

Acid-, Anion-, and Base-Catalyzed Solvolysis Reactions of a Water Soluble Bismuth(III) Porphyrin

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Introduction

The coordination chemistry and reactivity of bismuth(III) porphyrins is a relatively unexplored area.¹ Triebs² synthesized a Bi–NO₃ complex of mesoporphyrin-IX dimethylester using Bi(NO₃)₃ in refluxing pyridine, while under the same conditions two nitro groups were introduced into the etioporphyrin nucleus. Buchler and Lay³ made the Bi–NO₃ complex of octaethylporphyrin, and Brothers and co-workers⁴ prepared and studied the variable temperature ¹H NMR of bismuth(III) tetrakis(4-methylphenyl)porphyrin nitrate (Bi(TTP)NO₃). We report the synthesis of the first water soluble adduct, bismuth(III) tetrakis(*N*-methyl-3-pyridyl)porphyrin. Kinetic work indicates that while the removal of bismuth from this macrocycle is, as expected, catalyzed by protons, major anion and hydroxide contributions are also present. Such strong anion catalysis has been found before only with In(III)⁵ and Mg(II)⁶ porphyrins, and the hydroxide effect appears to be without precedent.

Experimental Section

In common with previous studies,^{1–4} pyridine was used for the synthesis of bismuth(III) tetrakis(3-pyridyl)porphyrin (Bi–3-P⁺). To 50 mL of refluxing pyridine containing 0.5 g (0.81 mm) of tetrakis(3-pyridyl)porphyrin (H₂-P) [Mid-Century Chemicals, Posen, IL] was added 5.2 g (10 mm) of Bi(NO₃)₃·5H₂O [Aldrich], and a further 2.3 g was introduced an hour later. After 2 h, the 465 nm Bi–3-P⁺ and the 417 nm H₂-P bands of the green solution showed no further changes with time. The mixture was evaporated, washed with water, and air-dried under the hood. All attempts at column chromatography using alumina or silica gel led to the decomposition of Bi–3-P⁺ into H₂-P. The impure solid was thus Soxhlet extracted first with methylene chloride to remove the excess H₂-P and then with methanol, in which the Bi–3-P⁺ (but not H₂-P) was extremely soluble. After filtration through a 0.45 μm Millipore filter, the visible and Soret bands of H₂-P were absent, and this compound in methanol was stable for months in the dark. Since traces of acetic, propionic, or hydrochloric acids in the air rapidly demetallate the solid nitrate salt, Bi–3-P⁺ is most profitably stored in solution. The absorption bands (nm) and their relative heights in methanol are 463.0 (19.8), 592.5 (1.13) and 637.5 (1.00).

To *N*-methylate Bi–3-P⁺ to form bismuth(III)-tetrakis(*N*-methyl-3-pyridyl)porphyrin (Bi–P⁺), an excess of methyl iodide⁷ was added to a portion of the methanolic Bi–3-P⁺ solution, the mixture was stirred overnight at room temperature, and excess methanol and CH₃I were then removed on a rotary evaporator. The solid was dissolved in water, filtered, and then passed through an anion exchange column in the nitrate form to remove the iodide ions. Intergration of the ¹H NMR spectra in D₂O of the free base of this porphyrin after removal of

bismuth confirmed tetra-*N*-methylation, with 8 H at 9.1 ppm (*β*-position on pyrroles) and 12 H at 4.8 ppm (*N*-methyl protons).

When made 1.0 M in HCl, the Bi–P⁺ produces the metal free diacid H₄-P²⁺, and since the extinction coefficients of the diacid are known,⁸ the extinction coefficients of Bi–P⁺ can readily be calculated. For Bi–P⁺ in water at pH 4.5, λ (nm), [log ε] values are 465.2 [5.04], 591.0 [2.75], and 637.5 [3.67]. The wavelengths are similar to those of Bi-(TTP)NO₃ in CH₂Cl₂ (469.4, 601.4, and 650.1 nm).⁴

The reaction kinetics at 25 °C were monitored on a Beckman DU-70 recording spectrophotometer, and the acids standardized by conventional methods. The notation Bi–P⁺ indicates the diaquo porphyrin complex, where the four positive charges at the porphyrin periphery are neglected for clarity.

Results

Making a Bi–P⁺ solution 0.20 M in HCl cleanly transforms Bi–P⁺ into the metal-free diacid species, which has bands at 431, 582, and 630 nm, and isosbestic points are found at 380, 447, 580, 607, and 685 nm during the course of the reaction. Thus Bi–P⁺ and H₄P²⁺ are the major absorbing species. With ~10^{–6} M Bi–P⁺ and >10^{–2} F acid levels, the kinetics followed in the Soret were first order in (Bi–P⁺) over more than 2 half-lives, characterized by a pseudo-first-order rate constant, *k*_{obs}. With an acid concentration of 0.20 F, the *k*_{obs} for HClO₄ was (4.0 ± 0.1) × 10^{–4} s^{–1}, and the relative rate constants were in the order HClO₄ (1.0) < HNO₃ (2.1) < HBF₄ (15.2) < HSO₄[–] (17.9) < HCl (4 × 10³), indicating that anions as well as protons were involved in the solvolysis process. Using HClO₄/NaClO₄ mixtures to maintain an ionic strength of 1.0, the variation of the observed first order rate constant, *k*_H, with (H⁺) [9.1 × 10^{–1} to 9.1 × 10^{–2} M] was of the form

$$k_H = a[H^+]^2/(b + [H^+]) \quad (1)$$

where *a* = (4.3 ± 0.6) × 10^{–3} M^{–1} s^{–1} and *b* = (3.0 ± 1.0) × 10^{–2} M. With an ionic strength of 1.0 (HClO₄/NaClO₄/NaX), we studied the variation of *k*_{obs} with pH and added amounts of NaX (X[–] = Cl[–], Br[–], and I[–]). The rate expression was

$$k_{obs} = k_H + k_a[H^+]^2[X^-] + k_b[H^+]^2[X^-]^2 \quad (2)$$

Figure 1 shows a linear plot of (*k*_{obs} – *k*_H)/([H⁺]²[Cl[–]]) vs [Cl[–]] from which the constants *k*_a and *k*_b were obtained. These values, along with the concentration ranges studied are listed in Table 1. At constant pH, *k*_{obs} increased with ionic strength.⁹

The liberation of Bi(III) from Bi–P⁺ was also catalyzed by hydroxide ions. From pH 6.5 to 8.5, with an ionic strength of 0.1 (NaClO₄) and 1.0 × 10^{–2} M Pipes buffer, the reactions were cleanly second order in (Bi–P⁺). In this pH range, the dependence of *k*_{obs2} on [OH[–]] was

$$k_{obs2} = k_c[OH^-]^2/(1 + k_d[OH^-]^2) \quad (3)$$

Figure 2 is a plot of *k*_{obs2} vs [OH[–]], and using a curve fitting program, *k*_c = (2.7 ± 0.2) × 10¹⁶ M^{–2} s^{–1} and *k*_d = (7.2 ± 1.8) × 10⁴ M.

Discussion

In aqueous solution, acid-catalyzed solvolysis reactions are usually first order in metalloporphyrin and either second order or between first and second order in [H⁺], as found in eq 1. Thus, one proton reacts in an equilibrium fashion with Bi–P⁺

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(9) In 0.10 M HNO₃, and using NaNO₃ to change the ionic strength (I) from 0.10 to 0.92, log(*k*_{obs}) = –4.26 + 3.24 {I^{1/2} / [1 + I^{1/2}]}.
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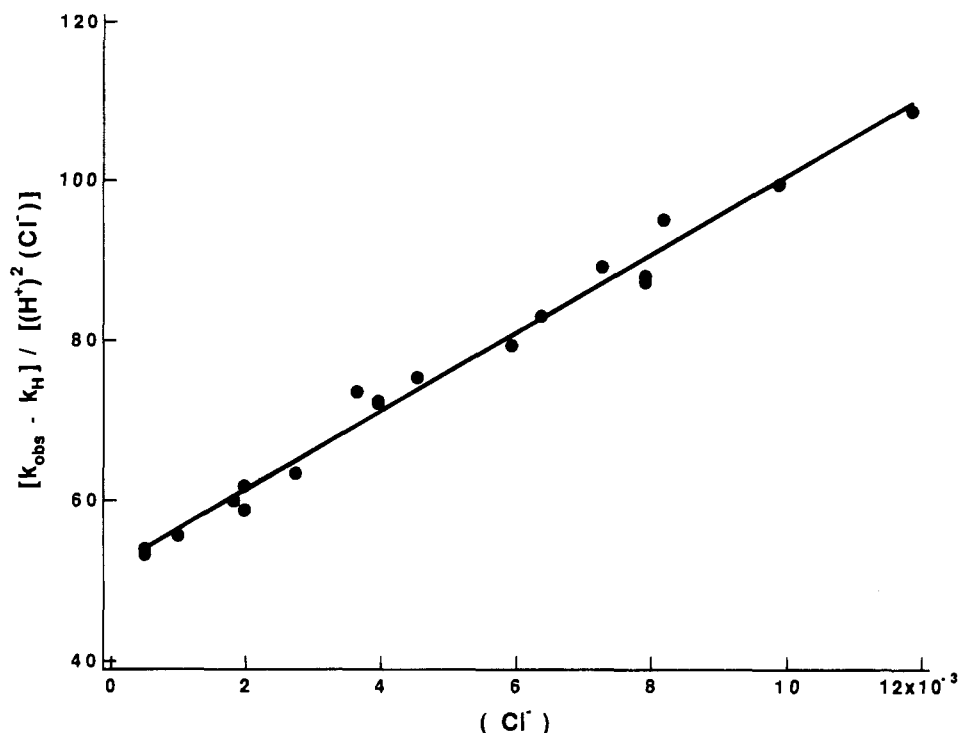


Figure 1. Plot of $\{[k_{\text{obs}} - k_{\text{H}}]/([\text{H}^+]^2[\text{Cl}^-])\}$ vs $[\text{Cl}^-]$ for the Bi-P⁺/HCl reaction, in accord with eq 2.

Table 1. Rate Constants for the Bi-P⁺/HX Reaction, 25 °C

X ⁻	k_{a} (M ⁻³ s ⁻¹) ^a	k_{b} (M ⁻⁴ s ⁻¹) ^a
Cl ⁻	$(5.2 \pm 0.1) \times 10^1$	$(4.9 \pm 0.1) \times 10^3$
Br ⁻	$(7.8 \pm 0.7) \times 10^1$	$(4.2 \pm 0.2) \times 10^4$
I ⁻	~0	$(3.8 \pm 0.1) \times 10^6$

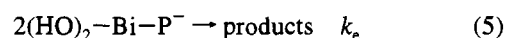
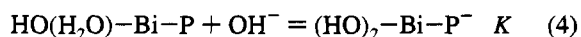
^a For chloride, $[\text{Cl}^-]$ from 1.2×10^{-2} to 4.6×10^{-4} M, $[\text{H}^+]$ from 8.6×10^{-2} to 3.5×10^{-1} M. For bromide, $[\text{Br}^-]$ from 6.5×10^{-3} to 2.3×10^{-4} M, $[\text{H}^+]$ from 9.1×10^{-2} to 2.8×10^{-1} M. For iodide, $[\text{I}^-]$ from 6.1×10^{-4} to 3.5×10^{-5} M, $[\text{H}^+]$ from 9.1×10^{-2} to 2.9×10^{-1} M. In all cases, $I = 1.0$ (NaClO₄/HClO₄/NaX).

to produce the (Bi-PH)²⁺ intermediate, which either reverts to reactants, or reacts with a second proton to form the product. This is the case¹⁰⁻¹¹ with Zn(II), Pb(II), Cd(II), Mg(II), Fe(II), and a series of lanthanide¹² porphyrins. For Zn-TPPS [tetrakis-(4-sulfonatophenyl)porphyrin], several groups^{11,13} have specifically looked for anion catalysis, and none has been found. In 0.20 F HX solutions, the relative order of anion effects for the Bi-P⁺ hydrolysis reaction is approximately ClO₄⁻ (1.0) < NO₃⁻ (2.1) < BF₄⁻ (15.2) < HSO₄⁻ (17.9) < Cl⁻ (4×10^3) < Br⁻ (4×10^4) < I⁻ (3.8×10^6). The Bi³⁺ ion is soft and too large (~110 pm) to fit into the porphyrin plane. In line with the soft acid character of Bi³⁺, the stability constants¹⁴ for BiX²⁺ species are 10^{1.9} (Cl⁻), 10^{2.3} (Br⁻) and 10^{3.6} (I⁻), while for BiX₄⁻, the order is 10^{5.5}, 10^{7.8}, and 10^{14.9} respectively. Thus Bi³⁺ prefers soft bases, and this appears to be the trend in anion catalysis found in this acid solvolysis study. Formally, the Bi³⁺ is coordinated to the four central porphyrin nitrogen atoms. Two protons break two of these Bi-N bonds, and the release of bismuth is further aided by the addition of one or two anions to the bound Bi³⁺, which effectively lowers the charge of the

outgoing ion. The overall mechanism involves equilibrium proton and anion attachments to Bi-P⁺, with the three rate-determining steps noted. Additional protons are added to the porphyrin and anions (up to BiX₆³⁻) to Bi(III) following the rate-determining steps.

Related behavior is found for In(III) porphyrins,⁵ which are stable for long periods of time in 5.3 M HClO₄. The addition of a trace of halide from NaX leads to the immediate production of the H₄P²⁺. The kinetics followed rate = $k[\text{In-P}^+](h_0)^{2.2}[\text{Cl}^-]^2$, similar to the third term in eq 2. The loss of Mg²⁺ from Mg(II)-TPPS is first order in porphyrin and acetate catalyzed, with one term second order in $[\text{H}^+]$, and the second having the form $[\text{H}^+][\text{OAc}^-]$.⁶ The Bi³⁺ is also removed from Bi-P⁺ by EDTA at pH 3, a reaction shown by the large Pb(II)¹⁵ and trivalent lanthanides¹⁶ complexed to porphyrins.

The anion hydroxide also catalyzes the removal of Bi from Bi-P⁺, and the process is different from the acid solvolysis reactions in being second order in $[\text{Bi-P}^+]$. We attempted to measure the pK_{a1} for the (H₂O)₂-Bi-P⁺/HO(H₂O)-Bi-P acid dissociation reaction, and from the very minor changes in spectra between pHs 6-2, pK_{a1} ~ 3.5. While the value for aquo-Bi³⁺ is ~1.5, metalloporphyrins have pK_{a1}s several units above the aquo ion, and their pK_{a2}s are ~3-5 units above pK_{a1}.^{17,18} Thus, considering only HO(H₂O)-Bi-P and (HO)₂-Bi-P⁻ above pH 6.5, one simple mechanism which fits the hydroxide catalyzed kinetics is



The dependence of the second order $k_{\text{obs}2}$ on $[\text{OH}^-]$ would be of the same form as eq 3, with $k_c = k_e K^2$ and $k_d = K$. Thus k_e

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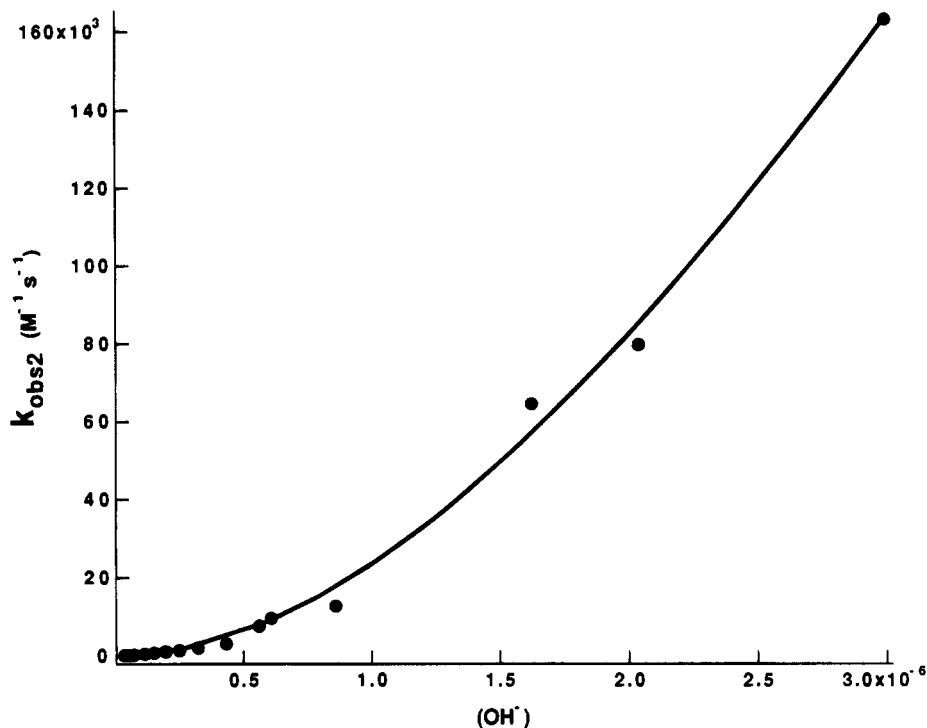


Figure 2. Graph of the second order rate constant $k_{\text{obs}2}$ vs $[\text{OH}^-]$ for the Bi-P⁺/OH⁻ process. The solid line is based on the calculated values of $k_{\text{obs}2}$ from eq 3, using the k_c and k_d parameters given in the text.

$= 5.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ and $K = 7.2 \times 10^4 \text{ M}^{-1}$. The $\text{p}K_{\text{a}2}$ for the $(\text{H}_2\text{O})(\text{OH})\text{-Bi-P}/(\text{HO})_2\text{-Bi-P}^-$ reaction is thus 9.6, not an unreasonable value. Iron(III) porphyrin oxo dimer formations are also second order in porphyrin, with the reactants $(\text{H}_2\text{O})_2\text{-Fe-P}^+$ and $(\text{HO})(\text{H}_2\text{O})\text{-Fe-P}$.¹⁹ The initial dependence is first order in $[\text{OH}^-]$ for such dimerizations, unlike the $[\text{OH}^-]^2$ behavior for the Bi-P dissociation. The removal of tungsten from W^{VO}-TPPS is second order in porphyrin, and attributed to the formation of an acid labile W^{VI}-TPPS from the rate-determining reaction of a W^{VO} with a W^{VO}(O₂) intermediate, an oxidative demetalation process.²⁰ The current Bi-P⁺ work appears to be the first kinetic study of a hydroxide-catalyzed porphyrin demetalation. Main group metalloporphyrins with long wavelength Soret bands, such as Bi-P⁺, are models for certain postulated porphyrin-based constituents of interstellar dust.^{21,22}

Many oligomeric Bi(III) complexes are known. For 10^{-5} M solutions, Bi(III) forms Bi^{3+} , $\text{Bi}(\text{OH})^{2+}$, $\text{Bi}(\text{OH})_2^+$, $\text{Bi}_6(\text{OH})_{12}^{6+}$, $\text{Bi}_9(\text{OH})_{20}^{7+}$ and $\text{Bi}_9(\text{OH})_{21}^{6+}$ from pH 0–5 and then $\text{Bi}_9(\text{OH})_{22}^{5+}$ and $\text{Bi}(\text{OH})_3$ in the neutral range, while $\text{Bi}(\text{OH})_4^-$ predominates in base.²³ The $\text{Bi}_6(\text{OH})_{12}^{6+}$ unit contains an octahedral array of bismuth ions, bridged on each edge by hydroxides. The activated complex for the Bi-P⁺ base solvolysis reaction is of the composition $[\text{P-Bi}-(\text{OH})_4\text{-Bi-P}]$. Faster reactions with further hydroxides produce more P-Bi-OH bonds at the expense of the Bi to porphyrin nitrogen attachments, ultimately leading to removal of the bismuth from the macrocycle. The second order dependence on Bi-P⁺ in base probably indicates the formation of $\text{Bi}-(\text{OH})_n\text{-Bi}$ bridges in the activated complex, foreshadowing the related structural units found in solution.

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