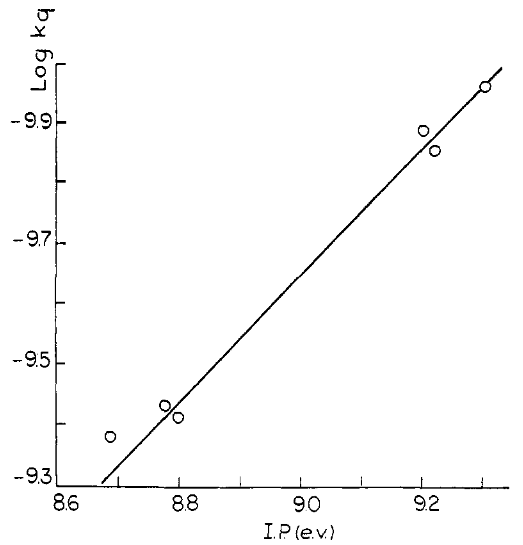

Figure 2. The ionization potential dependence of the oxygen quenching rate constants for several simple aromatic molecules.

processes could involve a contact-charge-transfer intermediate. Extrapolation of the present data to other systems may prove useful. As an example, the lack of observed oxygen quenching of the singlet state of many ketones may be due to their high ionization potentials.

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Acid-Catalyzed Solvolysis Reactions of Zinc Porphyrins Having Various Basicities and Zinc *N*-Methylporphyrins[1]

Sir:

The study of acid-catalyzed solvolysis reactions of metal chelates has mainly been confined to flexible multidentate ligand complexes where the possibility exists for the ligand to uncoil from around the coordinated metal ion.[2] With rigid macrocyclic ligands, however, the unraveling mechanism is inapplicable, and some recent work has been directed to this problem,[3] especially with porphyrin molecules.[4-9] A variety of mechanisms have been advanced to explain the differing kinetic behavior found in the acid-induced dissociations of Cu, Zn, Mn(II), and Mg porphyrins in various solvents. To this end, we present results on the kinetics of the acid-catalyzed dissociations of (A) zinc etioporphyrin(III) in methanol, (B) zinc *N*-methyletioporphyrin(III), and (C) 2,4-disubstituted zinc deuteroporphyrins of differing basicities.

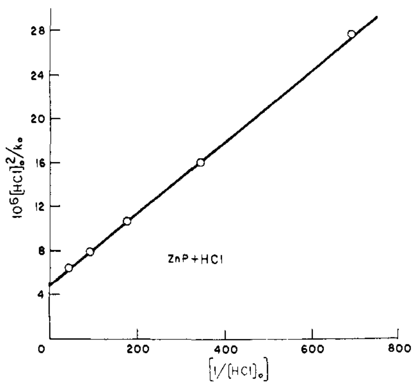

Figure 1. $[\text{HCl}]_0^2/k_{\text{obsd}}$ *vs.* $1/[\text{HCl}]_0$ for the reaction of zinc etioporphyrin with HCl in methanol, 25°.

The porphyrin and zinc complexes were prepared and purified by literature methods.[9,10] The kinetics were run at 25° in methanol acidified with HCl, using a Durrum stopped-flow apparatus or Cary 14, under pseudo-first-order conditions in porphyrin (*ca.* 10^{-5} *M*). Such rates were independent of water concentration below 0.2 *M*, but decreased by a factor of 10 to a limiting value at about 0.7 *M* H_2O. The dissociation of the zinc porphyrins into their acid forms was complete under the reaction conditions, and no reincorporation of Zn was observed.

At constant HCl concentrations, the additions of a two-, four-, or sixfold excess of NaCl or $(\text{Et}_4\text{N})\text{Cl}$ each increased the rate, with respect to the absence of added chloride, by the same amount of *ca.* 20%. Thus no rate term in chloride is evident in HCl–methanol. With 0.02 *F* HClO_4 the observed rate constant was approximately 500-fold lower than that with the same concentration of HCl. Both 0.02 *F* and 0.12 *F* $(\text{Et}_4\text{N})\text{Cl}$ in 0.02 *F* HClO_4–methanol showed the same solvolysis rate as produced by 0.02 *F* HCl–methanol itself. The observed rates with either HCl or HClO_4 were unaffected by a fivefold formal excess of $(\text{Et}_4\text{N})\text{ClO}_4$. These observations can be rationalized by assuming that HCl in methanol exists predominantly in an undissociated ion-pair form.[11] The following results were obtained for the HCl-catalyzed solvolysis reactions in methanol.

For zinc etioporphyrin(III) [ZnP], Figure 1 shows the linear plot of $[\text{HCl}]_0^2/k_{\text{obsd}}$ *vs.* $1/[\text{HCl}]_0$. This is consistent with the rate law

$$k_{\text{obsd}} = k_a[\text{HCl}]_0^3/(\rho_a + [\text{HCl}]_0) \qquad (1)$$

for which $k_a = (2.0 \pm 0.1) \times 10^{+5}\ F^{-2}\ \text{sec}^{-1}$ and $\rho_a = (6.6 \pm 0.2) \times 10^{-3}\ F$.

With zinc *N*-methyletioporphyrin(III) [Zn-*N*-MeP], Figure 2 shows the linear graph of $[\text{HCl}]_0/k_{\text{obsd}}$ *vs.*

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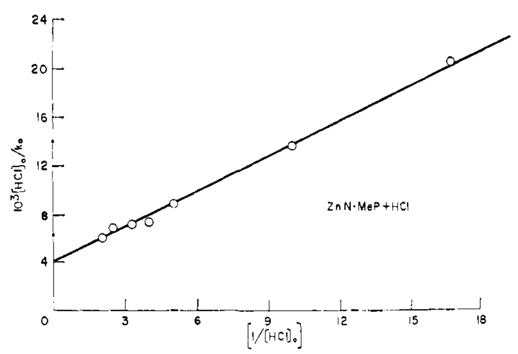

Figure 2. $[HCl]_0/k_{obsd}$ *vs.* $1/[HCl]_0$ for the reaction of zinc *N*-methyletioporphyrin with HCl in methanol, 25°.

$1/[HCl]_0$, for the formulation

$$k_{obsd} = k_b[HCl]_0^2/(\rho_b + [HCl]_0) \qquad (2)$$

with $k_b = (2.5 \pm 0.2) \times 10^2\ F^{-1}\ sec^{-1}$ and $\rho_b = (2.5 \pm 0.2) \times 10^{-1}\ F$.

The dimethyl esters of meso-, deutero-, proto-, and dibromodeuteroporphyrins having ethyl, hydrogen, vinyl, and bromo groups substituted on the 2,4-porphyrin positions were used to study the effect of porphyrin basicity on the rate of zinc ion displacement. At a constant acid concentration of $7.5 \times 10^{-3}\ F$, the first-order rate constants listed in Table I were obtained.

Table I. First-Order Rate Constants[a] for ZnP Dissociation at 25° in HCl-Methanol

Compound[b]	pK_3[c]	k, sec^{-1}
Zinc mesoporphyrin	5.85	1.59
Zinc deuteroporphyrin	5.50	5.73×10^{-1}
Zinc protoporphyrin	4.80	1.30×10^{-1}
Zinc dibromodeuteroporphyrin	3.0 ± 0.2	1.30×10^{-3}

[a] $[HCl]_0 = 7.5 \times 10^{-3}\ F$ in methanol. [b] Porphyrin dimethyl esters. [c] From ref 9, p 35.

The forms of the rate laws for zinc ion displacement are somewhat similar to that given by magnesium deuteroporphyrin in $HClO_4$-methanol.[5] The suggested mechanisms, with (zinc porphyrin·n-HCl) as a steady-state intermediate, are

$$\text{zinc porphyrin} + n\text{HCl} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} (\text{zinc porphyrin}\cdot n\text{HCl}) \qquad (3)$$

$$(\text{zinc porphyrin}\cdot n\text{HCl}) + \text{HCl} \xrightarrow{k_2} \text{products} \qquad (4)$$

For ZnP, $n = 2$, and $n = 1$ with Zn-*N*-MeP; thus ρ is k_{-1}/k_2 and k is k_1.

For Zn-*N*-MeP, a methyl group has been introduced on a central nitrogen atom in place of a proton. This makes the metal ion three- instead of four-coordinate with respect to the porphyrin. The effective basicity toward protons of *N*-methylporphyrins as opposed to porphyrins is also increased[12] owing to the bending of the porphyrin nucleus by the central methyl group, which tilts the lone pairs on the nitrogen atoms in a direction away from the porphyrin center. As shown, substitution of a methyl function for a proton decreases the acid dependence of demetalation by one proton.

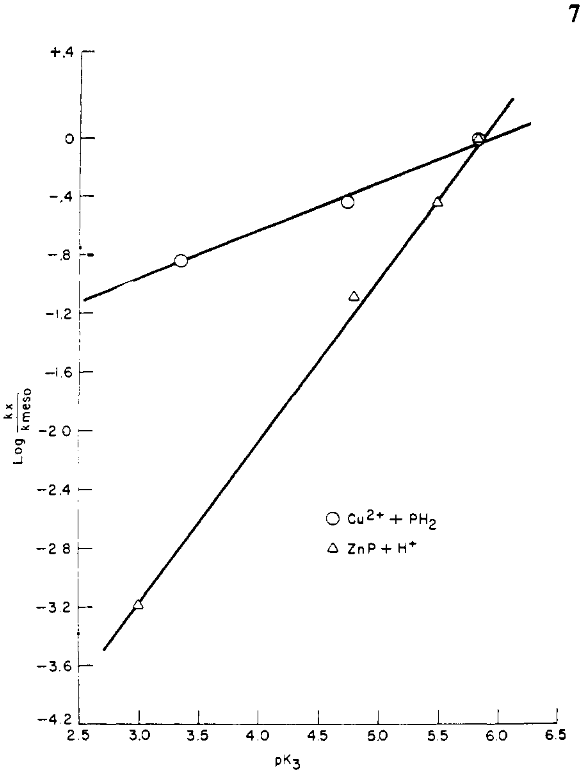

Figure 3. The dependence of the rates of formation of Cu(II) porphyrins and dissociation of Zn(II) porphyrins on porphyrin basicity.

The rate law for zinc ion removal from a water-soluble N-methylated tetrapyridylporphin in aqueous solution was found to be[7,8]

$$\text{rate} = k_d[\text{ZnTpyP}][H^+]^2[X^-]^2 \qquad (5)$$

with the efficiency of X^- in the order $Cl^- > Br^- > I^-$. Under the conditions of $[HCl]_0 \gg \rho_a$ in eq 1, the activated complexes for zinc ion removal from porphyrins in both aqueous and aqueous-methanolic solutions, as defined by the rate laws, have the same composition.

The rates of zinc ion dissociation increased markedly as the basicity of the porphyrin toward protons (pK_3) increased. Figure 3 shows the linear relationship between the logarithm of the ratio of the rate constants for the substituted deuteroporphyrin-mesoporphyrin reactions *vs.* pK_3. The rates of formation of metalloporphyrins also increase with porphyrin basicity.[9] Since it is known that the thermodynamic stability of a coordinated metal ion increases with porphyrin basicity,[13] it might have been expected that a more basic porphyrin would lose its metal ion more slowly than a less basic porphyrin. The contrary was found here and it appears that bond making overrides bond breaking in this reaction.

Crystal structures on porphyrin diacids,[14] the existence of *N*-methyl-, *N,N'*-dimethyl-, and *N,N',N''*-trimethylporphyrins,[15] and the atropisomerism found

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with tetraarylporphines[16,17] indicate the extreme flexibility of the porphyrin nucleus. We assume that the incoming protons attack the opposite pyrrole nitrogens, two protons for ZnP and one for Zn-*N*-MeP. This causes the porphyrin to bend, moving the opposite pyrrole planes downward and the other two upward, thus lifting the now two-coordinate zinc ion above and away from the porphyrin. The initial two- and one-proton attacks formally form the neutral free-base species of ZnP and Zn-*N*-MeP, balancing in a concerted fashion the incipient di- and uninegative porphyrin charges caused by the gradual removal of zinc. Halide ions could plausibly occupy the coordination positions vacated by the protonated nitrogen atoms, further reducing the amount of charge separation needed for dissociation. The rate increase with porphyrin basicity is reasonable in terms of proton attack at the nitrogen positions. The final step for both porphyrin types is a one-proton attack on either of the two remaining nitrogen atoms bonded to zinc, with the resulting one-coordinate zinc ion being readily displaced. The idea of successive porphyrin protonations and metal ion ligations (by H_2O and pyridine with[5] MgP) which balance charge, deform the porphyrin, and reduce the coordination number of the porphyrin to the metal ion is a possible model for solvolysis reactions of such rigid macrocyclic complexes.

Acknowledgments. We thank the U. S. Atomic Energy Comission for financial support and Miss Y. Majid for continued technical assistance.

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Temperature Dependence of the Ligand-Field Spectra of Some Five-Coordinate Complexes Containing Nickel(II), Palladium(II), and Platinum(II)[1]

Sir:

A substantial amount of electronic spectral data is now available for low-spin trigonal-bipyramidal complexes containing nickel(II),[2] palladium(II),[3] and platinum(II).[3] In a D_{3h} environment the two lowest energy bands ν_1 and ν_2 should correspond to the $^1A_1' \rightarrow {}^1E'$ and $^1A_1' \rightarrow {}^1E''$ transitions, respectively,[4,5] with the latter being orbitally forbidden. If the metal is in a C_{3v} environment both the $^1A_1 \rightarrow a^1E$ and $^1A_1 \rightarrow b^1E$ transitions are allowed, although the latter still has low intensity.[2] The lowest frequency band ν_1 is usually asymmetric,[6] and even may be split into a double peak[5,7] at room temperature. At this temperature the splitting of ν_1 has been interpreted as a result of a small ground-state distortion which removes the degeneracy of the $^1E'$ (or a^1E) state.[3-7]

We have carried out electronic spectral measurements at temperatures down to 77°K (or in some cases to 100°K) on solutions of complexes of the type $[Ni(CN)_2(PhPR_2)_3]$ (R = Me, OEt) and $[MX(L'L_3)]^+$, where M = Ni(II), Pd(II), Pt(II), X = a unidentate anion, and $L'L_3$ represents the quadridentate "tripod-like" ligands $(Me_2AsCH_2CH_2CH_2)_3L'$ (L′ = P, TAP; L′ = As, TAA), $(o\text{-}MeL\cdot C_6H_4)_3P$ (L = S, TSP; L = Se, TSeP), and $(o\text{-}Ph_2L\cdot C_6H_4)_3L'$ (L′ = L = P, QP; L′ = L = As, QAS). In all cases, on cooling, the asymmetric or split band ν_1 exhibits a dramatic increase in extinction coefficient and becomes more symmetrical.

The ligand-field spectrum of $[Ni(CN)_2\{PhP(OEt)_2\}_3]$ in 2-methyltetrahydrofuran–ethanol (2:1 by volume) is shown in Figure 1. The two bands (at 24,000 and 27,500 cm^{-1}) contributing to the $^1A_1' \rightarrow {}^1E'$ transition ν_1 at 295°K are found to merge as the temperature is decreased and a single symmetrical band is obtained at 77°K. The low-energy region of the electronic spectrum of [PtCl(QP)]Cl in 2-methyltetrahydrofuran–dichloromethane (9:1) is given in Figure 2; again ν_1 becomes more symmetrical as the temperature is lowered, but even at 100°K the $^1A_1 \rightarrow a^1E$ band envelope retains some asymmetry. The oscillator strength of ν_1 remains approximately independent of temperature for both compounds, as expected for a symmetry-allowed band.

The tendency of ν_1 to become more symmetrical at low temperatures is extremely unusual spectroscopic behavior and suggests that in solution there is either (1) a temperature-dependent static distortion of the ground state or (2) a Jahn–Teller distortion of the doubly degenerate excited state.

The energy difference between the idealized trigonal-bipyramidal and square-pyramidal structures of five-coordinate molecules, especially those containing monodentate ligands, is usually small.[8] As the potential energy surface connecting these two forms is irregular,[8] molecules of intermediate structure might be favored under certain solvent and temperature conditions.[9] The temperature variation of ν_1 using interpretation 1 could be analyzed in terms of an equilibrium between the two forms: regular trigonal bipyramid (D_{3h} or C_{3v}) $\rightleftharpoons$ distorted trigonal bipyramid(C_{2v} or C_s).

At temperatures between 295 and 77°K (or 100°K) an equilibrium mixture would be obtained, and three bands in the region of ν_1 would be predicted. In no case, however, have more than two bands been observed. A more satisfactory explanation of the temperature dependence of ν_1 using the ground-state distortion model is to consider that species of intermediate geometry are present at intermediate tem-

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(1) Part of this research was supported by the National Science Foundation.

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