fractions of each species (*e.g.*, 0.2–0.8); hence, no exchange is observable within the slow-exchange region of the epr time scale.[44,45]

The epr spectrum of Cu(bipy)(Tiron)$^{2-}$ (*cf.* Figure 2B) is unique, as in the case of the glassy epr spectra. It differs from both the spectra of the three Cu^{2+}–bipy complexes and the two Cu^{2+}–Tiron complexes. Thus we are assured that this is indeed a unique species, a ternary complex, at room temperature. The solution epr spectrum of Cu(8-HQ-5-S)$_2^{2-}$ is markedly similar to that of Cu(bipy)(Tiron)$^{2-}$, including ^{14}N superhyperfine structure on the highest field line, as is true for the latter species (*cf.* Figure 2B). This again confirms the great similarity between Cu(8-HQ-5-S)$_2^{2-}$ and the ternary complexes, as already concluded above, on the basis of glassy epr data.

The amounts of the ternary complex present, as observed in the three spectra of Figure 2B, do not agree very well with the amounts calculated from the stability data (*cf.* caption to Figure 2B).[8] This is probably again an ionic strength effect, since the two reactants are of opposite charge.

Acknowledgments.—Epr spectra were recorded in the Department of Biochemistry, Cornell University, and at Varian Associates, Palo Alto, Calif. The authors wish to thank Professor J. O. Edwards and the Department of Chemistry, Brown University, Providence, R. I., for use of the Cary 14 reflectance attachment, and Professor Henry Taube, Department of Chemistry, Stanford University, for use of the Faraday balance. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society (F. A. W.), the Schweizerischen Nationalfonds zur Förderung der wissenschaftlichen Forschung (H. S.), and the National Institute of Arthritis and Metabolic Diseases, U. S. Public Health Service, Research Grant Am-08721 and the State University of New York (D. B. M.) for support of this research.

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Kinetics of Zinc–Glycine Interactions in Aqueous Solution

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Received May 24, 1972

Two concentration and pH dependent relaxation times in the millisecond time region have been observed for the aqueous zinc–glycine system by means of temperature-jump spectrometry. The faster of the times was measured in dilute solutions. The process responsible was shown to be the formation of the monoglycinate complex from the reaction of zinc with free glycine anion. The overall second-order rate constant is 1.5×10^8 M^{-1} sec^{-1} at 25° and $I = 0.1$ M. The slower time, observed only in concentrated glycine solutions, was attributed to the formation of the bis glycinato complex accompanied by a rate-determining unimolecular rearrangement. The rate constant for the latter was estimated to be 93 sec^{-1}. The structure change is postulated to be tetrahedral → octahedral.

Introduction

Considerable information now exists for the kinetics of interactions of metal ions with organic and inorganic ligands.[1,2] In particular, much effort has been directed toward characterizing the solvent lifetimes within the inner coordination spheres of the alkaline earth cations and several of the first row transition elements (especially Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Cu^{2+}). Considerably less is known about the complexation kinetics of other metal ions.

An examination of the literature indicates that very few kinetic investigations have involved divalent zinc, with which this article is concerned. One of the first studies was that of Wilkins[3] between zinc(II) and an azo dye, pyridine-2-azo-*p*-dimethylaniline, for which he obtained a complexation rate constant of 4×10^6 M^{-1} sec^{-1} at 25°. Perhaps the most detailed study to date was that of Maass,[4] who reported kinetic data for the interactions between zinc(II) and acetate and sulfate by means of ultrasonic absorption measurements. The value of the characteristic ligand penetration rate constant (presumably equal to the solvent lifetime rate constant k_{H_2O} in the inner coordination sphere of the metal ion) ranged from 3×10^7 to 1×10^8 sec^{-1} at 25°. Other kinetic studies involving murexide,[4,5] 2-2′-dipyridyl, and 1,10-phenanthroline[6] have yielded complexation rate constants ranging from 1×10^6 to 7×10^7 M^{-1} sec^{-1}. Thus, several different investigations have come to substantially different conclusions as to the rate of ligand penetration into the primary coordination sphere for divalent zinc.

Divalent zinc is potentially an extremely interesting system in view of the structural possibilities proposed by Swift.[7] In a temperature-jump study of $Zn(NO_3)_2$, he reported a concentration-independent relaxation time ($\tau \approx 0.13$ sec at 25°). He attributed this time to a structural interconversion between tetrahedral $Zn(H_2O)_4^{2+}$ and another configuration, presumably octahedral. If this indeed is the cause of this relaxation, then it should be possible to obtain independent evidence for it by studying the interactions between zinc and a ligand which imposes a different geometry on the

(1) M. Eigen, *Pure Appl. Chem.*, **6**, 97 (1963).
(2) M. Eigen and R. G. Wilkins, *Advan. Chem. Ser.*, **No. 49**, 55 (1965).
(3) R. G. Wilkins, *Inorg. Chem.*, **3**, 520 (1964).
(4) G. Maass, *Z. Phys. Chem. (Frankfurt am Main)*, **60**, 138 (1968).
(5) A. Bewick and P. Robertson, *Trans. Faraday Soc.*, **63**, 678 (1967).
(6) R. Holyer, C. Hubbard, S. Kettle, and R. Wilkins, *Inorg. Chem.*, **4**, 929 (1965).
(7) T. J. Swift, *ibid.*, **3**, 526 (1964).

metal ion. Such a ligand is glycine, the bis complex of which with Zn^{2+} is octahedral.[8]

It was the purpose of this investigation to characterize the dynamics of the interactions between zinc ions, glycine, and water.

Experimental Section

Procedures and Materials.—All chemicals were of the highest quality available and used without further purification. Stock solutions of zinc nitrate (Fisher Scientific) and glycine (Nutritional Biochemicals) were prepared from triply distilled degassed water containing sufficient KNO_3 to maintain 0.1 ionic strength. All solutions were freshly prepared for each kinetic run. The pH was adjusted with KOH or HNO_3 in conjunction with a pH meter (Beckman Expandomatic). Spectra were taken on a Cary 15 to determine optimum measurement wavelengths for Methyl Red and Thymol Blue indicators. Kinetic measurements were made at 25° by the electrical discharge temperature-jump instrument obtained from Messanlagen Studiengesellshaft.[9] Its principle and operation have been described elsewhere.[10] Blanks, consisting of metal plus indicator and ligand plus indicator, in all instances showed no relaxation effect in the time ranges studied. Each relaxation effect was repeated at least three times (six to eight times for small effects).

Treatment of Data.—The equilibrium constants for the various complexing and proton-transfer processes are summarized in Table I. The equilibrium concentrations of the various species were obtained from the known amounts of ligand and metal ion and the value of the pH by means of an exact computer solution of the relevant equilibria.

Table I

Equilibrium Constants[a]

Reaction	Log K^b
$Zn^{2+} + gly^- = Zn(gly)^+$	5.03 (log K_1)
$Zn(gly)^+ + gly^- = Zn(gly)_2$	4.27 (log K_2)
$Zn(gly)_2 + gly^- = Zn(gly)_3^-$	2.31[c] (log K_3)
$H^+ + gly^- = Hgly$	9.60 (pK_{2a})
$Hgly + H^+ = H_2gly^+$	2.34 (pK_{1a})
$Zn^{2+} = ZnOH^+ + H^+$	−8.70

[a] L. Sillen and A. Martell, Ed., *Chem. Soc., Spec. Publ.*, **No. 17**, 377 (1964). [b] At 25° and $I = 0.1$ *M* unless stated otherwise. [c] C. Childs and D. Perrin, *J. Chem. Soc. A*, 1039 (1969), 37° and $I = 0.15$.

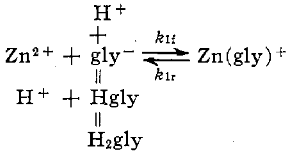
Photographs of each kinetic effect were enlarged to 8.5 × 11 in. The base line (t_∞ value) of each effect was estimated and the amplitudes measured at close intervals of time. The data were converted to a linear function by taking the logarithm of the amplitude. The relaxation time was determined from the preliminary value by a computer program which searched for the *best* base line by minimizing the squared errors in a weighted least-squares fit to a straight line. This gave a method of analyzing the data which was relatively independent of observer bias.

Results

Two concentration and pH dependent relaxation times were observed for the zinc–glycine system. One of these (τ_1) was observed in relatively dilute, slightly acidic solutions. The other (τ_2) could be detected only at very high glycine concentrations in alkaline solutions. Since τ_1 and τ_2 are attributed to very different processes, they will be discussed separately.

Low-Concentration Time (τ_1).—Kinetic data were obtained as a function of concentration and pH over the following ranges: Zn^0, 1×10^{-2}–1×10^{-4} *M;* gly^0, 1×10^{-3}–5×10^{-1} *M;* pH 4.5–6.0. Measured relaxation times varied from 50 μsec to 1 msec.

A variety of mechanisms were examined in detail. These included reactions between Zn^{2+} and free ligand or Zn^{2+} and protonated ligand (the zwitterion) for mono and bis complexation. Several permutations of each were made, *e.g.*, mono complex with bis as rapid preequilibrium, *vice versa*, etc. Of the various mechanistic possibilities, only a single one was found to be consistent with all the following data: the simple formation of the mono complex[11,12] in which the slow step is



$$\begin{array}{l} \quad\;\; H^+ \\ \quad\;\;\; + \\ Zn^{2+} + gly^- \underset{k_{1r}}{\overset{k_{1f}}{\rightleftharpoons}} Zn(gly)^+ \\ \quad\;\;\; \| \\ H^+ + Hgly \\ \quad\;\;\; \| \\ \quad\;\; H_2gly \end{array} \qquad (A)$$

represented by arrows, the rapid proton-transfer equilibria are represented by equal signs, and the subscripts f and r refer to forward and reverse rate constants. The relaxation time for this process is given by

$$\frac{1}{\tau_1} = k_{1f}\left(\frac{[Zn]}{1 + \beta} + [gly]\right) + k_{1r} \qquad (1)$$

where [Zn] and [gly] are the indicated equilibrium concentrations and β is a term correcting for the rapid proton-transfer equilibria of glycine and the pH indicator coupled to it

$$\beta = \frac{[H][(1 + \alpha)(K_{1a} + [H]) + [Hgly]]}{K_{2a}[K_{1a}(1 + \alpha) + 2[Hgly]] + [gly](K_{1a} + 2[H])}$$

and $\alpha = [In]/(K_{In} + [H])$. A graph of τ_1^{-1} *vs.* $[Zn]/(1 + \beta) + [gly]$ thus is a straight line of slope k_{1f} and intercept k_{1r} (Figure 1). The ratio of these values, as it must, returned the stability constant for the process. Conversion of the 0.1 ionic strength value of k_{1f} to the zero ionic strength value is given by $k_f = k_f^0\gamma_M\gamma_L/\gamma^\mp$ where γ_i are the indicated activity coefficients as estimated from the Davies equation,[13] and k_f^0 is the zero ionic strength rate constant. Constants are summarized in Table III.

High-Concentration Time (τ_2).—The second (slow) relaxation time was considerably more difficult to observe and in fact was not found in the original investigation in dilute solutions. Examination of equilibrium concentrations in the latter indicated that there were only small amounts of bis and tris complexes present. We found it necessary to increase the total glycine concentration and to raise the pH in order to achieve significant concentrations of higher complexes (see Table II). Under these conditions, one can calculate the value of τ_1 to be about 10^{-8} sec. The first complexation step is therefore under these conditions a rapid preequilibrium to the second time. We were not able to fit τ_2 to the concentration dependence predicted for simple bis or tris complexation. It was possible however quantitatively to fit the time to the formation of the bis complex accompanied by a rate-determining unimolecular rearrangement, step III–IV, according to the scheme

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[8] B. Low, F. Hirshfield, and F. Richards, *J. Amer. Chem. Soc.*, **81**, 4412 (1959).

[9] Göttingen, W. Germany.

[10] M. Eigen and L. DeMaeyer, *Tech. Org. Chem.* **8**, 895 (1963), and references contained therein.

[11] G. Hammes and J. Steinfeld, *J. Amer. Chem. Soc.*, **84**, 4639 (1962).

[12] A. F. Pearlmutter and J. E. Stuehr, *ibid.*, **90**, 858 (1968).

[13] C. W. Davies, "Ion Association," Butterworth, London, 1961.

$$\mathrm{Zn^{2+}} \overset{\mathrm{I}}{+} \mathrm{gly^-} = \overset{\mathrm{II}}{\mathrm{Zn(gly)^+}} + \mathrm{gly^-} = \overset{\mathrm{III}}{\mathrm{Zn(gly)_2}} \underset{k_r^{ra}}{\overset{k_f^{ra}}{\rightleftharpoons}}$$

$$\overset{\mathrm{IV}}{\mathrm{Zn(gly)_2'}} + \mathrm{gly^-} = \overset{\mathrm{V}}{\mathrm{Zn(gly)_3^-}} \qquad \text{(B)}$$

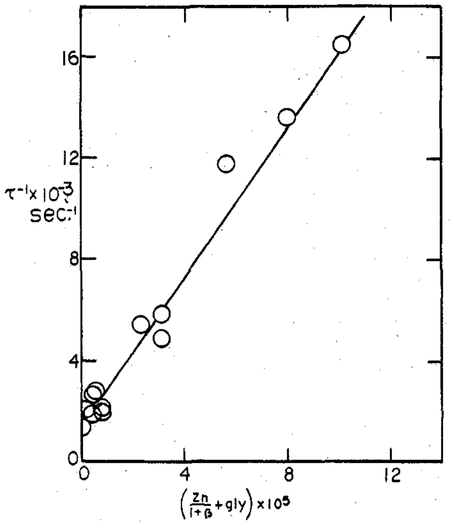

Figure 1.—Concentration dependence of the relaxation time for the formation of the monoglycinatozinc complex at 25°, $I = 0.1$. $k_f = 1.5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$, $k_r = 1.4 \times 10^3\ \mathrm{sec}$, $K_1 = k_f/k_r = 1.06 \times 10^5$, and K_1 (thermodynamic) $= 1.07 \times 10^5$.

TABLE II

KINETIC DATA FOR ZINC AND GLYCINE AT 25° AND AT $I = 0.1$

No.	$[\mathrm{Zn^0}]$, M^b	$[\mathrm{gly^0}]$, M^b	pH^c	τ_1^{-1}, sec$^{-1\,a}$	τ_2^{-1}, sec$^{-1\,d}$
1	0.010	0.010	4.61	2,050	
2	0.001	0.001	5.35	1,910	
3	0.001	0.050	4.64	2,160	
4	0.001	0.050	5.40	5,920	
5	0.0001	0.005	5.67	2,920	
6	0.00971	0.485	5.35	16,500	
7	0.001	0.050	4.95	2,060	
8	0.001	0.50	4.87	2,660	
9	0.001	0.050	5.32	5,480	
10	0.001	0.050	5.68	13,600	
11	0.001	0.001	4.90	1,350	
12	0.001	0.001	5.57	2,030	
13	0.001	0.001	5.92	4,880	
14	0.00962	0.481	5.12	11,800	
15	0.00921	0.461	5.38	20,700	
16	0.0194	1.94	9.25		49.5
17	0.112	1.87	9.24		52.5
18	0.181	1.80	9.25		46.2
19	0.0577	1.92	8.95		36.5
20	0.0577	1.92	9.08		38.5
21	0.0577	1.92	9.25		51.7
22	0.0577	1.92	9.49		64.5
23	0.0577	1.92	9.82		82.5

^{a} All solutions contain $3.0 \times 10^{-5}\ M$ Methyl Red indicator ($\log K = 4.95$, $I = 0.1$). ^{b} Overall concentrations. ^{c} Converted to H and OH by use of $\gamma_{\mathrm{H}} = 0.825$ and $\gamma_{\mathrm{OH}} = 0.745$. ^{d} All solutions contain $1.0 \times 10^{-5}\ M$ Thymol Blue indicator ($\log K = 8.96$, $I = 0.1$).

TABLE III

KINETIC RESULTS FOR THE FORMATION OF ZINC-GLYCINE COMPLEXES AT 25°^{a}

	Mono complexation	Bis rearrangement
k_f	$1.5 \times 10^8\ M^{-1}\ \mathrm{sec}^{-1}$ (3.9×10^8 at $I = 0$)	$9.3 \times 10\ \mathrm{sec}^{-1}$
k_r	$1.4 \times 10^3\ \mathrm{sec}^{-1}$	$1.9 \times 10^{-2}\ \mathrm{sec}^{-1}$
k_{1p}	$\sim 0.7 \times 10^8$	
K_{23}		3.8
K_{34}		4.9×10^3

^{a} Rate constants at $I = 0.1$ unless stated otherwise.

(the rapid proton-transfer preequilibria are not shown for simplicity). The superscript ra refers to the rearrangement step. The relaxation time for this process, with all others as rapid preequilibria, is given by

$$\tau_2\left(\frac{V}{R}\right) = \frac{1}{k_f^{ra}}\left(\frac{Q}{R}\right) + \frac{1}{k_r^{ra}} \qquad (2)$$

where Q, R, and V are cumbersome concentration- and pH-dependent functions derived from the preequilibria.[14] A graph of $\tau_2(V/R)$ *vs.* (Q/R) should give a straight line of slope $1/k_f^{ra}$ and intercept $1/k_r^{ra}$ (Figure 2). The stability constant K_{34} is, therefore, k_f^{ra}/k_r^{ra}. The rate and equilibrium constants for these processes are summarized in Table III.

Several observations drawn from the calculations are noteworthy. First, in principle scheme B should have four slow times visible to transient techniques at the proper experimental conditions. The times for steps I–II and III–IV are reported here; by the nature of the system, however, the times for steps II–III and IV–V are not visible. This is demonstrated as follows: the gross bis equilibrium constant (K_{24}) has the measured value 18,600. It is related to K_{23} and K_{34} by $K_{24} = K_{23}(1 + K_{34})$. The values of $\mathrm{Zn(gly)_2}$ and $\mathrm{Zn(gly)_2'}$ are given by $\mathrm{Zn(gly)_2'} = \mathrm{Zn(gly)_{2\Sigma}}[K_{34}/(1 + K_{34})]$ and $\mathrm{Zn(gly)_2} = \mathrm{Zn(gly)_{2\Sigma}}([1/(1 + K_{34}))]$ where $\mathrm{Zn(gly)_{2\Sigma}} = \mathrm{Zn(gly)_2} + \mathrm{Zn(gly)_2'}$ is the overall equilibrium bis concentration. A typical value of $\mathrm{Zn(gly)_{2\Sigma}}$ is about $1 \times 10^{-3}\ M$ in 2 M glycine and $5 \times 10^{-2}\ M$ zinc. With a value of $K_{34} = 4900$ the concentration of $\mathrm{Zn(gly)_2}$ is typically about $2 \times 10^{-7}\ M$; that is, virtually all of the bis complex is in the form $\mathrm{Zn(gly)_2'}$. The relaxation time for the formation of the tris complex (step IV–V) will be proportional to the sum of the concentrations of $\mathrm{Zn(gly)_2}$ and gly. The latter was typically 0.4 M. As a consequence, for a tris rate constant of the magnitude 10^5 or larger, the relaxation time would be 10 μsec or shorter under the conditions of the present experiments. Thus, of the four metal–ligand times, only two will be observable by T-jump spectroscopy.

Discussion

Unreactivity of the Zwitterion.—The possibility of any significant contribution to the relaxation time by complexation pathways involving the zwitterion and either the hydrated or hydroxylated metal ion was eliminated by lack of fit of the data to mathematical expressions describing such pathways. It is not sur-

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(14) If $K_{34} \gg 1$, then $K_{54} = K_3^{-1}(K_{34}/(1 + K_{34}))$ and $K_{32} = K_2^{-1}(1 + K_{34})$, $K_{54} \simeq K_3^{-1}$, and $K_{32} \simeq K_2^{-1} K_{34}$. The concentration functions in eq 2 are given by

$$V = [\mathrm{LML_2}] - K_3^{-1}[\mathrm{ML}]$$

$$R = [\mathrm{ML_2}]K_2^{-1} - \{[[\mathrm{ML}](K_3^{-1} + [\mathrm{L}])/(X_1 + X_2)]X_5K_2^{-1}\}$$

$$Q = [\mathrm{ML_2}][\mathrm{L}] - \{[[\mathrm{ML}](K_3^{-1} + [\mathrm{L}])/(X_1 + X_2)](X_3 + X_4)\}$$

where

$$X_1 = [\mathrm{L}][(K_3^{-1} + [\mathrm{L}])([\mathrm{HL}] + [\mathrm{OH}] + K'_{2a}) + [\mathrm{ML_2}]([\mathrm{HL}] + [\mathrm{OH}])]$$

$$X_2 = [\mathrm{ML}](K_3^{-1} + 2[\mathrm{L}])([\mathrm{HL}] + [\mathrm{OH}])$$

$$X_3 = K_3^{-1}[\mathrm{L}]([\mathrm{HL}] + [\mathrm{OH}] + K'_{2a})$$

$$X_4 = (K_3^{-1}[\mathrm{ML}] + [\mathrm{ML_2L}])([\mathrm{HL}] + [\mathrm{OH}])$$

$$X_5 = (K_3^{-1}([\mathrm{HL}] + [\mathrm{OH}] + K'_{2a}) + 2[\mathrm{ML_2}]([\mathrm{HL}] + [\mathrm{OH}])$$

$$\mathrm{L} = \mathrm{gly},\ \mathrm{M} = \mathrm{Zn},\ \mathrm{ML_2} = \mathrm{Zn(gly)_{2\Sigma}},\ K'_{2a} = K_{2a}/K_w$$

Contributions from equilibrium I–II and the indicator correction term were found to be negligibly small.

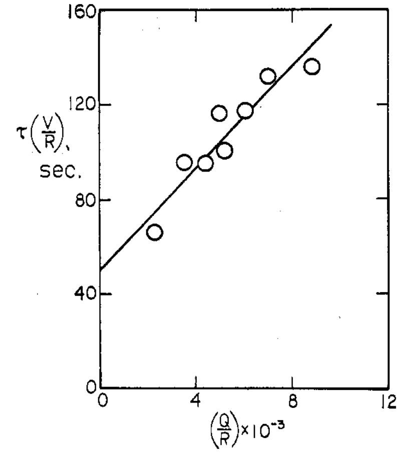

Figure 2.—Graph of $\tau(V/R)$ *vs.* Q/R according to eq 2 for the slow relaxation time.

prising that the metal ion reacts with the anionic form of the ligand and not with the protonated form of the ligand which predominates at the pH's studied. This is exactly the case found for simple amino acid complexation with nickel[11,15] and copper[12,16] ions. The fact that the amino group in the zwitterion is protonated effectively prevents the reaction with the amino group itself. As a consequence, as long as the ligand is in the zwitterionic form, only very labile complexes with the $-COO^-$ can form. The latter do not remain coordinated long enough for the $-NH_3^+$ group to deprotonate and then to close the ring and chelate (*cf.* the Zn-acetate system,[4] for which $\tau \approx 10^{-8}$ sec). As a consequence, the amino group must first deprotonate, after which chelation with both the carboxyl and amino group occurs.

Solvent Exchange Rate Constants.—It is now generally accepted that complex formation[17] occurs by the two step mechanism[18] C, in which the first step

$$\mathrm{M_{aq}}^{z+} + \mathrm{L_{aq}}^{z-} \overset{K_{os}}{=} \mathrm{M}^{z+}\mathrm{OH_2L}^{z-} \underset{k_r}{\overset{k_{1p}}{\rightleftharpoons}} \mathrm{ML_{aq}}^{(z+)+(z-)} + \mathrm{H_2O} \qquad \text{(C)}$$

represents the diffusion controlled formation of an outer-sphere complex with the metal ion and ligand still separated by one water molecule. The stability constant (essentially electrostatic) for the process is represented by K_{os}. The rate-determining step is the formation of the contact (inner sphere) complex.

The relation between the overall $I = 0$ forward rate constant k_f^0 and the ligand penetration rate constant k_{1p} for scheme C with a stationary state treatment of the intermediate is $k_{1p} = k_f^0/K_{os}$ where K_{os} is the electrostatic stability constant given by[19] $K_{os} = [4\pi a^3N/(3000)]\exp(-z_Az_Be^2/\epsilon akT)$ where z_i is the charge, ϵ the bulk dielectric constant, and a is the contact distance in the intermediate. For the reasonable values of a = 4-7 Å, K_{os} is practically constant at 5-6 M^{-1}. As a consequence, k_{1p} may be estimated as $\sim 0.7 \times 10^8$ sec^{-1} for the formation of the mono complex.

The value for the ligand penetration rate constant k_{1p} obtained in this study may be compared with those obtained from other detailed studies involving zinc. Maass[4] reported rate data for zinc acetate, for which the value of k_{1p} can be estimated[20] to be $(0.3\text{-}1.0) \times 10^8$ sec^{-1}. Rorabacher[21] in a temperature-jump study of zinc(II) with ammonia estimated the same constant to be 0.2×10^8 sec^{-1} at 11°. Comparison of these values with that for zinc and glycine (0.7×10^8 sec^{-1}) indicates that they are the same within probable error.[22]

Since ring closure of an intermediate complex which is bound to only one position of glycine will normally affect the rate only if ring closure is rate determining,[23] one may conclude that the rate constant for ring closure in glycine is rapid compared to that for the formation of the half-bonded intermediate. It is possible that the substantially reduced rate constants observed for the systems[6] 2,2′-dipyridyl and 1,10-phenanthroline result from ring-closure mechanisms being operative for these systems.

Structural Rearrangement.—The conclusion that τ_2 was associated with a combined bis complexation-structural change was based on several clear-cut observations. First, we were able to demonstrate, well in advance of observing τ_2, that the formation of the predominant bis complex had to be slow compared to τ_1. The data for the latter correlated well with the isolated mono complexation (Figure 1). If rate constants for the second relaxation time were made sufficiently large that τ_2 was within an order of magnitude of τ_1, then a progressively worse correlation with the data for the first step was observed. We concluded therefore that the second relaxation time had to be much longer than τ_1. Second, τ_2 was not seen under the same conditions as τ_1. It was necessary to greatly increase the glycine concentration and the pH. Even then, the second relaxation time was no shorter than about 10 msec. Third, if we tried to correlate the second relaxation time with the formation of the bis complex, a graph of τ_2^{-1} *vs.* the appropriate function of concentration yielded a smooth curve which strongly deviated from linearity at high concentrations. This curvature could be explicitly accounted for by assuming the rapid formation of $Zn(gly)_2$, followed by a rate-determining conversion to a different structure.

An assignment of the structures of $Zn(gly)_2$ and $Zn(gly)_2'$ can be proposed. It has been documented that complexes of zinc can exist in tetrahedral and octahedral structures as well as, in a limited number of cases, trigonal-bipyramidal and square-pyramidal structures.[24] The structural rearrangement of aqueous zinc

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(15) J. Cassatt and R. Wilkins, *J. Amer. Chem. Soc.*, **90**, 6045 (1968).

(16) W. Makinen, A. Pearlmutter, and J. Stuehr, *ibid.*, **91**, 4083 (1969).

(17) (a) H. Diebler and M. Eigen, *Z. Phys. Chem.* (*Frankfurt am Main*), **20**, 299 (1959); (b) M. Eigen, *Z. Elektrochem.*, **64**, 115 (1960); (c) M. Eigen and K. Tamm, *ibid.*, **66**, 93, 107 (1962).

(18) In principle, the last step consists of the following two steps: the formation of a complex bonded to glycine at one point followed by closure of the ring to form the chelate: K. Kustin, R. Pasternak, and E. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610; A. Kowalak, K. Kustin, R. Pasternak, and S. Petrucci, *ibid.*, **89**, 3126 (1967).

(19) (a) M. Eigen, *Z. Phys. Chem.* (Frankfurt *am Main*), **1**, 176 (1954); (b) R. Fuoss, *J. Amer. Chem. Soc.*, **80**, 5059 (1958).

(20) The value of k_{1p} as calculated by Maass is quite sensitive to the choice of overall stability constant. He obtained the rate constant k_r directly from ultrasonic data as 3×10^7 sec^{-1}. The overall stability constant $K_\Sigma = K_{os}(1 + K_{is})$ is in the range 10-20 at $I = 0$ [L. Sillen and A. Martell, Ed., *Chem. Soc., Spec. Publ.*, **No. 17** (1964)]. Since $K_{os} \cong 5$, K_{is} can range from 1 to 3 for this system. Thus, $k_{1p} = K_{23}k_r = (0.3\text{-}0.9) \times 10^8$ sec^{-1}, as stated.

(21) D. Rorabacher, *Inorg. Chem.*, **5**, 1891 (1966).

(22) Principally due to uncertainties in estimating K_{os} and differences in temperature.

(23) (a) K. Kustin, R. Pasternak, and E. Weinstock, *J. Amer. Chem. Soc.*, **88**, 4610 (1966); (b) A. Kowalak, K. Kustin, R. Pasternak, and S. Petrucci, *ibid.*, **89**, 3126 (1967).

ion proposed by Swift[7] is directly relevant to this study. From the temperature dependence of the concentration independent relaxation time ($\tau = 0.13$ sec at 25° in aqueous $Zn(NO_3)_2$), $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ were estimated to be 3.8 kcal/mol and −42 eu, respectively. Swift attributed this process to the tetrahedral–octahedral conversion. The relaxation times we observed for the formation of the zinc monoglycinate complex were in the 10^{-4} sec region and those for the bis rearrangement were much longer. We propose, therefore, that the bis rearrangement may be due to a change in structure similar to that observed by Swift.

The structure of bis(glycinato)zinc monohydrate has been studied by infrared and X-ray methods.[8,25] Both studies are in agreement; the structure of this complex is octahedral. The glycine anions are in a trans configuration coplanar to the central metal ion, while the other two coordination positions are occupied by carboxyl oxygens of neighboring glycine ligands. Also the axial bond lengths are longer than those in an equatorial position, and in this instance are occupied by water molecules. It seems reasonable, therefore, to assign an octahedral structure[26] to the $Zn(gly)_{2aq}'$ species of scheme B, where the waters of hydration occupy axial positions and the glycine ligands are equatorial. An octahedral configuration is also consistent with the presence of three bidentate ligands in the tris complex. Although the structure of zinc monoglycinate is not known, some comment can be made about its probable structure. It is more common for zinc to have a coordination number of four than six.[24] X-Ray studies have demonstrated that tetrachloro-[27] and tetracyanozincates[24] are tetrahedral. Moreover, it is known that diamminedichlorozinc is tetrahedral while hexaamminezinc(II) is octahedral.[24] That is, in this case increased coordination converts zinc from a tetrahedral to an octahedral structure. These considerations suggest that the $Zn(gly)^{+}_{aq}$ species of scheme B is tetrahedral and that $Zn(gly)_2'$ is octahedral. Our kinetic data are consistent with a structural change occurring after the formation of the monoglycinate complex. We propose therefore that this process involves the $Zn(gly)^+$ complex (in a probably tetrahedral configuration) being converted to the bis complex $Zn(gly)_2'$ (octahedral). If the suggestion of Krishnan and Plane[26]—that the bis complex is tetrahedral—is correct, then it would be necessary to propose the other structure for the mono complex. Nevertheless, the sequence resulting from the latter assignment (octahedral $Zn^{2+} \rightarrow$ octahedral $Zn(gly)^+ \rightarrow$ tetrahedral $Zn(gly)_2 \rightarrow$ octahedral $Zn(gly)_2$ in solid) is much less satisfying than the sequence proposed above. Kinetic data of course cannot distinguish between these possibilities.

Acknowledgment.—This work was supported by research grants from the Office of Saline Water (14-1273) and from the National Institutes of Health (GM 13116). The authors wish to express their thanks to Dr. Joseph L. Banyasz for helpful discussions.

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Metalloporphyrin Redox Chemistry. Unusual Electron-Transfer Behavior in the Oxidation of Lead Porphyrins

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Received February 22, 1972

Lead(II) octaethylporphyrin (PbOEP) undergoes two electrochemically reversible one-electron oxidations in dichloromethane, acetonitrile, or *n*-butyronitrile. In the product of the first oxidation, $PbOEP^+$, Pb(II) is covalently bound to the ring-oxidized π cation radical. However, loss of a second electron gives $PbOEP^{2+}$ which from its lability and spectral properties contains Pb(IV) weakly bound to OEP^{2-}. The properties of $PbOEP^{2+}$ are very similar to those of the ionic Ba^{2+} porphyrin complexes. The unusual pattern of oxidation is apparently a consequence of the tendency of Pb(II) to undergo net two-electron oxidation.

Introduction

An interest in the redox chemistry of metalloporphyrins is warranted by the likely involvement of ring-oxidized chlorophyll in photosynthesis and by the electron-transfer chemistry of the cytochromes. Recent work in this area has revealed two general patterns of oxidation.[2-7] For divalent metal ion complexes in which the metal ion is nonoxidizable or oxidized only with difficulty—this includes complexes of Zn^{2+}, Mg^{2+}, Cd^{2+}, and Cu^{2+}—oxidation proceeds by two reversible one-electron steps

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