5.81	5.52
	33.80	1.36×10^{-3}	6.65	6.71
Co^{2+}	1.22	1.36×10^{-6}	8.1	8.50
	2.45	1.36×10^{-6}	16.0	15.6
	3.63	1.36×10^{-6}	22.5	22.5
	4.90	1.36×10^{-6}	29.5	29.9
	6.31	1.36×10^{-6}	37.5	37.0
	1.22	4.28×10^{-6}	4.1	4.25
	2.45	4.28×10^{-6}	7.0	6.9
	3.63	4.28×10^{-6}	9.1	9.5
	4.90	4.28×10^{-6}	12.1	12.3
	6.13	4.28×10^{-6}	14.7	15.0
	1.22	1.36×10^{-5}	3.2	3.6
	2.45	1.36×10^{-5}	5.0	4.8
	3.63	1.36×10^{-5}	6.0	6.0
	4.90	1.36×10^{-5}	7.5	7.3
	6.13	1.36×10^{-5}	8.9	8.6

* [H_2hpto] = 2.5×10^{-4} mol dm^{-3}; measurements made at λ = 350 nm.

pH 3 a 10^{-2} mol dm^{-3} acetic acid–sodium acetate buffer was used to control the hydrogen ion concentration. Changing the buffer concentration had no apparent effect on the rate constants. No relaxations in the time range of the metal–ligand processes were observed in blank experiments involving only the ligand and buffers.

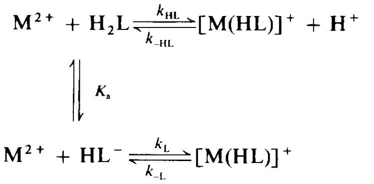
The conversion of the 1:1 to the 2:2 complexes were monitored by reacting solutions of [Ni(Hhpto)]$^+$ and [Co(Hhpto)]$^+$ with standard sodium hydroxide solutions and observing the increase in absorbance at 380 nm.

Hydrolysis reactions were carried out by reacting solutions containing both metal and ligand at an appropriate pH with solutions containing perchloric acid and observing the absorbance at a suitable wavelength.

All reactions were carried out at 25.0 ± 0.1 °C.

Results and Discussion

The absorbance of H_2hpto at 360 nm increases with pH at pH > 6.5. Clearly, this absorbance change is associated with ionization of the ligand. This is also the absorbance change observed in the stopped-flow apparatus following a pH jump from acidic pH to values in the range 8.5—10.5. However, in all cases the absorbance change was so rapid that rate constants could not be measured. Consequently, at these pH values, the rate of ionization must be $\geqslant 300$ s^{-1}. Bromination experiments gave similar results. When solutions of H_2hpto at pH 6.0 were reacted with solutions of Br_2 containing 1×10^{-3} mol dm^{-3} KBr (to prevent hydrolysis) most of the bromine was consumed instantly on the stopped-flow time-scale. A relatively slow reaction having a small amplitude probably resulted from reaction of Br_2 with the small amount of the ligand existing in the triketone form.



Scheme 1.

When solutions of H_2hpto were reacted with either Ni^{II} or Co^{II} an absorbance change corresponding to a single exponential was observed. The kinetic data are given in Tables 1 and 2. These data are consistent with the mechanism outlined in Scheme 1. Under pseudo-first-order conditions with metal in excess Scheme 1 predicts that $k_{obs.}$ will have the form of equation (1) (H_2L = heptane-2,4,6-trione) where $K_f = [M(HL)^+]/[M^{2+}][HL^-] = k_L/k_{-L}$ and K_a is the first dissociation constant of H_2hpto ($10^{-8.27}$).[4] Fitting the kinetic data to equation (1) gives values of k_{HL} = 180 ± 4 and 476 ± 25 dm^3 mol^{-1} s^{-1} for Ni^{2+} and Co^{2+} respectively and values of $k_L = 4.88\ (\pm 0.08) \times 10^4$ and $1.36\ (\pm 0.01) \times 10^6$ dm^3 mol^{-1} s^{-1} for Ni^{2+} and Co^{2+} respectively. Equation (1) predicts that a plot of $k_{obs.}\{[M^{2+}]([H^+] + K_a)^{-1} + (K_aK_f)^{-1}\}^{-1}$ against [H^+] should be linear with a slope of k_{HL} and intercept k_LK_a. Figures 1 and 2 show this to be true and even in the case of Ni^{II}, where the H^+ concentration was varied over four orders of magnitude, there is no deviation from linearity.

$$k_{obs.} = (k_{HL}[H^+] + k_LK_a)\left[\frac{[M^{2+}]}{K_a + [H^+]} + (K_aK_f)^{-1}\right] \quad (1)$$

When solutions containing metal and ligand at pH values where appreciable quantities of [M(HL)]$^+$ had formed were reacted with sodium hydroxide solutions of concentrations in the range 5×10^{-3} to 1.5×10^{-2} mol dm^{-3}, two separate reactions were observed. The rate constants were relatively well separated and no difficulty was encountered in evaluating the individual rate constants using the method described in the Experimental section. The rate constants were independent of both base and complex concentration. The values obtained were 6.07 and 0.21 s^{-1} for Ni^{2+} and 24.6 and 0.026 s^{-1} for Co^{2+}.

The mechanism of conversion of the 1:1 to the 2:2 complex must be discussed in the light of the kinetic data. The fact that changing the concentration of the 1:1 complex does not alter the rate constants implies that dimerisation is not involved in either of the rate-determining steps. In such cases the half-life of the reaction would be equal to $1/(2kA_0)$ where A_0 is the concentration of the 1:1 complex. The mechanism proposed is shown in Scheme 2. This is a two-step process, the faster of the two steps involving ionization of the [M(HL)]$^+$ species, while the slower of the two steps involves the formation of the 2:2 complex.

It is now accepted that in most cases ionization of intramolecularly hydrogen-bonded species involves a two-step process.[12] The first step represents the equilibrium between the 'open' and 'closed' forms of the hydrogen-bonded species, while the second step involves removal of the proton by the base. In the present case where hydroxide ion is the base, the overall reaction is thermodynamically favoured and $k_{obs.}$ has the form of equation (2). If the step involving k_2 behaves as a normal

$$k_{obs.} = k_1k_2[OH^-]/(k_{-1} + k_2[OH^-]) \quad (2)$$

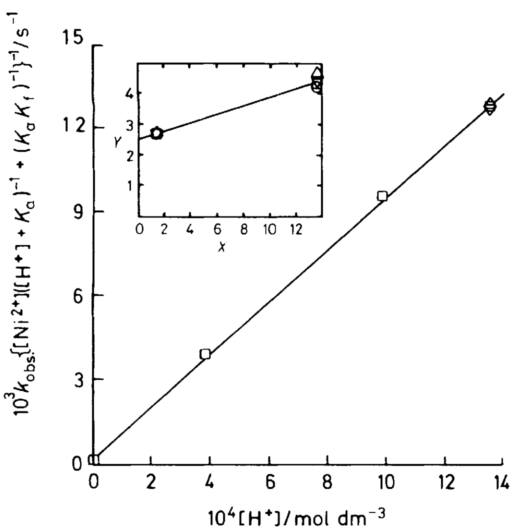


Figure 1. Plot of equation (1) for reaction of Ni^{II} with heptane-2,4,6-trione in methanol–water (70:30 v/v) at 25 °C and $I = 0.5$ mol dm^{-3}. $[Ni^{II}] = 5.60 \times 10^{-3}$ (□), 4.50×10^{-3} (○), 3.37×10^{-3} (△), 2.25×10^{-3} mol dm^{-3} (▽). Inset: $X = 10^7[H^+]$/mol dm^{-3}, $Y = 10^4k_{obs.}\{[Ni^{2+}]([H^+] + K_a)^{-1} + (K_aK_f)^{-1}\}^{-1}/s^{-1}$

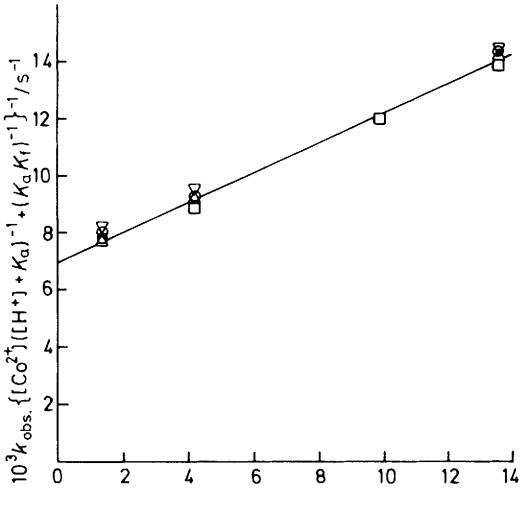
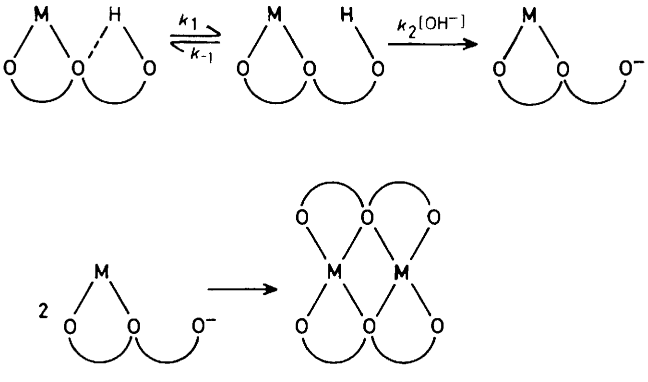
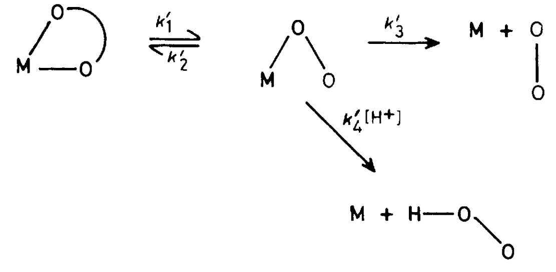


Figure 2. Plot of equation (1) for reaction of Co^{II} with heptane-2,4,6-trione in methanol–water (70:30 v/v) at 25 °C and $I = 0.5$ mol dm^{-3}. $[Co^{II}] = 6.13 \times 10^{-3}$ (□), 4.90×10^{-3} (○), 3.63×10^{-3} (△), 2.45×10^{-3} (▽) mol dm^{-3}

diffusion-controlled reaction, k_2 will have a value of *ca.* 2×10^{10} dm^3 mol^{-1} s^{-1} when OH^- is the base. In most examples investigated to date, $k_{obs.}$ is directly proportional to $[OH^-]$, and consequently the rate at which the open form reverts to the hydrogen-bonded species (k_{-1}) must be greater than the rate of proton removal from the open form by base. However, in the present case it appears that $k_2[OH^-] \gg k_{-1}$ so that $k_{obs.} = k_1$. Values of 6×10^7 s^{-1} have been estimated for k_{-1} in the case of substituted salicylic acids [12] so that at the high concentrations of hydroxide ion used here ($\geqslant 5 \times 10^{-3}$ mol dm^{-3}) it is not very surprising that $k_2[OH^-] \gg k_{-1}$. Thus the value of k_1 is 6.07 and 24.6 s^{-1} for $[Ni(HL)]^+$ and $[Co(HL)]^+$ respectively.



Scheme 2.



Scheme 3.

Table 2. Rate constants for reaction of Ni^{2+} and Co^{2+} with heptane-2,4,6-trione and for conversion of the 1:1 complex to the 2:2 complex, in methanol–water (70:30 v/v), at 25 °C and $I = 0.5$ mol dm^{-3} ($NaClO_4$)

Rate constant	Ni^{2+}	Co^{2+}
k_{HL}/dm^3 mol^{-1} s^{-1}	180 ± 4	476 ± 25
k_L/dm^3 mol^{-1} s^{-1}	$4.88(\pm 0.08) \times 10^4$	$1.36(\pm 0.01) \times 10^6$
k_{-HL}/dm^3 mol^{-1} s^{-1}	$4.97(\pm 0.24) \times 10^3$	$2.07(\pm 0.39) \times 10^4$
k_{-L}/s^{-1}		1.41 ± 0.6
k_{-L}(calc.)/s^{-1}	1.23×10^{-2}	1.18
$k_{1:1\rightarrow 2.2}$ (fast step)/s^{-1}	6.1 ± 0.12	24.6 ± 0.02
$k_{1:1\rightarrow 2.2}$ (slow step)/s^{-1}	0.21 ± 0.01	$2.6(\pm 0.4) \times 10^{-2}$

The slow step in the conversion must be associated with a rate-determining reorganisation of some form of a dimeric precursor complex to form the final dinuclear 2:2 complex.

When solutions of $[M(HL)]^+$ were reacted with solutions containing varying concentrations of hydrogen ion, a single reaction was observed. The kinetic data may be represented by equations (3) and (4) for Ni^{II} and Co^{II} respectively. The general

$$k_H^{Ni} = 0.0 + 4.97 \times 10^3[H^+] \tag{3}$$

$$k_H^{Co} = 1.41 + 2.07 \times 10^4[H^+] \tag{4}$$

mechanism for dissociation is shown in Scheme 3. For this mechanism $k_{obs.}$ has the form of equation (5). When $[H^+] = 0$,

$$k_{obs.} = \frac{k'_1(k'_3 + k'_4[H^+])}{k'_2 + k'_3 + k'_4[H^+]} \tag{5}$$

$k_H = k_{-L} = k'_1k'_3/(k'_2 + k'_3)$. At intermediate $[H^+]$, $k_{obs.}$ will vary linearly with hydrogen ion concentration while at high $[H^+]$, $k_{obs.} = k'_1$. The ratio k_{-L}/k_1 is the probability that a monodentate complex will either dissociate or be trapped by a proton. In the case of Co^{II} the value of k_{-L} calculated from k_L and K_f is in good agreement with the experimentally determined quantity. In the case of Ni^{II} a similar calculation gives the value of $k_{-L} = 1.23 \times 10^{-2}$ s^{-1}. This is too small to be experimentally detectable on the plot of $k_{obs.}$ against $[H^+]$.

Hydrolysis of the 2:2 complex results in a single reaction. The rate data are described by equations (6) and (7). In the case of

$$k_H^{Ni} = 0.35(\pm 0.02) + 60.6(\pm 2.1)\,[H^+] \qquad (6)$$

$$k_H^{Co} = 0.69(\pm 0.03) + 56.1(\pm 3.9)\,[H^+] \qquad (7)$$

both nickel and cobalt, the hydrolysis of the 2:2 complexes is slower than hydrolysis of the 1:1 complexes. This is consistent with the fact that only one reaction step is observed in the hydrolysis of the 2:2 complexes.

In methanol–water (70:30 v/v) solutions, the two predominant species of Ni^{2+} are $[Ni(H_2O)_6]^{2+}$ and $[Ni(H_2O)_5(CH_3OH)]^{2+}$.[12] In such a system at an ionic strength of 0.5 mol dm^{-3}, the outer-sphere association constants (K_0) for $+2/-1$ and $+2/0$ interactions are approximately 2 and 0.5 respectively. Taking the solvent-exchange rate $k^s_{6:0} = 2.8 \times 10^{-4}$ s^{-1} and $k^s_{5:1} = 1.38 \times 10^5$ s^{-1}, and using the calculated distribution of $[Ni(H_2O)_6]^{2+}$ and $[Ni(H_2O)_5(CH_3OH)]^{2+}$ an average solvent-exchange rate of 7.3×10^4 s^{-1} is calculated.[13] It must be realised that the values for both k_s and K_0 are only approximate, nevertheless they provide a useful basis for a comparison of the rate constants for complex formation. They do suggest that 'normal' complex formation reactions should be *ca.* 2.5 times as fast in methanol–water (70:30 v/v) as in water. Although detailed information on solvent-exchange rates of Co^{2+} in methanol–water mixtures is not available, it is not unreasonable to assume that similar considerations apply.

Using the above values for k_s the formation rate constants for reaction of Ni^{2+} with neutral (k_{HL}) and a mono-anionic ligand (k_L) are calculated to be 1.6×10^4 and 1.1×10^5 dm^3 mol^{-1} s^{-1} respectively. The corresponding values of k_{HL} and k_L for Co^{2+} are 6.6×10^5 and 4.4×10^6 dm^3 mol^{-1} s^{-1} respectively. From the data in Table 2, it is obvious that the experimental values for k_L are in fair agreement with the predicted values. The value for Ni^{2+} is lower by a factor of two while the value for Co^{2+} is lower by a factor of three. Taking the uncertainty in both the solvent-exchange rates and the outer-sphere association constant into account, the agreement must be considered satisfactory, and consequently it must be accepted that solvent exchange is the rate-determining step as in 'normal' complex formation to Ni^{2+} and Co^{2+}.

Complexation with the protonated neutral form of the ligand yields complex formation rate constants that are too slow by a factor of 89 in the case of Ni^{2+} and 1 387 in the case of Co^{2+}, when compared to the values calculated using K_0 and the solvent-exchange rates. Clearly a significant rate-retarding effect is in operation when the neutral H_2hpto is the incoming ligand. In this instance, conversion from the monobonded intermediate must now involve loss of solvent from the metal ion, proton loss, and ring closure. In view of the fact that the monoanion reacts normally, it is tempting to associate the reduction in rate constant with ring closure. However, due to the fact that the protonated ligand is probably a poor entering group, formation of the monobonded intermediate may also be slow, thus leading to a slow overall rate of complex formation.[14]

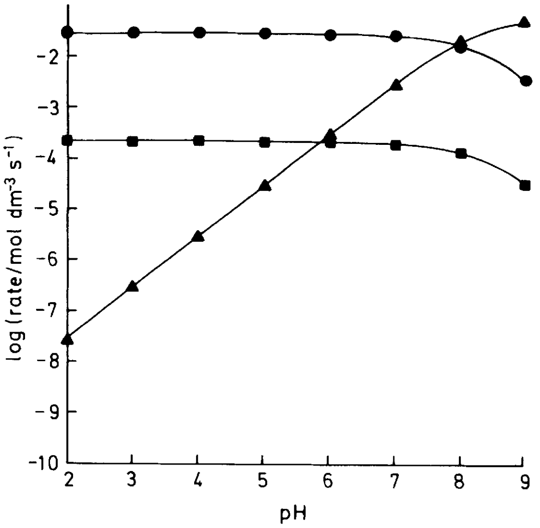


Figure 3. Relationship between initial rates and pH for the complex $[Ni(Hhpto)]^+$ in methanol–water (70:30 v/v) at 25 °C and I = 0.5 mol dm^{-3}: (rate $-$H)$_0$ (●), (rate M + HL)$_0$ (■), (rate M + L)$_0$ (▲)

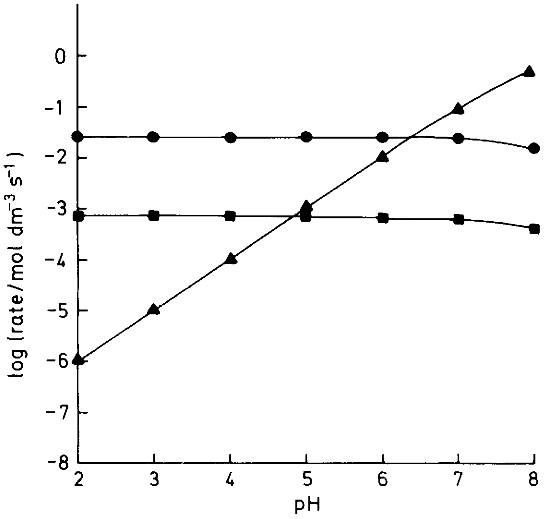


Figure 4. Relationship between initial rates and pH for the complex $[Co(Hhpto)]^+$ in methanol–water (70:30 v/v) at 25 °C and I = 0.5 mol dm^{-3}: key as in Figure 3

The non-base-catalysed rate constant for proton loss from uncomplexed H_2hpto may be estimated from the relationship $k_{-H}/k_H = K_a$ assuming that the rate constant for recombination of proton and the conjugate base, k_H, is diffusion controlled. Thus $k_{-H} = 107$ s^{-1}. It has recently been shown that when the pseudo-equilibrium of acid dissociation of the ligand fails during complex formation, incorrect values can be obtained for the complex-formation rate constants.[5,6] The requirement for maintenance of the pseudo-equilibrium is given by equation (8)

$$\begin{aligned}&(\text{rate } -\text{H}) > (\text{rate M} + \text{L}) \\ &\qquad\qquad \text{and } (\text{rate H}) > (\text{rate M} + \text{HL}) \qquad (8)\end{aligned}$$

where (rate $-$H) and (rate H) represent the rate of deprotonation and protonation of the ligand and (rate M + HL) and (rate M + L) represent the rates of reaction of the metal species with the protonated and deprotonated forms of the ligand respectively. The four rates are defined by equations (9)—(12). The quantities (rate M + HL), (rate $-$H), and (rate

$$(\text{rate } -\text{H}) = k_{-H}[H_2L] \qquad (9)$$

$$(\text{rate H}) = k_H[HL^-][H^+] \qquad (10)$$

$$(\text{rate M} + \text{HL}) = k_{\text{HL}}[\text{M}][\text{H}_2\text{L}] \qquad (11)$$

$$(\text{rate M} + \text{L}) = k_{\text{L}}[\text{M}][\text{HL}^-] \qquad (12)$$

H) all decrease and (rate M + L) increases with decreasing hydrogen ion concentration. Therefore, while the pseudo-equilibrium of the ligand may hold at high concentrations of hydrogen ion, it may fail at lower values. Figures 3 and 4 show the relationship between the initial rates and log [H$^+$] for the reactions of Ni^{2+} and Co^{2+} with H$_2$hpto. In the case of Ni^{2+} it is clear that the pseudo-equilibrium holds up to [H$^+$] = 10^{-8} mol dm^{-3}, while in the case of Co^{2+} the crossover occurs at approximately [H$^+$] = $10^{-6.5}$ mol dm^{-3}. The kinetic data for both Ni^{2+} and Co^{2+} were obtained below the crossover point of the (rate M + L)$_0$ and (rate −H)$_0$ curves. Thus, the data in Figures 3 and 4 support the validity of equation (8) and hence equation (1). The rate constants for proton loss from [M(HL)]$^+$, 6.07 and 24.6 s^{-1} for Ni^{2+} and Co^{2+} respectively, are quite small. However, a value of 1 s^{-1} has been reported for the rate of proton loss from the Ni^{2+} complex for (2,4-dihydroxyphenyl)-alanine.[15] Additionally β-diketones undergo slow proton-transfer reactions and the enol form of pentane-2,4-dione has a proton-dissociation rate constant of only 170 s^{-1}.[16] In the light of these data the values for the [M(HL)]$^+$ complexes of H$_2$hpto, where appreciable intramolecular hydrogen bonding would be expected, are very reasonable.

Due to the fact that the rate constants for dimerisation show no dependence on the complex concentration, little information about the mechanism can be deduced from the kinetic data. They do however demonstrate that the reaction involved at least one comparatively slow step, following the association of to form a dimeric precursor complex.

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Received 6*th February* 1985; *Paper* 5/212