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Reaction Mechanism of Mercury(II) with Protonated N-Substituted Porphyrin

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Kinetic and equilibrium studies on the complexation of mercury(II) ion with *N*-*p*-nitrobenzyl-5,10,15,20-tetrakis-(4-sulfonatophenyl)porphyrin, ($NO_2Bz(Htpps)^{4-}$; HP^{4-}) were carried out. The equilibrium constant, defined as $K_{HgP} = [HgP^{3-}][H^+][Hg^{2+}]^{-1}[HP^{4-}]^{-1}$, was determined spectrophotometrically in the pH range 2—3 and at temperatures of between 15 and 35 °C. The value of K_{HgP} was found to be $10^{6.28\pm0.04}$; and ΔH° and ΔS° values were 4.5±0.7 kJ mol^{-1} and 134±2 J mol^{-1} K^{-1}, respectively at 25 °C. The kinetic studies were carried out under a pseudo-first order condition in an aqueous medium at 10—35 °C, $I = 0.1(NaNO_3)$, $[HP^{4-}] = 3\times10^{-6}$, $[Hg(II)] = 4.74\times10^{-5}$ to 2.84×10^{-4}, [acetate buffer] $= 5\times10^{-3}$ to 1×10^{-1} mol dm^{-3}, and pH 4.2 to 5.6. The observed rate constant of the reaction was dependent of the total concentrations of mercury(II) and acetate buffer, but independent of the pH and ionic strength. The overall reaction was first order with respect to the total [Hg(II)] and $[HP^{4-}]$. The rate expression of the reaction is $d[HgP^{3-}]/dt = (k_1[Hg(OH)_2] + k_2[Hg(oac)_2])[H_2P^{3-}]$. The k_1 and k_2 values were found to be $(1.26\pm0.19)\times10^6$ and $(1.87\pm0.01)\times10^6$ mol^{-1} dm^3 s^{-1} (25.0 °C), and the activation enthalpies and entropyies were $\Delta H^\ddagger = 24.8\pm3.8$ kJ mol^{-1} and $\Delta S^\ddagger = -46\pm13$ J mol^{-1} K^{-1} for the k_1, and $\Delta H^\ddagger = 45.0\pm2.1$ kJ mol^{-1}, $\Delta S^\ddagger = 25.4\pm7.4$ J mol^{-1} K^{-1} for the k_2. The kinetic data revealed that dihydroxomercury(II) directly reacts with the protonated porphyrin with a small activation enthalpy and a negative activation entropy.

The kinetic and mechanistic aspects of the formation of metalloporphyrins are attractive in analytical chemistry for the determination of trace metals in different matrices.[1)] The mechanism for the formation of metalloporphyrin also provides useful information to biochemists regarding the metalation and dematalation of porphyrin in a living system. Sometimes information about the detailed reaction mechanism leads to the developement of a new drug that enhances or inhibits certain biochemical reactions. Therefore, investigating the metalation of porphyrin is important in analytical, inorganic, and biological science. Since the metalation of porphyrin is slower than that of open chain ligands,[2)] due to the rigidity of the porphyrin ring, several methods have been proposed[1)] to accelerate the rate of formation of metalloporphyrin. Among the factors which enhance the rate of metalation, N-substituents[3—5)] and large metal ions[6—9)] have attracted considerable attention.

Although N-substituted porphyrin was first reported in 1936,[10)] only a few studies have been made up to 1970. Efforts have been made regarding N-substituted porphyrin after the invention of a certain N-alkyl porphyrin in biological system using cytochrome P-450 enzymes.[11)] The effect of a distortion of the porphyrin planarity on the reactivity of the metal complex was studied by Hambright et al.,[3)] Lavallee et al.,[4)] and Tanaka et al.[5)] The metalation of N-substituted porphyrin has been investigated for Cu(II), Ni(II), Zn(II), Mn(II), Pb(II), etc. in organic media, but not much in aqueous media. N-substituted porphyrin has a higher basicity than that of non N-substituted porphyrin, and exists mainly in the protonated form, even at neutral pH.[12)] Mercury(II) is important from a toxicological point of view as well as its catalytic effect in metalation, showing the highest catalytic effect concerning the rate of incorporation of other metal ions in porphyrin, as previously reported.[13)] Mercury(II) exists predominantly in the hydrolyzed form at a pH above 3. The reactivity of protonated porphyrins and hydroxometal ions has not been clarified well, since the metalation of porphyrins has been investigated. Hence, our present work was designed to investigate the reaction between hydroxomercury(II) and protonated porphyrin. Here, we focus on the mechanism which regulates how the hydroxomercury(II) reacts with protonated $NO_2Bz(Htpps)^{4-}$ under certain experimental conditions.

Experimental

Reagent. *N*-*p*-nitrobenzyl-5,10,15,20-tetrakis(4-sulfonatophenyl)porphyrin, HP^{4-}, was synthesized, and purified in our laboratory.[12)] Its solution was prepared by dissolving the required quantities of HP^{4-} in ultrapure water. A mercury(II) solution was prepared from $Hg(NO_3)_2$ salt. The ionic strength of the solution was maintained using 0.1 mol dm^{-3} $NaNO_3$, which was purified by solvent extraction using phenyldiazenecarbothionic acid 2-phenylhydrazide (dithizone) in carbon tetrachloride to remove any foreign metal ions (Zn(II), Cu(II), Fe(II), and other heavy metal ions), and recrystallized from hot water. The pH of the solution was maintained by using 0.01 mol dm^{-3} solution of acetate buffer, which was also purified and recrystallized by the procedure described above.

Measurements. The visible absorption spectra were measured using a Shimadzu UV-visible spectrophotometer, and the reaction rate was studied using a Photal RA-401 stopped-flow spectrophotometer. The solution pH was measured using a Radiometer Ion 85 Ion Analyzer with a combined electrode (GK2401C). The pH meter and electrode system were calibrated in terms of $-\log[H^+]$ by a previously reported method.[14] All of the solutions were prepared using Milli-Q water.

The kinetic investigations were carried out under a pseudo-first order condition in the 4.2—5.6 pH range at constant ionic strength, $I=0.1$ mol dm^{-3} ($NaNO_3$) at 10—35 °C. The pH of the solutions was maintained using 0.01 mol dm^{-3} acetate buffer. The concentration of HP^{4-} was 3×10^{-6} mol dm^{-3}, and the Hg(II) concentration was varied in the range 4.74×10^{-5} to 2.84×10^{-4} mol dm^{-3}. The dependence of the buffer was checked by varying the concentration of the buffer over the range 5×10^{-3} to 1×10^{-1} mol dm^{-3}. The reaction was carried out by mixing two solutions, one containing HP^{4-}, buffer, and sodium nitrate, and the other containing $Hg(NO_3)_2$, buffer, and sodium nitrate; the change in the absorbance was monitored as a function of time. The reaction was studied at five different temperatures, and the activation parameters were evaluated from an Eyring Plot.

Results

Equilibrium of HgP^{3-} Formation. Since mercury(II) metal can exist as the aquamercury(II) ion at a pH less than 3, the equilibrium study was carried out at pH in the range 2—3 in order to avoid any complexity involving hydrolysis of mercury(II) at $I=0.1$ mol dm^{-3}. The formation constant of mercury(II) porphyrin was calculated by considering the following equilibrium:

$$Hg^{2+} + HP^{4-} \rightleftharpoons HgP^{3-} + H^+, \qquad (1)$$

where HgP^{3-} denotes the mercury(II) porphyrin of $NO_2Bz(Htpps)^{4-}$; HP^{4-}. To evaluate the equilibrium constant, the spectra were measured at different pH and concentrations of mercury(II), while the ionic strength of the solution was constant, and the concentration of HP^{4-} was 2.16×10^{-6} mol dm^{-3}. Since the mercury(II) porphyrin showed absorption maxima at 452 nm, all of the absorbances were measured at this wavelength. The equilibrium constant (K_{HgP}) was determined from the apparent molar absorptivity ($\bar{\varepsilon}$), which is equal to A/C, where A is the observed absorbance and C the total concentration of porphyrin.

$$\bar{\varepsilon} = (\varepsilon_1[HgP^{3-}] + \varepsilon_2[H_2P^{3-}] + \varepsilon_3[H_3P^{2-}])$$
$$([HgP^{3-}] + [H_2P^{3-}] + [H_3P^{2-}])^{-1}. \qquad (2)$$

The ε_1, ε_2, and ε_3 are the molar absorptivities of mercury(II) porphyrins (HgP^{3-}), monoprotonated (H_2P^{3-}), and diprotonated (H_3P^{2-}), respectively. Considering the protonation constants of porphyrin ($K_2=[H_2P^{3-}][HP^{4-}]^{-1}[H^+]^{-1}=10^{7.70}$, $K_3=[H_3P^{2-}][H_2P^{3-}]^{-1}[H^+]^{-1}=10^{2.51}$,[12]) and the hydrolysis constant of mercury(II) ($\log\beta_1^{OH}=-3.65$,[15] $\log\beta_2^{OH}=-5.915$,[15] where $\beta_n^{OH}=[Hg(OH)_n][H^+]^n[Hg^{2+}]^{-1}[H_2O]^{-n}$) we calculated the equilibrium constant (K_{HgP}) using a nonlinear least-squares minimization program. The value of K_{HgP} was found to be $10^{6.28\pm0.04}$ using the values of $\varepsilon_1=2.18\times10^5$, $\varepsilon_2=1.76\times10^5$ and $\varepsilon_3=3.43\times10^5$ mol^{-1} dm^3 cm^{-1} at 452 nm. The typical change in the apparent molar absorptivity with the concentration of mercury(II) and the pH is shown in Fig. 1.

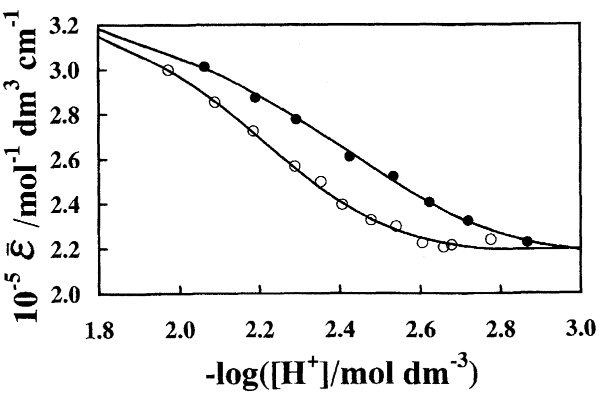


Fig. 1. A typical change in apparent molar absorptivity with $-\log[H^+]$ for the reaction of mercury(II) with nitrobenzylporphyrin at 452 nm at [Hg(II)]$=1.90\times10^{-4}$ (●) and 1.90×10^{-3} (○) mol dm^{-3}, and I=0.1 mol dm^{-3} ($NaNO_3$) at 25 °C.

The $NO_2Bz(Htpps)^{4-}$ can exist as diprotonated, monoprotonated or mercury(II) porphyrins according to the hydrogen-ion concentration. In order to visualize the species that exist in solution, the percent of species was calculated by considering the protonation constant of HP^{4-}, the formation constant of HgP^{3-}, and the hydrolysis constant of mercury(II); they are plotted as a function of the pH shown in Fig. 2, in which [Hg(II)]$=1.90\times10^{-3}$ mol dm^{-3}. Since the pH varied from 0—10, the diprotonated porphyrin (H_3P^{2-}) completely dissociates, and the formation of mercury(II) porphyrin (HgP^{3-}) starts at a pH of around 2, and completes at pH 4—7.

Kinetics of Formation of HgP^{3-}. The formation rate of HgP^{3-} was followed by a stopped-flow technique at pH 4.2—5.6. The observed rate of the reaction measured under a pseudo-first order condition was linearly related to the mercury(II) concentration (Fig. 3), indicating the first-order reaction with respect to the total [Hg(II)]. The observed rate increased by a smaller extent with the buffer concentration, and reached a plateau at a concentration above 2.5×10^{-2} mol dm^{-3} (Fig. 4). The observed rate was independent of the pH (Fig. 5) in the experimental pH range, in which the monoprotonated form of porphyrin

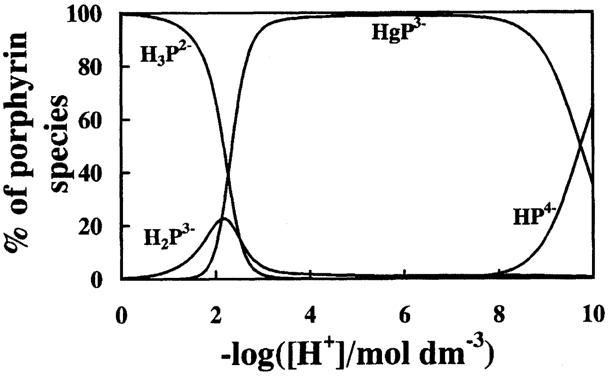


Fig. 2. Species distribution of $NO_2Bz(Htpps)^{4-}$ as a function of $-\log[H^+]$ at [Hg(II)]$=1.90\times10^{-3}$, $[oac]_t=1.00\times10^{-2}$ mol dm^{-3}, and I=0.1 mol dm^{-3} ($NaNO_3$) at 25 °C.

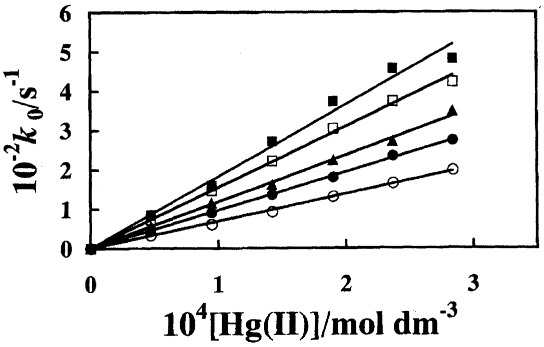


Fig. 3. Dependence of observed rate on the concentration of Hg(II) at 10 (○) 15 (●), 20 (□), and 30 (■) °C. $[NO_2Bz\text{-}(Htpps)^{4-}]=3.0\times10^{-6}$, $[oac]_t=1.00\times10^{-2}$ mol dm^{-3}, pH 4.76±0.05, and I=0.1 mol dm^{-3} ($NaNO_3$).

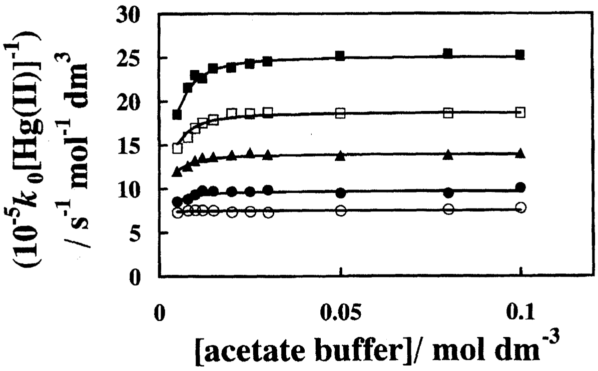


Fig. 4. Variation of observed rate constant with the concentration of acetate buffer at different temperatures: 12.6 (○), 17.0 (●), 21.3 (▲), 25.6 (□), and 31.7 (■) °C when $[Hg(II)]=1.90\times10^{-4}$, $[NO_2Bz(Htpps)^{4-}]=2.88\times10^{-6}$ mol dm^{-3}, pH 4.77±0.04, and I=0.1 mol dm^{-3} ($NaNO_3$).

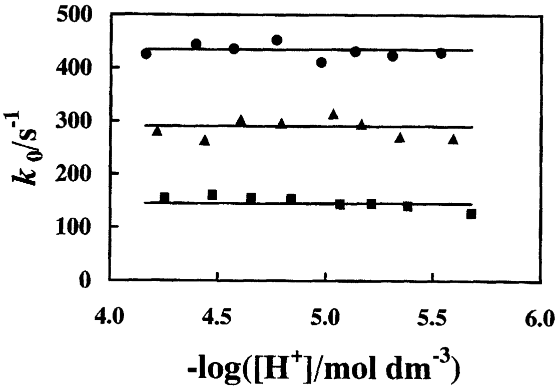


Fig. 5. Dependence of observed rate on the pH at $[NO_2Bz\text{-}(Htpps)^{4-}]=3.0\times10^{-6}$, and $[Hg(II)]=9.48\times10^{-5}$ (■), 1.90×10^{-4} (▲), 2.84×10^{-4} (●) mol dm^{-3}, $[oac]_t=1.00\times10^{-2}$ mol dm^{-3}, and I=0.1 mol dm^{-3} ($NaNO_3$) at 25 °C.

and dihydroxomercury(II) are the predominant species.[12,15,16] In the presence of an acetate buffer, although mono-, di-, tri-, and tetraacetatocomplexes may be possibly form,[17b] tri- and tetraacetatocomplexes are unfavorably formed, as discussed by Rossotti et al.[18] The stability constants of various mercury(II) species have been reported.[16,17,19] However, the values especially for the species of mercury(II) acetate are different for different investigations, and are inconsistent, making difficult it to reconcile all of the values. However, the values used in this case were $\log(\beta_1^{oac}/mol^{-1}\ dm^3)=4.22\pm0.01$[18] and $\log(\beta_2^{oac}/mol^{-2}\ dm^6)=8.44\pm0.02$ at 25.0 °C,[18,20] which were fitted well to the present experimental data, where $\beta_n^{oac}=[Hg(oac)_n][Hg^{2+}]^{-1}[oac]^{-n}$, in which oac denotes CH_3COO^-. Using these formation constants of mercury(II) acetate and the hydrolysis constants of $Hg(OH)^+$ and $Hg(OH)_2$, we calculated the fraction of all species of mercury(II) at pH 4—6 when the acetate buffer concentration was 0.01 mol dm^{-3}; we found that dihydroxo and diacetatocomplexes are predominant species at pH 4—6 and the existence of $Hg(OH)^+$ is 6.50×10^{-3}—5.50×10^{-4}%. We thus neglected the $Hg(OH)^+$ and assume that $Hg(OH)_2$ and $Hg(oac)_2$ are the reactive species, i.e. $k_0=k_1[Hg(OH)_2]+k_2\times[Hg(oac)_2]$.

Furthermore, the effect of the ionic strength on the reaction rate was investigated from I=0.01 to 0.1 mol dm^{-3}($NaNO_3$). A plot of $\log k_0$ vs. $I^{1/2}$ gave a slight increase in the k_0 values with a slope of 0.24. The negligible effect of the ionic strength on the reaction rate demonstrates the reaction of neutral species, such as $Hg(OH)_2$ and $Hg(oac)_2$, with the protonated porphyrin (H_2P^{3-}). If we assume that $Hg(OH)_2$ or $Hg(oac)_2$ reacts with the free base porphyrin (HP^{4-}), the observed rate should vary with the pH. In addition, if $Hg(OH)^+$ reacts with HP^{4-}, the observed rate constant would be independent of pH 4—6; however, the calculated rate constant is 3.44×10^{11} mol^{-1} dm^3 s^{-1} at pH 4—6. This value is abnormally high. The independence of the pH and ionic strength strongly suggests the absence of a contribution of the $Hg(OH)^+$ and $Hg(oac)^+$ ions in the rate-determining step i.e., only $Hg(OH)_2$ and $Hg(oac)_2$ directly react with the monocationic porphyrin.

From the above kinetic results we hypothesize the reaction mechanism involved in the present investigation given in Scheme 1:

According to Scheme 1, the reaction rate is expressed as

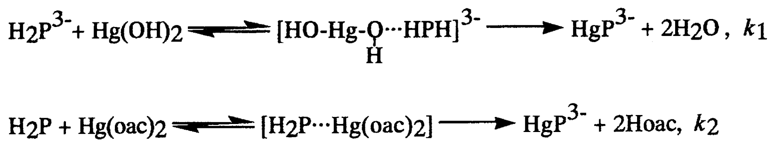
$$d[HgP^{3-}]/dt=(k_1[Hg(OH)_2]+k_2[Hg(oac)_2])[H_2P^{3-}]. \qquad (3)$$

The concentration of total mercury(II) $[Hg(II)]=[Hg(OH)_2]+[Hg(oac)_2]=(\beta_2^{OH}[H^+]^{-2}+\beta_2^{oac}[oac]^2)[Hg^{2+}]$. Therefore, Eq. 3 can be written as

$$k_0=\frac{(k_1\beta_2^{OH}[H^+]^{-2}+k_2\beta_2^{oac}[oac]^2)[Hg(II)]}{\beta_2^{OH}[H^+]^{-2}+\beta_2^{oac}[oac]^2}, \qquad (4)$$

where [oac] was calculated from the total concentration of the buffer, $[oac]_t$, which is correlated with the protonation constant of acetate as $[oac]_t=[Hoac]+[oac]=(K_1[H^+]+1)\times[oac]$ and $K_1=[Hoac][oac]^{-1}[H^+]^{-1}$.

At a low concentration of the acetate buffer, the dihydroxomercury(II) is predominant, and the second term of the numerator and denominator of Eq. 4 is negligible, i.e. $k_0/[Hg(II)]=k_1$. Similarly, at a high concentration of the



$$H_2P^{3-} + Hg(OH)_2 \rightleftharpoons [HO\text{-}Hg\text{-}\underset{H}{O}\cdots HPH]^{3-} \longrightarrow HgP^{3-} + 2H_2O,\ k_1$$

$$H_2P + Hg(oac)_2 \rightleftharpoons [H_2P\cdots Hg(oac)_2] \longrightarrow HgP^{3-} + 2Hoac,\ k_2$$

Scheme 1.

acetate buffer, the diacetatomercury(II) is predominant, and the first term is negligible, i.e. $k_0/[\mathrm{Hg(II)}]=k_2$.

The k_1 value was determined from the intercept of the plot of $k_0/[\mathrm{Hg(II)}]$ vs. [acetate buffer] shown in Fig. 4. The value of the intercept was found to be $(1.26\pm0.19)\times10^6$ mol^{-1} dm^3 s^{-1} at 25.0 °C, giving the value of the second-order rate constant for the k_1 path, when the concentration of the acetate buffer is zero, i.e. dihydroxomercury(II) is only the reactive species. On the other hand, at a high concentration of the acetate buffer, the values of $k_0/[\mathrm{Hg(II)}]$ are almost constant, and the average of these values was found to be $(1.87\pm0.01)\times10^6$ mol^{-1} dm^3 s^{-1} at 25.0 °C, giving the value of the second-order rate constant for the k_2 path. The solid lines in Fig. 4 were calculated from Eq. 4 using the values of k_1 and k_2 at different temperatures. The variations in the concentrations of $Hg(OH)_2$ and $Hg(oac)_2$ with pH 4—6 are opposite to each other; also since their reactivity is almost comparable ($(1.26\pm0.19)\times10^6$ and $(1.87\pm0.01)\times10^6$ mol^{-1} dm^3 s^{-1} at 25. 0 °C), the observed rates due to the variation in the pH (4.2—5.6) are almost independent (Fig. 5).

The activation parameters were calculated from the effect of the temperature, and are listed in Table 1.

Discussion

Although mercury(II) can easily coordinate with N-containing ligands, the situation is somehow complicated when mercury(II) reacts with porphyrin. A number of investigations have suggested that the reaction between mercury(II) and porphyrin produces different mercury(II) porphyrin species,[21—26] e.g. mononuclear, dinuclear, and doublesandwich types, according to the structure and concentration of porphyrin as well as the concentration of mercury(II) and the pH. In the case of $NO_2Bz(Htpps)^{4-}$, the bulky NO_2Bz– group demonstrates the incorporation of a metal ion to the porphyrin ring from its opposite side, suggesting a mononuclear precursor complex. The equilibrium constant was determined, and the value of K_{HgP} was found to be $10^{6.28\pm0.04}$ at 25 °C. The value of K_{HgP} indicates that the complex is about 5×10^5 and 3×10^8 times more stable than those of the corresponding Zn(II) and Cd(II) complexes, respectively.[27] Although the positive enthalpy (ΔH°) (Table 1) is unfavorable for complex formation, the large positive change in the entropy, due to the deformed structure of mercury(II) porphyrin, is favorable for complex formation.

The observed rate of formation of HgP^{3-} was directly related to the total concentration of mercury(II). The mercury(II) predominantly exists as $Hg(oac)_2$ and $Hg(OH)_2$ under the present experimental conditions. Since the first and second protonation constants of $NO_2Bz(Htpps)^{4-}$ are 7.70 and 2.51,[12] respectively, the monoprotonated (or cationic) porphyrin species is predominant at pH 4—6. The absence of a pH effect and ionic strength effect suggests the formation of HgP^{3-} by a direct interaction of neutral Hg(II) species with the monoprotonated porphyrin. The mechanism is supposed to be hydrogen-bonding between $Hg(OH)_2$ and the monoprotonated porphyrin for the k_1 path and the dissociative interchange mechanism for the k_2 path shown in Scheme 1.

In the case of N-substituted monoprotonated porphyrin, the two protonated rings are located adjacent to the N-substituted ring.[28] The bulky NO_2Bz– group tilts the porphyrin ring in such a way that the pyrrole ring bound to the NO_2Bz– group inclines upwards, and the pyrrole ring bound to the H-atom inclines downwards from the mean porphyrin plane. As the results, the electron-rich oxygen atom of $Hg(OH)_2$ easily approaches the porphyrin ring from the opposite side of the NO_2Bz– group and forms a hydrogen bond with the protonated porphyrin to remove the proton. The lone-pair electrons of the aryl substituted nitrogen atom become out of plane, which can easily coordinate to the mercury(II); subsequently, mercury(II) possesses a stable tetrahedral arrangement upon removing other pyrrolic protons and coordination with lone-pair electrons of the pyrrole nitrogens. The proposed reaction intermediate is shown in Fig. 6.

Another path, k_2, involves a preequilibrium followed by a dissosiative interchange (I_d) mechanism. Such a mechanism is consistent with the acetate-catalyzed metalation for the insertion of Zn(II) and Cu(II) to the porphyrin ring.[29,30]

The mechanism shown in Scheme 1 is further supported by the activation parameters listed in Table 1. The compar-

Table 1. The Equilibrium and Kinetic Parameters for the Reaction of Mercury(II) with $NO_2Bz(Htpps)^{4-}$[a)]

		ΔH°/kJ mol^{-1}	ΔS°/J K^{-1} mol^{-1}
K_{HgP}	$10^{6.28\pm0.04}$	4.5 ± 0.7	134 ± 2
		$\Delta H^\ddagger$/kJ mol^{-1}	$\Delta S^\ddagger$/J K^{-1} mol^{-1}
k_1/mol^{-1} dm^3 s^{-1}	$(1.26\pm0.19)\times10^{6\,\mathrm{b)}}$	24.8 ± 3.8	-46 ± 13
k_2/mol^{-1} dm^3 s^{-1}	$(1.87\pm0.01)\times10^{6\,\mathrm{b)}}$	45.0 ± 2.1	25.4 ± 7.4

a) I=0.1 mol dm^{-3} ($NaNO_3$). b) At 25.0 °C.

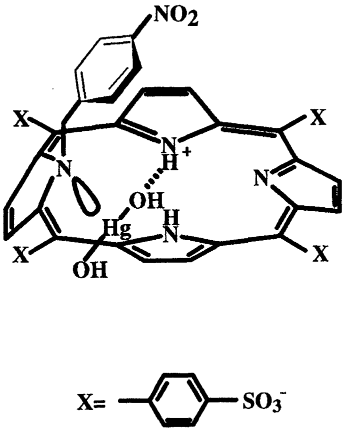


Fig. 6. The proposed intermediate of the reaction between dihydroxomercury(II) and the protonated N-substituted porphyrin.

atively low positive activation enthalpy and negative activation entropy suggest a hydrogen-bonding associative mechanism for the k_1 path. The large activation enthalpy and positive activation entropy suggest a dissociative interchange mechanism for the k_2 path.

Only a few kinetic studies have been performed for mercury(II) and porphyrin; in the case of N-substituted porphyrin, almost all kinetic studies have been related to *N*-methyl-5,10,15,20-tetraphenylporphyrin in organic media. Thus, from one investigation, it is difficult to reach any conclusion concerning the reactivities of the protonated porphyrin and hydrolyzed mercury(II) observed under the present experimental conditions. However, the present study for the first time describes the reactivity of protonated porphyrin concerning the formation of mercury(II) porphyrin.

Conclusion

The present equilibrium and kinetic studies of the reaction between dihydroxomercury(II) and protonated porphyrin clearly show the facile formation of an HgP^{3-} complex having large equilibrium and rate constants. Since deformation is the most important factor for metalation, the NO_2Bz-group changes the porphyrin configuration in such a way that the lone-pair electrons of the N-atom is almost ready to accommodate any metal ion. Moreover, the degree of deformation is enhanced by the addition of a proton in the protonated form due to a repulsion between the inner H-atoms. The electron-withdrawing effect of the NO_2Bz– group facilitates the removal of a proton during metalation. In this investigation, the combined effect of electron withdrawing and deformation shows the higher reactivity of protonated porphyrin towards mercury(II). The independence of the pH and ionic strength and the activation parameters suggest the direct reaction of dihydroxo- and diacetatomercury(II) with the monoprotonated porphyrin by an associative- and a dissociative- interchange mechanisms, respectively. In this study, the reactivity of protonated porphyrin is the first finding since the metalation of porphyrins was investigated.

Generally, the free base form of porphyrin is a more reactive species than the protonated porphyrin for the metalation of porphyrin. However, a hydrolyzed metal ion, like $Hg(OH)_2$, can associate with a protonated N-substituted porphyrin by the hydrogen-bonding formation between the metal hydroxo group and the proton of the porphyrin (Fig. 6). This interaction makes it easy for the hydrolyzed metal ion to react with protonated porphyrin.

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