Inorganica Chimica Acta, 100 (1985) L1–L3

The Dissociation of $[Cu(cyclen)]^{2+}$ in Acid Solution. A Kinetic Study

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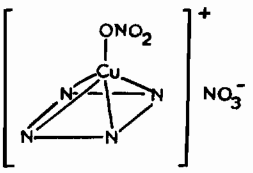
Received December 21, 1984

Recently there has been considerable interest in the dissociation of macrocyclic complexes in acidic solution [1–9]. Complexes of the 14-membered macrocyclic ligand cyclam (1,4,8,11-tetraazacyclotetradecane) are known to dissociate extremely slowly [2, 10], but dissociation from larger rings occurs much more readily [4–6]. Currently, no studies have been reported on macrocyclic complexes containing a 12-membered tetraaza ring. The copper(II) complex of cyclen(1,4,7,10-tetraazacyclododecane) is known from X-ray investigations [11] on $[Cu(cyclen)NO_3]NO_3$ to have the 'sitting atop' structure (**1**) in which the copper atom lies some 0.5 Å out of the plane of the four nitrogen donors.



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This structure could lead to increased lability in acidic solution. For this reason, we have studied the acidic dissociation kinetics over a temperature range.

Experimental

Cyclen·4HCl was prepared essentially as previously described [12]. The copper(II) complex of cyclen was prepared as follows. Cyclen·4HCl (0.5 g) was dissolved in water and an excess of basic copper(II) carbonate added. The slurry was heated on a water bath for *ca.* 0.5 h and filtered hot. Lithium perchlorate was added to the filtrate, and the volume slowly reduced on a water bath. On standing, blue needles of $[Cu(cyclen)](ClO_4)_2$ were obtained.

Kinetics

Solutions of perchloric acid were prepared from 70% perchloric acid and standardized using standard sodium hydroxide solution. The ionic strength was adjusted to 5 M by the addition of sodium perchlorate. The dissociation was normally monitored at *ca.* 268 nm where a strong charge transfer band occurs in $[Cu(cyclen)]^{2+}$. Plots of log $(A_t - A_\infty)$ were linear for several half lives and values of k_{obs} were evaluated from such plots. Interval scan spectra and kinetic measurements were made with a Perkin Elmer Lambda 5 UV-Vis spectrophotometer.

Results and Discussion

Copper(II)–cyclam was found to dissociate quite readily in 5 M $HClO_4$. A typical interval scan spectrum for the reaction is shown in Fig. 1. The reaction displays a clear isosbestic point, the position of which depends on the acidity of the solution. The reaction is cleanly first order in the concentration of $[Cu(cyclen)]^{2+}$. Initial studies of the dependence of the reaction on the acidity were carried out in the absence of any added electrolyte leading to the curved plot shown in Fig. 2. Further experiments indicated that the curvature was due to a medium effect. If the ionic strength of the solution was maintained at 5 M by addition of sodium perchlorate, the data shown in Table I were obtained. Under these conditions of constant ionic strength, the reaction is first order in $[H^+]$ with $k_H = k_{obs}/[H^+]$, Fig. 2, and

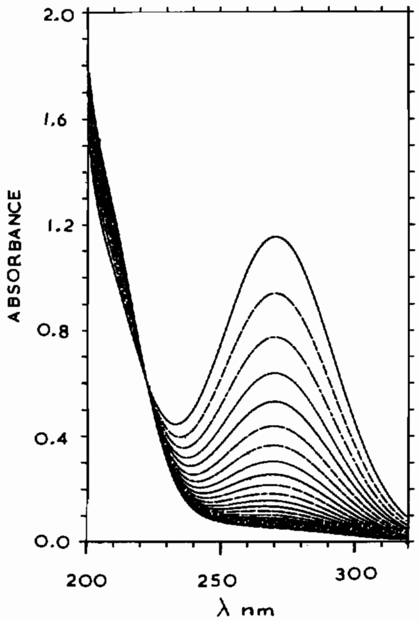

Fig. 1. Interval scan spectra for the dissociation of $[Cu(cyclen)]^{2+}$ in 5 M $HClO_4$ at 25 °C. The time interval between scans is 2 min.

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TABLE I. Dissociation of $[Cu(cyclen)]^{2+}$ in Perchloric Acid Solutions Adjusted to $I = 5$ M ($NaClO_4$).

Temp. (°C)	$[H^+]$ (M)	$10^4 k_{obs}$ (s^{-1})	$10^4 k_H$ ($M^{-1} s^{-1}$)
25	2.0	5.20	2.60
	3.0	7.68	2.56
	3.5	8.83	2.52
	4.0	10.10	2.52
	4.5	11.81	2.62
	5.0	12.12	2.42
30	3.5	14.63	4.18
	4.0	15.16	3.79
	4.5	19.21	4.26
	5.0	21.80	4.36
33	4.0	21.48	5.37
	4.5	23.38	5.19
	5.0	27.37	5.47
40	4.0	43.57	10.89
	4.5	51.2	11.37
	5.0	55.5	11.10

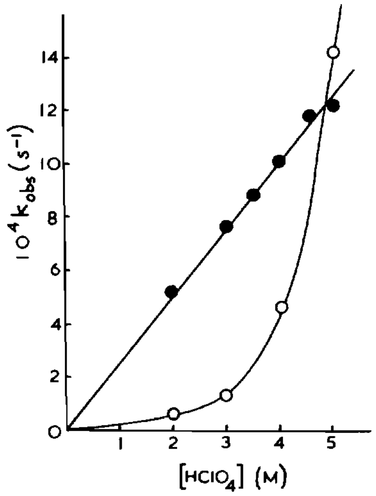


Fig. 2. Plot of k_{obs} *vs.* $[H^+]$ at 25 °C. The open circles are for solutions containing no added electrolyte. The filled circles are at a constant ionic strength of 5 M (adjusted with $NaClO_4$).

the rate expression takes the form rate = k_H[complex] $[H^+]$. Values of k_H were obtained at 25, 30, 33 and 40 °C giving the activation parameters $\Delta H^{\ddagger} = 74 \pm 2$ kJ mol^{-1} and $\Delta S^{\ddagger}_{298} = -67 \pm 8$ J K^{-1} mol^{-1} with a correlation coefficient of 0.9987, Table II. At 25 °C, $k_H = (2.54 \pm 0.07) \times 10^{-4}$ M^{-1} s^{-1} at I = 5.0 M.

It is probable that the acid catalysed reaction involves the steps:

TABLE II. Temperature Dependence of k_H ($I = 0.5$ M).[a]

Temp. (°C)	$10^4 k_H$ ($M^{-1} s^{-1}$)
25	2.54
30	4.15
33	5.34
40	11.12

[a] $\Delta H^{\ddagger} = 74 \pm 2$ kJ mol^{-1}; $\Delta S^{\ddagger}_{298} = -67 \pm 8$ J K^{-1} mol^{-1} (r = 0.9987).

$$[Cu(cyclen)]^{2+} + H^+ \overset{K}{\rightleftharpoons} [Cu(cyclenH^+)]^{3+} \quad (1)$$

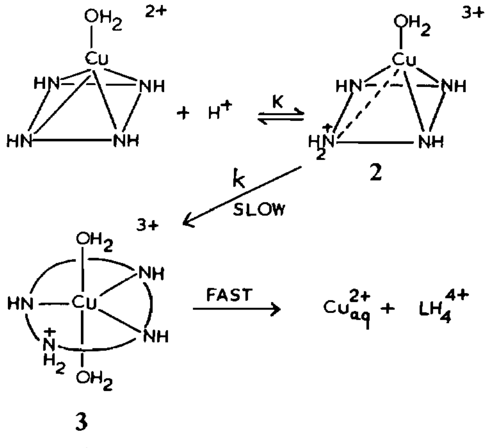
$$[Cu(cyclenH^+)]^{3+} + H_2O \xrightarrow{k} Cu^{2+}(aq.) + cyclenH^+ \quad (2)$$

the subsequent protonation steps being rapid to give $cyclenH_4^{4+}$. There is a rapid pre-equilibrium step, followed by a slow rate-determining dissociation. On the basis of eqns. (1) and (2):

$$k_{obs} = \frac{kK[H^+]}{(1 + K[H^+])} \quad (3)$$

When $K[H^+] \ll 1$, the reaction shows a first order dependence on $[H^+]$ with $k_H = kK$. The measured values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}_{298}$ thus relate to combined rate and equilibrium constants.

A possible mechanism for the acid catalysed reaction is shown in Scheme 1. As the kinetic data indicate that the equilibrium constant K is relatively small, protonation of a partly bound nitrogen atom is difficult (eqn. 1). Decomposition of the protonated species (2) is rate determining and may possibly involve a stereochemical change to the trigonal bipyramidal species (3) which then undergoes rapid decomposition to Cu^{2+} (aq.) and LH_4^{4+}.



Scheme 1. A possible reaction scheme for the dissociation of $[Cu(cyclen)H_2O]^{2+}$ in acidic solution.

As plots of k_{obs} *vs.* $[H^+]$ indicate no curvature at high acidities, there must be <10% of the protonated complex $[Cu(cyclamH^+)]^{3+}$ in 5 M $HClO_4$. The H^o value of 5 M $HClO_4$ is −2.23 [13], and use of the equation $pK_a = H^o - \log(B/BH^+)$ indicates that the pK_a of $[Cu(cyclenH^+)]^{3+}$ must be less than −3.2. As the equilibrium constant K will be given by eqn. (4), the rate variations observed between solutions having variable and constant ionic strength, presumably arise due to changes in K which arise due to variations in γ_{BH^+} and γ_B. Slow dissociation arises from a combination of low equilibrium constants for protonation and the difficulty in breaking the Cu–N bond. These effects lead to substantial values of $\Delta H^\ddagger$ and quite large negative entropies of activation.

$$K = \frac{[BH^+]}{[B]a_{H^+}} \times \frac{\gamma_{BH^+}}{\gamma_B} \qquad (4)$$

The distorted square pyramidal stereochemistry of copper(II)–cyclen complexes leads to quite rapid dissociation when comparisons are made with $[Cu(cyclam)]^{2+}$. In the case of the latter complex, Cabbiness and Margerum [2] have found that dissociation is extremely slow with $k_{obs} = 3.6 \times 19^{-7}$ s^{-1} ($t_{1/2}$ *ca.* 22 days) in 6.1 M HCl at 25 °C. If it is assumed that this reaction shows a first order dependence on $[H^+]$, an approximate value of k_H is 6×10^{-8} M^{-1} s^{-1}. Dissociation of $[Cu(cyclen)]^{2+}$ is some 10^4 times faster than that of $[Cu(cyclam)]^{2+}$ in acidic solution.

The ESR spectra [14] of $Cu(cyclen)(ClO_4)_2$ in MeCN and DMSO glasses (77 °K) are consistent with a square pyramidal stereochemistry in which the donor solvent occupies the axial site. The parallel signal of the X-band spectrum is split into four equally spaced hyperfine lines of which three are readily observable. By contrast the ESR spectrum of $Cu(cyclam)(ClO_4)_2$ in MeCN gives an isotropic signal at 77 °K indicating a truly planar stereochemistry. However, solvent interaction occurs in DMSO glasses as hyperfine splitting of the parallel signal occurs. In aqueous solution it can be safely assumed that $Cu(cyclen)(ClO_4)_2$ exists as $[Cu(cyclen)H_2O]^{2+}$ with a water ligand in the axial site.

Acknowledgement

We wish to thank the SERC for financial support.

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