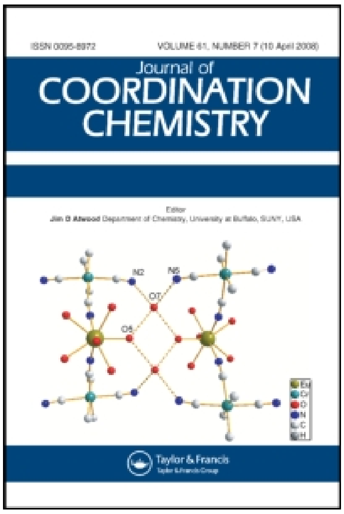

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Solution Equilibria and Kinetic Studies of the Copper(II) Promoted Hydrolysis of 8-Quinolyl Phosphate. A Large Rate Enhancement for the Hydrolysis of a Phosphate Monoester Dianion

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SOLUTION EQUILIBRIA AND KINETIC STUDIES OF THE COPPER(II) PROMOTED HYDROLYSIS OF 8-QUINOLYL PHOSPHATE. A LARGE RATE ENHANCEMENT FOR THE HYDROLYSIS OF A PHOSPHATE MONOESTER DIANION

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The dissociation constants of 8-quinolyl phosphate (H_3L^+) at 10°C and $I = 0.1$ mol dm^{-3} ($NaClO_4$) have been determined (pK$_a$ values <1.5, 4.12 and 6.46). At a 1:1 ligand to metal ratio, the interaction of copper(II) with 8-quinolyl phosphate can be described by the equilibria given below.

$$Cu^{2+} + H^+ + L^{2-} \rightleftarrows [CuHL]^+ \quad \log \beta_{111} = 9.13(3)$$
$$Cu^{2+} + L^{2-} \rightleftarrows [CuL]^0 \quad \log \beta_{110} = 5.38(1)$$
$$Cu^{2+} + H_2O + L^{2-} \rightleftarrows [CuL(OH)]^- + H^+ \quad \log \beta_{11-1} = -0.33(3)$$

The pK$_a$ values for the ionisation processes $[CuHL]^+ \rightleftarrows [CuL] + H^+$ and $[CuL(OH_2)] \rightleftarrows [CuL(OH)]^- + H^+$ are 3.75 and 5.71, respectively. Kinetic studies establish that in the copper(II)-promoted hydrolysis the complex [CuL] is the active species with $k_{CuL} = 2.7 \times 10^{-3}\,s^{-1}$ at 30°C and $I = 0.1$ mol dm^{-3}. Copper(II) ions promote the hydrolysis of the normally unreactive dianion L^{2-} of the phosphate monoester by a factor of *ca* 10^6.

Keywords: 8-Quinolyl phosphate, hydrolysis, copper(II), kinetics

INTRODUCTION

One of the striking observations of biological phosphate chemistry is that much of it appears to be subject to metal ion catalysis.[1,2] However, the role of the metal ion in promoting the hydrolysis reactions of phosphate derivatives including phosphate esters has been the subject of considerable speculation. Considerable progress has now been made in delineating mechanisms in reactions involving kinetically inert cobalt(III) complexes,[3,4-8] but the situation regarding the biologically important metal ions which give kinetically labile complexes is much less well defined.

Copper(II) ions have been observed to catalyse the hydrolysis of a number of phosphate monoesters including salicyl phosphate (I),[9,10] 8-quinolyl phosphate (II)[11,12] and 2(4(5)-imidazoyl)phenyl phosphate (III).[13] The catalytic effect observed with salicyl phosphate and 8-quinolyl phosphate was apparently quite small (*ca* 10

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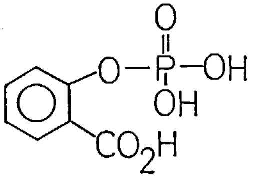
fold). However, we have recently shown that in the case of salicyl phosphate, copper(II) ions promote the hydrolysis of the dianion of the phosphate monoester by a factor of *ca* 10^8 at 25°C. The small rate enhancement initially noted arose because comparisons were made between the metal ion-promoted reaction and the intramolecular general acid-catalysed reaction of salicyl phosphate dianion. The present paper describes detailed studies of the copper(II)-promoted hydrolysis of 8-quinolyl phosphate.



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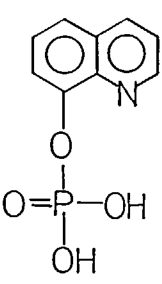

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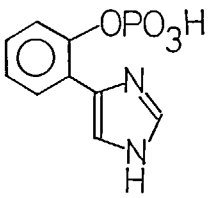


(III)

EXPERIMENTAL

8-Quinolyl phosphate was prepared by the reaction of $POCl_3$ with 8-hydroxyquinoline in pyridine solution, essentially as previously described.[12] The compound was recrystallised from H_2O/Ac_2O (1:1); m.p. 225°C. Anal.: Calc. for $C_9H_8NPO_4$: C, 48.0; H, 3.6; N, 6.2%. Found: C, 48.0; H, 3.5; N, 6.0%.

Potentiometric measurements

The potentiometric titrations with 8-quinolyl phosphate in the absence and in the presence of copper(II) perchlorate were carried out in an automatic system controlled by an Apple IIe computer and consisting of (i) a Radiometer PHM84 research pH meter, using a Beckman Futura glass electrode and an Ingold saturated sodium chloride-calomel reference electrode, fitted in an Ingold cell system, (ii) a Radiometer ABU80 Autoburette, equipped with a 2.5/0.25 cm^3 burette assembly, (iii) a Metrohm thermostatted cell, and (iv) a Huber MINISTAT digital thermostat. Typical concentrations used were in the range $(0.5–1.0) \times 10^{-3}$ mol dm^{-3}. The details of the experimental procedure have been published elsewhere.[15] The data were processed on a VAX 11/780 computer using the EXTEQUAD and MINISHORT programs,[16] two modified versions of the MINIQUAD[17] program. In the titration curves $-\log[H^+]$ was plotted *versus* B/L, the ratio of moles of standard base added (B) per mole of ligand (L). Negative values indicate excess acid.

Kinetics

The copper(II)-promoted hydrolysis of 8-quinolyl phosphate was studied using 2,6-dimethylpyridine-3-sulphonic acid (dmps)-NaOH buffer. Elias and coworkers[18] have shown that this is an excellent non-coordinating buffer which minimises metal-buffer interactions (K = 1.6 for $Cu^{2+} + L \rightleftharpoons CuL$). Hydrolysis in the presence of copper(II) was monitored at 315 nm using the buffer as the reference. Absorbance changes were logged directly by an Apple II computer interfaced with a Gilford 2400S spectrophotometer. Plots of $\log(A_t - A_\infty)$ were linear for several half-lives and values of k_{obs} were evaluated directly using the computing system. All kinetic runs were carried out in triplicate at $I = 0.1\ mol\,dm^{-3}$ adjusted with sodium perchlorate. The phosphate ester concentration used in the measurement was $9.46 \times 10^{-5}\ mol\,dm^{-3}$. The concentration of stock copper(II) perchlorate solutions was determined iodometrically. The pH of solutions prior to, and on completion of, hydrolysis were checked using a Radiometer PHM-64 Research pH meter. The maximum pH variation was ±0.02 pH units. Due to the large absorbance change in the reaction it was possible to determine rate constants with a high degree of precision.

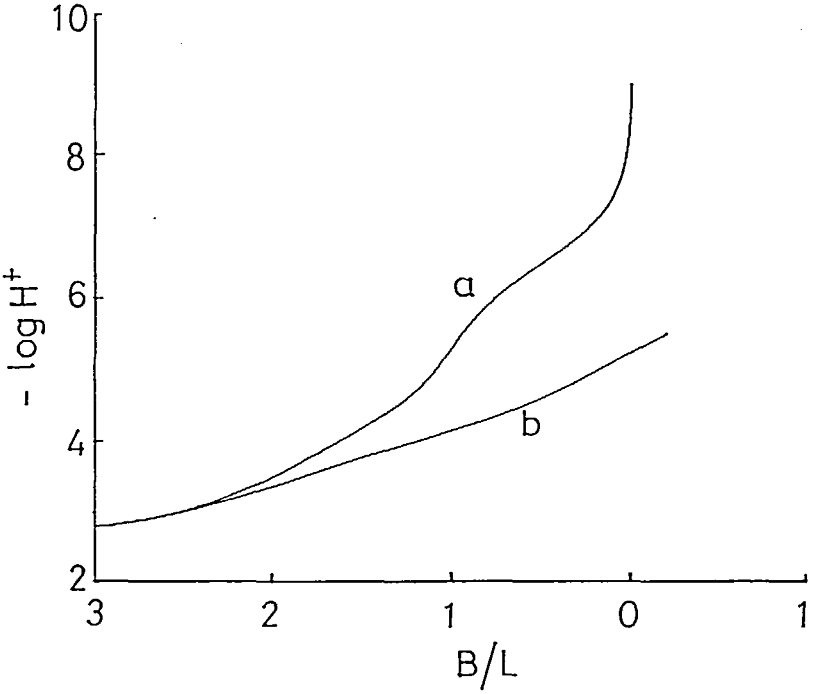


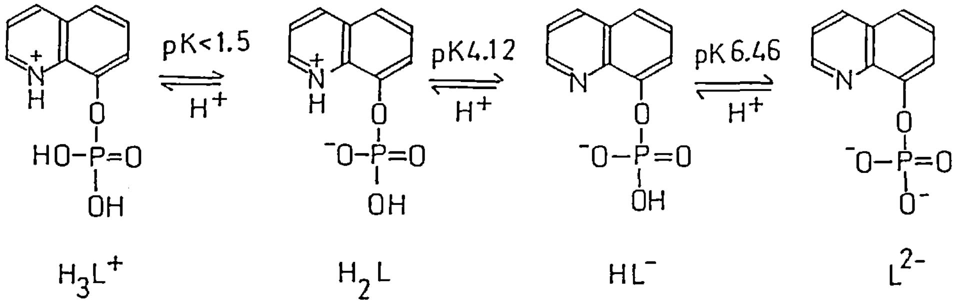
FIGURE 1 Titration curves for (a) 8-quinolyl phosphate; (b) 8-quinolyl phosphate and copper(II) perchlorate (1:1).

RESULTS AND DISCUSSION

The acid-base behaviour of 8-quinolyl phosphate (H_2L) at $I = 0.1\ mol\,dm^{-3}$ (Na ClO_4) was studied at 10.0 ± 0.1°C by potentiometric titration. In a typical experiment, Fig. 1, a solution of H_2L in excess acid ($HClO_4$) was titrated with standard base. In the $-\log[H^+]$ region investigated (*ca* 2.5 to 9.0), 8-quinolyl phosphate behaves as a triprotic ligand:

$$\begin{array}{ll} H^+ + L^{2-} \rightleftarrows HL^- & \log K_1 = 6.46(1) \\ H^+ + HL^- \rightleftarrows H_2L & \log K_2 = 4.12(1) \\ H^+ + H_2L \rightleftarrows H_3L^+ & \log K_3 < 1.5 \end{array}$$

These equilibria are illustrated in Scheme 1. The constants are in quite good agreement with those of Murakami and Sunamoto[12] (at 25°C, I = 0.1 mol dm^{-3} (K NO$_3$), $\log K_3 = 1.0$, $\log K_2 = 4.17$ and $\log K_3 = 6.42$).



Scheme 1 Ionisation equilibria of 8-quinolyl phosphate. The species distribution curve at 10°C is shown in Figure 2.

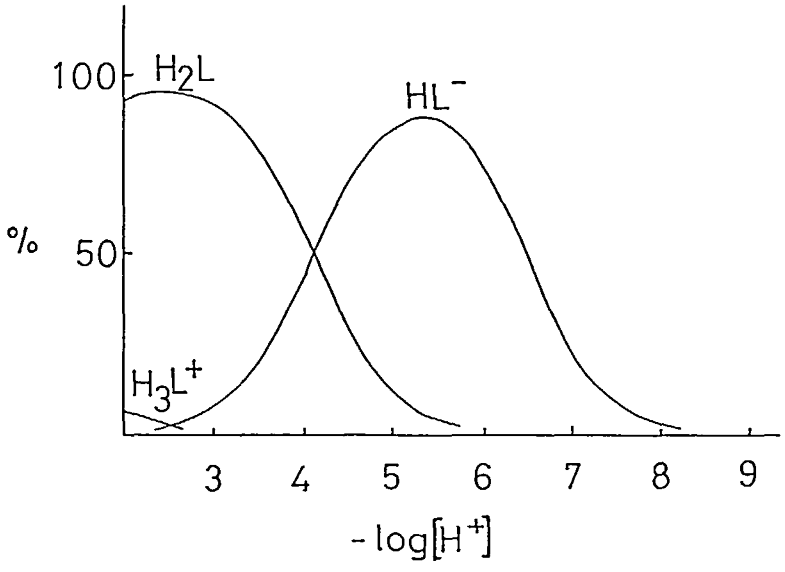


FIGURE 2 Species distribution curve for 8-quinolyl phosphate.

Complexation of 8-quinolyl phosphate with copper(II) was also studied at 10°C to minimise hydrolysis of the substrate (I = 0.1 mol dm^{-3}, NaClO$_4$). In a typical experiment a solution *ca* 10^{-3} mol dm^{-3} in H_2L and copper(II) perchlorate (molar ratio 1:1), containing excess acid ($HClO_4$) was titrated with standard sodium hydroxide. A pale yellow-green colour slowly developed on addition of base indicating complex formation in the pH range 2.8 to 5.5. Above pH 5.5 precipitation begins to occur.

The titration data (Fig. 1) can be fitted to the series of equilibria,[22]

$$Cu^{2+} + H^+ + L^{2-} \rightleftharpoons [CuHL]^+ \qquad \log \beta_{111} = 9.13(3)$$

$$Cu^{2+} + L^{2-} \rightleftharpoons [CuL]^\circ \qquad \log \beta_{110} = 5.38(1)$$

$$Cu^{2+} + H_2O + L^{2-} \rightleftharpoons [CuL(OH)]^- + H^+ \qquad \log \beta_{11-1} = 0.33(3)$$

The speciation curve is shown in Figure 3.

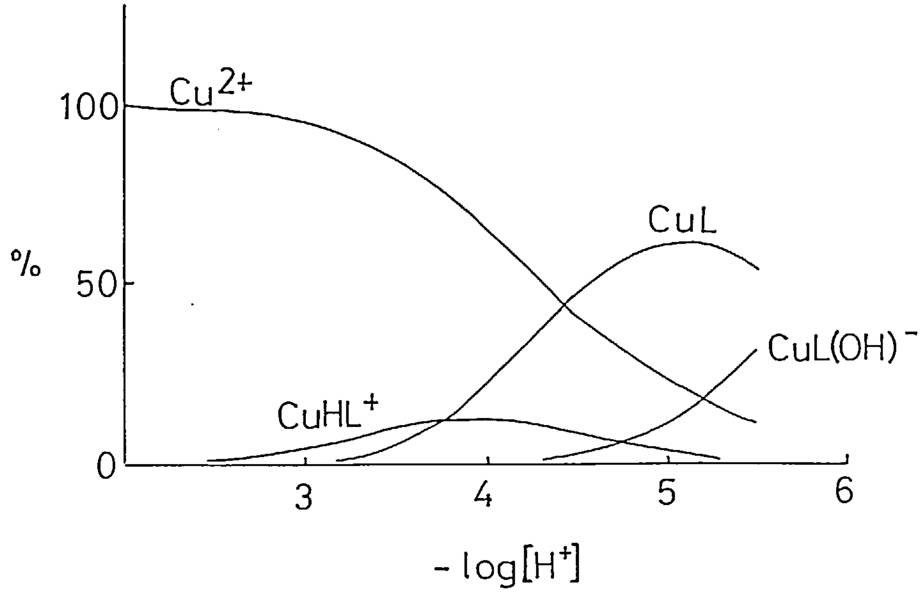
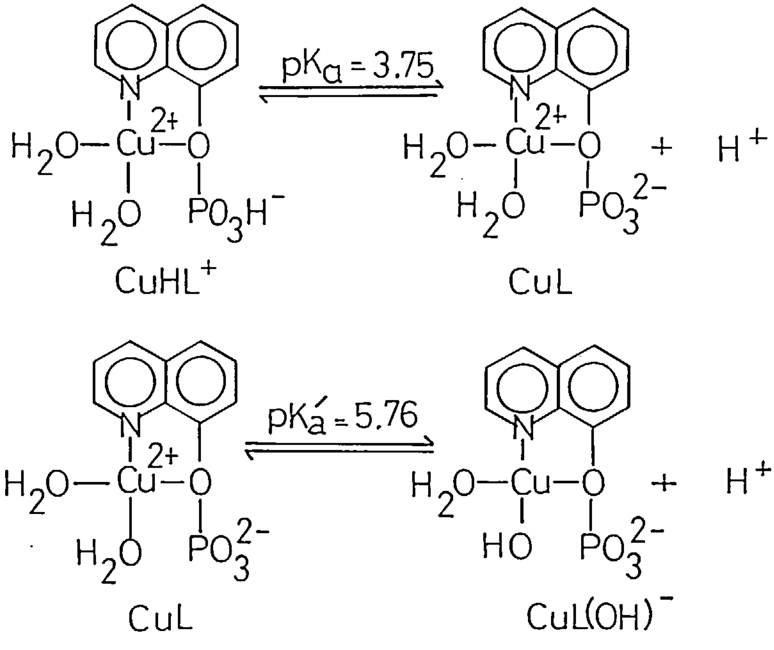


FIGURE 3 Species distribution curve for copper(II) complexes of 8-quinolyl phosphate at a 1:1 ligand to metal ratio; $[Cu^{2+}] = 1 \times 10^{-3}$ mol dm^{-3}.

The ionisation equilibria of the complexes are represented in Scheme 2. It can readily be shown that $pK_a = \log \beta_{111} - \log \beta_{110}$ and $pK_a' = \log \beta_{110} - \log \beta_{11-1}$, giving $pK_a = 3.75$ and $pK_a' = 5.71$. The complex $[CuL]^\circ$ reaches its maximum concentration (*ca* 60%) at pH 5, and $[CuHL]^+$ at pH 4 (*ca* 13%).

Kinetic Studies

Interval scan spectra established that quite rapid hydrolysis of 8-quinolyl phosphate occurred at pH 4.5 (30°C) in the presence of copper(II). The reaction displays clear isosbestic points at 341 and 274 nm with an absorbance decrease at 315 nm and an absorbance increase at 268 nm (Fig. 4). At pH 4.5 in the absence of copper(II) there was no change in the absorption spectrum of 8-quinolyl phosphate over a period of several days at 30°C. Hydrolysis in the presence of copper(II) was monitored using the decrease in absorbance at 315 nm. In the kinetic measurements the ester concentration was 9.46×10^{-5} mol dm^{-3} and the concentration of copper(II) was varied from 0.35 to 35×10^{-3} mol dm^{-3}. Plots of $\log(A_t - A_\infty)$ *versus* time were linear for several half lives and values of k_{obs} were derived from such plots.



Scheme 2 Ionisation equilibria of the 1:1 copper(II) complexes at 10°C.

Values of k_{obs} (the observed first order rate constant at constant pH) as a function of the copper(II) concentration at pH 4.59 are summarised in Table I.

TABLE I
Rate constants, k_{obs}, for the copper(II)-promoted hydrolysis of 8-quinolyl phosphate at 30°C and I = 0.1 mol dm^{-3} at pH 4.59; total ester concentration 9.46×10^{-5} mol dm^{-3}.

$10^3[Cu^{2+}]$ /mol dm^{-3}	10^3 k_{obs}/s^{-1}	$10^3[Cu^{2+}]$ /mol dm^{-3}	10^3 k_{obs}/s^{-1}
0.35	0.36	8.0	1.82
0.70	0.61	10.5	1.89
1.225	0.85	15.0	1.94
2.10	1.17	20.0	2.04
2.70	1.28	25.0	2.13
3.50	1.40	30.0	2.16
3.85	1.46	35.0	2.17
7.0	1.71		

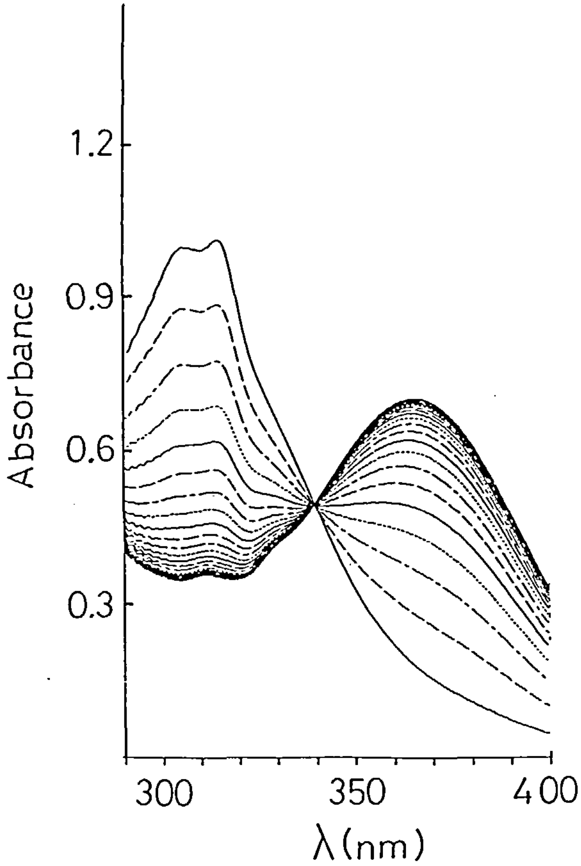


FIGURE 4 Interval scan spectra showing the hydrolysis of 8-quinolyl phosphate at 25°C. Reaction is in acetate buffer pH 4.96 with $[Cu^{2+}] = 10.5 \times 10^{-3}$ mol dm^{-3}; [ester] $= 0.35 \times 10^{-3}$ mol dm^{-3}. The time interval between scans is 5 mins. A solution of copper(II) perchlorate (10.5×10^{-3} mol dm^{-3}) was used as reference.

At high copper(II) concentrations ($>20 \times 10^{-3}$ mol dm^{-3}) saturation kinetics are observed with the reaction becoming independent of the copper(II) concentration (Fig. 5). The observed limiting rate is *ca* 2.15×10^{-3} s^{-1} at 30°C. At constant pH, the kinetic scheme can be defined by equations (*1*) and (*2*),

$$Cu^{2+} + L^{2-} \underset{k_M}{\overset{K_M}{\rightleftharpoons}} CuL \qquad (1)$$

$$CuL \longrightarrow \text{products} \qquad (2)$$

and it can readily be shown that,

$$k_{obs} = \frac{k_M K_M[Cu^{2+}]}{(1 + K_M[Cu^{2+}])} \qquad (3)$$

and

$$\frac{1}{k_{obs}} = \frac{1}{k_M} + \frac{1}{k_M K_M} \cdot \frac{1}{[Cu^{2+}]} \qquad (4)$$

A plot of $1/k_{obs}$ *versus* $1/[Cu^{2+}]$ should be linear with slope $1/k_M K_M$ and intercept $1/k_M$. Such a plot shows good linearity (Fig. 6). Least-squares analysis of the data gives an intercept of 4.6×10^2 s and a slope of 0.825 mol dm^{-3} with a correlation coefficient of 0.9995. These values give k_M (the limiting value of k_{obs}) = 2.17×10^{-3} s^{-1} and $K_M = 560$ dm^3 mol^{-1}. The constant K_M is a conditional formation constant, which is dependent upon pH.

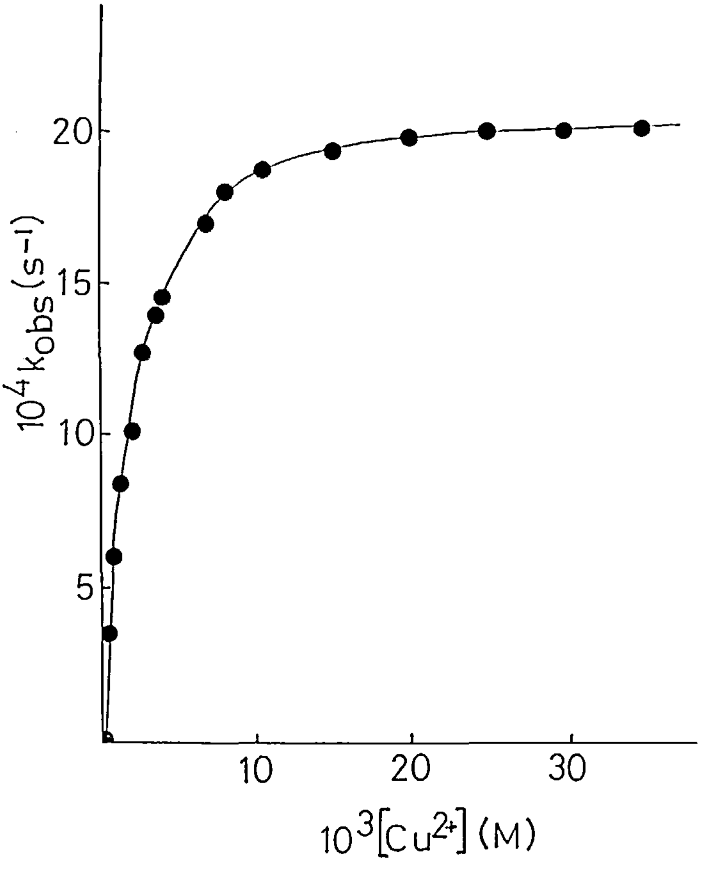


FIGURE 5 Plot of k_{obs} *versus* $[Cu^{2+}]$ at pH 4.59 and I = 0.1 mol dm^{-3} (30°C). Ester concentration is 9.46×10^{-5} mol dm^{-3} in dmps buffer.

Similar measurements were carried out at pH 4.05, Table II. At this lower pH saturation kinetics are also observed at high copper(II) concentrations with the limiting value of $k_{obs} = 1.20 \times 10^{-3}$ s^{-1} at 30°C.

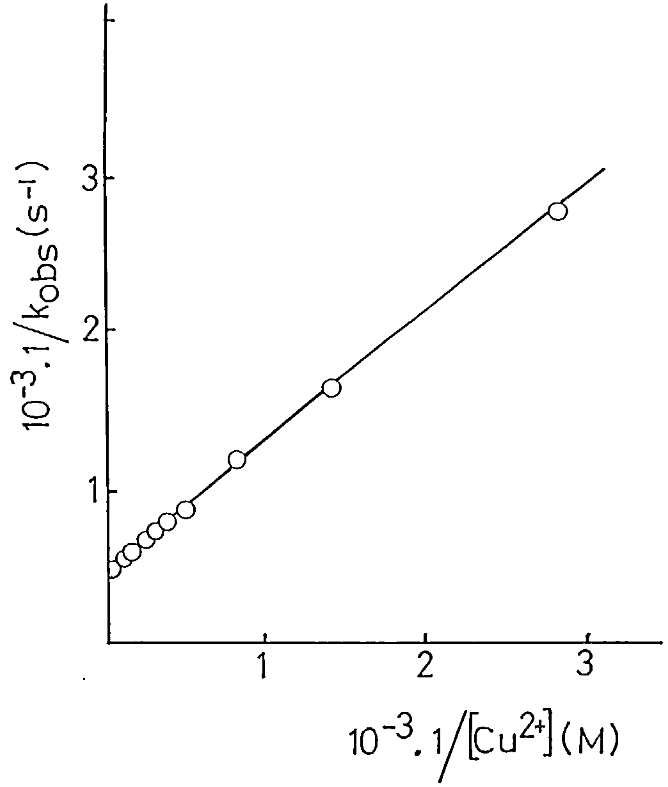


FIGURE 6 Plot of $1/[Cu^{2+}]$ *versus* $1/k_{obs}$ for the copper(II)-promoted hydrolysis at pH 4.59. The intercept 0.46×10^3 s gives a limiting value of $k_{obs} = 2.17 \times 10^{-3} s^{-1}$.

TABLE II

Rate constants, k_{obs}, for the copper(II)-promoted hydrolysis of 8-quinolyl phosphate at 30°C and $I = 0.1 \text{ mol dm}^{-3}$ at pH 4.05; total ester concentration $9.46 \times 10^{-5} \text{ mol dm}^{-3}$.

$10^3[Cu^{2+}]$ /mol dm^{-3}	$10^3 k_{obs}/s^{-1}$	$10^3[Cu^{2+}]$ /mol dm^{-3}	$10^3 k_{obs}/s^{-1}$
0.35	0.15	20.0	1.06
2.10	0.54	30.0	1.10
7.0	0.88	40.0	1.21
14.0	1.02	45.0	1.20

The pH dependence of the copper(II)-promoted hydrolysis was studied over the pH range 4.05–5.46 using a copper(II) concentration of $40 \times 10^{-3} \text{ mol dm}^{-3}$ to ensure that saturation kinetics were observed. The kinetic data are summarised in Table III. The reaction displays a bell-shaped pH rate profile with a maximum at pH *ca* 5 (Fig. 7). The pH rate profile closely mirrors the pH dependence of the CuL species shown in Fig. 3 and provides strong evidence that the copper(II) complex of the dianion of the ester is the active species in the hydrolytic reaction. The bell-shaped rate profile effectively excludes the participation of the $[CuLOH]^-$ species in a

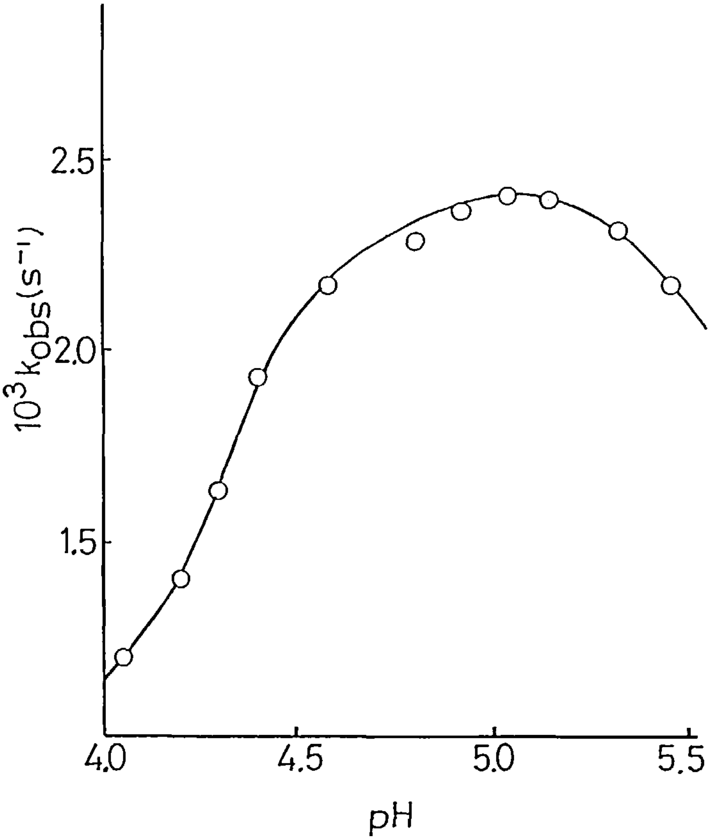


FIGURE 7 pH-Rate profile for the copper(II)-promoted hydrolysis using a copper(II) concentration of 4×10^{-2} mol dm^{-3}.

TABLE III
The pH dependence of the copper(II)-promoted hydrolysis of 8-quinolyl phosphate at 30°C and $I = 0.1$ *mol dm*$^{-3}$; *total ester concentration* 9.46×10^{-5} mol dm^{-3}, total copper(II) concentration 40×10^{-3} mol dm^{-3}.

pH	10^3 k_{obs}/s^{-1}	α_{CuL}	10^3 $k_{obs}/\alpha_{CuL}/s^{-1}$
4.05	1.20	0.63	1.9
4.20	1.41	0.71	2.0
4.30	1.64	0.74	2.2
4.40	1.93	0.77	2.5
4.50	2.16	0.80	2.7
4.58	2.17	0.81	2.7
4.81	2.29	0.82	2.8
4.92	2.37	0.81	2.9
5.04	2.41	0.79	3.0
5.14	2.40	0.77	3.1
5.32	2.32	0.70	3.3
5.46	2.17	0.63	3.4

reaction involving attack by coordinated hydroxide ion on the complexed ester. Such pathways have been identified in a number of cobalt(III) promoted hydrolyses of phosphates.[3]

The total ligand concentration (L_T) is given by expression (*5*).

$$L_T = [H_3L^+] + [H_2L] + [HL^-] + [L^{2-}] + [CuHL^+] + [CuL] + [CuLOH^-] \qquad (5)$$

The fractions (α) of the total ligand present as $[CuLH^+]$, $[CuL]$ and $[CuLOH^-]$ can be defined by equations (*6*) to (*8*).

$$\alpha_{CuLH^+} = [CuLH^+]/L_T \qquad (6)$$

$$\alpha_{CuL} = [CuL]/L_T \qquad (7)$$

$$\alpha_{CuLOH^-} = [CuLOH^-]/L_T \qquad (8)$$

Values of α were computed using a ligand concentration of 9.46×10^{-5} mol dm^{-3} and a copper(II) concentration of 40×10^{-3} mol dm^{-3} and these fractions are listed in Table IV.

TABLE IV

Values of α at a total ligand concentration of 9.46×10^{-5} mol dm^{-3} and a total copper(II) concentration of 40×10^{-3} mol dm^{-3} as a function of pH.

pH	$\alpha_{L^{2-}}$	α_{LH^-}	α_{LH_2}	$\alpha_{[CuLH]^+}$	$\alpha_{[CuL]}$	$\alpha_{[CuLOH]^-}$
4.05	0.000	0.017	0.020	0.317	0.632	0.014
4.20	0.000	0.013	0.011	0.248	0.705	0.022
4.30	0.000	0.011	0.007	0.209	0.743	0.029
4.40	0.000	0.009	0.005	0.173	0.774	0.038
4.50	0.000	0.008	0.003	0.142	0.798	0.049
4.58	0.000	0.006	0.002	0.119	0.812	0.061
4.81	0.000	0.003	0.001	0.070	0.821	0.105
4.92	0.000	0.002	0.001	0.055	0.811	0.130
5.04	0.000	0.002	0.000	0.041	0.791	0.166
5.14	0.000	0.002	0.000	0.031	0.765	0.202
5.32	0.000	0.001	0.000	0.020	0.698	0.281
5.46	0.000	0.000	0.000	0.010	0.630	0.360

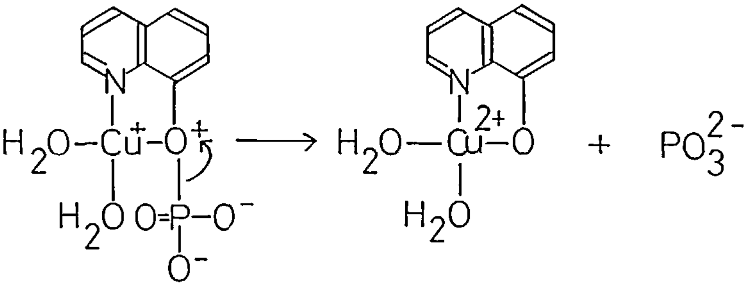
Values of α_{L2^-}, α_{LH^-} and α_{LH_2} are very small over the pH range 4.05 to 5.46 (Table 4).

The observed first-order rate constant at constant pH (k_{obs}) will be given by equation (*9*) if [CuL] is the only hydrolytically reactive species,

$$k_{obs} = k_{CuL} \cdot \alpha_{CuL} \qquad (9)$$

with $k_{CuL} = k_{obs}/\alpha_{CuL}$. Values of k_{CuL} are reasonably constant over the pH range 4.05 to 5.46 with k_{CuL} *ca* 2.7×10^{-3} s^{-1} (Table III).

It is probable that [CuL] has the structure (IV), which would provide Lewis acid catalysis by complexation of the leaving group to give the copper(II) complex of the oxinate anion, and the highly reactive metaphosphate species PO_3^{2-} which is rapidly hydrated.[19]



The metal ion effectively lowers the pK_a of the leaving group so that facile hydrolysis of the dianion of the phosphate ester occurs; this effect is normally only observed with leaving groups of $pK_a < 7$.[13] The dianion of a phosphate monoester is normally an extremely unreactive species in hydrolysis. Hydrolysis was too slow to be detectable at 30°C. However, measurements at 70°C using tris buffer (pH 7.44) adjusted to $I = 0.1\ \mathrm{mol\,dm^{-3}}$ gave an approximate value of $k = 5.6 \times 10^{-5}\ \mathrm{s^{-1}}$. At 30°C the rate constant is likely to be of the order of 10^{-8} to $10^{-9}\ \mathrm{s^{-1}}$. It is known that the rate constant for the hydrolysis of the dianion of phenyl phosphate is $4 \times 10^{-12}\ \mathrm{s^{-1}}$ at 39°C.[20] Although the rate enhancement observed in the copper(II)-promoted reaction cannot be accurately defined it is probable that it is greater than 10^6 fold.[†]

ACKNOWLEDGEMENTS

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[†] Fife and Pujari (ref. 21) have recently shown that divalent metal ions such as Cu(II), Ni(II), Co(II) and Zn(II) exert a pronounced catalytic effect on the hydrolysis of the phosphate dianion species of 2-(1,10-phenanthrolyl)phosphate. A dianion reaction cannot be observed in the absence of the metal ion. The copper(II) complex of the 2-(1,10-phenanthrolyl)phosphate dianion hydrolyses, at 40°C, more than 10^8 times faster than the phenylphosphate dianion and 6×10^4 times faster than the *p*-nitrophenylphosphate dianion.

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22. A recent publication (M.M. Armstrong, U. Kramer, P.W. Linder, R.G. Torrington, and T.A. Modro, *J. Coord. Chem.*, **20**, 81 (1989)) describes equilibrium studies of the protonation of 8-quinolyl phosphate, 1-naphthyl phosphate and 8-quinolyl methyl phosphate and their complexation with copper(II), zinc(II), nickel(II), cobalt(II) and manganese(II) at 25°C and $I = 0.150\,\mathrm{mol\,dm^{-3}}$. The data for copper(II) are broadly in agreement with the present results.