Activation Parameters for the Formation of Copper(II) Complexes with 2,2′-Bipyridyl-type Ligands

By THOMAS S. ROCHE and RALPH G. WILKINS*

(*State University of New York at Buffalo, Buffalo, N.Y.* 14214)

Summary The first activation parameters have been measured for the reaction of Cu^{2+}_{aq} with 2,2′-bipyridyl, 1,10-phenanthroline, and 2,2′,2″-terpyridyl, and/or some of their protonated forms.

THE formation of most copper(II) complexes in aqueous solution is extremely rapid, and this has doubtless discouraged their rate measurement, which generally require relaxation methods. A handful of single-temperature rate constants and one activation energy value have been reported.[1-5] The sound-absorption by aqueous solutions of copper(II) sulphate and acetate[2] has provided data on the rate constant k_0 for the exchange of co-ordinated water by ligand within the outer-sphere complex Cu^{2+}, L^{n-} (see equation 1). The latter is formed by a diffusion-controlled reaction between the reacting ions.[6] For these

$$Cu^{2+}_{aq} + L^{n-}_{aq} \overset{K_0}{\rightleftharpoons} Cu^{2+}, L^{n-} \overset{k_0}{\rightleftharpoons} CuL^{(2-n)+} \qquad (1)$$

two systems, as well as a number of others in which chelating ligands are involved, [1,3-5] k_0 can be estimated to be in the range 3×10^8—1×10^9 s^{-1}. It is not yet established whether this value refers to water loss from the very labile axial water of the tetragonal Cu^{2+}_{aq} ion, or to the rapid inversion of the structure leading to axial and equatorial water interchange.[3,4,7]

We have measured the rates of reaction of Cu^{2+} with 2,2′-bipyridyl (bipy), 1,10-phenanthroline (phen), and 2,2′,2″-terpyridyl (terpy) at pH 1—2·5 by stopped-flow methods. The reactions could be studied directly in the 280—330 nm region, thus avoiding the complication of added indicators to follow the change.[2-4] No reactant or product hydroxy-species were involved under the conditions used. All reactions were second-order and forced to completion.

For the reaction of a mixture of bidentate ligand L (k_L) and the protonated form LH (k_{LH}) with Cu^{2+} ion, the observed second-order rate constant k_{obs} is related to $[H^+]$ and K_a, the ionization constant of LH, by (2). In all

$$k_{obs}\,(K_a + [H^+])[H^+]^{-1} = k_{LH} + k_L K_a [H^+]^{-1} \qquad (2)$$

cases $K_a \ll [H^+]$. From the linear plots of k_{obs} against $[H^+]^{-1}$ were obtained k_{LH} (intercept) and $k_L K_a$ (slope). For terpy the expression corresponding to equation (2) is more complicated.[8] However, a plot of k_{obs} against $[H^+]^{-1}$ at low pH gave k_{LH_2} (intercept) and $k_{LH} K_{LH_2}$ (slope).

A series of kinetic experiments at 1—25°, in conjunction with literature values for pK_a and ΔH_{LH}, gave the results shown in the Table. The negligible contribution of phen H^+ and terpy H_2^{2+} to the reaction rate allowed accurate data to be obtained for that of phen and terpy H^+. Activation parameters could be obtained for bipy H^+ but not for the temperature coefficient for the rate constant for bipy. At higher pH (>3) the reaction of Cu^{2+} with terpy is not straightforward, and previous approximate values[9] for k_{terpy} should be ignored. Our results for bipy and bipy H^+ at 25° are in very good agreement with recent temperature-jump measurements by Diebler[5] [*ca.* 4×10^7 and $2{\cdot}9\ (\pm 0{\cdot}4) \times 10^5$ at 25°, respectively]. For the reaction of Cu^{2+} with bipy and phen, formation rate constants of 2×10^7 and 4×10^7 $M^{-1}\,s^{-1}$ at 25° can be estimated from dissociative and thermodynamic data.[9]

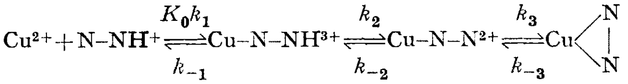
Rate data for copper(II) *reactions* ($\mu = 1{\cdot}0$M)

Ligand	k_{25} $M^{-1}\,s^{-1}$	$\Delta H^\ddagger$ kcal. mol^{-1}	$\Delta S^\ddagger$ e.u
phen	$6{\cdot}4(\pm 0{\cdot}5) \times 10^7$	$5{\cdot}1 \pm 1{\cdot}0$	-6 ± 3
phen H^+	$< 5 \times 10^2$	—	—
bipy	$5{\cdot}0(\pm 0{\cdot}8) \times 10^7$	—	—
bipy H^+	$2{\cdot}6(\pm 0{\cdot}2) \times 10^5$	$4{\cdot}3 \pm 1{\cdot}2$	-19 ± 4
terpy H^+	$8{\cdot}0(\pm 0{\cdot}7) \times 10^5$	$4{\cdot}7 \pm 0{\cdot}9$	-15 ± 3
terpy H_2^{2+}	$< 5 \times 10^2$	—	—

The reaction of phen with a number of bivalent metal ions can be understood on the basis of equation (1) with a value for K_0 of *ca.* 0·1.[10] Application of this to the Cu^{II} situation gives $k_0 = ca.\ 6 \times 10^8$ s^{-1}, which suggests that formation of the Cu^{II}–phen complex is controlled by first-bond formation. The slightly lower value for the bipy reaction (consistently found[9,10]) may reflect a degree of steric control in this more flexible ligand.

For the reaction of the monoprotonated form (represented N–NH$^+$ in the scheme) with Cu^{2+} ion, the expression (3) can be deduced. k_{LH} was independent of pH, and thus the last term in the denominator in equation (3) was negligible and ring-closure was never rate-determining.[4,5] Thus $k_{LH} = K_0 k_1 k_2 (k_2 + k_{-1})^{-1}$. The low values for the rate constants for bipy H^+, terpy H^+, (and en H^+; ref. 4) probably reside in $k_{-1} \gg k_2$ and show up as a large negative

$\Delta S^{\ddagger}$. The effective blocking of the donor sites in phen H^{+} and terpy $\mathbf{H}_2^{2+}$ (ref. 11) probably results in a very low



$$\mathrm{Cu^{2+} + N{-}NH^{+}} \underset{k_{-1}}{\overset{K_0k_1}{\rightleftharpoons}} \mathrm{Cu{-}N{-}NH^{3+}} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{Cu{-}N{-}N^{2+}} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \mathrm{Cu(N{-}N)}$$

$$k_{\mathrm{LH}} = \frac{K_0k_1k_2k_3}{k_2k_3 + k_{-1}k_3 + k_{-1}k_2\,[\mathrm{H}^{+}]} \qquad (3)$$

K_0k_1 value, and thus in overall rate constants which are less than 5×10^{2} M^{-1} s^{-1}. All $\Delta H^{\ddagger}$ values are low (*cf.* $\Delta H^{\ddagger} = 5{\cdot}5$ $\Delta S^{\ddagger} = -3$ e.u. for the $\mathrm{Cu^{2+}}$–murexide reaction[1]) as might be expected from the structure of the aquated copper ion. The reactivity sequence phen > bipy > terpy H^{+} > bipy H^{+} > phen H^{+} $\simeq$ terpy H_2^{2+} has been also observed in their reaction with $\mathrm{Ni^{2+}}$ ion. At high acidities however, the value of k_{LH} was pH-dependent because of the lowered values of k_3.[8,12]

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