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Kinetics of Inner-Sphere Solvent Exchange on the Aquocopper(II) Ion: Indirect Determination from Kinetics of Copper(II) Reacting with Ammonia in Aqueous Solution

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For an estimation of the kinetic parameters for inner-sphere solvent exchange on $Cu(H_2O)_6^{2+}$, the kinetics of this metal ion reacting with NH_3 to form the monoammine complex $Cu(NH_3)(H_2O)_5^{2+}$ have been measured in aqueous solution at 5, 15, and 25 °C by using the temperature-jump relaxation method. The kinetic parameters determined for the formation and dissociation reactions are respectively as follows: $k(25\ °C) = 2.3 \times 10^8\ M^{-1}\ s^{-1}$, $2.0 \times 10^4\ s^{-1}$; ΔH^* (kcal mol^{-1}) = 4.5, 9.5; ΔS^* (eu) = −5, −7. On the basis of the data for the formation reaction and evidence supporting the hypothesis that this reaction proceeds by a dissociative mechanism, the kinetic parameters for inner-sphere solvent exchange on the aquocopper(II) ion are calculated to be $k_{ex} = 2.0 \times 10^9\ s^{-1}$ at 25 °C, $\Delta H^*_{ex} = 4.5$ kcal mol^{-1}, and $\Delta S^* = -1$ eu.

Introduction

For divalent aquometal ions, the exchange of inner-sphere solvent molecules with the surrounding bulk solvent

$$M(H_2O)_n + H_2O^* \xrightleftharpoons{nk_{ex}} M(H_2O^*)(H_2O)_{n-1} + H_2O \qquad (1)$$

represents a fundamental process whose kinetic characteristics have been shown to govern directly both the rates of complex formation reactions[1] and the rates of inner-sphere electron-exchange processes.[2] Because of their importance in interpreting kinetic behavior, intensive efforts have been made to determine the k_{ex} values (where k_{ex} is the exchange rate constant *per coordination site*) for nearly all stable aquometal ion species.[1,3,4]

Despite repeated efforts, however, the k_{ex} value for $Cu(H_2O)_6^{2+}$ has remained in doubt. As shown in Table I, at least eight attempts have been made to determine this value directly by means of either NMR or sound absorption techniques.[5-12] The most frequently cited values (represented by entries 4–7) cover a 40-fold range. We believe that *all of these values are incorrect*, suffering from either experimental or interpretive errors (see footnotes to Table I).

The errors associated with the reported k_{ex} values for $Cu(H_2O)_6^{2+}$ are largely attributable to the inner-sphere Jahn–Teller distortion which is inherent in this d^9 species.

The axial elongation along one orthogonal axis yields two Cu–H_2O bonds which are extraordinarily labile. Moreover, this distortion is dynamic with the rapid inversion of the elongated axis occurring on a time scale ($\simeq 10^{-11}$ s)[13] much shorter than the time scale for solvent exchange itself. As a result, all six Cu–H_2O bonds appear to be labilized such that only a single k_{ex} value is to be anticipated.[12]

Table I. Experimental Values Reported for the Inner-Sphere Solvent-Exchange Rate Constant for Aquocopper(II) Ion at 25 °C

no.	k_{ex}, s^{-1}	method	year	ref	remarks
1	$\geq 6 \times 10^5$	^{17}O NMR	1959	5	detection limit[a]
2	$\geq 3.3 \times 10^6$	^{17}O NMR	1961	6	detection limit[a]
3	$>5 \times 10^7$	sound abs	1962	7	detection limit[a]
4	2×10^8	^{17}O NMR	1962	8	experimental error[b]
5	8.3×10^9	^{17}O NMR	1965	9	assumed slow inversion[c]
6	2×10^8	sound abs	1968	10	diffusion controlled[d]
7	2×10^8	sound abs	1968	11	diffusion controlled[d]
8	$\sim 5 \times 10^9$	ESR, NMR	1972	12	estimated value[e]

[a] Value reported represents upper detection limit of experimental approach used. [b] Value reported is presumably in error due to experimental difficulties (cf. ref 8b and 9). [c] Value reported erroneously assumed slow Jahn-Teller inversion (see text). [d] Based on use of SO_4^{2-} as substituting ligand; value is presumably in error due to diffusion-limiting kinetics. [e] Estimated value claimed to be within an order of magnitude of actual value.

The most exhaustive study conducted to date on $Cu(H_2O)_6^{2+}$ water exchange is that of Merideth and Connick,[9] who measured the NMR transverse relaxation times of ^{17}O-enriched water over the extended temperature range of −59.6 to +150 °C. The 25 °C k_{ex} value which they reported from their high-temperature studies (entry 5 in Table I) results, in fact, from their assumption that Jahn–Teller inversion was slow relative to axial solvent exchange. When rapid inversion (a model which they considered and rejected) is taken into account, their high-temperature data yield $k_{ex} = 2.8 \times 10^9\ s^{-1}$ at 25 °C.[9b] This corrected value must be considered susceptible to error, however, since the relaxation times exhibited curvature at higher temperatures, the source of which could not be identified.

In determining the activation parameters for water exchange on $Cu(H_2O)_6^{2+}$, Merideth and Connick were forced to rely solely on their low-temperature (<0 °C) measurements which are carried out in semiaqueous solutions (5.27 M $HClO_4$). Unfortunately, these conditions yielded a 25 °C k_{ex} value which was less than one-fifth that obtained from the high-temperature data.[9b] It was suggested that this discrepancy might be due to complexation of Cu(II) by perchlorate. If such were the case, however, the calculated activation values would not be representative of $Cu(H_2O)_6^{2+}$.

Merideth and Connick's work has never been formally published, and no other reliable activation parameters for water exchange on $Cu(H_2O)_6^{2+}$ have appeared in the literature. Thus, these values are generally considered to be unknown.

In our laboratory, the absence of reliable solvent-exchange activation parameters has proved to be a severe handicap in attempting mechanistic interpretations on a number of Cu(II)

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reactions currently under study. To rectify this, we have launched a concerted effort to determine such values. In view of the difficulties encountered in evaluating k_{ex} for aquocopper(II) from direct solvent-exchange measurements,[12] we have chosen to study simple ligand–solvent substitution, taking advantage of the two-step mechanism postulated by Eigen for such reactions,[4,7] viz., eq 2. The application of the steady-state

$$\mathrm{M(H_2O)_6{}^{2+} + L} \underset{k_{-o}}{\overset{k_o}{\rightleftharpoons}} \underset{\substack{\text{outer-sphere} \\ \text{complex} \\ \text{(contact pair)}}}{\mathrm{M(H_2O)_6{}^{2+}, L}} \xrightarrow{k_1} \mathrm{ML(H_2O)_5{}^{2+} + H_2O} \quad (2)$$

approximation to the outer-sphere complex yields the relationship

$$k_f = k_o k_1/(k_{-o} + k_1) \quad (3)$$

where k_f is the observed overall formation rate constant. Under conditions where $k_{-o} \ll k_1$, such reactions become diffusion controlled (i.e., $k_f = k_o$). On the other hand, if $k_{-o} \gg k_1$, then

$$k_f = k_o k_1/k_{-o} = K_o k_1 \quad (4)$$

where K_o is the equilibrium constant for outer-sphere complex formation from the solvent-separated reactants.

For hexaaquo, divalent metal ions, such substitution reactions appear to be largely dissociative such that $k_1 \simeq k_{ex}$ *in the absence of steric effects*. Thus, if eq 4 prevails, k_{ex} values may be approximated from ligand-substitution kinetics with the level of uncertainty in the value thus generated being directly dependent on the accuracy with which K_o may be calculated.

In earlier work[14] we have argued that NH_3 represents an ideal nucleophile for such studies, being virtually free of electrostatic and steric interactions when reacting with hexaaquo metal ions. In temperature-jump relaxation studies involving ammonia substitution on $Co(H_2O)_6{}^{2+}$, $Ni(H_2O)_6{}^{2+}$, and $Zn(H_2O)_6{}^{2+}$,[14] the calculated values for k_{ex} obtained via eq 4 and the associated activation parameters were shown to be within experimental error of the values determined by other workers for direct outer-sphere to inner-sphere exchange by either sound absorption[7] or NMR[8] techniques. However, at that time no relaxation measurements could be obtained for the corresponding reaction with $Cu(H_2O)_6{}^{2+}$.

Subsequently, Diebler and Rosen[15] have demonstrated that experimental data for the Cu(II)–NH_3 reaction can be obtained from temperature-jump relaxation studies conducted at much lower pH. Their reported k_f value is consistent with a 25 °C k_{ex} value of 2×10^9 s^{-1}. As we have noted in an independent study,[16] this k_{ex} value appears to be consistent with the majority of substitution reactions involving $Cu(H_2O)_6{}^{2+}$ and is consistent with Merideth and Connick's high-temperature data when interpreted in terms of the rapid inversion model.

In the current work, we have made a concerted effort to extend the study of Diebler and Rosen to cover the temperature range of 5–25 °C in order to generate viable activation parameters. This temperature range was limited by the fact that the relaxation times were too short to be measured at higher temperatures, and lower temperatures would have required a significant increase in salt concentration. The latter appeared to be particularly undesirable in view of the differing data obtained by Merideth and Connick in high perchlorate concentrations. Moreover, independent studies in this laboratory on other Cu(II) reactions have revealed dramatic variations in substitution rate constants as a function of perchlorate concentration.[17] Thus, every effort was made to operate at low ionic concentrations even though larger relaxation amplitudes could have been obtained in more concentrated ionic media.

Table II. Equilibrium Constant Values Utilized in this Work for $\mu = 0.10$ M

T, °C	$\log K_H{}^{m\,a}$	$\log K_{In}{}^{m\,b}$	$\log K_{ML}{}^{c}$
5	9.89	4.90	4.32
15	9.56	4.78	4.19
22	9.35		4.10
25	9.26	4.67	4.06

[a] $K_H{}^m = [NH_4{}^+]/a_H[NH_3]$; values listed were calculated from the corresponding concentration constants reported by Bates and Pinching (Bates, R. G.; Pinching, G. D. *J. Res. Natl. Bur. Stand.* **1949**, *42*, 419) as corrected to 0.10 M ionic strength by using the correction factor established by Bjerrum (Bjerrum, J. "Metal Ammine Formation in Aqueous Solution"; P. Haase and Son: Copenhagen, 1957). [b] $K_{In}{}^m = [HIn]/a_H[In^-]$; values listed are for bromocresol green indicator and were determined spectrophotometrically. [c] $K_{ML} = [CuNH_3{}^{2+}]/[Cu^{2+}][NH_3]$; values listed were calculated from the experimental values of Bjerrum (cited in footnote *a*) with the use of his corrections for ionic strength and temperature.

Experimental Section

Reagents. $Cu(ClO_4)_2$ was prepared by adding reagent grade, concentrated (73.6%) $HClO_4$ (G. F. Smith Chemical Co.) dropwise to a stirred aqueous slurry of reagent grade $CuCO_3$ (Fisher Scientific Co.). The evolved CO_2 and excess water were removed by gentle boiling, and $Cu(ClO_4)_2 \cdot 6H_2O$ was then recrystallized twice from hot water. Reagent grade NH_4ClO_4 (G. F. Smith Chemical Co.) appeared to be free of interfering contaminants and was used without further purification. Reagent grade bromocresol green indicator (J. T. Baker Chemical Co.) was also used without further purification.

Stock Solutions. All solutions were prepared by using distilled, deionized water. Stock solutions of $Cu(ClO_4)_2$ were standardized by titration with EDTA. Stock solutions of NH_4ClO_4, which were used to control the ionic strength as well as to provide the source of NH_3, were prepared by weight and were not otherwise standardized since NH_3 was largely protonated under the experimental conditions used and small errors in $[NH_3]$ had no effect upon the kinetic data. Final pH adjustments were made at 22 °C with concentrated NaOH and $HClO_4$ solutions by using an Orion Model 801-A pH meter equipped with a gel-filled calomel electrode as a reference electrode to prevent precipitation of $KClO_4$ at the junction. The hydrogen ion activity attained following the temperature jump was approximated in each case from the relationship[14]

$$a_H' = \left(\frac{K_H{}^m K_{ML}'}{K_H{}^{m\prime} K_{ML}}\right) a_H \quad (5)$$

In eq 5, a_H represents the measured hydrogen ion activity at 22 °C and K_{ML} and $K_H{}^m$ are the 22 °C values of the $Cu(NH_3)^{2+}$ stability constant and the mixed-mode protonation constant for ammonia, respectively, while the primed symbols represent the corresponding values at the experimental temperature achieved following the temperature jump. All values utilized are listed in Table II.

Kinetic Measurements. Relaxation measurements were made with a Joule-heating temperature-jump relaxation spectrometer which has been previously described.[18] The temperature rise time for this instrument is about 3 μs, and the attendant noise limited measurements to relaxation times of 10 μs or longer. The final temperature achieved was calibrated to within ±0.2 °C by correlating spectrophotometric transmission data to thermistor resistance in a series of static measurements. Bromocresol green was used as a coupled indicator to monitor the reaction kinetics. This indicator provided optimal signals within the region of pH 4.5 and, as a sulfonphthalein having substituents at all positions ortho to the phenolic oxygens, did not exhibit

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Table III. Kinetic Relaxation Data for the Reaction of Aquocopper(II) Ion with Ammonia at $\mu = 0.10$ M (NH_4ClO_4)

C_M, mM[a]	A, mM[b]	$10^{-4}\tau^{-1}$, s^{-1}	C_M, mM[a]	A, mM[b]	$10^{-4}\tau^{-1}$, s^{-1}
		5 °C, pH 4.62			
4.22	0.0708	1.10	10.6	0.176	1.77
6.33	0.106	1.28	12.7	0.211	2.05
8.44	0.141	1.53			
		15 °C, pH 4.43			
4.22	0.0645	1.77	12.7	0.192	3.20
6.33	0.0964	2.29	14.8	0.224	3.38
8.44	0.128	2.62	16.9	0.256	3.84
10.6	0.160	2.88	21.1	0.319	5.00
		25 °C, pH 4.46			
2.08	0.0522	2.29	14.8	0.361	6.05
4.24	0.105	2.88	17.7	0.431	6.77
7.41	0.182	4.61	20.8	0.507	7.66
10.6	0.259	5.48			

[a] $C_M = [Cu(H_2O)_6^{2+}] + [Cu(NH_3)^{2+}]$. [b] See eq 6a.

observable interactions with Cu(II).[19] Test solutions containing either Cu(II) with indicator or NH_3 with indicator showed no relaxation effects at time ranges resolvable by the instrument, and solutions containing all three components showed a single relaxation curve with relaxation times which were independent of indicator concentration. The mixed-mode protonation constants for bromocresol green as determined spectrophotometrically are included in Table II.

Results

In accordance with the study of Diebler and Rosen[15] and earlier studies in this laboratory on the reaction of NH_3 with related transition-metal ions,[14,18] the single observable relaxation in solutions containing Cu(II), NH_3, and indicator was attributed to the reaction of $Cu(H_2O)_6^{2+}$ with NH_3 to form the monoammine complex, yielding the relaxation equation (6), where $[\overline{Cu}]$ and $[\overline{NH_3}]$ represent the equilibrium con-

$$1/\tau = k_f\left(\frac{[\overline{Cu}]}{1+\alpha} + [\overline{NH_3}]\right) + k_d \tag{6}$$

$$= k_f A + k_d \tag{6a}$$

centrations of uncomplexed reactants and the quantity $(1 + \alpha)$ is introduced to correct for the effect of the protonation side reactions (with NH_3 and the indicator) upon the change in $[NH_3]$ relative to the change in [Cu]. The α parameter can be calculated from relationship[14] 7, where $[\overline{H}]$ and $[\overline{In}]$

$$\frac{\partial[H]}{\partial[NH_3]} = \alpha = \frac{K_H[\overline{H}]\{K_{In}[\overline{In}] + K_{In}[\overline{H}] + 1\}}{K_H[\overline{NH_3}]\{K_{In}[\overline{H}] + 1\} + K_{In}[\overline{In}] + K_{In}[\overline{H}] + 1} \tag{7}$$

represent the equilibrium concentrations of hydrogen ion and deprotonated indicator, respectively, and K_H and K_{In} represent concentration constants ($K_H = \gamma_H K_H{}^m$; $K_{In} = \gamma_H K_{In}{}^m$; $\gamma_H = 0.80$ was used throughout).

The experimentally obtained relaxation times, each representing the median value of four or more replicate relaxation curves, are listed in Table III for all three experimental temperatures. Also listed are the values calculated for the quantity A as defined by eq 6 and 6a. The formation and dissociation rate constants at each temperature were then calculated from these data by means of eq 6a with linear least-squares regression analysis. The resultant plots are shown in Figure 1.

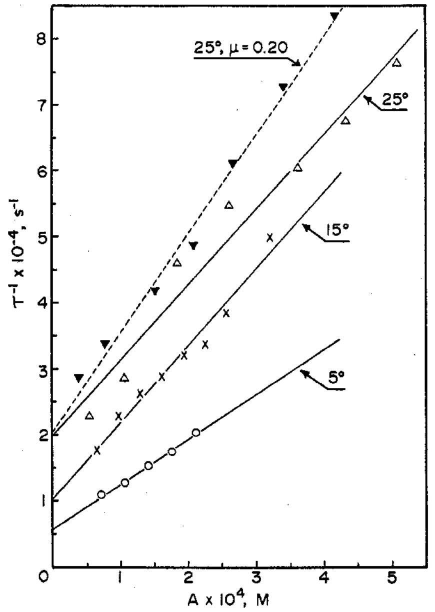

Figure 1. Resolution of the relaxation data for the aquocopper(II) ion reacting with ammonia in aqueous solution at $\mu = 0.10$ M. Plot of eq 6a: ○, 5 °C; ×, 15 °C; △, 25 °C. The solid triangles (dashed line) represent data from a corresponding study at 25 °C and $\mu = 0.20$ M: Jambor, L. G. Ph.D. Dissertation, Wayne State University, 1975. (Note the similarity in intercepts for the two 25 °C data sets yielding virtually identical k_d values.)

Table IV. Resolved Rate Constants and Activation Parameters for the Reaction of Aquocopper(II) Ion with Ammonia at $\mu = 0.10$ M

T, °C	$10^{-4}k_d$, s^{-1}	$10^{-8}k_f$(exptl), $M^{-1}\ s^{-1}$	$10^{-8}k_f$(calcd), $M^{-1}\ s^{-1}$ [a]
5	0.59 ± 0.04	0.67 ± 0.03	1.2_3
15	1.05 ± 0.15	1.11 ± 0.07	1.6_1
25	2.01 ± 0.30	1.08 ± 0.09	2.2_9
$\Delta H^\ddagger$, kcal mol^{-1}	9.5 ± 0.5		4.5 ± 0.4
$\Delta S^\ddagger$, eu	−7		−5

[a] See text.

At the relatively low pH values used in this study, the concentration of free unprotonated NH_3 is extremely small such that the quantity represented as A in eq 6a is essentially equal to $[\overline{Cu}]/(1 + \alpha)$. Furthermore, at these low pH values, $\alpha \gg 1$, yielding

$$A \simeq [\overline{Cu}]/\alpha \simeq C_{Cu}/\alpha \tag{8}$$

where C_{Cu} represents the total Cu(II) concentration in solution.

Of all the parameters dealt with in this study, the values calculated for α are most susceptible to error since the terms involving the indicator constant ($K_{In}[\overline{In}]$ and $K_{In}[\overline{H}]$ are dominant under the experimental conditions used and the values used for this constant are not highly accurate. From eq 8 it is apparent that any errors inherent in α will directly affect the calculated values of A. However, it should be noted that *all experimental solutions at a single temperature contained identical concentrations of hydrogen ion and indicator.* As a result, the value of α was constant for all experimental solutions at a single temperature such that *any error in α should affect the A values of all solutions proportionately.* Thus, whereas the slopes determined from the plots in Figure 1 may well be in error, the intercepts (yielding k_d values) should be virtually unaffected (i.e., as $[\overline{Cu}] \rightarrow 0$, $\tau^{-1} \rightarrow k_d$). These considerations lead us to conclude that the k_d values determined experimentally are well characterized whereas the k_f values are not.

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[19] Sulfonphththalein indicators having unsubstituted ortho positions (relative to the phenolic oxygens), such as thymol blue and phenol blue, have been observed to interact weakly with Co(II): Taylor, R. W. Ph.D. Dissertation, Wayne State University, 1973.

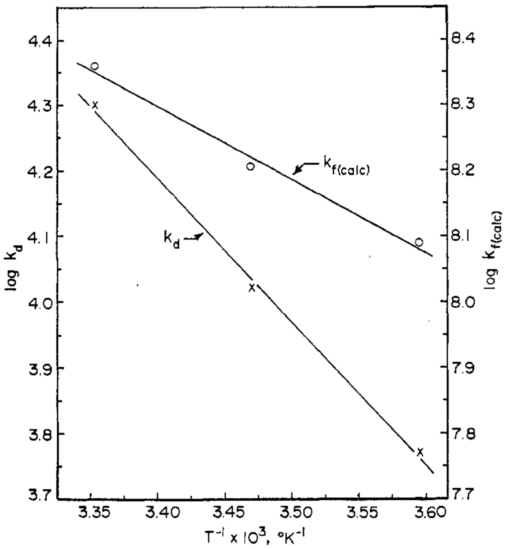

Figure 2. Arrhenius plots for k_d and k_f(calcd) based on rate constants determined in this study.

With increasing temperature, the experimental relaxation times increased markedly and could barely be resolved by the instrument. Thus, the data for 25 °C yield a much greater uncertainty for the k_d intercept. However, an independent 25 °C study of the Cu(II)–NH_3 reaction conducted in our laboratory at an earlier date[20] utilized a slightly higher ionic strength, which yielded larger relaxation amplitudes. As illustrated in Figure 1, the precision of these data (which also involved different pH, indicator, and reactant concentrations) was markedly improved, yielding a larger slope but a *virtually identical intercept*. Thus, the k_d value generated in this study for 25 °C is presumed to be reasonably accurate despite the relatively poor precision.

Due to the uncertainties in the experimentally determined k_f values as noted above, the resolved k_d values were used to derive calculated k_f values, with the use of the excellent stability constants determined by Bjerrum (Table II), according to the relationship

$$k_f(\text{calcd}) = k_d K_{ML} \qquad (9)$$

These calculated k_f values, along with the experimental k_f and k_d values, are listed in Table IV.

Both the k_f(calcd) and k_d values yield linear Arrhenius plots (Figure 2). The resultant values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for both rate constants are included in Table IV.

Discussion

For ammonia reacting with the aquated, divalent, first-row transition-metal ions, the center-to-center distance of closest approach in the outer-sphere complex, a, is relatively well established as 4 Å.[14–18] For a neutral ligand such as NH_3, the electrostatic contribution to the k_o and k_{-o} terms in reaction 1 are insignificant[21] so that these constants may be calculated according to the simplified expressions

$$k_o = 4\pi a D_{AB} N_A \times 10^{-3} \simeq 6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$$

$$k_{-o} = 3D_{AB}/a^2 \simeq 4 \times 10^{10} \text{ s}^{-1}$$

where D_{AB} is the sum of the diffusion coefficients for the two reactants (usually assumed to be about 2×10^{-5} cm^2 s^{-1} in water at 25 °C),[22] N_A is Avogadro's number, and a is expressed in centimeters.

Table V. Kinetic Parameters for Inner-Sphere Solvent Exchange on $Cu(H_2O)_6^{2+}$

	this work (μ = 0.10)	Merideth and Connick[11] (rapid Jahn–Teller inversion model) high temp (μ = 0.10)	low temp (μ = 5.27)
k_{ex}, s^{-1} (25 °C)	2.0×10^9	2.8×10^9	0.5×10^9
$\Delta H_{ex}^{\ddagger}$, kcal mol^{-1}	4.5		4.3
$\Delta S_{ex}^{\ddagger}$, eu	−1		−2

These values indicate that the Cu(II)–NH_3 reaction is not diffusion controlled (i.e., $k_f \ll k_o$) and that there is no significant buildup of the outer-sphere complex. Under such circumstances eq 4 may be presumed to be applicable to this system, yielding $k_1 = 1.5 \times 10^9$ s^{-1} at 25 °C.

Similar values of k_1 can be calculated from the reported rate constants for $Cu(H_2O)_6^{2+}$ reacting with acetate,[10] glycinate,[23] imidazole,[15] fluoride,[24] and chloroacetate.[25] In view of the large difference in the nucleophilicity of ammonia and these other ligands, these results lend strong support to the proposition that all of these reactions occur by a dissociative mechanism.

Moreover, the large magnitude of this k_1 value indicates that reactions involving dinegative ligands will cause decreases in k_{-o} sufficient to result in diffusion-controlled reactions (eq 3). This is presumed to account for the erroneous values of k_{ex} generated from studies involving SO_4^{2-} substitution on $Cu(H_2O)_6^{2+}$ (entries 6 and 7 in Table I).

Following the suggestion by Neely and Connick that k_{ex} should actually approximate $^4/_3 k_1$,[26] we conclude that $k_{ex} \simeq 2.0 \times 10^9$ s^{-1} for $Cu(H_2O)_6^{2+}$ at 25 °C. Since the value of K_o is independent of temperature in the absence of electrostatic interactions between the reacting partners, the temperature dependence of k_{ex} should also directly parallel that of k_f(calcd), yielding the activation parameters $\Delta H_{ex}^{\ddagger}$ = 4.5 kcal mol^{-1} and $\Delta S_{ex}^{\ddagger}$ = −1 eu.

In Table V the kinetic parameters derived in this work for water exchange on $Cu(H_2O)_6^{2+}$ are compared to the values obtained by Merideth and Connick assuming rapid Jahn–Teller inversion. In view of the approximations made in both studies, the close agreement between the two sets of values is startling.[27] Analysis of the uncertainties inherent in the treatment of the two data sets suggests that the values obtained indirectly from ammonia substitution kinetics are at least as reliable as the NMR relaxation results. The close correlations between the values obtained from these independent studies lend strong support to the veracity of both data sets.

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Registry No. $Cu(H_2O)_6^{2+}$, 14946-74-8; NH_3, 7664-41-7; $Cu(NH_3)(H_2O)_5^{2+}$, 51139-42-5.

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(27) It is significant to note that the current study was, in fact, completed without prior knowledge of the actual activation parameters generated by Merideth and Connick; thus, the agreement between the two sets of values is totally uninfluenced by any preconception of the *correct* values to be derived.