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High Affinity of a Macrobicyclic Cu(II) Complex to Halide Ions and Application of the Complex in Kinetics of the Menschutkin Reaction

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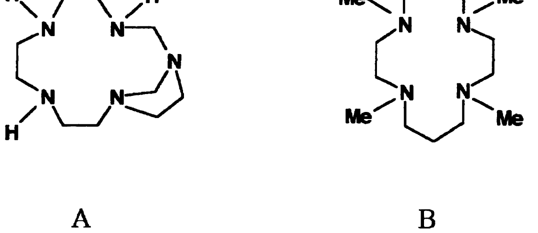
Synopsis. The equilibrium constants (K) for the reaction $[Cu(A)]^{2+}+X^- \rightleftharpoons [Cu(A)X]^+$ (A=1,3,6,9,12-pentaazabicyclo[10.2.1] pentadecane; $X^-=Br^-$ or Cl^-) in acetonitrile, DMF, and DMSO have been determined at 25°C. The large K values ($>8.8\times10^4$) and other results show that the copper(II) complex can be used as a probe for kinetic study of the Menschutkin reaction even in the basic solvents.

Although the kinetics of the reaction between alkyl halides and amines, as the Menschutkin reaction, have usually been studied by conductometry,[1—4] it is somewhat difficult to determine the concentration of the leaving halide ion from the conductance of the salt generated in the reaction. A recent report[5] showed that the Menschutkin reaction in nitrobenzene, a noncoordinating solvent, can be easily monitored by the spectral change of the square planar nickel(II) complex $[Ni(B)]^{2+}$ (B=1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane), which reacts with halide ions (X^-) to form $[Ni(B)X]^+$ in the solution, without relying on conductometry (Chart 1). However, the spectrophotometric method using the nickel(II) complex can not be utilized when the reaction takes place in coordinating solvents such as acetonitrile (AN), *N,N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and water.[5] This can be attributed to the fact that, in these solutions, the solvent molecule is readily coordinated to the nickel(II) complex and is rarely substituted by the halide ion.[5,6]

Previously, we reported the synthesis of the pentaazabicycloalkane copper(II) complexes $[Cu(A)]^{2+}$ and $[Cu(A)Cl]^+$.[7] It has been observed that the chloride ion of $[Cu(A)Cl]^+$ is rarely removed from the coordination sphere in AN. In this work, the equilibrium constants of the adducts of $[Cu(A)]^{2+}$ with the halide ions Br^- and Cl^- in AN, DMF, and DMSO have been determined to see that the copper(II) complex can be used as a probe for the kinetic study of the Menschutkin reaction in the basic solvents.



A B

Chart 1.

Experimental

Materials and Instruments. $[Cu(A)](ClO_4)_2$ and $[Cu(A)Cl]ClO_4$ were prepared by the published method.[7] The other reagents were commercially obtained.

Electronic spectra were recorded with a Kontron Uvikon 860 UV-vis spectrophotometer. Conductance measurements were performed by using a Metrohm Herisau Conductometer E518. Infrared spectra were obtained on a Shimadzu IR-440 spectrophotometer. Elemental analyses were performed by Kolon R & D Center, Kumi, Korea.

Equilibrium Constants Determinations. The spectrophotometric measurements and calculations of the equilibrium constants for Eq. 1 were carried out by the methods described previously.[8,9] The halide ion salts used for the equilibrium study were LiBr and LiCl.

Kinetic Measurements. The spectrophotometric measurements of the reaction (Eq. 2) by using $[Cu(A)](ClO_4)_2$ as a probe were performed near 560 and/or 650 nm, which corresponding to the maximum absorptions of $[Cu(A)]^{2+}$ and $[Cu(A)X]^+$, respectively. The concentrations of *p*-nitrobenzyl bromide (PNB), pyridine (Py), and the copper(II) complex were 1.0×10^{-3}, 4.0×10^{-2}—1.0×10^{-1}, and 1.2×10^{-3} M, respectively (1 M=1 mol dm^{-3}). Plots of $\ln(A_t-A_\infty)$ or $\ln(A_\infty-A_t)$ vs. time had good linearity. The A_∞ values for the absorbance were measured after more than 10 half-lives. The kinetic measurements and calculations of the second-order rate constants for the reaction by conductometry were carried out as described in previous reports.[1—4] The reaction temperature was maintained at 25±0.1°C.

Synthesis of $[Cu(A)Br]ClO_4$. Excess NaBr was added to a hot aqueous solution saturated with $[Cu(A)](ClO_4)_2$. On cooling the blue solid was precipitated. The solid was filtered off, washed with methanol, and air-dried. Yield: ca. 90%. Anal. Calcd for $CuC_{10}H_{23}N_5BrClO_4$: C, 26.3; H, 5.08; N, 15.3%. Found: C, 26.7; H, 5.11; N, 15.2%. IR $\nu_{N-H}=3255$ cm^{-1}.

Results and Discussion

The visible spectra (Table 1) show that the maximum absorptions for the five-coordinated complex $[Cu(A)X]^+$ (X=Br or Cl) dissolved in AN, DMF, and DMSO appear at ca. 90 nm longer wavelength than those of $[Cu(A)]^{2+}$. The conductance data of $[Cu(A)(X)]^+$ in the nonaqueous solutions indicate that the complexes are 1 : 1 electrolytes. In aqueous solutions, the spectra and molar conductance data of the five-coordinated complexes are quite similar to those for $[Cu(A)]^{2+}$. These

Table 1. Electronic Spectra and Molar Conductance Data of the Cu(II) Complexes$^{a)}$

Complex	$\lambda_{\max}$/nm(ϵ/M^{-1}cm^{-1})		Λ_M/ohm^{-1} mol^{-1} cm^2	
[Cu(A)](ClO$_4$)$_2$	560(285)	566(241)$^{b)}$	270	141$^{b)}$
	576(254)$^{c)}$	565(261)$^{d)}$	70$^{c)}$	234$^{d)}$
[Cu(A)Br]ClO$_4$	644(268)	645(280)$^{b)}$	138	68$^{b)}$
	629(274)$^{c)}$	564(253)$^{d)}$	42$^{c)}$	205$^{d)}$
[Cu(A)Cl]ClO$_4$	659(288)	659(304)$^{b)}$	153	74$^{b)}$
	648(303)$^{c)}$	563(261)$^{d)}$	38$^{c)}$	215$^{d)}$

a) In AN solutions at 25°C unless otherwise specified. b) In DMF solutions. c) In DMSO solutions. d) In aqueous solutions.

spectral data strongly indicate that the halide ion of the $[\mathrm{Cu(A)X}]^+$ is easily removed from the coordination sphere in water but is rarely removed in AN, DMF, and DMSO.

In the visible spectra (Fig. 1) of the mixture of $[\mathrm{Cu(A)}]^{2+}$ and Br^- in AN, it is seen that the increase of the concentration of the halide ion causes the absorption increase near 650 nm with an isosbestic point near 600 nm. The similar spectra have also been observed in DMF and DMSO solutions of the mixtures and in the solutions of mixtures of the copper(II) complex and Cl^-. The equilibrium constants (K) for the reaction (Eq. 1) in the solutions have been determined at 25°C by published methods[8,9] and are listed in Table 2.

$$[\mathrm{Cu(A)}]^{2+} + \mathrm{X}^- \overset{K}{\rightleftharpoons} [\mathrm{Cu(A)X}]^+ \qquad (1)$$

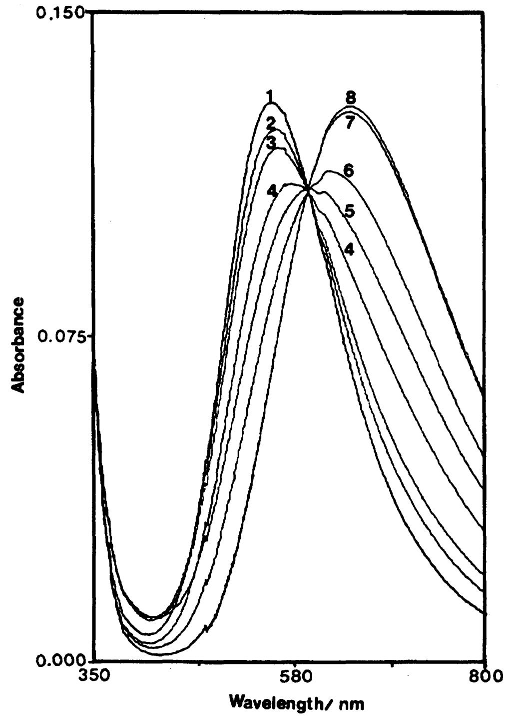


Fig. 1. Visible spectra of mixtures of $[\mathrm{Cu(A)}]^{2+}$(4.4×10^{-4} M) and LiBr in AN solutions. [LiBr]=0(1), 4.6×10^{-5}(2), 7.7×10^{-5}(3), 1.5×10^{-4}(4), 2.3×10^{-4}(5), 3.1×10^{-4}(6), 4.6×10^{-4}(7), or 6.1×10^{-4} M(8).

Table 2. Equilibrium Constants for the System $[\mathrm{Cu(A)}]^{2+} + \mathrm{X}^- \rightleftharpoons [\mathrm{Cu(A)X}]^+$ in Various Solutions at 25°C

Salt	Solvent			
	AN$^{a)}$	DMF$^{a)}$	DMSO$^{a)}$	H$_2$O$^{b)}$
LiBr	1.5×10^5	1.0×10^5	3.3×10^5	21.3
LiCl	1.3×10^5	8.8×10^4	1.5×10^5	11.1

a) [Complex]=4.4×10^{-4} M; [LiX]=4.8×10^{-5}—6.8×10^{-4} M. b) [Complex]=4.4×10^{-4} M; [LiX]=1.0×10^{-2}—2.0×10^{-1} M.

It is interesting to see that the K values in the solvents except water are 8.8×10^4—3.3×10^5, which are larger than those (ca. 10^4) for the $[\mathrm{Ni(B)}]^{2+}$–X^- system in nitrobenzene.[5] Much larger values of K in the nonaqueous solvents, compared to those in water, may be resulted from the lower dielectric constants of the solvents and the lower solvation of the halide ions.[8] The larger K values for Br^- than those for Cl^- correspond to the reported results that the axial coordinating ability of monodentate anion to square planar copper(II) complexes of macrocyclic ligands largely depends on the basicity and the softness of the anion.[10,11] The rate of the coodination of the halide ion to the square planar copper(II) complex was too fast to be measured by ordinary methods. The addition of various amines such as Py, triethylamine, and trimethylamine or various organic halides such as PNB, 1,2-dichloroethane, and benzyl chloride to the nonaqueous solutions of $[\mathrm{Cu(A)}]^{2+}$ caused no apparent spectral change indicating uncoordination of the species at the axial position of the complex. These results strongly indicate that $[\mathrm{Cu(A)}]^{2+}$ can be utilized as a probe in the spectrophotometric titration of the halide ions even in the coodinating solvents except water.

$$p-\mathrm{O_2N\text{-}C_6H_4CH_2Br} + \mathrm{NC_5H_5} \rightarrow$$
$$p-\mathrm{O_2N\text{-}C_6H_4CH_2N^+C_5H_5Br^-} \qquad (2)$$

The reaction (Eq. 2) between PNB and Py in AN, DMF, and DMSO solutions was examined spectrophotometrically by using the copper(II) complex. The time-dependent spectra of the mixtures of PNB (1.0×10^{-3} M), Py (0.04—0.1 M), and $[\mathrm{Cu(A)}]^{2+}$ (1.2×10^{-3} M) in the solutions also showed the absorp-

Table 3. Second Order Rate Constants for the Reaction (Eq. 2) in Various Solutions at 25°C

Solvent	$k^{a)}/\mathrm{M^{-1}\ s^{-1}}$	$k'^{a)}/\mathrm{M^{-1}\ s^{-1}}$	k/k'
AN	7.1×10^{-5}(1)	5.3×10^{-5}(1)	1.3
DMF	1.4×10^{-4}(2)	1.1×10^{-4}(2)	1.3
DMSO	4.5×10^{-4}(6.3)	3.6×10^{-4}(6.8)	1.3

a) Relative values in parenthesis.

tion increase near 650 nm due to $[\mathrm{Cu(A)Br}]^+$ and the decrease at 560 nm with an isosbestic point, likewise the spectra of the mixture of $[\mathrm{Cu(A)}]^{2+}$ and Br^-. The reaction rates were measured by the time-dependent spectra. The second-order rate constants (k) obtained at 25°C by this method are listed in Table 3, along with those (k') measured by conductometry in the absence of the copper(II) complex. It is seen that the k value inceases with the solvent in the order AN (1)<DMF(2)<DMSO(6.3), which is quite similar to that for k'. The comparision of these data also shows that the k value in each solvent is ca. 1.3 times larger than the k' value. The similar trend was also observed when $[\mathrm{Ni(B)}]^{2+}$ was used as a probe for the reaction of bromoethane or 1,2-dichloroethane with Py in nitrobenzene.[5] It has not been clearly understood that the larger values of k, compared to k', are arised from whether the different kinetic method or the "special salt effect".[12] However, this work shows that the Menschutkin reaction even in the basic solvents such as AN, DMF, and DMSO can be readily monitored by the spectral change of the square planar complex $[\mathrm{Cu(A)}]^{2+}$, which has high affinity to the halide ions in the solutions.[13] Furthermore, the copper(II) complex can be easily prepared by the simple one-pot metal template condensation reaction.[7]

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13) Since the reaction between benzyl chloride and Py is very slow, quantitative measurements for the reaction were not attempted. However, the large K values for the $[\mathrm{Cu(A)}]^{2+}$–Cl^- system and qualitative measurements showed that the reaction in the nonaqueous solutions can also be monitored by the spectral change of the Cu(II) complex.