modes are expected for C_{2v} complexes but frequently fewer are observed.[17] We find an X-insensitive band at approximately 240 cm^{-1} (Figure 1) which we have assigned to $\nu_{\text{Co–(4-DMAP)}}$ and two bands (Table IV) for the Cl and Br complexes which are assigned to $\nu_{\text{Co–Cl}}$ and $\nu_{\text{Co–Br}}$. We have not resolved $\nu_{\text{Co–I}}$ or $\nu_{\text{Co–NCSe}}$ absorptions from the low-frequency ligand bands (Figure 1). Assignments for $\nu_{\text{Co–NCO}}$ and $\nu_{\text{Co–NCS}}$ have also been made at 370 and 330 and 325 cm^{-1}, respectively.

Ligand field spectral data given in Table V are rather typical of CoN_2X_2 complexes.[1] Two absorptions are observed. The first, in the near-infrared region centered at approximately 7500–8500 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1(^4F)$, ν_2, transition and the second, centered at approximately 16 000 cm^{-1} is assigned to the $^4A_2 \rightarrow {}^4T_1(^4P)$, ν_3, transition. By using the crystal field matrix elements of König[19] and by weighting the individual components of the bands according to their spin–orbit coupling energies, we have calculated values for the tetrahedral crystal field splitting parameters Dq^{tet} and B. The series of Dq^{tet} values follows the classical spectrochemical series NCSe > NCS > NCO > Cl ~Br > I. Because the overall splitting of ν_2 and ν_3 is considerably larger than $6\lambda_0$,[20] we have calculated the second-order distortion parameter Ds[21] by using the electrostatic matrix elements given by Flamini et al.[22] These values of Ds decrease in the order NCO > I > Br > NCS ~ Cl > NCSe. The fact that this series does not correlate with the normal spectrochemical series may indicate that the model[22] used to calculate Ds is inadequate for these complexes.

Conclusion

We have determined that 4-DMAP forms pseudotetrahedral complexes with Co(II) halides and pseudohalides and have concluded that these compounds are similar to other C_{2v} Co(II) complexes containing substituted pyridine ligands. Future investigations are planned to obtain the mass spectral fragmentation patterns and ^{13}C NMR spectra of these complexes. In addition we are planning a study of the corresponding 2-DMAP and 3-DMAP complexes.

Registry No. $Co(4\text{-DMAP})_2Cl_2$, 62660-95-1; $Co(4\text{-DMAP})_2Br_2$, 62882-88-6; $Co(4\text{-DMAP})_2I_2$, 62882-87-5; $Co(4\text{-DMAP})_2(NCO)_2$, 62882-86-4; $Co(4\text{-DMAP})_2(NCS)_2$, 62882-85-3; $Co(4\text{-DMAP})_2(NCSe)_2$, 62882-84-2; 4-DMAP, 1122-58-3.

Supplementary Material Available: A listing of the x-ray powder diffraction d spacings, Table I (2 pages). Ordering information is given on any current masthead page.

References and Notes

(1) M. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.*, **84**, 1543 (1962); A. B. P. Lever and S. M. Nelson, *J. Chem. Soc. A*, 859 (1966); and references therein.
(2) J. M. Haigh, N. P. Slabbert, and D. A. Thornton, *J. Mol. Struct.*, **7**, 199 (1971).
(3) L. C. Nathan and R. O. Ragsdale, *Inorg. Chim. Acta*, **10**, 177 (1974).
(4) J. H. Nelson, R. G. Garvey, and R. O. Ragsdale, *J. Heterocycl. Chem.*, **4**, 591 (1967).
(5) A preliminary report on the synthesis and characterization of the pseudohalide complexes has appeared: J. M. Land, J. A. Stubbs, and J. T. Wrobleski, Abstracts, 12th Midwest Regional Meeting of the American Chemical Society, 1976, No. 419, p 47. The spectrum of the chloride complex in several media has been published: J. T. Wrobleski and G. J. Long, *Appl. Spectrosc.*, **31**, 177 (1977).
(6) Supplementary material.
(7) F. E. Mabbs and D. J. Machin, "Magnetism and Transition Metal Complexes", Chapman and Hall, London, 1973, p 5.
(8) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).
(9) J. M. Land and J. T. Wrobleski, *J. Chem. Educ.*, in press.
(10) A. R. Katritzky and J. N. Gardner, *J. Chem. Soc.*, 2198 (1958).
(11) J. M. Essery and K. Schofield, *J. Chem. Soc.*, 3939 (1961).
(12) C. W. N. Cumper and A. Singleton, *J. Chem. Soc. B*, 1096 (1967).
(13) R. Frampton, C. D. Johnson, and A. R. Katritzky, *Justus Liebigs Ann. Chem.*, **749**, 12 (1971).
(14) B. N. Figgis, "Introduction to Ligand Fields", Interscience, New York, N.Y., 1966, p 276.
(15) C. J. Ballhausen, "Introduction to Ligand Field Theory", McGraw-Hill, New York, N.Y., 1962, p 170.
(16) R. J. H. Clark and C. J. Williams, *Inorg. Chem.*, **4**, 350 (1965); D. H. Brown, K. P. Forrest, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc. A*, 2146 (1968); R. J. H. Clark and C. S. Williams, *Chem. Ind. (London)*, 1317 (1964); N. S. Gill and H. J. Kingdon, *Aust. J. Chem.*, **19**, 2197 (1966).
(17) J. R. Ferraro, "Low-Frequency Vibrations of Inorganic and Coordination Compounds", Plenum Press, New York, N.Y., 1971, p 205.
(18) Reference 14, p 239.
(19) E. König, *Struct. Bonding (Berlin)*, **9**, 175 (1971).
(20) Reference 15, p 127.
(21) M. Gerloch and R. C. Slade, "Ligand-Field Parameters", Cambridge University Press, London, 1973, p 147.
(22) A. Flamini, L. Sestili, and C. Furlani, *Inorg. Chim. Acta*, **5**, 241 (1971).

Contribution from the Department of Chemistry,
Indiana–Purdue University at Indianapolis, Indianapolis, Indiana 46205

Hydrolysis Kinetics of (−)-Sparteine–Copper(II) Halides[1a–c]

W. A. CADY,* ERWIN BOSCHMANN,* RYO SHON CHOI,[1d] JOSEPH F. HEIDELMAN, and SHARON L. SMITH

Received January 28, 1977 AIC700749

The hydrolysis kinetics of the reactions of (−)-sparteine–copper(II) chloride and (−)-sparteine–copper(II) bromide were studied to determine a possible mechanism for the process. Of particular interest were the slowness of the reaction and the catalytic effect of halide ions on the hydrolysis reaction. The parameters investigated were concentration, temperature, and halide concentration, which have positive effects on the rate, and the pH and ionic strength, which have minimal effects. The results suggest a mechanism in which the rate-determining step is a conformational inversion from a cisoid to a transoid form of the sparteine moiety followed by a subsequent attack by water or a halide ion. The reactions proceed according to the rate law $-d[C_{15}H_{26}N_2\cdot CuX_2]/dt = [(k_1k_2 + k_1k_3X)/(k_{-1} + k_2 + k_3X)][C_{15}H_{26}N_2\cdot CuX_2]$. From measurements over the 25–55 °C temperature range the $\Delta H^{\ddagger}$ values are found to be 16.0 and 23.1 kcal/mol, and the $\Delta S^{\ddagger}$ values are −24.4 and −1.45 eu, for the chloro and bromo complexes, respectively. The difference in kinetic behavior is explained in terms of halide size differences and the nucleophilicity differences of the halide ions.

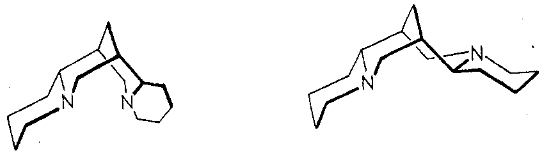
Introduction

Recently there has been increased interest in the chemistry of sparteine alkaloids, $C_{15}H_{26}N_2$, and their metal salt adducts.[2-11] Particular interest in the chemistry of these alkaloids has arisen because of their biological and physiological use in the stimulation of muscular action in the heart, lung, and uterus.[12] Since the ions of metals such as calcium[13a] and magnesium[13b] appear to play a sensitive role in muscle activity, the complex formation process may affect in some manner the equilibria or kinetic processes involving these metal ions.[14] To provide additional information for understanding and elucidating the detailed mechanism of this effect as well as extending our knowledge of the reaction processes of these alkaloids, we investigated the kinetics of the hydrolysis of two copper halide adducts.

An x-ray analysis has shown that the $CuCl_2$ adducts of the sparteine diastereomers are locked into a tetrahedral configuration about the copper.[8] Optical[9,15] as well as electron spin resonance[9] studies confirm the tetrahedral coordination geometry of the (−)-sparteine–copper(II) halide complexes not only in the solid state but also in solution which is rare for copper(II). This relatively stable structural configuration of these complexes may make them useful models in the study of type I copper(II) ions in metalloproteins.[9] The compact tetrahedral structure of the copper complex makes attack on the copper rather difficult and hydrolysis rather slow. Although quite stable in nonaqueous media the $CuCl_2$ adducts of the three sparteine diastereomers have been shown to hydrolyze slowly according to the reaction[15]

$$C_{15}H_{26}N_2 \cdot CuCl_2 + 2H_2O \rightarrow C_{15}H_{26}N_2 \cdot 2H^{2+} + 2Cl^- + Cu(OH)_2 \quad (1)$$

Our results reported here on the kinetics of hydrolysis of $CuCl_2$ and $CuBr_2$ complexes of (−)-sparteine (I) confirm this and



I

show the reaction to be product catalyzed.

Experimental Section

Reagents and Solutions. Copper(II) chloride and copper(II) bromide complexes were prepared as described elsewhere.[15] Aqueous solutions of the complexes were prepared as follows. The powdered sample was weighed out to the nearest 0.0001 g and, at fixed times (several minutes) just prior to a run, dissolved in previously distilled and boiled water to give 0.5-L solutions (2.00×10^{-3} M sparteine·$CuCl_2$ and 1.64×10^{-4} M sparteine·$CuBr_2$). The ionic strength of all solutions was adjusted with chloride-free sodium nitrate (Matheson Coleman and Bell, reagent grade; total chlorine 0.001%) to 0.17. Sodium chloride and sodium bromide salts were used in the halide-dependence studies for sparteine·$CuCl_2$ and sparteine·$CuBr_2$, respectively, at 25 °C, adjusting the ionic strength with $NaNO_3$ to 0.17 for all ions. Additional data were obtained in the sparteine·$CuBr_2$–bromide ion study through the hydrolysis study of a solution containing a 10:1 concentration ratio of 1.64×10^{-3} M $Hg(NO_3)_2$ to 1.64×10^{-4} M sparteine·$CuBr_2$, which ensured virtually complete removal of bromide ion in solution. As always, the ionic strength was maintained constant at 0.17 using $NaNO_3$.

For the temperature studies the solvent was brought to within ±2 °C of the desired solution temperature prior to mixing the reagents. After mixing, the solution was then allowed to equilibrate in an Haake automatic temperature-control bath to the desired temperature (±0.2 °C) before the first measurement was taken.

Measurements and Calculations. The rates of hydrolysis were determined by observing the disappearance of the (−)-sparteine·CuX_2 complex using a Cary 118 UV–visible spectrophotometer[16] with 1-cm quartz matched cells. The reactions were followed at 700 and 320 nm, for the chloro and bromo complexes, respectively. These wavelengths are at the absorption maxima for the reactants; the hydrolysis products do not absorb at either of these wavelengths. Since the rates of hydrolysis are relatively slow, the spectra of the reactants were scanned during some runs and showed no change in the shape of the reactant spectra or the peak position as the reaction progressed nor any evidence of photochemical reaction. A reference solution consisting of 0.17 M $NaNO_3$ when no halide ion was added to the system or of NaCl or NaBr plus sufficient $NaNO_3$ to give an ionic strength of 0.17 when halide was added to the system was used to eliminate baseline effects which might possibly be introduced by the salts. During hydrolysis the chloro and bromo complex solutions changed from bright green and blue-green, respectively, to faint blue and colorless solutions, with the eventual formation of $Cu(OH)_2$ precipitate. To avoid scattering interference from $Cu(OH)_2$, only the initial rates were studied. Previously measurements were performed over a longer period of time by centrifuging the solution to remove the $Cu(OH)_2$.[15] We found that we could obtain more reproducible results by carefully measuring the initial rates before significant nucleation of the $Cu(OH)_2$ occurs. Attempts to eliminate this interference through complexation of liberated cupric ions or correction for scattering gave poor and nonreproducible results. Typically, for systems at 25 °C with no halide ion added, data were collected for about 20 min for the chloro complex and for about 2 h for the bromo complex before significant precipitation occurred vitiating any further chemical analysis. The time difference between the two complexes was due in part to the difference in initial concentration of the complex. The studies on the effect of ionic strength were carefully carried out using ionic strength values from 0 to 0.50 for the chloro complex and from 0 to 0.34 for the bromo complex (conditions: [sparteine·$CuCl_2$] = 2.00×10^{-3} M, [sparteine·$CuBr_2$] = 1.64×10^{-4} M, pH 5.7, temperature 25.0 ± 0.2 °C).

The pH studies were made with a Beckman Model LS pH meter. The pH range from 3 to 10 was covered (conditions: [sparteine·$CuCl_2$] = 2.00×10^{-3} M, [sparteine·$CuBr_2$] = 1.64×10^{-4} M, ionic strength 0.17, temperature 25.0 ± 0.2 °C) using HNO_3 and NaOH. An attempt to buffer the solution to the smooth muscle fluid pH of 7.4 was unsuccessful, since all buffers tested affected the sparteine complex, as indicated by a shift in the absorption maxima. The pH was also monitored during the course of some of the hydrolysis reactions (28 h). A solution identical with the reaction solution but without the sparteine complex was followed for comparison during the reaction.

A plot of the log of the initial rate vs. the log of the (−)-sparteine·CuX_2 concentration proved the hydrolysis to be first order in the sparteine adduct concentration. The rate constant k_{obsd} for this pseudo-first-order process (see eq 2) was obtained from the slope of

$$-d[C_{15}H_{26}N_2 \cdot CuX_2]/dt = k_{obsd}[C_{15}H_{26}N_2 \cdot CuX_2] \quad (2)$$

the plots of the log of the absorbance of $C_{15}H_{26}N_2 \cdot CuX_2$ vs. time for a number of initial concentrations between 1.1×10^{-4} and 3.8×10^{-4} M for the bromo complex and between 5.0×10^{-4} and 20×10^{-4} M for the chloro complex. A best straight-line fit was obtained from the data (typically 5–12 readings per data point) by a least-squares computer fit.

The values for k_{obsd} were obtained in the temperature range 25–55 °C and used in the usual fashion[17] to obtain the thermodynamic activation parameters.

Results and Discussion

The reaction of (−)-sparteine·CuX_2 with water follows the stoichiometry of eq 1 and obeys the general rate law given by eq 2. The parameters studied were pH, ionic strength, reactant and halide concentration, and temperature, the last three of which influenced the rate significantly. When fixed, these parameters were set at or near biological levels.

Although it took several minutes to completely dissolve the sparteine complex, there was no evidence of any rapid preequilibria in the hydrolysis reaction. The order of the reaction was determined from the initial rate data with only the ionic strength adjusted to its standard value (conditions: pH 5.7, ionic strength 0.17, temperature 25.0 ± 0.2 °C). The observed first-order rate constants were found to be $k_{obsd} = (4.80 \pm 0.05) \times 10^{-5}\ s^{-1}$ ($t_{1/2} = 4.01$ h) for the chloro complex and $k_{obsd} = (3.08 \pm 0.22) \times 10^{-5}\ s^{-1}$ ($t_{1/2} = 6.24$ h) for the bromo complex. The results for the chloro complex are nearly the same as those obtained earlier;[15,18] the major difference is due to the lower accuracy of the previous method where the data were collected over a longer period of time, beyond the point where precipitation of $Cu(OH)_2$ becomes a problem. Also, better control of temperature is maintained here since the sample is never removed from the temperature bath when spectroscopic measurements are made.

A study of the effect of pH showed the hydrolysis of the complexes to be insensitive to this parameter. In the pH range 3–10, the chloro complex experiences little variation in rate constant, while the bromo complex is somewhat more sensitive, changing in k_{obsd} values from 3.1×10^{-5} to 4.4×10^{-5} s^{-1}, in going from the acidic to the basic solution. If the hydrolysis mechanism involved simply the breaking of the N–Cu bond as the rate-determining step, one might expect the reaction should show acid catalysis. The lack of dependence on the hydrogen ion concentration is due to the fact that the rigid sparteine structure keeps the tertiary amino groups sterically hindered from hydrogen ion attack. This effect has been seen with other rigid bidentate systems, such as phenanthroline with various metals.[19]

The pH change due to the hydrolysis of the complex over a 28-h period was observed to increase to a maximum value and then rapidly drop to an intermediate value. For instance, during one run with the initial chloro complex concentration of 2.00×10^{-3} M, the pH rose from 5.60 to 6.60 during the first 235 min. The solution then turned cloudy and the pH dropped rapidly to 6.05 where it remained approximately constant for the next 24 h. Assuming no $Cu(OH)_2$ precipitation and using $pK_{a1} = 10.8$ and $pK_{a2} = 4.6$ for the sparteine,[15] the pH maximum at 235 min is predicted to be 7.0. These values of the pK_a of sparteine along with the K_{sp} of $Cu(OH)_2$[20] predict the final pH of the solution to be 6.15. Since the time at which precipitation occurred varied a great deal between the various runs, care was always taken to terminate the collection of spectroscopic rate data well before this time.

The ionic strength of 0.17 was chosen for our studies since it parallels that of smooth muscle fluids. In order to determine whether the rate of hydrolysis is affected by changes in ionic strength, careful studies were carried out using ionic strength values from 0 to 0.50 for the chloro complex and from 0 to 0.34 for the bromo complex. The results show little sensitivity to ionic strength except at very low values where the bromo complex gives an increase in k_{obsd} by a factor of about 2 with decreasing ionic strength. These results also show that $NaNO_3$ does not participate in the reaction. There is no apparent stabilization of the activated complex or intermediate that might be expected if either involved charge separation or ionization.

By comparing the spectra of both complexes during the hydrolysis process, including far into the reaction when centrifuging is necessary before the spectra can be taken, the position and shape of the peaks are found to be unchanged and to remain clearly different for the two complexes. Apparently the halide ions are not exchanging rapidly with the OH^- ions as might be expected with copper. Although OH^- has a formation constant with Cu^{2+} of about 7 orders of magnitude greater than Cl^-,[20] this large driving force does not appear to determine the rate of halide loss in this case but simply the extent of reaction.

The rate of hydrolysis shows a marked dependence on halide ion concentration. Studies were carried out on the rate of hydrolysis of sparteine·$CuCl_2$ as a function of chloride ion concentration and the hydrolysis of sparteine·$CuBr_2$ as a function of bromide ion concentration. The results are shown in Figures 1 and 2 and clearly indicate the reaction to be a product-catalyzed one. The variation of k_{obsd} for the chloro complex with chloride concentration indicates that the chloride ion does not have as strong an effect on the chloro complex as the bromide ion has on the bromo complex. k_{obsd} for the bromo system becomes too great to measure by the methods employed here before any leveling off occurs.

By extrapolating the plot of k_{obsd} of either complex vs. added halide ion concentration to zero added halide, it is apparent that there are two processes occurring—halide ion catalyzed hydrolysis and also the noncatalyzed direct hydrolysis. The rate constant discussed above for the hydrolysis with no added halide ion and indicated in Figures 1 and 2 involves both processes even though only the initial rate was measured. To check the reliability of the trend, the rate of hydrolysis of the sparteine·$CuBr_2$ complex was measured in the presence of mercuric ion, which complexes strongly with bromide (mercuric bromide formation constants: $K_1 = 1.1 \times 10^9$, $K_2 = 1.9 \times 10^8$, $K_3 = 260$, $K_4 = 18$).[21] Hg^{2+} thus rapidly removes the bromide released into solution by hydrolysis of the complex. The extrapolated k value at zero bromide concentration falls in line with the k value measured in this manner. This mild Lewis acid does not extract the bromide ion or increase the hydrolysis rate as might be expected if the rate-determining step involved loss of halide.

A mechanism consistent with the observed slowness of the hydrolysis, the halide ion catalysis, and the effect of ionic strength is shown by eq 3 and 4 for the chloro system. The

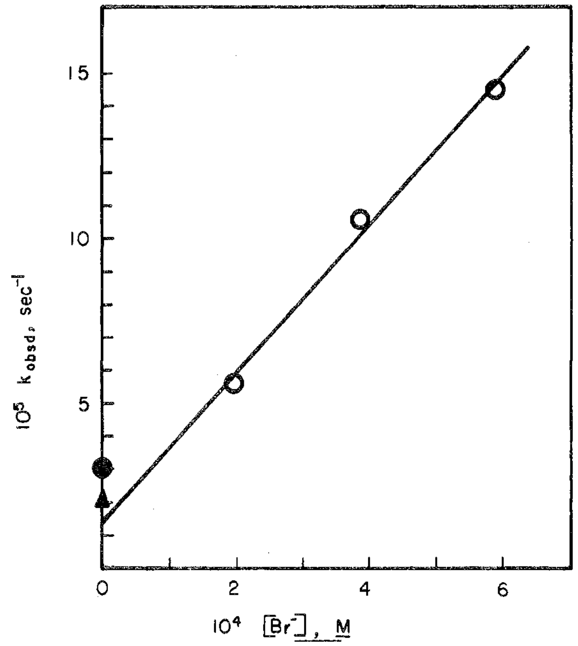


Figure 1. Plot of k_{obsd} vs. $[Br^-]$ added. k_{obsd} for the case with no added Br^- is shown by ● and k_{obsd} for the case with mercuric ion added is shown by ▲. Experimental conditions are [sparteine·$CuBr_2$] = 1.64×10^{-4} M, pH 5.7, ionic strength 0.17, and temperature 25.0 ± 0.2 °C.

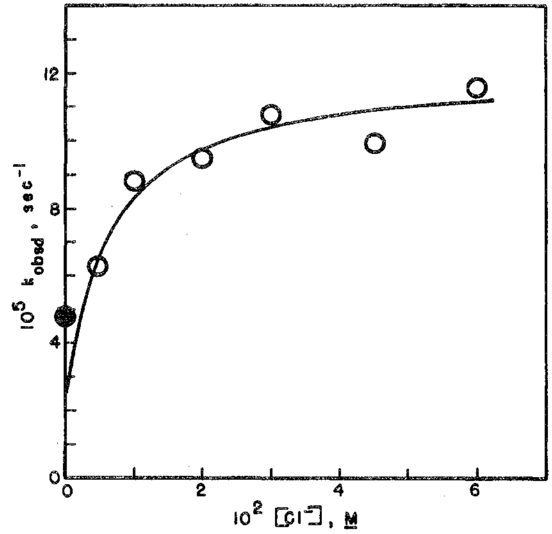
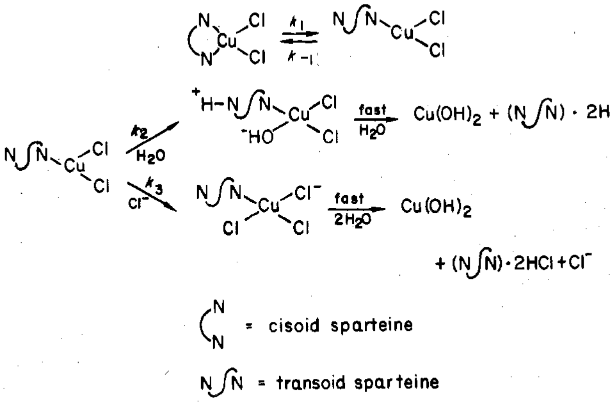


Figure 2. Plot of k_{obsd} vs. $[Cl^-]$ added. k_{obsd} for the case with no added Cl^- is shown by ●. Experimental conditions are [sparteine·$CuCl_2$] = 2.00×10^{-3} M, pH 5.7, ionic strength 0.17, and temperature 25.0 ± 0.2 °C.



(3)

(4)

last steps labeled "fast" are probably a sequence of rapid steps to the product precipitate and sparteine–hydrogen halide. The rate-determining steps, however, are the conformational inversion of the sparteine from the cisoid form required for coordination to the transoid form (the preferred form of the free base[22]) and direct water addition and chloride addition processes. A similar transoid–cisoid inversion has been used to explain the slow rate for the coordination exchange of sparteine with dineopentylmagnesium.[7] The slow rate and a mechanism that involves breaking a N–Cu bond rather than a Cl–Cu bond in the initial step is probably due to solvent effects.[23] The large organic ligand in the compact tetrahedral complex tends to break up the solvent shell of the complex, so that in order to go to a transition state involving a separation of charge a much greater demand is placed on solvation.

For the mechanism, eq 3 and 4, k_{obsd} is given by

$$k_{\text{obsd}} = \frac{k_1 k_2 + k_1 k_3 [\text{Cl}^-]}{k_{-1} + k_2 + k_3 [\text{Cl}^-]} \tag{5}$$

By a least-squares computer fit of eq 5 to the observed values, the curve in Figure 2 was determined. From the fit we obtain $k_1 = 1.21 \times 10^{-4}\ \text{s}^{-1}$, $k_2/k_3 = 1.11 \times 10^{-3}$ M, and $k_{-1}/k_3 = 4.97 \times 10^{-3}$ M. We do not have data to find k_{-1}, k_2, and k_3 separately but only their ratios.

We believe the bromo system follows the same mechanism as the chloro system (eq 3 and 4); however, the catalytic rate process for the bromo complex increases much more rapidly with bromide ion concentration than the chloro complex with chloride concentration. Thus, expanding k_{obsd} for small bromide ion concentration gives

$$k_{\text{obsd}} = \frac{k_1 k_2}{k_{-1} + k_2} + \frac{k_1 k_{-1} k_3}{(k_{-1} + k_2)^2} [\text{Br}^-] \tag{6}$$

A linear least-squares fit of eq 6 to the experimental data yields $k_1 k_2/(k_{-1} + k_2) = 1.34 \times 10^{-5}\ \text{s}^{-1}$ and $k_1 k_{-1} k_3/(k_{-1} + k_2)^2 = 0.229\ \text{s}^{-1}\ \text{M}^{-1}$.

The fact that the bromide ion plays a much greater role than the chloride ion for the catalytic route is surprising from a steric point of view. The bulky, more polarizable bromide ion is involved in a nucleophilic attack on the copper complex now made possible by the loosening of the structure with the inversion to the transoid sparteine form. In fact, rather than simple addition of bromide ion at this stage as shown in eq 4, the sparteine may be simultaneously eliminated in a concerted reaction. The fact that Br^- attacks Cu^{2+} more readily than Cl^- is supported by the ratio of the formation constants[21] of $CuBr^+$ to $CuCl^-$: 1.6. Bromide ion is in general a better nucleophile than chloride ion and both are better than water.

Table I. Thermodynamic Parameters for the Hydrolysis of Sparteine·CuX_2

	Sparteine·$CuCl_2$	Sparteine·$CuBr_2$
$\Delta H^{\ddagger}$, kcal/mol	16.0 ± 1.9	23.1 ± 2.9
$\Delta S^{\ddagger}$, eu	−24.4 ± 6.2	−1.5 ± 9.0
$\Delta G^{\ddagger}_{298}$, kcal/mol	23.3 ± 2.7	23.5 ± 4.0

In order to determine the values for the activation parameters, a series of studies was carried out from 25 to 55 °C with no halide ion added. Plots of log k_{obsd} vs. $1/T$ are linear over this temperature range and a least-squares computer fit of the data yields the thermodynamic activation parameters for the two complexes given in Table I. $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the empirical activation parameters referring to the temperature dependence of k_{obsd} with no halide ion added to the system. The large enthalpy of activation observed here is consistent with the conformational inversion process. The difference in the activation energy between the two complexes is primarily due to the difference in the role k_3 plays in k_{obsd}. For the bromo complex k_3 is much greater and thus contributes to the temperature dependence of k_{obsd} more than for the chloro complex.

Registry No. Sparteine·$CuCl_2$, 39733-84-1; sparteine·$CuBr_2$, 62882-83-1; Br^-, 24959-67-9; Cl^-, 16887-00-6.

References and Notes

(1) (a) Presented, in part, before the First Chemical Congress of the North American Continent, Mexico City, Dec 1975; see Abstracts, INOR No. 76. (b) This is part III in a series; for part I see ref 15 and for part II see ref 11. (c) Work supported, in part, by grants from Eli Lilly and Co., Indianapolis, Ind., and the Indiana University Foundation. (d) NSF Undergraduate Research Participant, summer, 1975.

(2) J. M. H. Pinkerton and L. K. Steinrauf, *J. Org. Chem.*, **32**, 1828 (1967).

(3) J. D. Morrison and H. S. Mosher, "Asymmetric Organic Reactions", Prentice-Hall, Englewood Cliffs, N.J., 1971, pp 393, 415, 432.

(4) T. Aratani, T. Gonda, and N. Nozaki, *Tetrahedron*, **26**, 545 (1970); H. Nozaki, T. Aratani, T. Toraya, and R. Noyori, *ibid.*, **27**, 905 (1971).

(5) S. F. Mason and R. D. Peacock, *J. Chem. Soc., Dalton Trans.*, 226 (1973).

(6) G. Fraenkel, C. Cottrell, J. Ray, and J. Russell, *Chem. Commun.*, 273 (1971).

(7) G. Fraenkel, B. Appleman, and J. G. Ray, *J. Am. Chem. Soc.*, **96**, 5113 (1974).

(8) L. S. Childers, K. Folting, L. L. Merritt, Jr., and W. E. Streib, *Acta Crystallogr., Sect. B*, **31**, 924 (1975).

(9) S. Choi, R. D. Bereman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).

(10) D. H. Busch, private communication.

(11) E. Boschmann, G. A. Nypaver, J. P. Majors, S. M. Ealy, and M. Van Horn, *J. Coord. Chem.*, in press.

(12) E. L. McCawley in "The Alkaloids, Chemistry and Physiology", Vol. V, V. R. H. F. Manske, Ed., Academic Press, New York, N.Y., 1955, p 93; M. J. Dallemagne and C. Heymans, *ibid.*, p 123; A. K. Reynolds, *ibid.*, p 179; K. De Voe, *Am. J. Obstet. Gynecol.*, **105**, 304 (1969).

(13) (a) B. Katz, "Nerve, Muscle and Synapse", McGraw-Hill, New York, N.Y., 1966, pp 133, 164; S. Ebashi, M. Endo, and I. Ohtsuki, *Q. Rev. Biophys.*, **2**, 351 (1969); (b) A. Muhlrad, M. Kovacs, and G. Megyi, *Biochim. Biophys. Acta*, **107**, 507 (1965).

(14) F. Mercier and P. Caramaounas, *C. R. Seances Soc. Biol. Ses. Fil.*, **115**, 1641 (1934).

(15) E. Boschmann, L. M. Weinstock, and M. Carmack, *Inorg. Chem.*, **13**, 1297 (1974).

(16) Purchased in part by funds from NSF Instructional Scientific Equipment Grant GY 10123.

(17) K. J. Laidler, "Chemical Kinetics", 2nd ed., McGraw-Hill, New York, N.Y., 1965, p 88.

(18) The units of the rate constant *k* in Table I of ref 15 should read min^{-1} and not sec^{-1}.

(19) See for instance R. G. Pearson and O. A. Gansow, *Inorg. Chem.*, **7**, 1373 (1968), and references therein.

(20) L. G. Sillén, *Chem. Soc., Spec. Publ.*, No. **25**, Suppl. 1, 26, 67 (1971).

(21) L. Meites, Ed., "Handbook of Analytical Chemistry", McGraw-Hill, New York, N.Y., 1963, pp 1-39.

(22) F. Bohlmann, D. Schumann, and C. Arndt, *Tetrahedron Lett.*, 2705 (1965); M. Wiewiórowski and T. Skolik, *Bull. Acad. Pol. Sci., Ser. Sci. Chim.*, **11** (2), 69 (1963); M. Wiewiórowski, O. E. Edwards, and M. D. Bratek-Wiewiórowski, *Can. J. Chem.*, **45**, 1447 (1967).

(23) T.-L. Ni and C. S. Gardner, *Inorg. Chem.*, **6**, 1071 (1967), and references therein.