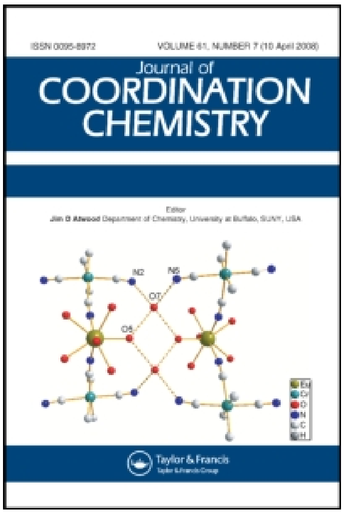

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THE KINETICS OF THE REACTION BETWEEN Cu(II) AND 2-HYDROXY-ACETOPHENONE

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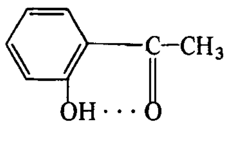
INTRODUCTION

In continuation of our program of investigating the rate of complex formation between internally hydrogen-bonded acids and metal ions which are known to form highly labile complexes[2–5] we have studied the system Cu(II)-2-hydroxy-acetophenone. The formula of the ligand is



and will be abbreviated as HL, and that of its deprotonated form as L^-.

EXPERIMENTAL

All kinetic experiments were carried out by the temperature jump method. The ionic strength was 0.1 M throughout and the temperature 25°C. Experimental details are described elsewhere.[2]

RESULTS

Equilibrium Constants

A spectrophotometric determination[2] of the dissociation constant of HL, carried out at $\lambda = 370$ nm and seven values of pH between 9.12 and 10.86 yielded

$$K_c = (4.2 \pm 0.8) \times 10^{-11}\ \mathrm{M}$$

If A is the absorbance of a solution containing ligand in total concentration b, and Cu(II) in total concentration a, with $b \gg a$, then we can write[2]

$$\frac{a}{A - \epsilon_{HL}b} = \frac{1}{\epsilon_{CuL} - \epsilon_{HL}} + \frac{1}{(\epsilon_{CuL} - \epsilon_{HL})}\frac{[H^+]}{bK_1} \qquad (1)$$

with

$$K_1 = \frac{[CuL]\,[H^+]}{[Cu]\,[HL]} \qquad (2)$$

(For the sake of brevity, we omit charges in the expression for concentration except for the hydrogen ion.) Eq. (1) would be valid if Cu^{2+} were completely unhydrolyzed. It is also valid when Cu^{2+} and CuL^+ hydrolyze to the *same*, small, but not negligible, extent (assumption (i)), that is to say

$$[Cu]/[CuOH] = [CuL]/[CuOHL] = [H^+]/K_{Cu} \qquad (3)$$

where

$$K_{Cu} = \frac{[CuOH]\,[H^+]}{[Cu]} \qquad (4)$$

On the other hand, if we assume that the complex does not hydrolyse at all, whereas Cu^{2+} does (assumption (ii)), the first term on the right hand side of Eq. (1) has to be multiplied by $[1 + (K_{Cu}/K_1 b)]$. *In either case*, a plot of $a/(A - \epsilon_{HL}b)$ against $[H^+]/b$, at constant b, should give a straight line (provided the pH is low enough for [L] to be very much lower than [HL], so that the molar absorption of the ligand is uninfluenced by pH; since $\epsilon_L \gg \epsilon_{HL}$ at the wavelength chosen, we found this condition to hold only up to pH ~ 8). From the ratio between intercept and slope we get K_1, or $K_1 + K_{Cu}/b$, respectively.

The results of three series of experiments with $b = (3.6; 4.6; 6.9) \times 10^{-4}$ M at $\lambda = 380$ nm differed from each other more strongly than might be expected from the standard deviations of each series taken separately. On the basis of assumption (i) we get as the mean of the three series

$$K_1 = 2.53 \times 10^{-4}$$

with a standard deviation of the mean of ±1.57×10^{-4}. As we shall see, this high standard deviation does not materially affect our conclusions. The value of K_{Cu} does not seem to be reliably known,[6] but if we assume it to be $\sim 10^{-7}$, then in two of the three series the ratio between intercept and slope becomes smaller than K_{Cu}/b. On the basis of assumption (ii), this would leave a negative value for K_1, which is of course impossible. If we take a lower value for K_{Cu},[7] then K_1 remains positive, but its standard deviation would be even higher than on the first assumption. We conclude that assumption (i) is nearer to representing the true state of affairs, that is to say, Cu^{2+} and CuL^+ hydrolyse to a similar extent.

Kinetic Results

The results of two series of experiments, at $a = b = 2 \times 10^{-4}$ M, and at $a = b = 4 \times 10^{-4}$ M, showed that $1/\pi$ decreases with increasing pH, passes through a minimum, and then increases with further increase of pH. A reaction scheme which explains this behavior is

$$\begin{array}{llll}
Cu^{2+} + HL & \rightleftharpoons & CuL^+ + H^+; & \\
\upharpoonleft\downharpoonright & & K_1 & (I) \\
CuOH^+ + HL & \rightleftharpoons & CuL^+ + H_2O; & \\
\upharpoonleft\downharpoonright \quad \upharpoonleft\downharpoonright & & K_2 = K_1/K_{Cu} & (II) \\
Cu^{2+} + L^- & \rightleftharpoons & CuL^+; & \\
\upharpoonleft\downharpoonright & & K_2' = K_c & (II') \\
CuOH^2 + L^- & \rightleftharpoons & CuOHL; & \\
 & & K_3 = K_1/K_c & (III)
\end{array}$$

This leads to a reciprocal relaxation time of[8,9]

$$1/\tau = (k_1 [H^+]/K_{Cu} + k_2 + k_2' K_c/K_{Cu} + k_3 K_c/[H^+]) \times B \quad (5)$$

where k_1, k_2, k_2' and k_3 are the forward rate constants of reactions I, II, II′ and III, respectively, and

$$B = [CuOH]\,[\delta_{HL}/(-\delta)] + [HL]\,[\delta_{CuOH}/(-\delta)] + (K_{Cu}/K_1)[\delta_{CuL}/\delta) \quad (6)$$

The meaning of δ_i is the difference between equilibrium concentration and instantaneous concentration of substance i, and $(-\delta) \equiv \delta_{HL} + \delta_L = \delta_{Cu} + \delta_{CuOH}$. Since the protolytic equilibria are all fast, the ratios appearing in Eq. (6) are independent of the extent of reaction, and can be calculated from the conservation conditions together with the knowledge that the protolytic equilibria are maintained while the complex formation proceeds. The expression for $(1/\tau)/B$ was treated as a linear regression in the two variables $[H^+]$ and $1/[H^+]$, and the rate constants were obtained from the regression coefficients. With assumption (i)[10] and[11] $K_{Cu} = 10^{-7}$ M, this yields

$$k_1/K_{Cu} = (3.21 \pm 0.35) \times 10^{11}\ M^{-2}\,sec^{-1};$$

$$k_1 = 3.2 \times 10^4\ M^{-1}\,sec^{-1}$$

$$k_3 K_c = (1.74 \pm 0.33) \times 10^{-2}\ sec^{-1};$$

$$k_3 = 4.1 \times 10^8\ M^{-1}\,sec^{-1}$$

$$k_2 + k_2' K_c/K_{Cu} = (1.33 \pm 0.41) \times 10^5\ M^{-1}\,sec^{-1}$$

With the aid of these values, we synthesized the curve shown in Figure 1. It will be noted that the points representing the experiments carried out at the lower concentration lie almost universally below this

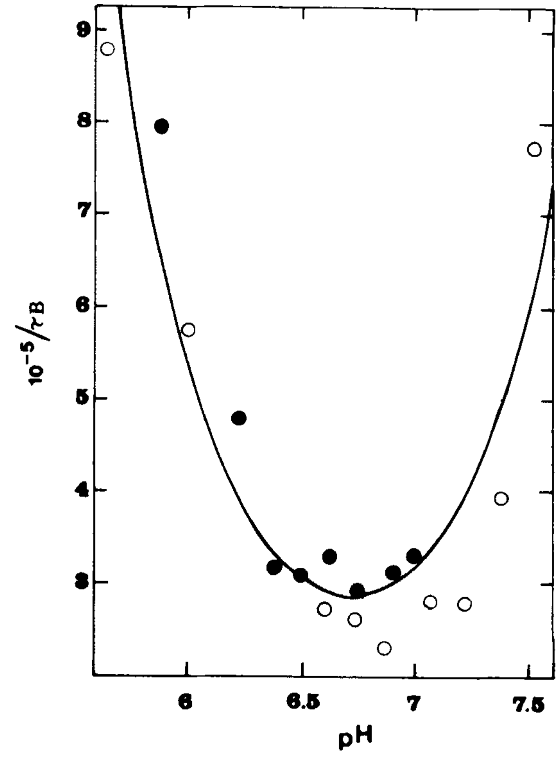


FIGURE 1 The dependence of $1/\tau B$ on pH (where B is defined in equation (6)). Dots: $a = b = 4 \times 10^{-4}$ M; open circles: $a = b = 10 \times 10^{-4}$ M.

line, whereas those representing the experiments at the higher concentration lie above. This hints at the possibility of the formation of a higher complex[4]. We should like to stress, however, that the discrepancy between the two series can *not* be due to our values of K_1 being incorrect. Varying K_1 within wide limits, we could not make the two series coincide.

DISCUSSION

The value of k_1 is lower by a factor of $\sim 10^3$ than the value which would be "normal" for a reaction between Cu^{2+} and an uncharged ligand;[12] this important result is in keeping with previous findings (see, for example, Refs. 2, 3, 5 and 13) when the ligand contained an internally bonded hydrogen.

Reactions II and II′ have the same pH-dependence and it is impossible to determine their individual contributions. In the present case, they may well be of the same order of magnitude. In view of the fact that we have recently[5] found that $NiOH^+$ reacts with internally hydrogen-bonded ligands at a higher rate than does Ni^{2+}, the value of $k_2 \sim 10^5$ M^{-1} sec^{-1} would not be unreasonable for the reaction between $CuOH^+$ and HL. On the other hand, if reaction II′ is the sole contributor to the $[H^+]$-independent path, we get $k_2{}' \sim 3 \times 10^8$ M^{-1} sec^{-1}, a reasonable value for a reaction between Cu^{2+} and a "normal" monovalent ligand.[12] This problem of "proton ambiguity"[14] has been extensively discussed for the case of Fe(III) (see, for instance, Ref. 15).

The relative reactivity of $CuOH^+$ still seems to be a matter for discussion. Margerum and coworkers[7] explain the pH dependence of the reaction between Cu(II) and EDTA-complexes by assuming $CuOH^+$ to react much faster than Cu^{2+}, whereas Rorabacher and coworkers[16] did not find any kinetic contribution of $CuOH^+$ up to pH 5.5. Our value of k_3 means[11] that, with the "*normal*" ligand L^-, $CuOH^+$ reacts at approximately the same rate as does Cu^{2+}. This confirms the theory that the labilizing influence of OH^- on the remaining water molecules in the inner sphere is confined to metal ions for which hydrolysis proceeds at a much higher rate than does substitution.[12]

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10. On assumption (ii), the ratios of the δ's, as well as [CuOH] and [HL], would have slightly different values. This would lead to values of the regression ceefficients differing from those listed above by less than two standard deviations.
11. If we assume K_{Cu} to be lower than 10^{-7} M, then B as defined in equation (6) becomes lower, though not in proportion to the change in K_{Cu}. The regression coefficients and, therefore, k_2 and k_3 become higher, whereas k_1 and $k_2{}'$ become somewhat lower.
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