Metal-catalysed Ionization of a Cyclic 1,3-Diketone. The Effects of Nickel(II) and Copper(II) on the Ionization of 2-Acetylcyclohexanone

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The kinetics and mechanisms of the reactions of nickel(II) and copper(II) with 2-acetylcyclohexanone to form metal–enolate complexes have been investigated in methanol–water solution (70:30 v/v) at 25 °C and ionic strength 0.5 mol dm^{-3}. A mechanism is proposed which accounts satisfactorily for the kinetic data. Nickel(II) reacts exclusively with the enol tautomer of the ligand with a rate constant of 0.114 dm^3 mol^{-1} s^{-1}. Copper(II) reacts with both the keto and enol tautomers of the ligand with rate constants of 0.929 and 1.27 × 10^3 dm^3 mol^{-1} s^{-1}, respectively. The catalytic effect of both Ni^{2+} and Cu^{2+} on the ionization rate constants of the keto and enol tautomers of the ligand have been calculated.

The reversible base-catalysed transformation of β-diketones into their enolic forms is a reaction whose mechanism is well established.[1–8] The rate of enolization can be measured by the rate of halogen uptake from solution because on the time-scale of the enolizations, any of the enol tautomer present reacts instantaneously with halogen. Although the enolization reaction is subject to general-base catalysis,[9–11] no acid catalysis occurs in the case of β-diketones.[12,13]

The kinetics and mechanisms of the reactions of metal and oxometal ions with a variety of β-diketones have been the subject of a number of investigations.[14] A variety of kinetic behaviour is exhibited in these reactions. Complexation can take place by reaction of the metal species with either of the two possible tautomers or with the enolate ion. Which actually occurs is dependent on both the metal species and the β-diketone involved. In general, the reactions between the metal species and either of the two possible tautomers are slower than would be expected on the basis of the Eigen–Wilkins–Tamm mechanism[15,16] which predicts that the rate of complex formation should be approximately equal to $(3/4)k_sK_o$ where k_s is the rate of solvent exchange, K_o is the outer-sphere association constant and (3/4) is a statistical factor.[17] These reactions are probably slow because of rate-determining proton transfer. However, reaction of the enolate ion with most metal species generally proceeds at rates comparable to those predicted by the Eigen–Wilkins–Tamm mechanism.[14–16]

To date, no detailed kinetic studies of the reactions of metal ions with cyclic β-diketones have been reported. Both the keto–enol equilibrium and the rates of enolization of 2-acetylcyclohexanone have been previously investigated in aqueous solution.[18] It was shown that the rate of enolization was much slower than that of most linear 1,3-diketones and that it was base-catalysed. No acid-catalysis effect was observed. Consequently it was of interest to investigate the extent to which the enolization reaction would be catalysed by transition-metal ions such as Cu^{2+} and Ni^{2+}. We have investigated the reactions of nickel(II) and copper(II) with 2-acetylcyclohexanone in methanol–water solution (70:30 v/v). The ligand and its metal complexes have sufficient solubility in this medium to enable the complex formation reactions to be studied.

Experimental

$Ni(ClO_4)_2{\cdot}6H_2O$ (Johnson Matthey) was used as the source of nickel(II). Stock solutions were standardized by titration with ethylenediaminetetraacetate using bromopyrogallol red as an indicator.

$Cu(NO_3)_2{\cdot}3H_2O$ (May and Baker) was used as the source of copper(II). Stock solutions were standardized by titration with sodium thiosulfate in the presence of starch indicator. The sodium thiosulfate had been previously standardized against potassium iodate.

Reagent-grade 2-acetylcyclohexanone (Aldrich) was freshly distilled under reduced pressure prior to use. Stock solutions were standardized by titration with standard sodium hydroxide using SUPERQUAD[19] to determine the end-points.

Perchloric acid was used as the source of hydrogen ions and all solutions were adjusted to an ionic strength of 0.5 mol dm^{-3} by the addition of $NaClO_4$.

Reagent-grade methanol was distilled from magnesium and iodine prior to use. Methanol–water solutions were prepared by addition of water (300 g) to a volumetric flask (1000 cm^3) and followed by dilution to the mark with dry methanol. These are referred to in the text as methanol–water (70:30 v/v).

UV–VIS spectra were recorded on a Shimadzu UV260 spectrophotometer. pH Measurements were made using a PT16 pH meter equipped with a Russell combination electrode. The filling solution of the reference section was 3 mol dm^{-3} aqueous sodium chloride. The pH meter was calibrated to read hydrogen-ion concentration directly by titrating solutions of perchloric acid (0.001–0.005 mol dm^{-3}) with standard sodium hydroxide solution. The end-points of these titrations together with the electrode correction factor were determined using a computer program based on the method of Johansson.[20]

Metal-ion and proton stability constants were determined by the potentiometric technique. Titrations were carried out in jacketed titration vessels through which water at 25 °C was circulated. All titrations were carried out in an atmosphere of oxygen-free nitrogen. Details of the titrations are shown in Table 1. Data refinement was carried out using SUPERQUAD.[19]

When metal ions react with either the keto or enol tautomers of β-diketones in solution, the final product is invariably the metal–enolate complex irrespective of which tautomer of the uncoordinated ligand predominates. The rate-constants for the complex formation reactions were measured with a HiTech SF-20 stopped-flow apparatus which was interfaced to a BBC microcomputer. Pseudo-first-order rate constants were calculated by fitting the absorbance data (70–100 data points) to eqn. (1) using a three-parameter curve-fitting routine in which the absorbance at time zero, A_o, the absorbance at infinity time,

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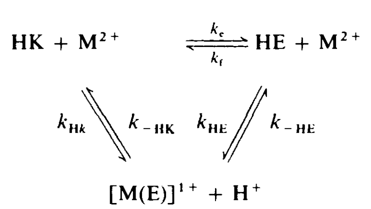
Table 1 Ratio of enol to keto tautomers, equilibrium constants with Cu^{2+} and Ni^{2+} and rate constants for keto–enol tautomerism reactions of 2-acetylcyclohexanone in methanol–water (70:30 v/v) at 25 °C and $I = 0.5$ mol dm^{-3} $NaClO_4$

	Ni^{2+}	Cu^{2+}
Solution composition		
$[T_L]$ range	0.005–0.0194 mol dm^{-3}	
$[T_M]$ range	0.005–0.010 mol dm^{-3}	
Ionic strength	0.5 mol dm^{-3} ($NaClO_4$)	
pH range		
Protonation	9.3–11.4	
Complexation	4.9–7.3	2.6–4.0
Experimental method	pH titration[a]	
Temperature	25 °C	
Method of calculation	Superquad[20]	
Total No. of data points		
Protonation	58[b]	
Complexation	58[b]	55[b]
K_{HA}[c]	9.54×10^{-11} mol dm^{-3}	
K_{HE}	1.35×10^{-11} mol dm^{-3}	
K_{HK}	2.04×10^{-11} mol dm^{-3}	
k_e	3.25×10^{-4} s^{-1}	
k_f	2.15×10^{-4} s^{-1}	
$[HE]/[HK] = k_e/k_f$	1.51	
$\log \beta_1$	6.50 (±0.01)	9.36 (±0.01)
K_1[d]	2.57×10^{-5}	3.46×10^{-2}
K_E	4.27×10^{-5}	5.36×10^{-2}
K_K	6.45×10^{-5}	8.68×10^{-2}

[a] Calibrated in concentrations. [b] Three titrations. [c] $1/K_{HA} = 1/K_{HE} + 1/K_{HK}$. [d] $1/K_1 = 1/K_E + 1/K_K$, where $K_1 = \beta_1 K_{HA}$.



Scheme 1

A_∞, and the rate constant, k, were treated as variables. Data for from three to four half-lives were utilized in these calculations.

$$A = A_\infty[1 - \exp(-kt)] + A_0\exp(kt) \qquad (1)$$

The reported rate constants are the average of at least three determinations. The standard deviation in individual runs was usually less than one percent.

The enolization of β-diketones does not normally proceed by the direct transfer of a proton from carbon to oxygen. Instead, the enolate ion is formed as an intermediate as shown in eqn. (2). In eqn. (2), k_c is diffusion-controlled ($\approx 3 \times 10^{10}$ dm^3 mol^{-1} s^{-1}) and $k_c \gg k_b$. The equilibrium between the keto and enol tautomers is usually represented as in eqn. (3) where k_e is the rate of enolization and k_f is the rate of ketonization. In terms of

$$H_2O + H\text{–} \underset{k_b}{\overset{k_a}{\rightleftharpoons}} H_3O^+ + E^- \underset{k_d}{\overset{k_c}{\rightleftharpoons}} EH + H_2O \qquad (2)$$

$$HK \underset{k_f}{\overset{k_e}{\rightleftharpoons}} HE \qquad (3)$$

the ionization scheme [eqn. (2), $k_e = k_a$ and $k_f = K_{HE}k_b$ where K_{HE} is the dissociation constant of the enol tautomer.

The rate of enolization of 2-acetylcyclohexanone was studied by a bromination procedure. If the bromine reacts instantly with the enol tautomer, the bromination will reach the limiting rate given by eqn. (4). In this situation, the concentration of HK

$$-d[Br_2]/dt = -d[HK]/dt = k_e[HK] \qquad (4)$$

is given by eqn. (5) where A is the absorbance due to bromine at any time t at the observation wavelength (452 nm), ε (103) is the extinction coefficient of bromine at the observation wavelength, l is the pathlength and a and b are the total ligand and bromine concentrations, respectively, at time zero.

$$[HK] = A/(\varepsilon l) + a - b \qquad (5)$$

Substitution of eqn. (5) into eqn. (4) followed by integration gives eqn. (6) where C is a constant. A plot of the left-hand side

$$\ln[A/(\varepsilon l) + a - b] = k_e t + C \qquad (6)$$

of eqn. (6) against time gives a straight line of slope k_e and intercept C. The enolization rate constant was determined spectrophotometrically. Aliquots (25 cm^3) of a solution containing 2-acetylcyclohexanone (*ca.* 2.5×10^{-3} mol dm^{-3}) at an ionic strength of 0.5 mol dm^{-3} $NaClO_4$ (adjusted with $NaClO_4$ and $HClO_4$) were placed in the thermostatted cell compartment of the spectrophotometer. When the temperature of the solution in the cuvette had reached 25 °C, 50 or 60 mm^3 of a bromine solution (*ca.* 0.125 mol dm^{-3}) were added following which the absorbance at 452 nm was recorded as a function of time for approximately 30 min. The absorbances were digitized at 2 min intervals using the resident program in the spectrophotometer. Each of the bromine solutions contained 0.001 mol dm^{-3} NaBr in order to suppress hydrolysis of the bromine. In order to determine the effect of hydrogen-ion concentration on the rate of bromination, the reaction was studied at hydrogen-ion concentrations of 0.01 and 0.10 mol dm^{-3}.

The value of k_f, the rate of ketonization of 2-acetylcyclohexanone, was determined by reacting a solution of the ligand which had been adjusted to a pH of approximately 11 with sodium hydroxide and which contained appreciable quantities of the enolate ion, with excess perchloric acid. The enolate ion is rapidly protonated and the subsequent readjustment of the equilibrium to the equilibrium concentrations of keto and enol tautomers was monitored spectrophotometrically at 290 nm. A first-order plot of these absorbance changes gives ($k_e + k_f$) from which k_f can be readily evaluated.

Results

Table 1 gives the experimental conditions and the equilibrium data for the Ni^{2+} and Cu^{2+} 1:1 complexes formed with 2-acetylcyclohexanone (HL). The proton equilibrium data together with the rate constants for enolization (k_e) and ketonization (k_f) of the ligand are also included.

Tables 2 and 3, respectively, contain the kinetic data for reaction of Cu^{2+} and Ni^{2+} with HL. The general mechanism proposed to account for the kinetic data is shown in Scheme 1. In this Scheme HK and HE represent the keto and enol tautomers of the ligand, respectively, while M^{2+} represents the metal ion.

In Scheme 1, k_{HE} and k_{HK} are the rate constants for reaction of the metal ion with the keto and enol tautomers, respectively, k_{-HE} and k_{-HK} are the rate constants for complex dissociation, while $K_E = k_{HE}/k_{-HE}$ and $K_K = k_{HK}/k_{-HK}$. The general solution of the secular equations obtained from Scheme 1 yields

Table 2 Rate constants[a] for the reaction of Cu^{2+} with 2-acetylcyclohexanone[b] in methanol–water (70:30 v/v) at 25 °C and I = 0.5 mol dm^{-3} $NaClO_4$

$[Cu^{2+}]/10^{-3}$ mol dm^{-3}	$[H^+]/10^{-3}$ mol dm^{-3}	k_{obs}/ s^{-1} [c]	k_{obs}/ s^{-1} [d]
4.08	1.08	31.9	0.69
4.08	2.16	53.1	0.78
4.08	3.24	74.0	0.84
4.08	4.32	96.1	0.74
4.08	5.40	114	0.70
6.10	1.08	38.8	0.78
6.10	2.16	57.5	0.94
6.10	3.24	76.9	1.02
6.10	4.32	100	0.96
6.10	5.40	120	1.01
8.16	1.08	45.5	1.14
8.16	2.16	65.7	1.20
8.16	3.24	79.9	1.25
8.16	4.32	102	1.31
8.16	5.40	129	1.27
10.2	2.16	72.0	1.37
10.2	3.24	91.9	1.45
10.2	4.32	112	1.57
10.2	5.40	132	1.68

[a] λ = 330 nm. [b] [2-Acetylcyclohexanone] = 2 × 10^{-4} mol dm^{-3}. [c] Fast reaction. [d] Slow reaction.

Table 3 Rate constants[a] for the reaction of Ni^{2+} with 2-acetylcyclohexanone[b] in methanol–water (70:30 v/v) at 25 °C and I = 0.5 mol dm^{-3} $NaClO_4$

$[Ni^{2+}]/10^{-2}$ mol dm^{-3}	$[H^+]$/ mol dm^{-3}	k_{obs}/ s^{-1}
0.998	0.991	2.36
0.998	1.982	5.04
0.998	2.973	7.53
0.998	4.955	12.5
1.975	0.991	2.38
1.975	1.982	5.16
1.975	2.973	7.75
1.975	4.955	12.9
2.963	0.911	2.43
2.963	1.982	5.18
2.963	2.973	7.91
2.963	4.955	13.4
3.950	1.982	5.38
3.950	2.973	8.04
3.950	4.955	13.2
4.930	0.991	2.58
4.930	1.982	5.50
4.930	2.973	8.40
4.930	4.955	14.6

[a] λ = 335 nm. [b] [2-Acetylcyclohexanone] = 2 × 10^{-4} mol dm^{-3}.

eqns. (7), (8) and (9).[21,22] The λ_1 solution is trivial and need not be considered further.

$$\lambda_1 = 0 \tag{7}$$

$$\lambda_2 = 0.5\,(p + q) \tag{8}$$

$$\lambda_3 = 0.5\,(p - q) \tag{9}$$

$$p = k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + (k_{-HE} + k_{-HK})[H^+] \tag{10}$$

$$q = (p^2 - 4b)^{\frac{1}{2}} \tag{11}$$

$$b = k_e\{k_{HE}[M^{2+}] + (k_{-HK} + k_{-HE})[H^+]\} + k_{HK}[M^{2+}]\{k_f + k_{HE}[M^{2+}] + k_{-HE}[H^+]\} + k_f(k_{-HE} + k_{-HK})[H^+] + k_{HE}k_{-HK}[M^{2+}][H^+] \tag{12}$$

Factoring the q term [eqn. (11)], expanding the factor $[1 - (4b/p^2)]^{\frac{1}{2}}$ using the binomial expansion and retaining only the first two terms gives eqn. (13).

$$q = p - 2b/p \tag{13}$$

It is apparent that the mechanism in Scheme 1 may give a maximum of two relaxations for reaction of the keto and enol tautomers, respectively, irrespective of whether the reaction is monitored in the forward direction (complex formation) or the reverse direction (hydrolysis). The faster of these two relaxations is described by eqn. (14) while the slower is described by eqn. (15).

$$\lambda_2 = p - b/p \tag{14}$$

$$\lambda_3 = b/p \tag{15}$$

Substituting for p and b in eqns. (14) and (15) from eqns. (10) and (12), respectively, while noting that $K_E = k_{HE}/k_{-HE}$ and $K_K = k_{HK}/k_{-HK}$ and rearranging the terms gives eqns. (16) and (17) for the fast and slow relaxations, respectively.

An examination of the data published to date[14] shows that in general, the enol tautomer of β-diketones is considerably more reactive than the keto tautomer. This is expected because reaction of the keto tautomer involves deprotonation at carbon whereas the enol tautomer is deprotonated at oxygen in a much faster reaction. Therefore one can reasonably assume that $k_{HE} \gg k_{HK}$. When this simplification is incorporated into eqn. (16), eqn. (18) is obtained. Eqn. (18) contains only one unknown parameter, k_{HE}.

$$\lambda_2 = k_e + k_f + k_{HE}[M^{2+}] + k_{HE}[H^+]/K_E - \frac{[M^{2+}]k_e k_{HE}\{1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E\}}{k_e + k_f + k_{HE}[M^{2+}] + k_{HE}[H^+]/K_E} \tag{18}$$

Reaction of Copper(II) *with 2-Acetylcyclohexanone.*—When solutions containing Cu^{2+} were reacted with solutions containing 2-acetylcyclohexanone in a stopped-flow apparatus, two consecutive first-order reactions were observed. They were sufficiently well separated to enable the individual rate constants to be determined using eqn. (1). When the kinetic data for the faster of the two observed relaxations (Table 2) are fitted to eqn. (18), a value of 1.27(±0.02) × 10^3 dm^3 mol^{-1} s^{-1} is obtained for k_{HE}. The value of k_{HK}, 0.929(±0.02) dm^3 mol^{-1} s^{-1} is obtained by fitting the kinetic data for the slow relaxation to eqn. (17) while keeping the value of k_{HE} obtained above constant.

In previous investigations of the reactions of metal ions with β-diketones, an inverse acid relationship was sometimes found for k_{HE}, eqn. (19). In the absence of appreciable hydrolysis of

$$k_{HE} = a + b/[H^+] \tag{19}$$

the metal species, this was ascribed to a reaction pathway in which the metal species reacted with the enolate ion which is obtained on loss of a proton. It was further noted that in most instances, this pathway proceeded with rate constants close to those predicted on the basis of the Eigen–Wilkins–Tamm mechanism.[15,16] Based on this assumption, it can be readily shown that under the experimental conditions used in the present experiment, the inverse acid pathway would not compete with the pathway involving a direct reaction between the Cu^{2+} and the enol tautomer. A pH of approximately 5 would be required for the inverse acid pathway to be significant. At

$$\lambda_2 = k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+] - \frac{[M^{2+}](k_e k_{HE} + k_f k_{HK} + k_{HE}k_{HK}[M^{2+}])\{1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E)\}}{k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+]} \quad (16)$$

$$\lambda_3 = \frac{[M^{2+}](k_e k_{HE} + k_f k_{HK} + k_{HE}k_{HK}[M^{2+}])\{1 + ([H^+]/[M^{2+}])(1/K_K + 1/K_E)\}}{k_e + k_f + (k_{HE} + k_{HK})[M^{2+}] + \{k_{HK}/K_K + k_{HE}/K_E\}[H^+]} \quad (17)$$

this pH buffers would be required to control the pH and it has recently been shown that supposedly non-coordinating buffers such as cacodylic acid can catalyse complex formation reactions of metal complexes with β-diketones.[23] Catalysis by cacodylate buffers presumably occurs because the rate-determining steps in these reactions are deprotonation of keto or enol 'precursor complexes'.

Reaction of Nickel(II) *with 2-Acetylcyclohexanone*.—When solutions containing Ni^{2+} were reacted with solutions of 2-acetylcyclohexanone in the stopped-flow apparatus, a single first-order reaction was observed which accounted for the total absorbance change between reactants and products. When the kinetic data are fitted to eqn. (18), a value of 0.114(±0.001) $dm^3\ mol^{-1}\ s^{-1}$ is obtained for k_{HE}.

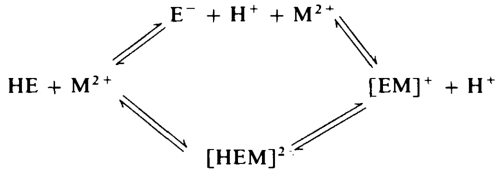
Discussion

The values of k_e and k_f obtained in the present investigation may be compared with the values previously obtained in water,[18] 7.13×10^{-3} and $2.9 \times 10^{-3}\ s^{-1}$, respectively. These values give an enol:keto ratio of 0.41 compared with the 1.51 obtained in methanol–water (70:30 v/v). This is as expected, because in general the enol:keto ratio of β-diketones increases with decreasing polarity of the solvent. The rate constant for ionization of the keto tautomer ($k_a = k_e$) is smaller by more than one order of magnitude than any previously reported values while the rate constant for loss of a proton from the enol tautomer (k_d) is almost two orders of magnitude less than any previously reported values.[14] The slow rate of loss of proton from the keto tautomer can be ascribed to the fact that the C-2 of HL has only one proton attached compared with the two in the other β-diketones. More importantly, the acidic proton is attached to a ring carbon and it has been shown for monocyclic ketones that this reduces reactivity relative to an acyclic ketone, probably because of the formation of the enolate double bond in a six-membered ring.

Table 4 contains a summary of the rate constants for reaction of Cu^{2+} and Ni^{2+} with a variety of β-diketones. The rate constants for reaction of both metal ions to form the 1:1 complexes are lower than any previously reported values for their reactions with a 1,3-diketone ligand. It is immediately obvious that the complex formation rate constants determined are considerably lower than would be expected on the basis of the outer-sphere association constants and the rate of solvent exchange. Using the rates of solvent exchange determined by Rorabacher[31] and the Rorabacher modification[32] of the Eigen–Fuoss equation,[33,34] the rate of complex formation of Ni^{2+} with an uncharged ligand in methanol–water (70:30 v/v) has been previously estimated to be approximately $1.6 \times 10^4\ dm^3\ mol^{-1}\ s^{-1}$.[35] The rate constant obtained for reaction of Ni^{2+} with the enol tautomer of 2-acetylcyclohexanone is approximately five orders of magnitude less than the predicted value.

Various reasons have been proposed for the relatively slow rate of reaction of protonated ligands and in particular enols of β-diketones with metal ions.[14,16,24,29] These include the presence of strong intramolecular hydrogen bonds which convert the ligand into a poor entering group, the energetics of proton release from a unidentate intermediate which may slow down the rate of ring closure or ring strain associated with the formation of a six-membered ring. The last-mentioned factor may be disregarded on the basis that the reactions of metal ions with the enolate form of β-diketones proceed at rates close to those predicted by the Eigen–Wilkins–Tamm mechanism.[14] This is so even in the case of relatively labile metal ions such as Cu^{2+}.[27]

For many complex-formation reactions, the rate constants for loss of a proton by the ligand are considerably greater than the rates of complex formation with the deprotonated form of the ligand. For example, the rate of proton loss from ethanoic acid[36] is $8.2 \times 10^5\ s^{-1}$ while the rate of reaction of Ni^{2+} with CH_3COO^- is $1.5 \times 10^5\ dm^3\ mol^{-1}\ s^{-1}$.[16] However, in the case of β-diketones, the rates of proton loss from either the keto or enol tautomers are either less than or of similar magnitude to the rates of complex formation. Consequently, it is reasonable to treat the complex formation reaction as a metal-catalysed proton transfer reaction in which the metal first reacts with the ligand to form a loose precursor complex which then loses a proton to complete the complex formation reaction. Associative and dissociative mechanisms for the proton exchange reactions are shown below.



The dissociative pathway will occur at low metal and low proton concentrations and the associative pathway when these concentrations are high. The pH/metal-ion concentration for a change of mechanism will depend on the relative stabilities of the enolate anion and the enol precursor complex. As already stated, the dissociative mechanism would show an inverse pH dependence.

Table 5 shows the results of calculations made on the above basis for the reactions studied here. The rate of complex formation, k_{HL}, is compared with the rate of proton loss from both the keto and enol tautomers. Owing to the fact that Cu^{2+} reacts directly with both the keto and enol tautomers, a direct comparison can be made between the catalytic effect of the metal ion on the rate of proton loss from both tautomers. Interestingly, the effect is broadly similar for both of them. In the case of Ni^{2+}, only a single reaction is observed for conversion of the ligand into the metal complex and only k_{HE} could be determined. The ratio of k_{HE}/k_{-H} is less than unity, suggesting that Ni^{2+} is not an effective catalyst in these reactions.

It has previously been pointed out[14] that the following reactivity order obtains for the apparent rate constants for metal complexation of the various forms of β-diketones present in solution:

$$\text{enolate} \gg \text{enol} > \text{keto}$$

Many metal ions only react with either the enolate ion or the enol tautomer and do not catalyse deprotonation of the keto form. In general, it is only metal ions such as Cu^{2+}, Fe^{3+}, $[VO]^{2+}$ and $[UO_2]^{2+}$ which form complexes of relatively high stability or very labile metal ions such as Co^{2+} which react

Table 4 Rate constants for formation of 1:1 complexes of Ni^{2+} and Cu^{2+} with β-diketones

Metal	β-diketone ligand	Solvent	k_{HL}/mol dm^{-3}	Ref.
Ni^{2+}	Htftbd[a] (enol)	H_2O	2.3	24
Ni^{2+}	Hpd[b] (enol)	H_2O	19.3	25
Ni^{2+}	Hpd (enol)	MeOH–H_2O[f]	17.0	25
Ni^{2+}	Htfpd[c] (enol)	H_2O	1.7	26
Ni^{2+}	Hpbd[d] (enol)	MeOH–H_2O[f]	3.21	27
Ni^{2+}	Hhptd[e] (enol)	MeOH–H_2O[f]	10.0	28
Ni^{2+}	HL (enol)	MeOH–H_2O[f]	0.114	This work
Cu^{2+}	Hpd (keto)	H_2O	12.0	29
Cu^{2+}	Hpd (keto)	MeOH	1300.0	29
Cu^{2+}	Hpd (enol)	H_2O	2.0×10^4	29
Cu^{2+}	Hpd (keto)	MeOH	2.0×10^4	29
Cu^{2+}	Hpbd (enol)	MeON–H_2O[f]	5.0×10^3	27
Cu^{2+}	Hhptd (enol)	H_2O	1.14×10^4	30
Cu^{2+}	Hhptd (keto)	H_2O	8.89	30
Cu^{2+}	HL (enol)	MeOH–H_2O[f]	1.27×10^3	This work
Cu^{2+}	HL (keto)	MeOH–H_2O[f]	0.93	This work

[a] 4,4,4-Trifluoro-1-(2-thienyl)butane-1,3-dione. [b] Pentane-2,4-dione. [c] 1,1,1-Trifluoropentane-2,4-dione. [d] 1-Phenylbutane-1,3-dione. [e] Heptane-3,5-dione. [f] 70:30 (v/v).

Table 5 Catalytic effect of Ni^{2+} and Cu^{2+} on the rate of ionization of 2-acetylcyclohexanone in methanol–water (70:30 v/v) at 25 °C and I = 0.5 mol dm^{-3} $NaClO_4$

Metal	Tautomer	k_{-H}	k_{HL}	k_{HL}/k_{-H}
Ni^{2+}	Enol	0.405	0.114	0.28
Cu^{2+}	Enol	0.405	1.27×10^3	3.14×10^3
Cu^{2+}	Keto	3.25×10^{-4}	0.929	2.86×10^3

(*a*) (*b*)

Fig. 1

directly with the keto tautomers of β-diketones. Pearson and Anderson[29] originally proposed the idea of a precursor complex of the type shown in Fig. 1(*a*) as the logical precursor complex to the transition state in the reaction between Cu^{2+} and the keto tautomer of pentane-2,4-dione. Indeed such complexes have actually been isolated and characterized.[37,38] The acidic proton is still attached to this precursor complex. The complex formation reaction is then completed by loss of a proton from the 3-position to give the final complex which contains a coordinated enolate ion. The copper(II) ion obviously acts as a catalyst in this step as the overall reaction is more than three thousand times more rapid than loss of a proton from the uncoordinated ligand (Table 5). A similar type of precursor complex can be formulated for the reaction between the enol tautomer and the metal ion. A probable structure is shown in Fig. 1(*b*). Again, the rate of reaction of Cu^{2+} with the enol tautomer is some three thousand times more rapid than the rate of ionization of the enol tautomer. A relatively large deuterium isotope effect was observed for the reaction between the keto tautomer of pentane-2,4-dione and Cu^{2+}, strongly suggesting that proton removal is a relatively important step in the overall reaction.[29]

Obviously Ni^{2+} is a much poorer catalyst than Cu^{2+} in assisting the removal of a proton from a precursor complex of the type depicted in Fig. 1(*b*). This is not entirely unexpected in view of the relatively low value of the reduction potential of Ni^{2+} (−0.25 V) compared with Cu^{2+} (0.35 V). In general, a stability order consistent with the reduction potential of the metal ion is observed for complexes of 3d transition-metal ions with ligands having oxygen and nitrogen donor atoms.[39] The increased stability of the copper(II) precursor complex is responsible for its increased tendency to lose a proton as reflected in the increased catalytic effect of the Cu^{2+} ion.

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