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Kinetics and Equilibria of Mercury(II) Complexes with Phenanthroline, Bipyridyl, and OH^- in Aqueous Solution. *T*-Jump Study with a Novel Computational Technique for Multistep Relaxation Processes

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The equilibria of the complex formation reactions of Hg^{2+} with phen, bpy, and OH^- have been determined by pH titrations. Typically various complexes coexist in aqueous solution, mainly $Hg(phen)^{2+}$, $Hg(phen)_2^{2+}$, $Hg(phen)_3^{2+}$, $Hg(phen)(OH)^+$, $Hg(OH)_2$, or the analogous bpy species. Temperature-jump investigations in the pH range 1–10 allowed detailed elucidation of the ligand-exchange reactions of the bidentate ligands against OH^- and the formation of the 1:2 and 1:3 complexes. Typically in these reaction systems one relaxation time (in certain systems two) could be detected. Due to the overlapping equilibria, it is not obvious which step is rate-determining. Using a novel numerical approach for multistep relaxation, we developed an interactive Fortran program that allows an efficient and straightforward test of all the various possibilities. In the intermediate and alkaline pH range the rate-determining step of the ligand-exchange reactions with OH^- is governed by the concentration distribution of the reactive species. In the exergonic direction these processes correspond to diffusion-controlled reactions. In acidic solutions the 1:2 complexation occurs mainly by direct reaction with the protonated ligands. The rate constants for bpy and phen correspond to diffusion-controlled reactions whereas those for $Hbpy^+$ and $Hphen^+$ are 2 and 3 orders of magnitude below that limit. In the pH range 4–6 the formation of $Hg(phen)_3^{2+}$ could be studied separately. The reaction of the probably tetrahedral $Hg(phen)_2^{2+}$, which leads to $Hg(phen)_3^{2+}$, shows an unexpected second-order dependence on [phen].

Introduction

It is well-known that Hg(II) complexes are very labile. In particular the study of the kinetics and mechanisms of ligand-exchange reactions with CH_3Hg^{II} complexes has shown that in many cases the diffusion-controlled limit is reached.[1] From the type of rate-equilibria correlations obtained for a variety of ligands it could be concluded that these reactions follow an associative (Ia) mechanism.[1,2] The methyl group strongly favours the digonal coordination. Therefore, the question arose if this low coordination number is responsible for the extreme substitution lability of the Hg(II) complexes. Hg(II) with no alkyl or aryl ligand shows a pronounced variety of coordination geometries including all coordination numbers between 2 and 6. This structural diversity should provide the rare possibility to study the consequences of a variable coordination number on the reactivity of complexes with the same metal center. Surprisingly, since the early ligand-exchange study by Eigen and Eyring,[3] very few kinetic investigations have been applied to Hg(II) complexes.[4] This is perhaps understandable because flow methods cannot be used due to the fast equilibrations. However, chemical relaxation methods should be well suited for these studies, especially for systems like Hg(II), where typically various complexes coexist in stepwise equilibria. The chemical relaxation methods (e.g., the temperature-jump method) proved to be important tools for the study of the kinetics of elementary steps of coupled reactions in solution. Although the experimental procedures are not very complicated, they are not widespread. Methods and theory have been extensively discussed in the literature.[5,6] However, to our knowledge no straightforward practical procedure to evaluate the experimental relaxation times, τ, of a multistep reaction system to get the relevant rate constants for a set of postulated mechanisms is published. Even for systems where various simplifying assumptions, such as steady-state conditions or coupled preequilibria, are possible, the laborious derivation of the expressions for the relaxation times leads to rather complicated analytical expressions.

In this paper we present an easy and efficient method to handle the assumptions of various preequilibria and steady states for a general multistep mechanism. The main difference from the usually applied methods is that no closed analytical expression is derived. Rather, numerical terms for the rate-determining step are calculated. This procedure facilitates the testing of the concentration dependence of $1/\tau$ expressions for alternative mechanisms. An interactive Fortran program KINET was developed and has been applied to evaluate the rate constants for the various reactions of Hg(II) complexes with 1,10-phenanthroline (phen), 2,2-bipyridyl (bpy), and OH^- over the whole pH range between 1 and 10. These reactions include ligand-exchange processes that are associated with a change of the coordination number. The *T*-jump method also proved to be a powerful tool for characterizing mixed-ligand complexes of the type $Hg(phen)(OH)^+$ and $Hg(bpy)(OH)^+$.

Method of Data Treatment

The kinetics of multistep systems near the equilibrium state can be described by linear differential equations yielding the characteristic time constants (spectra of relaxation times). The methods and theory have been discussed by several authors, e.g., by Eigen and De Maeyer[5] and Bernasconi.[6] Since it is generally neither possible nor desirable to obtain exact analytical expressions for the relaxation times and relaxation amplitudes, approximate relationships are generally used to analyze relaxation experiments. For example, it is usually assumed that certain reaction steps are in equilibrium while the observed reaction proceeds or sometimes steady-state conditions are applied. For certain systems such necessary assumptions lead to complicated analytical expressions for the $1/\tau$ dependencies of the equilibrium concentrations and the kinetic constants. Of course, a rigorous comparison of theory and experimental data can only be done if exact solutions of the relaxation equations are available. But this is only possible if all kinetic, thermodynamic, and other constants (e.g., molar extinction coefficients) are known, which is normally not the case.

In this paper we present a method that allows one to evaluate relaxation data of multistep-reaction mechanisms in a much easier way. Instead of employing closed analytical expressions, a numerical term is calculated for the rate-determining step (the slowest normal mode relaxation time). According to Castellan,[7] Ilgenfritz,[8] and others, the set of independent differential equations that describes any reaction mechanism can be reduced if new dependencies are introduced by the assumption that certain reaction steps equilibrate rapidly. This implies that these fast steps are decoupled from the slower equilibrating steps, namely, the rate-determining steps. The fast steps are therefore unaffected by the slower ones.

(1) Erni, I. W.; Geier, G. *Helv. Chim. Acta* **1979**, *62*, 1007.
(2) Raycheba, J. M. T.; Geier, G. *Inorg. Chem.* **1979**, *18*, 2486.
(3) Eigen, M.; Eyring, E. M. *Inorg. Chem.* **1963**, *2*, 636.
(4) Tamura, K.; Harada, S.; Hiraissh, M.; Yasunaga, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2928.
(5) Eigen, M.; De Maeyer, L. In *Technique of Organic Chemistry*; Weissberger, A., Ed.; Interscience: New York, 1963; Vol. VIII, part 2, p 895.
(6) Bernasconi, C. F. *Relaxation Kinetics*; Academic: New York, 1976.
(7) Castellan, G. W. *Ber. Bunsen-Ges. Phys. Chem.* **1963**, *67*, 898.
(8) Ilgenfritz, G. In *Molecular Biology, Biochemistry, and Biophysics*; Pecht, I., Riegler, R., Eds.; Springer: Berlin, Heidelberg, New York, 1977; Vol. 24, p 1.

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Every individually measurable relaxation time can be analyzed by a single linear differential equation, eq 1. In the case of the

$$\frac{1}{\delta c_j}\left(\frac{\mathrm{d}(\delta c_j)}{\mathrm{d}t}\right) \equiv \frac{\delta \dot{c}_j}{\delta c_j} = -\frac{1}{\tau} \tag{1}$$

superposition of two or more relaxing effects, the relaxation times should be different by at least a factor of 10 in order to treat them as uncoupled relaxation processes. It will be shown in the following that $1/\tau$ can be factorized in two terms, for example

$$1/\tau = k_{rs}F_{rs} \tag{2}$$

where k_{rs} is the observed rate constant with the corresponding order of the reaction from state r to state s. F_{rs} is called the concentration function for the reaction from r to s as rate-determining step. F_{rs} is a function of only thermodynamic properties (concentrations and equilibrium constants). As it is not known at the beginning of the investigation which step is the rate-determining one, various reaction steps will be tested in this respect. Each reaction tested as being rate determining will be called the test reaction.

Derivation of the $1/\tau$ Relation. The reaction equation for the reversible rate-determining step under test can be written as

$$\sum_{i=1}^{N} \nu_i \mathrm{X}_i = 0$$

where ν_i is the stoichiometric coefficient of the species X_i and N species are involved directly in the test reaction. If one has to consider some side reactions (e.g., fast-equilibrating reactions), the number of kinetically relevant species may increase to R. Since the rate-determining step is treated as a "pseudo-single-step" system, we need $R - 1$ equations of mass balance and fast preequilibria to solve the differential equation, eq 3, for the advancement parameter ξ_{rs}.[9] The advancement of the test reaction, ξ_{rs}, is defined by $c_i = \nu_i\xi_{rs}$, where c_i is the concentration of X_i, and $\nu_i^{\mathrm{E}} = |\nu_i|$ for an educt species X_i or 0 for a product species X_i, respectively, and $\nu_i^{\mathrm{P}} = 0$ for an educt species X_i or $|\nu_i|$ for a product species X_i, respectively. Taking into account that the relaxing system is close to equilibrium, the differential equation, eq 3, can be expanded to a Taylor series. By neglecting quadratic and higher terms, one gets eq 4 where c_i° represents the equilibrium con-

$$\dot{\xi}_{rs} = -k_{rs}\prod_{i=1}^{N} c_i^{\nu_i^{\mathrm{E}}} + k_{sr}\prod_{i=1}^{N} c_i^{\nu_i^{\mathrm{P}}} \tag{3}$$

$$\dot{\xi}_{rs}(c_1 \ldots c_N) \cong \dot{\xi}_{rs}(c_1^\circ \ldots c_N^\circ) + \sum_{i=1}^{N} \frac{\partial \dot{\xi}_{rs}(c_1^\circ \ldots c_N^\circ)}{\partial c_i}(c_i - c_i^\circ) \tag{4}$$

centration of X_i. Since $\dot{\xi}_{rs}(c_1^\circ \ldots c_N^\circ) = 0$, and the definitions $-\delta\dot{\xi}_{rs} = \dot{\xi}_{rs}(c_1 \ldots c_N) - \dot{\xi}_{rs}(c_1^\circ \ldots c_N^\circ)$ and $\delta c_i = c_i - c_i^\circ$ are given, the differential equation, eq 4, can be rewritten:

$$-\delta\dot{\xi}_{rs} = k_{rs}\sum_{k=1}^{N}\left[\nu_k^{\mathrm{E}} c_k^{\circ\,(\nu_k^{\mathrm{E}}-1)}\prod_{\substack{i=1\\ i\neq k}}^{N} c_i^{\circ\,\nu_i^{\mathrm{E}}}\right]\delta c_k - k_{sr}\sum_{k=1}^{N}\left[\nu_k^{\mathrm{P}} c_k^{\circ\,(\nu_k^{\mathrm{P}}-1)}\prod_{\substack{i=1\\ i\neq k}}^{N} c_i^{\circ\,\nu_i^{\mathrm{P}}}\right]\delta c_k \tag{5}$$

Substituting $\delta\dot{\xi}_{rs}$ by $(1/\nu_j)\delta\dot{c}_j$ and dividing by δc_j leads to the final differential equation, eq 6, where j means any species X_j involved

$$-\frac{1}{\nu_j}\left(\frac{\delta\dot{c}_j}{\delta c_j}\right) = \frac{1}{\tau} = k_{rs}\left\{\sum_{k}^{N}\left[\nu_k^{\mathrm{E}} c_k^{\circ\,(\nu_k^{\mathrm{E}}-1)}\prod_{\substack{i=1\\ i\neq k}}^{N} c_i^{\circ\,\nu_i^{\mathrm{E}}}\right]\frac{\delta c_k}{\delta c_j} - \frac{k_{sr}}{k_{rs}}\sum_{k}^{N}\left[\nu_k^{\mathrm{P}} c_k^{\circ\,(\nu_k^{\mathrm{P}}-1)}\prod_{\substack{i=1\\ i\neq k}}^{N} c_i^{\circ\,\nu_i^{\mathrm{P}}}\right]\frac{\delta c_k}{\delta c_j}\right\} \tag{6}$$

in the test reaction. The final result from eq 6, $1/\tau = k_{rs}\{F_{rs}\}$, corresponds to the already presented eq 2.

Discussion of the $1/\tau$ Relation. The quotient $k_{sr}/k_{rs} = K_{sr}$ is the equilibrium constant for the reverse test reaction. The ratios $(\delta c_i)/(\delta c_j)$ in F_{rs} do not contain any kinetic parameters. They are uniquely determined by the linearized "equilibrium" conditions of the fast-equilibrating steps, and the mass balance equations.[8] These can be written as

$$\sum_{i=1}^{R} w_{im} c_i^\circ = \text{constant, with } m = 1, \ldots, M$$

or in linearized form

$$\sum_{i=1}^{R} w_{im}\frac{\delta c_i}{\delta c_j} = 0 \tag{7}$$

where w_{im} are the coefficients of the mass balance equations. The equilibrium conditions can be described by eq 8, or in linearized

$$\prod_{i=1}^{R} c_i^{\circ\,v_{il}} = K_l, \text{ with } l = 1, \ldots, L \tag{8}$$

form by eq 9, where v_{il} are the stoichiometric coefficients of the

$$\sum_{i=1}^{R} v_{il}\frac{1}{c_i^\circ}\left(\frac{\delta c_i}{\delta c_j}\right) = 0 = \sum_{i=1}^{R} u_{il}\frac{\delta c_i}{\delta c_j} \tag{9}$$

fast-equilibrating reactions. u_{il} is equal to the stoichiometric coefficient divided by the corresponding equilibrium concentration.

In matrix notation the two sets of equations can be combined to the system of $M + L = R - 1$ inhomogenous linear equations, eq 10. The order of the species $\mathrm{X}_1, \ldots, \mathrm{X}_R$ is maintained. Index

$$\begin{pmatrix} w_{11} & \cdots & w_{1R} \\ \vdots & & \vdots \\ w_{M1} & \cdots & w_{MR} \\ \hline u_{11} & \cdots & u_{1R} \\ \vdots & & \vdots \\ u_{L1} & \cdots & u_{LR} \end{pmatrix}\begin{pmatrix} \frac{\delta c_1}{\delta c_1} = 1 \\ \cdot \\ \cdot \\ \frac{\delta c_R}{\delta c_1} \end{pmatrix} = \begin{pmatrix} 0 \\ \cdot \\ \cdot \\ \cdot \\ 0 \end{pmatrix} \tag{10}$$

$$\begin{pmatrix} \mathbf{W} \\ \hline \mathbf{U} \end{pmatrix}\begin{pmatrix} \mathbf{d} \end{pmatrix} = 0$$

1 is reserved for a species directly involved in the test reaction. Therefore, $\mathbf{d}$ is the vector of the ratios $\delta c_i/\delta c_1$. $\mathbf{W}$ is the matrix of the mass balance equations. $\mathbf{U}$ is the matrix of the fast-established preequilibria.

This system of inhomogenous linear equations can easily be solved by an appropriate numerical method.[10] This numerical method replaces the traditional approach in the field of relaxation kinetics, which consists of the successive elimination of the variables $(\delta c_i/\delta c_1)$ until a closed analytical expression for $\delta\dot{c}_1/\delta c_1$ or $1/\tau$ is obtained. The "traditional" procedure is very time consuming. Moreover, prediction of the effects of experimental conditions on the relaxation time by use of these expressions is often restricted. For example, the assumption of a steady state or a buffered species is not valid over the entire range of concentrations. (For the complexity of analytical expressions of F_{rs}, compare, for instance, the numerous examples given in Czerlinski's book.[11])

Since in a general multistep reaction mechanism the rate-determining step is not known at the beginning of the investigation, the possibility of each step being rate determining has to be compared with the experimental data. This is performed with the interactive program KINET on a HP-1000 computer equipped with a Fortran 77 compiler and an RTE 6 operating system.[12] The first step in this program is the calculation of the concentrations of all the species in solution from known equilibrium constants and total concentrations (Newton algorithm). Then

(9) The definition of advancements, ξ', is actually based on mole numbers. The variable ξ introduced in eq 3 is thus related to the advancements by $\xi = \xi'/V$, where V is the volume; see ref 8.

(10) IMSL-Library, Edition 9, 1982, Houston, TX.
(11) Czerlinski, G. H. *Chemical Relaxation*; Marcel Dekker, New York: 1966.
(12) The program KINET is available upon request from the authors.

Table I. pH Titrations of Hg/phen and Hg/bpy Solutions

10^3[Hg]$_t$, M	10^3[N-N]$_t$, M	no. of titrations	no. of data points	
			a	*b*
2		2	10[c]	
2	1	2	24	18
1	1	2	22	17
1	2	2	8	21[d]
1	3	2	9[e]	18

[a] Acid range of the titration curves (evaluation of β_1, β_2, and β_{11}). [b] Alkaline range of the titration curves (evaluation of β_2, β_3, β_{11}, and β_{21}). [c] Evaluation of the pK_a values of Hg^{2+}. [d] Evaluation in the alkaline range only. [e] Evaluation of K_3 in the acid range.

the user interactively inputs the kinetically important species (X_1, ..., X_R) that are part of the reaction mechanism including any side reaction. Afterward he inputs the slowest step (test reaction) by means of the stoichiometric coefficients. The description of the mechanism is completed by the definition of the matrix of the mass balances (coefficients, w_{im}, only), and the matrix of the fast-equilibrating reactions (only stoichiometric coefficients, v_{il}, are needed. The division by c_i° is effected within the program). The calculation of the concentration function F_{rs} is then performed for all the experimental samples by means of the IMSL subroutine LEQT1F.[10] The results are transferred to a commercially available program, MATLAB,[13] where the graphical correlation of experimental and calculated time constants can be examined interactively on a graphics terminal (HP 2648A). This procedure can be performed for any other test reaction until the best chemically consistent correlation is found. The observed rate constant, k_{rs}, is usually a rate constant for a single reaction step (e.g., from the slope of a straight line through the origin if $1/\tau$ vs. F_{rs} is plotted). It may, however, consist of more than one term in cases where consecutive steady states or parallel reaction paths are contributing to the rate determining step. Here, conventional methods to derive k_{obsd} are appropriate for the evaluation of k_{rs}.

Experimental Section

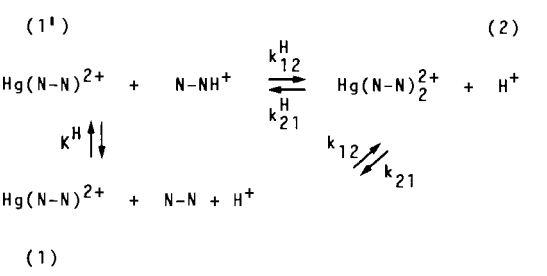
Chemicals. A stock solution of 0.05 M $Hg(NO_3)_2$ (Merck) was used for preparing all the samples containing either 1,10-phenanthroline or 2,2'-bipyridyl (both from Fluka, puriss). The ionic strength of I = 0.1 M was maintained with KSO_3CH_3, which was obtained by recrystallization of the crude product from the neutralization of HSO_3CH_3 (Fluka, puriss) with aqueous KOH.

Equilibrium Measurements. The determinations of the equilibrium constants were carried out by potentiometric pH titrations following the method of Anderegg.[14,15] The pH values of the solutions were defined by using the concentration of the hydrogen ions, pH = −log [H^+], in the standard state used, given by the supporting electrolyte (0.1 M KSO_3CH_3) in pure water. The instrumental setup was previously described.[16] The total concentrations used for the titrations are given in Table I. The calculations of the constants were performed with the KVARI program.[17]

Kinetic Measurements. The temperature-jump experiments were performed by means of a double beam instrument by Messanlagen Studiengesellschaft, Göttingen, West Germany. The temperature-jump apparatus was interfaced to a HP-1000 computer through a transient recorder (Maurer, TM 110 and TM 1009, Luzern, Switzerland).[18] All kinetic measurements were performed at 25 °C, and I = 0.1 M (KSO_3CH_3). The pH of each solution was measured with a glass electrode, which was standardized as described elsewhere.[16] The pH of the solutions was varied by adding small amounts of HSO_3CH_3 or KOH (0.1 M). The relaxation times were resolved from the digital kinetic data on a HP-1000 computer using the EVALU program.[18] The τ values were reproducible within 10%.

The formation of the 1:2 complexes, $Hg(N\text{-}N)_2^{2+}$ with N-N = phen or bpy, was examined in acidic solutions (pH 1–3) by monitoring the absorbance change of the protonated ligands, $N\text{-}NH^+$, and the coordinated ligands, $Hg(N\text{-}N)_2^{2+}$. The ligand-exchange reactions between N-N and OH^- were examined in the pH region above 7 (absorbance change between free and coordinated N-N). With phen two separate relaxations occured. The slow one was also detected in the intermediate pH region (pH 4–6). With bpy only one (fast) relaxation was detected throughout the whole pH region.

Scheme I



Results and Discussion

Equilibrium Studies. Because the complexes of Hg(II) with the ligands phen and bpy are very stable, it is not possible to determine the complex formation constant directly by means of the pH method. On the other hand, it is well-known that the hydrolysis produces only soluble $Hg(OH)_2$[19] in contrast to other metal ions where polynuclear species are formed. Therefore, the ligand-exchange reaction with OH^- ion, eq 11, is well suited for

$$Hg(N\text{-}N)_n^{2+} + 2OH^- \rightleftharpoons Hg(OH)_2 + n\text{N-N} \qquad (11)$$

studying the stability of the $Hg(N\text{-}N)_n^{2+}$ complexes (n = 1–3). Anderegg[14] introduced this method many years ago. However, he neglected the occurence of mixed-ligand complexes. Since our kinetic studies showed that such species, e.g., $Hg(N\text{-}N)(OH)^+$, are very important intermediates, we have undertaken a reinvestigation of this equilibrium study. Due to solubility problems in 0.1 M $NaNO_3$[14] we used 0.1 M KSO_3CH_3 as the inert electrolyte. Our results and data from the literature are summarized in Table II. Our β_1 value for Hg^{II}(bpy) is noticeably smaller than that of the literature. This is probably a consequence of the pHg method, which was applied by Anderegg for the determination of this particular constant. He assumed that no Hg(I)–bpy complexes are present. On the other hand, Davidson[20] found that the normal application of the pHg method yields an equilibrium constant that is too large in the case of aniline because Hg(I) complexes are formed. In fact $Hg_2(phen)(NO_3)_2$ could be obtained from aqueous solution and characterized by X-ray diffraction.[21] In this connection it is interesting to note that Wilkins[22] mentioned in a kinetics paper that Anderegg's β_1 value might be too large. The formation rate constant (k_f, eq 12) that Wilkins

$$Hg^{2+} + bpy \underset{k_d}{\overset{k_f}{\rightleftharpoons}} Hg(bpy)^{2+} \qquad (12)$$

calculated from the dissociation rate constant (log k_d = 1.4) yields an "alarmingly high" value of 1×10^{11} M^{-1} s^{-1}. On the basis of our β_1 value, $k_f = 5 \times 10^9$ M^{-1} s^{-1} is obtained, which is reasonably in line with a diffusion-controlled reaction for water substitution in CH_3Hg^+.[1]

The other new result of the equilibrium study is the fact that mixed-ligand complexes, namely $Hg(N\text{-}N)(OH)^+$, $Hg(N\text{-}N)_2(OH)^+$, and possibly $Hg(N\text{-}N)(OH)_2$ exist in significant concentrations. The relative large uncertainties in the β_{11} values result from the correlation between β_2 and β_{11} in the calculation of the equilibrium constants. However, our kinetic study proves not only qualitatively the existence of mixed complexes but agrees also significantly with the numerical values for β_{11}. Additional

(13) Moler, C. "MATLAB", University of New Mexico.
(14) Anderegg, G. *Helv. Chim. Acta* **1963**, *46*, 2397.
(15) We thank Prof. G. Anderegg and his group for the guidance and advice in carrying out the titrations.
(16) Anderegg, G.; Wanner, H. *Inorg. Chim. Acta* **1986**, *113*, 101.
(17) Anderegg, G. "KVARI Algol program", ETH Zürich, CH-8092 Zürich, Switzerland.
(18) Gross, H. Dissertation No. 7482, ETH Zürich, 1984.
(19) *Stability Constants of Metal Ion Complexes*; Special Publication No. 17; The Chemical Society: London, 1964.
(20) Wirth, T. H.; Davidson, N. *J. Am. Chem. Soc.* **1964**, *86*, 4314.
(21) Elder, R. C.; Halpern, J.; Pond, J. S. *J. Am. Chem. Soc.* **1967**, *89*, 68.
(22) Wilkins, R. G.; Holyer, R. H.; Hubbard, C. D.; Kettle, S. F. A. *Inorg. Chem.* **1965**, *4*, 929.

Table II. Stability Constants of Hg(II) Complexes with phen and bpy and Mixed-Ligand Complexes with OH^- at 25 °C and I = 0.1 M (KSO_3CH_3)

reaction	constant	ligand L: phen[c]	bpy[d]	OH^-[e]
$Hg^{2+} + L \rightleftarrows HgL^{2+}$	$\log \beta_1$	9.85 (0.3)[a]	8.30 (0.2)[a]	10.20 (0.08)[a]
			9.64[b]	10.0[b]
$Hg^{2+} + 2L \rightleftarrows HgL_2^{2+}$	$\log \beta_2$	19.04 (0.05)[a]	16.33 (0.05)[a]	21.20 (0.03)[a]
		19.65[b]	16.70[b]	21.40[b]
$Hg^{2+} + 3L \rightleftarrows HgL_3^{2+}$	$\log \beta_3$	23.13 (0.05)[a]	19.04 (0.08)[a]	
		23.35[b]	19.54[b]	
$Hg^{2+} + L + OH^- \rightleftarrows HgL(OH)^+$	$\log \beta_{11}$	19.85 (0.30)[a]	18.15 (0.30)[a]	
$Hg^{2+} + 2L + OH^- \rightleftarrows HgL_2(OH)^+$	$\log \beta_{21}$	23.35 (0.30)[a]	<20.65[a]	
$Hg^{2+} + L + 2OH^- \rightleftarrows HgL(OH)_2$	$\log \beta_{12}$	<24.2[a]		

[a] This work, uncertainty in brackets. [b] Reference 13; I = 0.1 M ($NaNO_3$) at 20 °C. [c] pK_a(phen) = 4.89 (0.01), $\log \chi_2 = \log([(phen)_2H]/[H][phen]^2) = 6.68$ (0.22), ref 15. [d] pK_a(bpy) = 4.38 (0.01), ref 15. [e] pK_w = 13.75 (0.02).

Table III. Temperature-Jump Data of the 1:2 Complex Formation Reactions at 25 °C and I = 0.1 M ($(K,H)SO_3CH_3$)

	pH	$10^3[Hg]_t$, M	$10^3[N\text{-}N]_t$, M	$10^{-2}(1/\tau)$, s^{-1}	10^5F_{12}, M
phen	1.00	5.00	10.00	32.2	34.2
	1.00	0.500	1.000	8.79	10.3
	1.00	0.050	0.100	2.71	2.95
	1.00	0.005	0.010	0.625	0.703
	2.11	1.00	2.00	23.7	4.23
	1.75	1.00	2.00	18.3	6.37
	2.16	0.10	0.200	4.96	1.24
	1.80	0.10	0.200	5.05	1.85
bpy	1.92	1.00	2.00	217	10.3
	2.14	1.00	2.00	141	8.04
	2.57	1.00	2.00	100	4.91
	3.02	1.00	2.00	95.2	2.92

Table IV. Logarithms of Rate Constants (M^{-1} s^{-1}; s^{-1}) for the Formation and Dissociation of $Hg(phen)_2^{2+}$ and $Hg(bpy)_2^{2+}$[a]

	phen	bpy
$\log k_{12}$	~10.4	~9.5
$\log k_{21}$	1.2	~1.5
$\log k_{12}^H$	6.76	8.29
$\log k_{21}^H$	2.46	4.64

[a] Conditions: 25 °C; I = 0.1 M ($(K,H)SO_3CH_3$). Estimated error: ±0.2 log unit.

methods, namely UV and ^1H NMR spectroscopy[18] support the results from the pH titrations.

Kinetic Studies. (A) 1:2 Complex Formation. Due to the high stabilities of $Hg(phen)_2^{2+}$ and $Hg(bpy)_2^{2+}$, dissociation occurs only in strongly acidic solutions, where the free ligands are protonated. This means that the temperature-jump method can only be applied under conditions where the protonated ligands react with Hg(II). In fact, $Hbpy^+$ dominates the kinetics of the 1:2 complex formation in such solutions, whereas with phen both pathways occur; cf. Scheme I. Since the protonation $\mathbf{1} \rightleftharpoons \mathbf{1}'$ (with the protonation constants K^H) is rapid under the conditions used,[23] the reciprocal relaxation time $1/\tau$ is given by eq 13, where F_{12} is the concentration function, cf. eq 2. The experimental results are summarized in Table III. For a fixed pH $1/\tau$ correlates linearly with F_{12}. With increasing pH the slope increases which proves that k_{12}^{obsd} shows two terms as given in eq 13. A linear least-squares analysis

$$1/\tau = k_{12}^{obsd}F_{12} = (k_{12}^H + k_{12}/K^H[H])F_{12} \qquad (13)$$

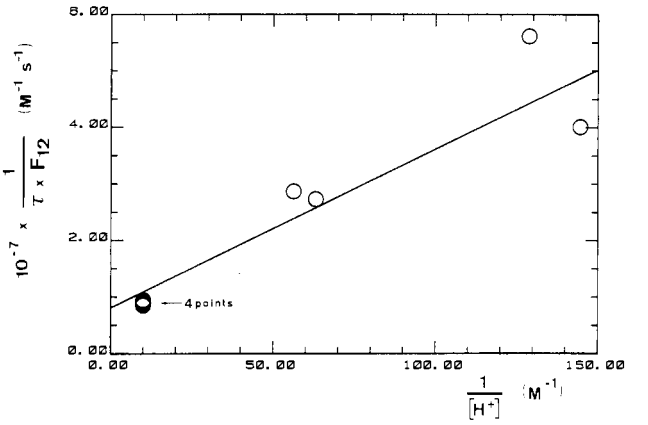
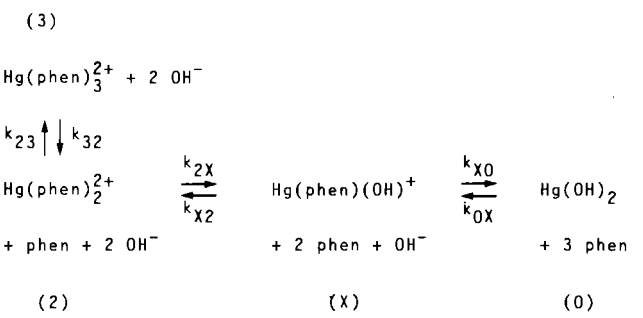


Figure 1. Analysis of the formation of $Hg(phen)_2^{2+}$ according to eq 13.

Scheme II



of the data in Figure 1 yields the kinetic constants given in Table IV. The value of k_{12} for phen ($\log k_{12}$ = 10.4) seems to be too large for even a diffusion-controlled reaction. However, one has to take into account that the stability constant K_1 is not very accurate, which leads to some uncertainties in the calculations of the concentrations of the reactive species and of F_{12}. k_{12} for bpy is only an approximate value ($\log k_{12} \approx 9.5$) because the contribution to $1/\tau$ of the free ligand is very small. Nevertheless, there seems to be no significant difference in rate constants for 1:1 complex formation (calculated from Wilkins'[22] dissociation rate constant; cf. equilibrium part) and for 1:2 complex formation. Both reactions are probably diffusion-controlled, and the corresponding rate constants for water substitution must be almost as high as 10^{10} s^{-1}. The same order of magnitude was found for water substitution in $CH_3HgOH_2^+$.[1] The ratio k_{12}/k_{12}^H, a measure for the decreased rates with the protonated bidentate ligands, is larger for phen (1.2×10^3) than for bpy (80). This reflects the higher flexibility of bpy. Similar ratios were found for complex formation reactions with other metal ions.[24]

(B) Kinetics of the Ligand-Exchange Reactions of $Hg(N\text{-}N)_n^{2+}$ with OH^-. N-N = phen. The exchange of phen by OH^- takes

(23) A reviewer has asked us to comment on the papers of Ando et al. (Ando, I.; Ujimoto, K.; Kurihara, H. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 713, 2881). These authors stated that pyridine and pyridine derivatives show quite slow protolytic behavior. E.g. with phen they obtained for the protonation rate constant $k_{11'} = 2.5 \times 10^4$ M^{-1} s^{-1}. We have checked these protolytic reactions with phen, bpy, and pyridine and found that the relaxation times are within the heating time of our apparatus (<2 × 10^{-6} s). Consequently, a lower limit for $k_{11'}$ can be estimated (>7 × 10^9 M^{-1} s^{-1} for phen), which is in line with numerous papers including the early article by Eigen (Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1). We have no explanation for the data reported by Ando et al.

(24) Margerum, D. W.; Gayley, G. R.; Weatherburn, D. C.; Pagenkopf, G. K. In *Coordination Chemistry*; ACS Monograph 174; American Chemical Society: Washington, DC, 1978; Vol. 2, p 53.

Table V. Temperature-Jump Data in the Hg/phen/OH^- System at 25 °C and I = 0.1 M (KSO_3CH_3)[a]

pH	10^5[Hg]$_t$, M	10^5[phen]$_t$, M	$10^{-3}(1/\tau)$, s^{-1}	10^5F_{2X}, M
7.17	3.75	7.52	3.07	0.240
7.86	3.75	7.52	14.4	0.633
8.58	3.75	7.52	36.5	1.83
9.13	3.75	7.52	65.3	3.05
7.16	2.00	6.00	84.1	0.279
7.86	2.00	6.00	16.7	0.487
8.22	2.00	6.00	22.4	0.812
8.44	2.00	6.00	27.9	1.12
8.55	2.00	6.00	36.6	1.30
8.75	2.00	6.00	52.8	1.62
9.16	2.00	6.00	58.5	2.81
6.93	4.00	5.00	1.77	0.127
7.17	4.00	5.00	2.77	0.184
7.43	4.00	5.00	3.86	0.263
7.59	4.00	5.00	4.78	0.326
7.87	4.00	5.00	7.77	0.477
8.21	4.00	5.00	13.7	0.797
8.55	4.00	5.00	30.4	1.31
8.74	4.00	5.00	37.5	1.66
9.15	4.00	5.00	55.1	2.84
8.25	1.50	10.0	24.3	1.11
8.55	1.50	10.00	25.2	1.56
8.75	1.50	10.00	32.8	1.93
9.13	1.50	10.00	46.7	2.94

[a] All solutions contain Bistris buffer (the total concentration is 1 × 10^{-3} M except in the first five solutions where the concentration is 5 × 10^{-4} M).

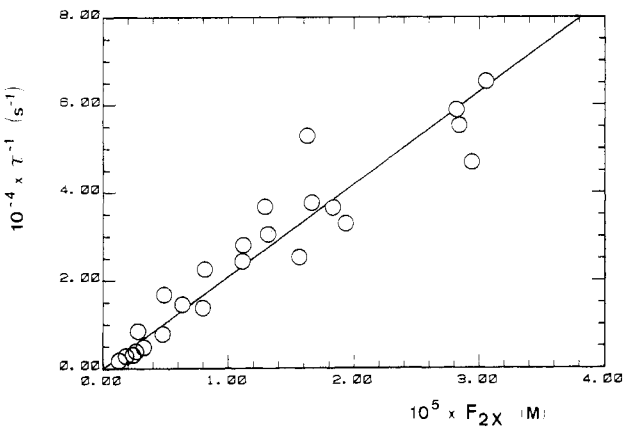


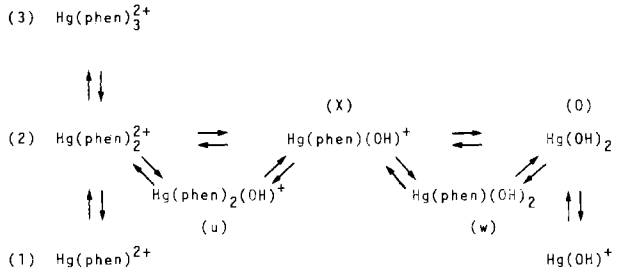
Figure 2. Resolution of k_{2X} from relaxation data for the Hg/phen/OH^- system.

place in the pH range 7–10, where two T-jump relaxations were always detected. In agreement with the relative size of the relaxation amplitude, the fast relaxation time could be assigned to the overall reaction, eq 14. The slower relaxation time is discussed

$$\mathrm{Hg(phen)}_n^{2+} + 2\mathrm{OH}^- \rightleftharpoons \mathrm{Hg(OH)_2} + n\mathrm{phen} \qquad n = 2, 3 \tag{14}$$

in section C because it corresponds to a reaction in which no OH^- ligand is involved. This can be demonstrated by measurements of solutions with a large excess of phen. In a pH region where the exchange reaction with OH^- does not yet occur, the slow relaxation is still observed. Detailed mechanistic analysis of the kinetic data with the help of the program KINET showed that Scheme II is relevant for the mechanism of the fast process. Under the experimental conditions used, all protolytic side reactions with phen and the present buffer can be treated as preequilibria. The possibility of all the various steps being rate determining was tested. A good fit is only obtained if the reaction step **2** ⇌ **X** is treated as rate limiting, whereas for **X** ⇌ **O** the equilibrium is established and **2** ⇌ **3** is a "slow" step. The relaxation of such a reaction system is described by $1/\tau = k_{2X}F_{2X}$ (cf. data treatment part). The plot of $1/\tau$ vs. F_{2X} (Figure 2, Table V) is sensitive to the

Scheme III



stability constant of the mixed-ligand complex $Hg(phen)(OH)^+$. K_{2X} was varied within 2 orders of magnitude. The best fit is obtained with log K_{2X} = 0.80, which is in agreement with the potentiometrically determined β_{11} value. With log K_{2X} values, which are smaller or larger by 0.3 log units, curved plots are obtained. The slope of the straight line in Figure 2 yields k_{2X} = 2.1 × 10^9 M^{-1} s^{-1}, and for k_{X2} one gets 3.3 × 10^8 M^{-1} s^{-1}. The rate constant of this ligand-exchange reaction is close to the limiting value for a diffusion-controlled process. Therefore, the rate constants for **X** ⇌ **O** cannot be much above these values. Actually, this reaction step can be treated as preequilibrium if $k_{XO} \geq 2 \times 10^9$ M^{-1} s^{-1} and $k_{XO} \geq 9 \times 10^7$ M^{-1} s^{-1} (with K_{XO} = 20). This shows that this reaction is governed by the concentration distribution of the reactive species.

In the following discussion, various alternative mechanisms will be considered. Because at the beginning of this study not even the mixed-ligand complex $Hg(phen)(OH)^+$ was established, a variety of steps including the dissociation pathway over the 1:1 complex had to be checked. The corresponding elementary reactions that were analyzed with regard to rate-limiting steps are presented in Scheme III (For simplicity, only the Hg-containing species are included in this scheme). The high stability of the 1:2 complex with $k_{21} = k_{12}/K_{12} \leq 1$ M^{-1} s^{-1} would give rise to relaxation times above 1 s if dissociation occurred. In the concentration range used, no such slow relaxation was detected. Therefore, this pathway could be excluded. According to their stability constants (cf. Table II) and therefore low concentrations, the steady-state approximation can be applied to the intermediate species **w** and **u** in the concentration range used in this study. The direct pathway (k_{2X}') is not distinguishable from the indirect one via **u**, as indicated by eq 15. By similar arguments the pathways

$$k_{2X} = k_{2X}' + \frac{k_{2u}k_{uX}}{k_{u2} + k_{uX}} \qquad k_{X2} = k_{X2}' + \frac{k_{Xu}k_{u2}}{k_{u2} + k_{uX}} \tag{15}$$

from **O** to **X** are not resolvable in their direct and indirect parts. We have no indications that $Hg(phen)_3^{2+}$ can react directly with OH^-. A few samples, as listed in Table V, contain appreciable concentrations of the 1:3 complex. However, the $1/\tau$ values do not deviate from the correlation in Figure 2. Therefore, the reaction mechanism may be reduced to Scheme II, which is already given. To localize the rate-determining step within this simplified mechanistic scheme all possibilities were tested for correlations of $1/\tau$ vs. F_{rs} by means of the program KINET. It is interesting to note that these tests also provide a check of the potentiometrically determined equilibrium constants of the Hg(II) complexes. The plots of $1/\tau$ vs. F_{rs} are indicative not only of the rate-determining step but also of the reliability of the equilibrium concentrations of the species and therefore the accuracy of the stability constants.

It is rather surprising that the rate constants for both steps from **2** to **O** are close to the maximum possible value of diffusion-controlled reactions. In spite of the fact that Hg(II) complexes with quite different structures are involved (presumably tetrahedral $Hg(phen)_2^{2+}$, $Hg(phen)(OH)^+$ with coordination number three, and digonal $Hg(OH)_2$) they all turn out to be extremely labile. The analogous ligand-exchange reaction of phen with OH^- at methylmercury(II) is also diffusion-controlled.[25] However, the

(25) Geier, G.; Erni, I. W.; Steiner, R. *Helv. Chim. Acta* **1977**, *60*, 9.

Table VI. Temperature-Jump Data in the Hg/bpy/OH^- System at 25 °C and I = 0.1 M (KSO_3CH_3)[a]

pH	$10^4[Hg]_t$, M	$10^4[bpy]_t$, M	$10^{-3}(1/\tau)$, s^{-1}	10^4F_{OX}, M
8.70	0.30	0.80	50.0	87.4
8.38	0.30	0.80	21.5	39.9
8.03	0.30	0.80	10.1	16.4
7.54	0.30	0.80	3.51	4.74
7.14	0.30	0.80	1.48	1.91
6.17	0.30	0.80	0.524	0.351
5.47	0.30	0.80	0.346	0.200
8.03	0.30	0.40	11.0	17.4
7.56	0.30	0.40	3.21	5.17
7.14	0.30	0.40	1.60	2.01
6.51	0.30	0.40	0.800	0.699
6.19	0.30	0.40	0.541	0.446
5.57	0.30	0.40	0.493	0.185
8.76	0.50	2.00	56.4	98.3
8.45	0.50	2.00	29.8	52.4
8.06	0.50	2.00	12.6	23.4
7.55	0.50	2.00	4.26	6.37
7.14	0.50	2.00	2.13	2.36
6.52	0.50	2.00	1.79	1.12

[a] All solutions contain Bistris buffer (5×10^{-4} M total concentration).

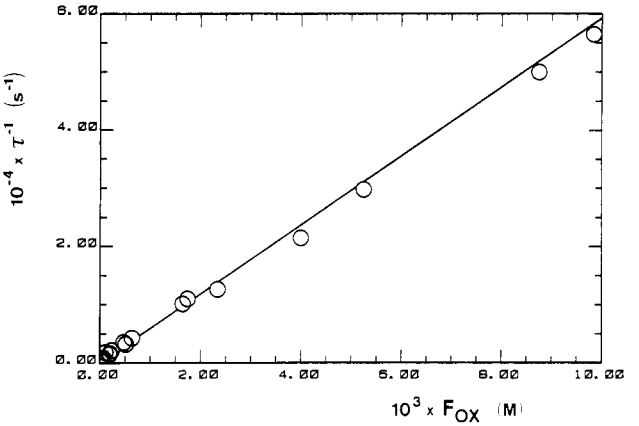


Figure 3. Resolution of k_{OX} from relaxation data for the Hg/bpy/OH^- system.

exchange reactions of unidentate ligands with OH^- show rates that are clearly below the maximum limit.[1]

N-N = bpy. In contrast to the phen system for the analogous exchange reaction of bpy by OH^-, eq 14, only one relaxation was detected. As a result of the lower stability of the bpy complexes, the reactions occur in a lower pH region (pH 6–8), and the 1:3 complex is too weak to be present under the experimental conditions used (cf. Table II). Scheme II can be simplified accordingly. Analogous to the phen system the kinetic data were analyzed with the help of the KINET program. A good fit is obtained by plotting $1/\tau$ vs. F_{OX} (cf. Figure 3 and Table VI). From the slope of the straight line one obtains $k_{OX} = 5.8 \times 10^6$ M^{-1} s^{-1}. For the calculation of F_{OX} the equilibrium constant log $K_{OX} = -3.1$ was used, which is in agreement with the potentiometrically determined stability constants (cf. Table II). Correspondingly, one gets $k_{XO} = 6.3 \times 10^9$ M^{-1} s^{-1}. For the alternative plot $1/\tau$ vs. F_{2X} no linear correlation is obtained. This is understandable if one considers that $Hg(bpy)(OH)^+$ is present in only small concentrations. The step $\mathbf{X} \rightleftharpoons \mathbf{O}$ becomes rate-limiting though the constant k_{XO} corresponds to an almost diffusion-controlled process. If $k_{2X} \geq k_{XO}$ the step $\mathbf{2} \rightleftharpoons \mathbf{X}$ is in an equilibrium state because the concentration of $Hg(bpy)_2^{2+}$ is always greater than that of $Hg(bpy)(OH)^+$ under the experimental conditions. To summarize, the enormous reactivities of $Hg(bpy)_2^{2+}$ and $Hg(bpy)(OH)^+$ toward OH^- are very similar to those of the corresponding phen complexes.

(C) "Slow" Relaxation in the $Hg(phen)_2^{2+}/Hg(phen)_3^{2+}$ System. In Hg(II)–phen solutions with pH values between 5 and 10, two relaxations are detected. As described in section B the fast one with the larger amplitude can be assigned to the exchange reaction in which the mixed-ligand complex $Hg(phen)(OH)^+$ is involved. The slower relaxation (τ between 1 and 15 ms) always has a much smaller amplitude. The amplitude of the signal increases with an increasing amount of $Hg(phen)_3^{2+}$. With sufficient concentration of phen, the equilibria can be shifted such that between pH 4 and 6 mainly $Hg(phen)_3^{2+}$, $Hg(phen)_2^{2+}$, and free phen are present, whereas the concentrations of the complexes with the OH^- ligands are negligible. In these solutions the fast relaxation is no longer detectable, but the slow relaxation has a rather large amplitude and can be determined with the usual precision. In Table VIII these τ values are listed together with the total concentrations of the reactants. It is quite obvious that this relaxation is to be assigned to a reaction in which $Hg(phen)_3^{2+}$ is involved. Surprisingly the $1/\tau$ values cannot be correlated with the concentration function F_{23}, which corresponds to a simple $Hg(phen)_3^{2+}$ formation reaction (cf. Scheme II) in which the protonation reactions are in preequilibrium. In Figure 4 it is seen that the curved shape of the plot $1/\tau$ vs. [phen] indicates a quadratic dependence on [phen]. This shows that a mechanism is operating where two phen molecules are required for the complex formation reaction. The simplest overall reaction would be presented by eq 16. The

$$Hg(phen)_2^{2+} + 2phen \overset{k_{23}^{obsd}}{\rightleftharpoons} Hg(phen)_3^{2+} + phen \quad (16)$$

corresponding correlation is $1/\tau = k_{23}^{obsd}F_{23}'$ where F_{23}' is the

Table VII. Logarithms of the Rate Constants (M^{-1} s^{-1}) of the Reactions with the Mixed-Ligand Complexes $Hg(N\text{-}N)(OH)^+$ at 25 °C and I = 0.1 M (KSO_3CH_3)[a]

reaction	constants	
$Hg(phen)_2^{2+} + OH^- \underset{k_{X2}}{\overset{k_{2X}}{\rightleftharpoons}} Hg(phen)(OH)^+ + phen$	log k_{2X} 9.3	log k_{X2} 8.5
$Hg(bpy)(OH)^+ + OH^- \underset{k_{OX}}{\overset{k_{XO}}{\rightleftharpoons}} Hg(OH)_2 + bpy$	log k_{XO} 9.8	log k_{OX} 6.8

[a] The estimated error of the rate constants is ±0.2 log unit.

Table VIII. Temperature-Jump Data in the $Hg(phen)_2^{2+}/Hg(phen)_3^{2+}$ System at 25 °C and I = 0.1 M (KSO_3CH_3)

pH	$10^3[Hg]_t$, M	$10^3[phen]_t$, M	$10^{-2}(1/\tau)$, s^{-1}	10^4F_{23}, M	$10^8F_{23}'$, M
5.82	0.33	1.00	2.95	3.35	4.19
4.55	0.33	1.00	1.29	2.79	1.73
4.04	0.33	1.00	0.797	1.89	0.585
3.74	0.33	1.00	0.758	1.39	0.257
3.46	0.33	1.00	0.667	1.10	0.119
5.81	0.66	2.00	9.70	4.68	9.02
5.28	0.66	2.00	8.58	4.58	7.68
4.62	0.66	2.00	4.13	4.26	4.54
4.04	0.66	2.00	1.66	3.01	1.57
4.50	3.30	10.00	23.0	10.4	27.0

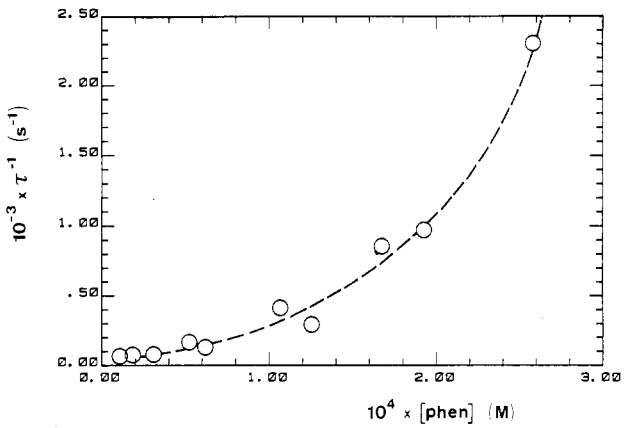


Figure 4. Variation of $1/\tau$ with [phen] in the $Hg(phen)_2^{2+}/Hg(phen)_3^{2+}$ system.

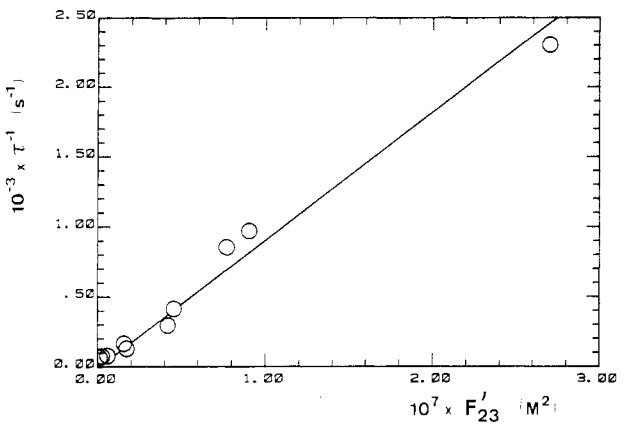
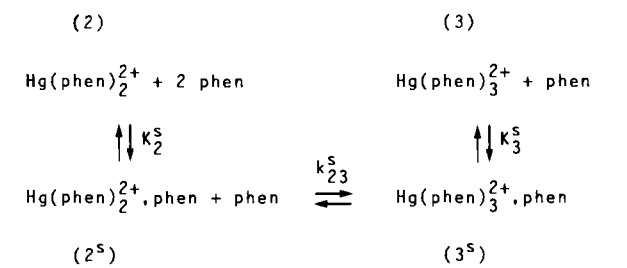


Figure 5. Resolution of k_{23}^{obsd} from relaxation data for the Hg(phen)$_2^{2+}$/Hg(phen)$_3^{2+}$ system.

Scheme IV



concentration function that takes into account the second-order dependence in [phen]. The protonation of phen can be considered as a fast reaction. Figure 5 shows that a good linear correlation is obtained indeed. From the slope of the straight line one gets $k_{23}^{obsd} = 9.0 \times 10^9$ M^{-2} s^{-1}. The question arises as to the reason for such an unexpected catalytic process. To our knowledge there is no published kinetic study of the reaction between the 1:2 and 1:3 phen complex of any metal ion. If an octahedral Hg(phen)$_2$(OH$_2$)$_2^{2+}$ were involved one could hardly see any reason for such an unusual rate law. However, Hg(phen)$_2^{2+}$ is probably tetrahedral, which is rather common for Hg(II) complexes with N donors. An X-ray structural analysis of [Hg(phen)$_2$][NO$_3$]$_2$ shows a distorted tetrahedral geometry,[26] whereas for Hg(phen)$_2$(SCN)$_2$ a distorted octahedral structure was found.[27] Most likely, the tetrahedral Hg(phen)$_2^{2+}$ exhibits a relative inertness. A certain inertness was found for other tetrahedral d^{10} complexes, e.g., chelates of Cu(I), Ag(I), and Au(I) with bidentate phosphines. ^{31}P NMR measurements showed that the ligand-exchange reactions are much slower than those with unidentate ligands.[28] On the basis of the unambiguous second-order dependence on [phen] we propose that the tetrahedral Hg(phen)$_2^{2+}$ complex is activated by stacking interaction of an uncoordinated phen with a coordinated one. This fast step opens the entrance into the coordination sphere of Hg(II) where a further phen is coordinated to yield an octahedral Hg(phen)$_3^{2+}$ complex; cf. Scheme IV. Stacking interaction with phen and phen complexes is a well-known phenomenon. For example, in the solid state such stacking is clearly indicated in [Sr(phen)$_2$(OH$_2$)$_4$][ClO$_4$]$_2$·2phen and [Ba(phen)$_2$(OH$_2$)$_4$][ClO$_4$]$_2$·2phen.[29] ^{1}H NMR studies revealed self-stacking in aqueous solutions of Hphen$^+$,[30] phen, Zn(phen)$^{2+}$,[31] and Ru(phen)$_3^{2+}$.[32] Recently it was shown that flattening distortions in tetrahedral complexes of Cu(I) and Ag(I) with tetramethylbipyridyl can be traced to stacking interactions involving the heteroaromatic rings.[33] This type of distortion may be seen in connection with the proposed activation of Hg(phen)$_2^{2+}$. It should be mentioned that the type of stacking interaction described by Margerum[34] is different. He found enhanced rate constants for mixed-ligand-complex formations when free and coordinated heteroaromatic ligands are involved. This effect is due to stabilization of outer-sphere complexes. In our reaction system the stacked ligand is not coordinated directly to the Hg(II) as the reaction proceeds, but a further phen is finally bound.

By means of ^{1}H NMR measurements we have tried to check the proposed stacking interaction in the Hg(II) system, between pH 1 and 12. The chemical shifts are clearly dependent on the concentrations of phen and the Hg(II) complexes. The spectra show averaged signals that are typical for dynamic systems with fast ligand-exchange reactions on the NMR time scale (which is in qualitative agreement with the T-jump kinetics). It is not possible to decide if, in addition to the complex formation reactions, stacking interactions with further phen molecules occur.

In accordance with the postulated mechanism in Scheme IV the evaluated third-order rate constant may be interpreted as $k_{23}^{obsd} = K_2^s k_{23}^s$ for small K_2^s. K_2^s is the equilibrium constant for the fast association of a phen at the periphery of Hg(phen)$_2^{2+}$, and k_{23}^s is the rate constant for the reaction with a further phen, which leads to the stacked Hg(phen)$_3^{2+}$,phen. The latter complex is in rapidly established equilibrium with the normal octahedral Hg(phen)$_3^{2+}$ and free phen. In reference to the stacking interaction in solutions with various phen species,[30-32] K_2^s may be estimated between 10 and 10^2. This means that under the experimental conditions in our kinetic study approximately 1% of the complexes were present in the activated stacked forms. The second-order rate constant k_{23}^s is only a factor of 10^{-2} below the diffusion-controlled limit.

The question arises why the Hg(II)/bpy system does not show similar effects. As already mentioned all the T-jump experiments with bpy give rise to only one relaxation, which could be assigned to the ligand-exchange reaction in which the mixed-ligand complex Hg(bpy)(OH)$^+$ is involved. Due to the much lower stability of Hg(bpy)$_3^{2+}$, its concentration was always negligible. Also with other phenanthrolines we could not detect a second relaxation. For example, we used 2,9-dimethyl-1,10-phenanthroline, which easily forms tetrahedral 1:2 complexes, whereas octahedral 1:3 complexes are not favorable by steric reasons.

Finally, we should mention some rejected mechanistic alternatives. The second-order [phen] dependence is also understandable if one assumes that a phen molecule reacts in a first step unidentatively with Hg(phen)$_2^{2+}$. In a rate-determining second step a further phen is bound as a chelate ligand, and following this one phen is released. However, it seems unlikely that the rigid phen ligand is suitable to activate Hg(phen)$_2^{2+}$ by unidentate coordination. A further alternative in correspondence with a second-order [phen] dependence would be a mechanism in which a dimeric phen species would be a reactant. In fact such dimers are known.[31] However, in the concentration range used for our experiments the concentration of the dimer is very small and does not agree with the $1/\tau$ dependence.

Acknowledgment. This work was supported by grants from the Swiss National Science Foundation (Project Nos. 2.101-0.81 and 2.830-0.83).

Registry No. Hg^{2+}, 14302-87-5; OH$^-$, 14280-30-9; phen, 66-71-7; bpy, 366-18-7.

(26) Grdenic, D.; Kamenar, B.; Hergold-Brundic, A. *Cryst. Struct. Commun.* **1978**, *7*, 245.
(27) Beauchamp, A. L.; Saperas, B.; Rivest, R. *Can. J. Chem.* **1974**, *52*, 2923.
(28) Berners Price, S. J.; Brevard, C.; Pagelot, A.; Sadler, P. J. *Inorg. Chem.* **1986**, *25*, 596.
(29) Smith, G.; Kennard, C. H. L.; White, A. H. *J. Chem. Soc., Dalton Trans.* **1977**, 1184.
(30) Mitchell, P. R. *J. Am. Chem. Soc.* **1980**, *102*, 1180.
(31) Mitchell, P. R. *J. Chem. Soc., Dalton Trans.* **1980**, 1079.
(32) Masuda, Y.; Yamatera, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 58.
(33) Goodwin, K. V.; McMillin, D. R.; Robinson, W. R. *Inorg. Chem.* **1986**, *25*, 2033.
(34) Reference 24, p 142.