2.59 Å.);[28] longer Fe–Fe distances are observed in $Fe_3(CO)_{12}$ (*ca.* 2.75 Å.),[17b] and $Fe_2(CO)_8^{2-}$ (2.88 Å.).[29] The variation of iron–iron distances can be rationalized in terms of the amount of negative charge localized on the metal atom through coördination with the other ligands. In general, greater metal–metal distances correspond to a higher localized negative charge.

Acknowledgments.—The authors are grateful to Mr. G. S. D. King of Union Carbide European Research Associates and Mr. Paul Sutton of Wisconsin for helpful discussions. The X-ray work was financially supported by the National Science Foundation (Grant No. 86-3474).

[29] O. S. Mills, private communication, 1961; R. S. Nyholm, *Proc. Chem. Soc. (London)*, 273 (1961).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND RESEARCH LABORATORY OF ELECTRONICS, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE, MASSACHUSETTS]

Relaxation Spectra of Some Nickel(II) and Cobalt(II) Complexes[1]

BY GORDON G. HAMMES AND JEFFREY I. STEINFELD

RECEIVED JULY 9, 1962

The rate constants for the formation and dissociation of Ni(II) and Co(II) complexes with one, two and three glycine, diglycine, or imidazole molecules have been determined by the temperature-jump technique. The approximate time scale of the reactions studied ranged from 0.1 to 500 msec. The rate-determining step of the complex-building reaction, following initial formation of an ion pair, is the dissociation of a water molecule from the inner hydration sphere of the metal ion. The measured rate constants can be normalized with respect to electrostatic and steric factors by dividing out the calculated ion-pair equilibrium constant. The rate constant of dissociation thus obtained is characteristic of a given metal ion, and, in nearly all the reactions studied, was 20 to 25 times greater for Co(II) than for Ni(II). The difference in activation energies corresponding to this rate ratio is of the order of magnitude predicted on the basis of crystal-field theories. For glycine, these normalized rate constants tend to increase in reactions involving the higher complexes, indicating a loosening of the hydration shell due to the fact that the glycine is bound to the metal *via* the negatively charged carboxyl group. These rate constants are independent of the number of ligands bound if the bonding takes place *via* uncharged groups.

Introduction

Although the equilibrium properties of transition metal ion complexes have received considerable attention,[2] relatively few systematic kinetic studies have been carried out on any of these complexes other than those of Co(III) and Pt(II). This is primarily due to the fact that most of the reactions of complexes of other transition metal ions proceed too fast to be studied by conventional techniques. However, the recent application of relaxation methods to simple metal complex systems[3–4] indicates that these new fast reaction techniques are applicable to multi-ligand metal complexes as well.

In the present study, the temperature jump method[5,6] has been used to study the reactions of Ni(II) and Co(II) with glycine, glycylglycine (diglycine) and imidazole. In each case, the metal ions are known to bind several of the ligand molecules and the equilibrium quotients for the individual complex formation steps have been determined.[1,7–10] The rate constants obtained in this study are consistent with the detailed mechanism proposed by Eigen and co-workers for simple systems,[3,4] namely, that the rate of release of water molecules from the inner coördination sphere of the metal ion is the rate controlling step in the overall rate of complex formation. However, this rate of dissociation is greatly dependent on the number and mode of bonding of ligand molecules on the metal. In fact, the variation of this rate constant with successive degrees of association of the ligand with the metal permits some conclusions to be drawn concerning the structure of the complexes.

The metal ions Co(II) and Ni(II) were selected for study because the ratio of their rates of reaction in similar bonding situations is a direct measure of the difference in their crystal field activation energies.[11,12] Moreover, the observed ratios of rate constants can provide a measure of the difference in crystal field stabilization energy in cases where *ab initio* calculations of this quantity are exceedingly difficult.

Finally, relatively simple systems such as those studied can serve as model systems for problems of biochemical interest, such as metal ion activation of enzymes, and the association of metals with proteins and polynucleotides. Kinetic properties, especially at the molecular level, are potentially capable of yielding more specific information than equilibrium properties.

Experimental

The temperature jump apparatus used has been described in considerable detail elsewhere.[13] The only significant change made is that a single beam of light is now employed, rather than a double beam. A null detection method is still made possible by offsetting the initial photomultiplier voltage with a potentiometer powered by dry cells. This

---

[1] This work was supported in part by the U. S. Army Signal Corps, Air Force, Office of Scientific Research, and Office of Naval Research and in part by the National Institutes of Health (RG7803).

[2] See for example J. Bjerrum, G. Schwarzenbach and L. G. Sillén, "Stability Constants of Metal Ion Complexes," Chemical Society, London, 1957.

[3] M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960).

[4] (a) M. Eigen and K. Tamm, *ibid.*, **66**, 93 (1962); (b) M. Eigen and K. Tamm, *ibid.*, **66**, 107 (1962).

[5] G. Czerlinski and M. Eigen, *ibid.*, **63**, 652 (1959).

[6] H. Diebler, Dissertation, Universität Göttingen, 1960.

[7] R. B. Martin, M. Chamberlin and J. T. Edsall, *J. Am. Chem. Soc.*, **82**, 495 (1960).

[8] J. B. Gilbert, M. C. Otey and J. Z. Hearon, *ibid.*, **77**, 2599 (1955).

[9] C. Tanford, D. C. Kirk, Jr., and M. V. Chantooni, Jr., *ibid.*, **76**, 5325 (1954).

[10] R. Mathur and H. Lal, *J. Phys. Chem.*, **63**, 439 (1959).

[11] R. G. Pearson, *ibid.*, **63**, 321 (1959).

[12] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, New York, N. Y., 1958.

[13] G. G. Hammes and P. Fasella, *J. Am. Chem. Soc.*, in preparation.

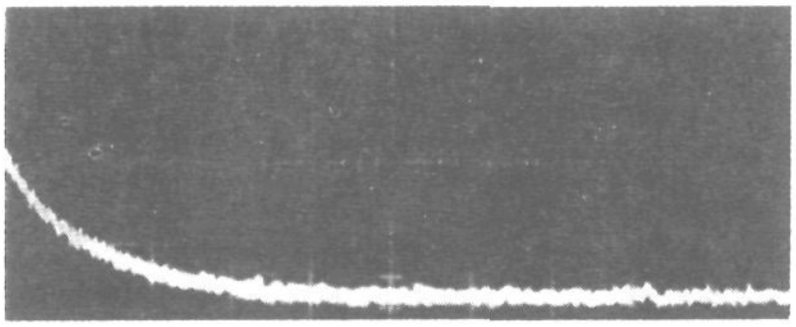

Fig. 1.—Relaxation effect in Co(II)–diglycine system: $\Sigma\mathrm{Co}^{++} = 1.11 \times 10^{-3}$ *M*, $\Sigma\mathrm{L} = 0.534 \times 10^{-3}$ *M*, pH 7.7, $\mu = 0.15$ with phenol red as indicator. The abscissa scale is 1 msec. per major division and the vertical scale is in arbitrary units of absorbency. The relaxation effect corresponds to an increase in absorbance with time.

improvement has resulted in an increase of the signal to noise ratio by a factor of two. Each solution studied was prepared by mixing appropriate amounts of aqueous stock solutions of the metal nitrate, the neutral ligand and a colorimetric pH indicator. The glycine and diglycine were from Calbiochem (Grade A) and the imidazole was supplied by Nutritional Biochemicals. All other chemicals, except for the pH indicators, were reagent grade. The solutions were prepared with freshly boiled conductivity water. Indicators employed were phenol red for the diglycine and imidazole systems and phenolphthalein for the glycine system, each approximately 10^{-5} *M* in total concentration. The ionic strength of each solution was adjusted to the desired level by addition of $\mathrm{KNO_3}$. Finally the solution was brought to the desired pH by dropwise addition of dilute NaOH and/or dilute $\mathrm{HNO_3}$.

The temperature jump experiments were carried out and the relaxation times calculated as described previously.[13] In all cases the metal–indicator and ligand–indicator systems were tested independently to be sure that metal–ligand interactions were being measured. A representative relaxation effect is shown in Fig. 1. The system and conditions employed are given in the figure legend.

Results and Treatment of Data

The experimental conditions and a summary of the pertinent observed relaxation times for the various systems studied are shown in Tables I and II. The experimental error in the relaxation times is about ± 10%.

For a metal complex formation reaction of the type

$$\mathrm{ML}_{n-1} + \mathrm{L} \underset{k_{-n}}{\overset{k_n}{\rightleftarrows}} \mathrm{ML}_n \qquad (1)$$

with the equilibrium quotient $K_n = k_n/k_{-n}$ (*n* is equal to a positive integer), the reciprocal relaxation time is[3]

$$\frac{1}{\tau_n} = k_n[(\mathrm{ML}_{n-1}) + (\mathrm{L})] + k_{-n} \qquad (2)$$

Here the concentrations are those present at equilibrium. If the extent of reaction is followed by a colored pH indicator, In, and the ligand has ionizable groups, the appropriate protolytic equilibria must be included in the reaction mechanism

$$\mathrm{LH}^+ = \mathrm{L} + \mathrm{H}^+$$
$$\mathrm{HIn}^+ = \mathrm{In} + \mathrm{H}^+$$

TABLE I

RELAXATION SPECTRA OF NICKEL(II) COMPLEXES AT 25°

10^3 ΣNi (*M*)	10^3 ΣL (*M*)	*p*H	τ_1 (msec.) Obsd.	τ_1 (msec.) Calcd.	τ_2 (msec.) Obsd.	τ_2 (msec.) Calcd.
			Glycine, $\mu = 0.15$			
1.44	7.19	9.0	17.5	19.6	...	...
1.51	6.01	9.3	21.2	19.2	...	...
1.51	5.76	9.6	19.2	19.2	...	...
1.51	5.01	9.8	17.7	19.2	...	...
0.516	2.37	9.3	33.4	32.6	...	...
.516	1.76	9.8	38.2	32.7	...	...
.312	1.07	9.3	39.8^a	41.5	147	140
.312	0.87	9.8	47.1	42.0	...	142
			Diglycine, $\mu = 0.15$			
28.8	114	8.2	8.8	7.8	...	...
20.5	70.5	8.2	8.9	10.1	...	...
20.5	92.5	7.7	9.3	10.1	...	...
11.5	32.9	8.2	11.4^a	15.7	19.8	21.4
11.5	41.5	7.7	...	15.7	18.9	21.4
5.84	16.8	8.2	21.7	18.2	...	66
11.7	28.6	8.2	12.6	13.7	...	59
0.65	0.98	8.2	86.8	90	...	250
0.49	0.48	8.2	101	101	...	312
			Imidazole, $\mu = 0.15$			
0.947	1.33	7.1	85^a	82.5	141	140
1.90	1.85	7.1	70^a	69	127	113
1.46	2.28	7.1	Sum of 3 $1/\tau_{\mathrm{obs}}$ = 41.4 msec.$^{-1}$			
			Sum of 3 $1/\tau_{\mathrm{calc}}$ = 41.8 msec.$^{-1}$			

[a] Relatively uncertain due to small amplitude of effect.

TABLE II

RELAXATION SPECTRA OF COBALT(II) COMPLEXES AT 25°

10^3 ΣCo (*M*)	10^3 ΣL (*M*)	*p*H	τ_1 (msec.) Obsd.	τ_1 (msec.) Calcd.	τ_2 (msec.) Obsd.	τ_2 (msec.) Calcd.
			Glycine, $\mu = 0.10$			
3.28	13.2	9.5	0.11	0.14	..	0.14
2.96	8.95	9.5	0.15	0.16	0.36	0.30
2.96	13.1	9.0	..	0.16	0.27	0.30
1.46	4.14	9.5	0.26	0.20	0.50	0.49
0.306	0.664	9.5	1.1	1.0	..	18
0.175	0.306	9.5	1.3	1.6	..	23
			Diglycine, $\mu = 0.15$			
2.31	3.52	8.2	0.75	0.75	..	1.48
1.60	1.65	8.2	0.80	1.10	..	1.66
1.23	0.637	8.2	1.2	1.03	..	...
0.556	.257	8.2	1.3	1.45	..	...
1.11	.314	8.2	1.2	1.1	..	...
1.11	.534	7.7	1.1	1.1	..	...
			Imidazole, $\mu = 0.15$			
3.24	5.41	7.1	..	0.62	0.90	0.98
2.59	2.64	7.1	0.75	0.69	..	1.10
1.29	2.32	7.1	0.80	0.69	1.40	1.36
1.14	0.847	7.5	1.35	1.40	..	...
1.14	1.15	7.1	1.40	1.40	..	...

Since these protolytic reactions reach equilibrium much faster than the metal complex reactions under consideration here, they can be assumed to be at equilibrium at all times. By straightforward calculations utilizing mass conservation and equilibrium concentration relationships, it can be shown that the reciprocal relaxation time is now

$$\frac{1}{\tau_n} = k_n\left[\frac{[\mathrm{ML}_{n-1}]}{1+\alpha} + [\mathrm{L}]\right] + k_{-n} \qquad (3)$$

where

$$\alpha = \frac{\delta[\mathrm{LH}]}{\delta[\mathrm{L}]} = \frac{[\mathrm{H}^+]}{K_\mathrm{L} + [\mathrm{L}]\left[\dfrac{K_\mathrm{I} + [\mathrm{H}^+]}{K_\mathrm{I} + [\mathrm{H}^+] + [\mathrm{In}]}\right]}$$

Here δ designates the deviation from equilibrium of the variable under consideration, and K_L and K_I

are the ionization constants for the ligand and indicator respectively. The quantity α is negligible in all but a few of the experiments.

In the systems of interest here, an additional complication is introduced by the fact that, in general, a system of consecutive complex-building reactions must be taken into account. In all cases, except the imidazole systems, the experimental conditions can be adjusted so that only two such equilibria are important. That is, in addition to equation 1, the following reaction occurs

$$\mathrm{ML_n} + \mathrm{L} \underset{k_{-(n+1)}}{\overset{k_{n+1}}{\rightleftarrows}} \mathrm{ML}_{n+1} \qquad (4)$$

The rate equations of this system near equilibrium can be written as

$$\begin{aligned}-\frac{\mathrm{d}\,\delta[\mathrm{ML}_{n-1}]}{\mathrm{d}t} &= \{k_{-n} + k_n[(\mathrm{L}) + (\mathrm{ML}_{n-1})]\}\delta[\mathrm{ML}_{n-1}] + \\ &\qquad [k_{-n} - k_n(\mathrm{ML}_{n-1})]\delta[\mathrm{ML}_{n+1}] \\ &= a_{11}\delta[\mathrm{ML}_{n-1}] + a_{12}\delta[\mathrm{ML}_{n+1}] \\ -\frac{\mathrm{d}\,\delta[\mathrm{ML}_{n+1}]}{\mathrm{d}t} &= k_{n+1}[(\mathrm{L}) - (\mathrm{ML}_n)]\delta[\mathrm{ML}_{n-1}] + \\ &\qquad \{k_{-(n+1)} + k_{n+1}[(\mathrm{L}) + (\mathrm{ML}_n)]\}\delta[\mathrm{ML}_{n+1}] \\ &= a_{21}\delta[\mathrm{ML}_{n-1}] + a_{22}\delta[\mathrm{ML}_{n+1}]\end{aligned}$$

where the a's are defined by the above equations. The relaxation times can be found by solving the secular determinant

$$\begin{vmatrix} a_{11} - \frac{1}{\tau} & a_{12} \\ a_{21} & a_{22} - \frac{1}{\tau} \end{vmatrix} = 0$$

The result is

$$\frac{1}{\tau_{n,n+1}} = \frac{1}{2}(a_{11} + a_{22}) \pm \sqrt{(a_{11} + a_{22})^2 - 4(a_{11}a_{22} - a_{12}a_{21})} \qquad (5)$$

For a system of m-order coupling, the rate equations are of the form

$$-\frac{\mathrm{d}\,\delta x_i}{\mathrm{d}t} = \sum_{k=1}^{m} a_{ik}\delta x_k$$

The system of equations can be solved by making a transformation to new concentration variables, y_i, possessing a diagonal matrix such that

$$-\,\mathrm{d}\,\delta y_i/\mathrm{d}t = \delta y_i/\tau_i$$

This is equivalent to solving the matrix equation

$$\mathbf{A}\delta\mathbf{x} = (1/\tau)\delta\mathbf{x}$$

satisfied by the secular determinant $[\mathbf{A} - (1/\tau)\mathbf{I}] = 0$. Here $\mathbf{A}$ is the coefficient matrix $[a_{ik}]$, $\mathbf{I}$ is the unitary matrix and $\delta\mathbf{x}$ is the column vector $[\delta x_i]$. The exact solution for $m > 2$ is quite complex and only one such case ($m = 3$) was resolvable experimentally. The indicator coupling discussed above enters into these more complicated reaction schemes in a similar manner to that for the single metal-complex reaction: each term involving the concentration of a metal ion or metal–complex species is divided by the factor $1 + \alpha$. It should be noted that in many cases only one of the relaxation times for coupled systems is observed. This is due to the fact that one of the normal concentration variables (y_i) is the sum of two concentrations while the other is a difference.[14] Thus the magnitude of one of the effects is sometimes too small to be seen. In addition, it was sometimes impossible to resolve experimentally all of the coupled relaxation times. These cases are not included in the tables.

Equations 2 and 5 have been used to calculate the relaxation times for a number of trial values of the rate constants for each system making use of the known equilibrium quotients. The rate constants given in Table III are those which give a best fit to all the observed relaxation times; the relaxation times calculated with these parameters are given in Tables I and II alongside the observed relaxation times for each system studied. The precision of the rate constants is about ± 25%.

TABLE III

RATE CONSTANTS OF METAL COMPLEX REACTIONS[a]

Metal	n	Glycine	Diglycine	Imidazole
		$k_n(M^{-1}\text{ sec.}^{-1})$		
Ni^{++}	1	1.5×10^{4}[b]	2.1×10^{4}	5.0×10^{3}
	2	6.0×10^{4}	4.0×10^{3}	4.3×10^{3}
	3	4.2×10^{4}	3.3×10^{3}	2.4×10^{3}
Co^{++}	1	4.6×10^{5}[b]	4.6×10^{5}	1.3×10^{5}
	2	2.2×10^{6}	9.0×10^{4}	1.1×10^{5}
	3	9.0×10^{5}	...	...
		$k_{-n}(\text{sec.}^{-1})$		
Ni^{++}	1	0.024[b]	2.6	2.7
	2	0.95	2.0	8.9
	3	10.4	33	17
Co^{++}	1	10[b]	420	507
	2	360	475	1265
	3	3800	...	...

[a] See Tables I and II for experimental conditions. [b] Estimated from other data; see text for details.

Several of the entries and omissions in Table III require special comment. For the nickel–glycine system with $n = 1$, a direct measurement of the rate constants was not possible because the concentration of reactants required to separate this step from higher order complexes was too small to show a relaxation effect. However, stopped flow data on the acid catalyzed decomposition of nickel-glycine complexes have been reported by Shamsudden Ahmed and Wilkins.[15,16] If their rate constants for n equal to 2 and 3 are compared with the noncatalyzed constants determined in the present study, the acid catalyzed constants are found to be approximately 22 times faster. Thus the noncatalytic constants for $n = 1$ can be estimated by dividing the rate constants calculated from the stopped flow data by 22. The results of this procedure are tabulated with the other rate constants. Similarly, for cobalt-glycine with $n = 1$, a direct measurement of the rate constants was not possible. By analogy with the nickel system and other systems previously studied,[3] the value of k_1 should be approximately the same as that for cobalt–diglycine, with $n = 1$. The rate constants obtained with this assumption are also given in Table III.

For the nickel–imidazole system, three relaxation times are sometimes observed. An exact analysis of the corresponding cubic secular equation would be

---

(14) J. I. Steinfeld, B.S. Thesis, MIT, 1962.

(15) A. K. Shamsudden Ahmed and R. G. Wilkins, *Proc. Chem. Soc. (London)*, 399 (1959).

(16) A. K. Shamsudden Ahmed and R. G. Wilkins, *J. Chem. Soc.*, 3700 (1959).

very difficult; therefore the rate constants for the step $n = 3$ were determined by making use of the diagonal sum rule. This rule states that the sum of the three diagonal terms of **A** is equal to the sum of the three eigenvalues, which are the measured reciprocal relaxation times. In the present case this results in the equation

$$1/\tau_1 + 1/\tau_2 + 1/\tau_3 = k_{-1} + k_{-2} + k_{-3} + k_1[(\mathrm{Im}) + (\mathrm{Ni})] + k_2[(\mathrm{Im}) + (\mathrm{NiIm})] + k_3[(\mathrm{Im}) + (\mathrm{NiIm_2})]$$

which can be solved for k_3 and k_{-3} since K_3 and all other quantities in the equation can be determined independently. Unfortunately, for the analogous case in the cobalt–imidazole system the three relaxation times could not be resolved experimentally. Attempts to obtain rate constants for systems with $n > 3$ were also unsuccessful. Finally, for cobalt–diglycine with $n = 3$, the equilibrium quotient has not been reported; presumably it is too small to be measured by conventional techniques.

Discussion

Eigen and Tamm,[3,4] in their kinetic studies of divalent metal ions with simple anionic species, have proposed a mechanism which involves the initial formation of an ion pair from the hydrated uncomplexed or partially complexed metal ion with the ligand followed by dissociation of a water molecule from the inner hydration shell of the metal ion species. This last process is the rate determining step in the formation of the complex. The mechanism can be written schematically (neglecting charges) for a typical complex building reaction as

$$\mathrm{M(aq)} + \mathrm{L(aq)} \rightleftarrows \mathrm{M(aq)L} \qquad (6)$$

$$\mathrm{M(aq)L} \underset{k_{-0}}{\overset{k_0}{\rightleftarrows}} \mathrm{ML(aq)} + \mathrm{H_2O} \qquad (7)$$

Actually, the reaction in equation 6 has been shown to consist of at least two discrete steps (for 2–2 electrolytes) involving two stages of aquation of the ion pair[3,4]; however for our purposes this can be written as one step since the overall equilibrium in equation 6 is adjusted fast compared to that in equation 7. Because the ion pair equilibrium is adjusted so rapidly, the rate equation for the overall reaction is

$$\frac{\mathrm{d[ML](aq)]}}{\mathrm{d}t} = k_0K_0[\mathrm{M(aq)}][\mathrm{L(aq)}] - k_{-0}[\mathrm{ML(aq)}]$$

where

$$K_0 = \frac{[\mathrm{M(aq)L}]}{[\mathrm{M(aq)}][\mathrm{L(aq)}]}$$

Thus the measured rate constants, k_n and $k_{-\mathrm{n}}$, are equal to k_0K_0 and k_{-0}, respectively. The rate constant k_0 then represents the unimolecular dissociation of a water molecule from the inner coördination shell of the metal ion, while k_{-0} represents the rate of breaking a metal–ligand bond upon interaction with solvent molecules. For bidentate ligands, an additional step must be added to equations 6 and 7

$$\mathrm{ML(aq)} \underset{k_{-0}'}{\overset{k_0'}{\rightleftarrows}} \mathrm{ML(aq)}^* + \mathrm{H_2O} \qquad (8)$$

where ML(aq) represents a species with one coördinate bond and ML(aq)* represents a fully chelated species. If the intermediate ML(aq) is assumed to be in a steady state, it can be shown that $k_\mathrm{n} = k_0'k_0K_0/(k_{-0}+k_0')$ and $k_{-\mathrm{n}} = k_{-0}'k_{-0}/(k_{-0}+k_0')$. If $k_0' >> k_{-0}$, the overall rate of complex formation is determined by the rate of expulsion of the first water molecule from the inner hydration sphere and the overall rate of dissociation represents a complex process roughly related to the rate of dissociation of a metal–ligand bond.

Unfortunately K_0 cannot be determined independently, nor can it be calculated exactly from theory; however, a reasonable approximation to this constant can be obtained by using the Bjerrum ion-pair constant with activity coefficients[17,18] or its equivalent calculated from diffusion theory.[3,19] The results for spherically symmetric ions, can be expressed as

$$K_0 = \frac{4\pi Na^3}{3000}\, e^{-U(a)/kT} \qquad (9)$$

where $U(a)$ is the Debye–Hückel interionic potential

$$U(a) = \frac{z_1z_2e^2}{aD} - \frac{z_1z_2e^2\kappa}{D(1 + \kappa a)} \qquad (10)$$

and

$$\kappa^2 = \frac{8\pi Ne^2}{1000\, DkT}\,\mu$$

In the above equations μ is the ionic strength, N is Avogadro's number, a is the distance of closest approach of the ion pair partners, z is the charge on the ith ion, e is the electron charge, kT is the Boltzmann energy factor, and D is the dielectric constant of the solvent. If the ion is not spherically symmetrical, K_0 must be multiplied by a steric factor, S which is taken to be simply the fraction of the six octahedral coördination positions on the metal ion occupied by water and thus available for bonding. If n is the number of sites occupied by water molecules, then S is equal to $n/6$. This method for calculating K_0 involves many approximations including use of an interionic potential known to be in error at the concentrations under consideration, use of a macroscopic dielectric constant at the molecular level, neglect of all binding forces other than electrostatic, use of a simplified steric factor, and use of the somewhat arbitrary parameter, a, the distance of closest approach. However, the resulting values of K_0 are probably valid within a factor of two or three.

Assuming a value for a of 5 Å. (approximately the internuclear distance of a coördinate bond plus the effective thickness of a water molecule), K_0 can be calculated for the various complexes and k_0 can be calculated from the experimentally determined rate constants. The results obtained are given in Table IV. These rate constants, then, describe the process of the elimination of a water molecule from an ion-pair and are precise at least to within a factor of two or three, reflecting the error made in the calculation of K_0.

Note that for $n = 1$, the bidentate and monodentate ligands have approximately the same k_0, in-

---

(17) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publ. Corp., New York, N. Y., 1950, p. 42.

(18) R. Fuoss, *J. Am. Chem. Soc.*, **80**, 5059 (1958).

(19) G. G. Hammes, unpublished calculations.

TABLE IV

CALCULATED VALUES OF k_0(SEC.$^{-1}$)

Metal	n	Glycine	Diglycine	Imidazole
Ni^{++}	1	0.9×10^4	1.2×10^4	1.6×10^4
	2	1.2×10^5	0.8×10^4	1.6×10^4
	3	4.0×10^5	2.9×10^4	1.1×10^4
Co^{++}	1	2.6×10^5	2.6×10^5	4.4×10^5
	2	4.4×10^6	1.8×10^5	4.1×10^5
	3	8.6×10^6	...	...

dicating the same rate controlling step. On the other hand, the corresponding values of k_{-1} are somewhat different. In terms of the previous discussion, this indicates that $k_0' >> k_{-0}$ (although this conclusion is not unequivocal). Also the values of k_0 obtained for $n = 1$ are in reasonable agreement with those obtained by other methods.[3,4,20,21]

For the complexes of glycine with nickel and cobalt, the rate constants in Table IV increase with successive degree of association of ligand with metal. This can be interpreted as a loosening of the water molecules in the primary hydration sheath, which is caused by the drainage of positive charge from the metal ion by the covalent bond formed between it and the negatively charged carboxyl groups of the glycine ion. The corresponding increase in dissociation rates similarly represents a loosening of the bond formed with the ligand itself.

This increase in rate constants is not observed, however, with the complexes of diglycine. The small observed variation lies within the experimental error and the assumptions made in treating the data. This indicates that bonding must take place through the uncharged portions of the molecule, rather than the carboxyl group. Similar conclusions, namely that bonding takes place through the amino nitrogen and the oxygen of the peptide carbonyl group, have been reached by Rosenberg,[22] on the basis of infrared studies, and by Datta, Leberman and Rabin[23] through an analysis of equilibrium data. A corresponding lack of variation is demonstrated by the rate constants for the first two dissociation steps; the enhanced value of k_{-3} for nickel–diglycine is probably the result of steric and electrostatic interactions occurring when three bulky diglycine molecules are forced into close proximity around the metal ion. The behavior observed with imidazole is similar to that found with diglycine.

The ratio of rate constants for Co(II) and Ni(II) in identical bonding systems is a measure of their difference in activation energy, ΔE_a. This means that

$$\Delta E_a = RT \ln k_{0\text{Co}}/k_{0\text{Ni}}$$

In the case of k_0, the ratio of rate constants is approximately 25 for almost all cases. This corresponds to a ΔE_a of 1.9 kcal./mole. On the other hand, the ratio of the rates of complex dissociation is about 200 (although the experimental deviation is considerable) which yields a ΔE_a of about 3.1 kcal./mole. The calculated value of the difference in crystal-field activation energy for the hexa-aquo ions is about 4.9 kcal./mole[11,12] which is only in fair agreement with experiment. However, considering the complexity of the actual situation, better agreement is not to be expected.

The fact that the ratio of rate constants for Co(II) and Ni(II) with a given ligand is roughly constant can be utilized if the rate constants for only one metal are known. For example, the complex of Co(II) with a third diglycine molecule has not been amenable to experimental study. The rate constants k_3 and k_{-3} can be estimated simply by multiplying the corresponding constants for the Ni(II) diglycine system by 25 and 200, respectively. The results are $k_3 \approx 7 \times 10^4\ M^{-1}$ sec.$^{-1}$, $k_{-3} \approx 7 \times 10^3$ sec.$^{-1}$ and the stability constant $K_3 \approx 10\ M^{-1}$. The predicted smallness of the stability constant explains the difficulty of measuring it experimentally.

Since the mode of ligand bonding determines the rate of water dissociation from the metal ion's hydration shell, the effect of various ligands on this rate is predictable. The cases of bonding through no charges and a -1 charge on the ligand are covered specifically by this study. However, it is not too difficult to guess that bonding through two or more negatively charged groups should loosen the water molecules on the metal even more.

In the pH range covered in these experiments, acid–base catalysis of the complex-ion reactions was not detected. However, there was a suggestion that a base catalyzed path is available for Co^{+2} and glycine, with $n = 1$, at pH's of 9.5 or greater. A small effect with a relaxation time of about 2 msec. was observed at pH 9.5 and low glycine and metal concentrations. This relaxation time is much too short to have anything to do with the mechanisms discussed here. Unfortunately an extended study of the pH dependence for this reaction was not possible so that the occurrence of base catalysis at high pH's must remain little more than speculation at this time. These studies are being extended to other metals and ligands, including macromolecules.

[20] R. E. Connick and R. E. Poulson, *J. Chem. Phys.*, **30**, 759 (1959).

[21] R. E. Connick and E. D. Stover, *J. Phys. Chem.*, **65**, 2075 (1961).

[22] A. Rosenberg, *Acta. Chem. Scand.*, **11**, 1390 (1957).

[23] S. P. Datta, R. Leberman and B. R. Rabin, *Trans. Faraday Soc*. **55**. 1982 (1959).