(8) S. C. Tang, S. Koch, G. N. Weinstein, R. W. Lane, and R. R. Holm, *Inorg. Chem.*, **12**, 2589 (1973).
(9) L. F. Lindoy and D. H. Busch, *Prep. Inorg. React.*, **6**, 1 (1971).
(10) TIM = 2,3,9,10-tetramethyl-1,4,8,11-tetraazacyclotetradeca-1,3,8,10-tetraene ($Me_4[14]$-1,3,8,10-tetraeneN_4).
(11) D. A. Baldwin and N. J. Rose, Abstracts, 157th National Meeting of the American Chemical Society, Minneapolis, Minn., April 1969, No. INOR 20.
(12) D. A. Baldwin, R. M. Pfeiffer, D. W. Reichgott, and N. J. Rose, *J. Am. Chem. Soc.*, **95**, 5152 (1973).
(13) S. C. Jackels, K. Farmery, E. K. Barefield, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **11**, 2893 (1972).
(14) K. Bowman, D. P. Riley, D. H. Busch, and P. W. R. Corfield, *J. Am. Chem. Soc.*, **97**, 5036 (1975).
(15) J. P. Collman, R. R. Gagne, C. A. Reed, T. R. Halbert, G. Lang, and W. T. Robinson, *J. Am. Chem. Soc.*, **97**, 1427 (1975).
(16) V. Katović, L. T. Taylor, and D. H. Busch, *J. Am. Chem. Soc.*, **91**, 2122 (1969).
(17) C. K. Chang and T. G. Traylor, *J. Am. Chem. Soc.*, **95**, 5810 (1973).
(18) After this work was completed an interesting report of the preparation of a dihydroxy macrocyclic tetramine appeared.[19] The procedure however was different from that used in this work and is not as suitable for the preparation of unsymmetrical tetramines.
(19) E. K. Barefield, F. Wagner, and K. Hodges, *Inorg. Chem.*, **15**, 1370 (1976).
(20) W. C. Drinkard, H. F. Bauer, and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **82**, 2992 (1960).
(21) B. Das Sarma, G. T. Tennenhouse, and J. C. Bailar, *J. Am. Chem. Soc.*, **90**, 1362 (1968).
(22) J. A. Broomhead, *J. Am. Chem. Soc.*, **90**, 4480 (1968).
(23) R. A. Krause and S. D. Goldby, *Adv. Chem. Ser.*, **No. 37**, 143 (1963).
(24) L. T. Taylor, N. J. Rose, and D. H. Busch, *Inorg. Chem.*, **7**, 785 (1968).
(25) M. C. Thompson and D. H. Busch, *J. Am. Chem. Soc.*, **86**, 3651 (1964).

Contribution from the Ames Laboratory and Chemistry Department,
Iowa State University, Ames, Iowa 50011

Kinetics and Mechanism of the Demetalation of Iron(III) Porphyrins Catalyzed by Iron(II)[1]

JAMES H. ESPENSON* and RICHARD J. CHRISTENSEN

Received February 25, 1977 AIC701510

The demetalation of iron(III) porphyrins by HCl in acetic acid is catalyzed by iron(II). Rate determinations for three compounds support a mechanism consisting of two steps: reduction to the iron(II) porphyrin and decomposition of the latter by HCl. The first step follows the rate law $k_1[\mathrm{ClFe^{III}P}][\mathrm{Fe(II)}][\mathrm{HCl}]$ and the second $k_2[\mathrm{Fe^{II}P}][\mathrm{HCl}]^n$, with n = 2 or 3 depending upon the porphyrin. Depending on concentration variables, either of the steps may be rate determining. The role of the iron(II) porphyrin as an intermediate is supported by measurements of its competitive reactions with HCl and with iron(III).

Introduction

Demetalation of iron(III) porphyrins in acetic acid is shown in eq 1, where P represents the porphyrin and H_4P^{2+} its

$$\mathrm{ClFe^{III}P + 5HCl = HFeCl_4 + H_4P^{2+} + 2Cl^-} \tag{1}$$

completely protonated dication. Demetalation does not proceed spontaneously,[2] however, requiring addition of a reducing agent to act as catalyst, such as an iron(II) salt,[2a] tin(II) chloride,[3] metallic mercury,[4] and diazomethane.[5]

In contrast to this slow demetalation, iron(II) porphyrins are readily demetalated by HCl. On the basis of such qualitative observations, Fischer et al.[6] proposed that the sequence of reactions 2 and 3 constitutes the mechanism by

$$\mathrm{ClFe^{III}P + Fe(II) \rightleftarrows Fe^{II}P + Fe(III)} \tag{2}$$

$$\mathrm{Fe^{II}P + 4HCl \rightarrow Fe(II) + H_4P^{2+}} \tag{3}$$

which iron(II) catalyzes reaction 1, as well as the reason for the requirement that salts of iron(II), not iron(III), be used in the synthesis of iron(III) porphyrins.[6]

The proposed sequence has not been verified, although Morell and Stewart[7] carried out some semiquantitative measurements to establish conditions under which iron(III) porphyrins might be demetalated rapidly and quantitatively at room temperature. They found that the extent of demetalation in a given time period increased with the concentrations of Fe(II) and of HCl (above 0.550 M HCl the rate then decreases, although $[H_2O]$ was not constant during that variation). They also noted that chlorohemin *a* was always demetalated to a greater extent than the less strongly oxidizing chloroiron(III) protoporphyrin IX, consistent with the electron-transfer process of reaction 2 being the first step in the sequence.

We have carried out kinetic studies to determine the effects of the pertinent concentration variables–$\mathrm{ClFe^{III}(P)}$, Fe(II), Fe(III), HCl, and (to some extent) H_2O. In addition experiments were conducted on the fate of independently prepared $\mathrm{Fe^{II}P}$ in the presence of varying concentrations of Fe(III) and/or HCl, since $\mathrm{Fe^{II}P}$ occurs as an intermediate in the proposed mechanism. The studies were carried out with the iron porphyrins shown in Figure 1; the deuteroporphyrin IX dimethyl ester complex (**1a**, ClFeDPE) and its 2,4-dibromo derivative (**1b**, ClFeDBDPE) were used, with a less extensive study of the Fe(III) complex of $\alpha,\beta,\gamma,\delta$-tetraphenylporphine (**2**, ClFeTPP). The measurements were made at 24.8 °C in acetic acid containing 5% water by volume ($[H_2O]$ = 2.80 M).

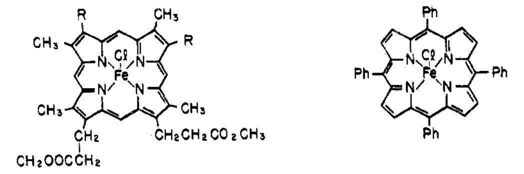
Results

General Observations. Both HCl and Fe(II) are required to effect demetalation of the $\mathrm{ClFe^{III}P}$ complexes shown in Figure 1. Demetalation in acetic acid containing 5% water proceeds with half-times of 10–1600 s for the ranges of $\mathrm{Fe^{II}}$ (typically 10^{-4} to 10^{-2} M) and HCl (0.05–1.3 M) employed.

The spectral changes accompanying the reaction are marked by the disappearance of bands characteristic of the $\mathrm{Fe^{III}(P)Cl}$ species and the growth of bands characteristic of the H_4P^{2+} dication. Appropriate isosbestic points were maintained throughout,[8] substantiating the presence of only two porphyrin species at appreciable concentration throughout the course of the reaction. Typical spectral scans at various time intervals are given in Figure 2 for Fe(DPE)Cl and in Figure 3 for Fe(DBDPE)Cl and Fe(TPP)Cl.

Only very slight dissociation of HCl occurs in glacial acetic acid.[9] The state of ionization of HCl upon addition of 5% H_2O (=2.80 M H_2O) is not known although, by assuming HCl acts as a weak electrolyte, an internally consistent formulation was realized.

The predominant species of nonporphyrin iron(III) in this medium is $HFeCl_4$. Solutions of $Fe(OAc)_3$ in acetic acid containing 0.42 M HCl and 2.80 M H_2O obey Beer's law over a concentration range 1.2×10^{-4} to 1.2×10^{-2} M. The same spectrum results from either LiCl or HCl, remains independent of added excess chloride, and matches closely that of $HFeCl_4$



Ia, R = H
Ib, R = Br

2

Figure 1. Porphyrin structures.

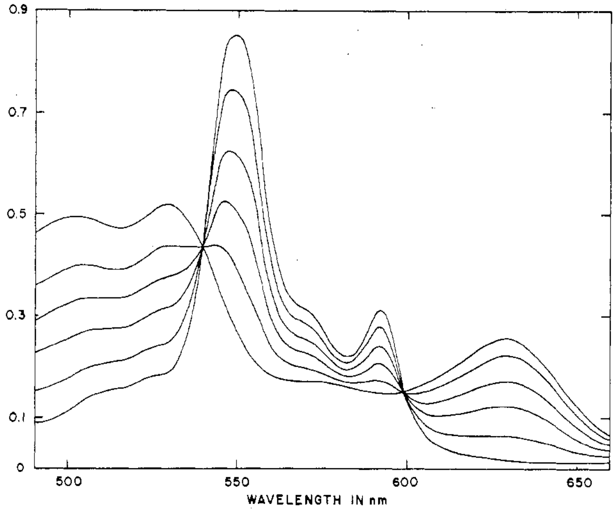


Figure 2. Spectral scans (25-mm optical path) of the reaction of 2.4 × 10^{-5} M Fe(DPE)Cl with 1.2 × 10^{-3} M $FeCl_2$, 0.472 M HCl, and 2.80 M H_2O in acetic acid at 24.8 °C. Reading upwards at the 550-nm peak of the porphyrin dication, spectra were taken 0, 210, 460, 810, 1510, and ca. 7000 s after mixing.

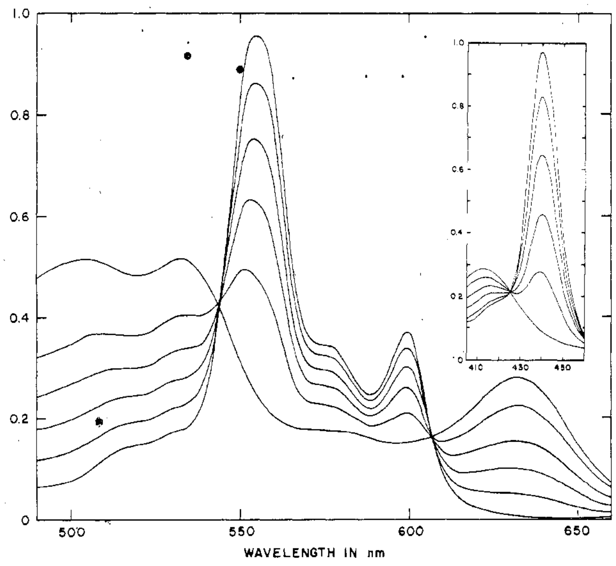


Figure 3. Spectral scans (25-mm cell) of the reaction of 2.6 × 10^{-5} M Fe(DBDPE)Cl with 5.69 × 10^{-4} M $FeCl_2$, 0.128 M HCl, and 2.80 M H_2O in acetic acid at 24.8 °C. Reading upwards at 550 nm, the spectra were recorded at 0, 90, 300, 590, 1070, and ca. 4000 s after mixing. The inset shows similar scans for the reaction of 1 × 10^{-6} M $ClFe^{III}TPP$ with 5.26 × 10^{-4} M $FeCl_2$ and 0.123 M HCl; reading upwards at 440 nm, the times are 0, 140, 340, 640, 1240, and ca. 5000 s after mixing.

in both aqueous[10] and nonaqueous[10b,11] media. The HCl concentrations reported in our experiments are therefore the values after allowing for formation of $HFeCl_4$. (These corrections are small but are significant owing to the strong HCl dependence of certain reaction steps.)

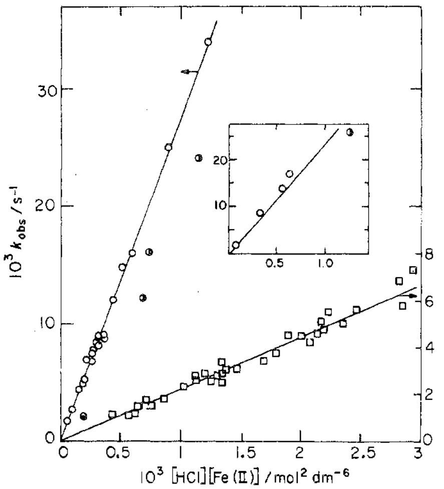


Figure 4. Plots of the pseudo-first-order rate constants for the demetalation of $ClFe^{III}DPE$ (squares) and $ClFe^{III}DBDPE$ (circles) vs. the product of HCl and Fe(II) concentrations for kinetic data at 25.0 °C in acetic acid with 5 wt % H_2O. Points lying off the line for the latter complex are at <0.1 M HCl (◒) and >0.7 M HCl (◐)—see text and ref 13. Inset: $ClFe^{III}TPP$.

Kinetics of Demetalation in the Absence of Added $HFeCl_4$. The reactions followed pseudo-first-order kinetics (eq 4), as

$$-d[ClFe^{III}P]/dt = k_{obsd}[ClFe^{III}P] \qquad (4)$$

verified by the linearity of the semilogarithmic rate plots to at least 88% reaction and by the invariance of k_{obsd} over a wide range of initial concentration of $ClFe^{III}P$.[12]

Values of k_{obsd} are correlated reasonably well by a first-order dependence on [HCl] and on [Fe(II)] (eq 5 and Figure 4).

$$-d[ClFe^{III}P]/dt = k_1[ClFe^{III}P][Fe(II)][HCl] \qquad (5)$$

Data for $ClFe^{III}DPE$ follow this relation over the entire concentration range. Demetalation of $ClFe^{III}DBDBE$ follows eq 5 at all [Fe(II)] over a range 0.1–0.7 M HCl.[13,14] Values of $k_1/dm^6\ mol^{-2}\ s^{-1}$ are as follows: $ClFe^{III}DPE$, 2.19 ± 0.13 (33 runs); $ClFe^{III}DBDPE$, 27.3 ± 1.5 (20 runs); $ClFe^{III}TPP$, 29 ± 3 (5 runs).

Certain other variables were tested, among them the source of iron(III) porphyrin (which was immaterial—see Experimental Section and supplementary materials[12]), the monitoring wavelength (also immaterial), and [H_2O]. Modest variation of water is unimportant for $ClFe^{III}DPE$; values of $k_1/M^{-2}\ s^{-1}$ ([H_2O]) are 4.87 (1.90), 1.90 (2.48), 2.13 (2.80), and 2.17 (2.91). Similar data[14] for $ClFe^{III}DBDPE$ show a somewhat greater variation: 112 $M^{-2}\ s^{-1}$ (1.14 M H_2O), 43 (2.24), 27.3 (2.80), 18 (3.35), and 7.6 (4.46).

Demetalation of the iron(III) porphyrin catalyzed by iron(II) does not occur when all the HCl is replaced by LiCl. Substitution of a part of the HCl by LiCl has no effect, however, and the rate expressions of eq 5 are obeyed (to within 10%) replacing [HCl] by the sum of [HCl] + [LiCl], or $[Cl]_T$, up to $[Cl]_T$ of ca. 0.6 M.

Iron(II)-catalyzed demetalation also does not occur with a noncomplexing acid alone, such as *p*-toluenesulfonic acid. In the presence of HCl or LiCl, however, addition of this acid decreases the reaction rate. For $ClFe^{III}DPE$ for example, the apparent second-order rate constant at 0.13 M HCl and 0.65 M TsOH was 0.13 ± 0.02 $M^{-1}\ s^{-1}$, compared to 0.28 $M^{-1}\ s^{-1}$ in 0.13 M HCl alone. A similar but smaller inhibition was noted in the case of $ClFe^{III}DBDPE$.

Kinetic Effects of Added $HFeCl_4$. Marked rate retardation is caused by $HFeCl_4$ added independently at concentrations much higher than those generated during demetalation. The magnitude of the effect can be gauged by noting the decrease

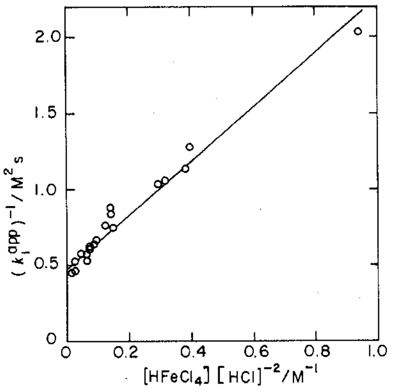


Figure 5. A plot according to eq 7 (with $n = 2$) illustrating the effect of $HFeCl_4$ and HCl on the demetalation of $ClFe^{III}DPE$.

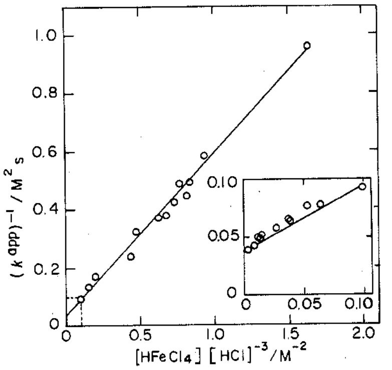


Figure 6. A plot of eq 7 (with $n = 3$) illustrating the dependence of the rate of demetalation of $ClFe^{III}DBDPE$ upon $[HFeCl_4]$ and [HCl].

in the apparent value of k_1. For $ClFe^{III}DPE$, values[12] of k_1^{app} ranged from 0.49 to 2.2 $M^{-2}\ s^{-1}$ (over the concentration ranges $2.8 \times 10^{-3} < [HFeCl_4] < 3.8 \times 10^{-2}$ M and $0.201 < [HCl] < 1.04$ M), compared to 2.19 $M^{-2}\ s^{-1}$ in the absence of $HFeCl_4$. For $ClFe^{III}DBDPE$, a similar study[12] gives k_1^{app} from 1.05 to 25.9 $M^{-2}\ s^{-1}$ (for $1 \times 10^{-4} < [HFeCl_4]_0 < 2.6 \times 10^{-2}$ M and $0.223 < [HCl] < 0.563$ M), compared to 27.3 $M^{-2}\ s^{-1}$ without added $HFeCl_4$.

Data for both complexes can be fit to a similar equation, eq 6, although the HCl dependences of the denominator term

$$\frac{-d[ClFe^{III}P]}{dt} = \frac{k_1[ClFe^{III}P][Fe(II)][HCl]}{1 + \kappa[HFeCl_4]/[HCl]^n} \qquad (6)$$

are different, being $n = 2$ for $ClFe^{III}DPE$ and $n = 3$ for $ClFe^{III}DBDPE$.

Rearrangement to the form shown in eq 7 provides a relation

$$\frac{[Fe(II)][HCl]}{k_{obsd}} = \frac{1}{k_1^{app}} = \frac{1}{k_1} + \frac{\kappa}{k_1}\frac{[HFeCl_4]}{[HCl]^n} \qquad (7)$$

useful for graphical correlation. Figures 5 and 6 depict the suggested linear plots.

The least-squares parameters for $ClFe^{III}DPE$, with $n = 2$, are $k_1 = 2.08 \pm 0.07$ $M^{-2}\ s^{-1}$ and $\kappa = 3.7 \pm 0.2$ M (19 runs). The former agrees with the value of k_1 from the experiments without added $HFeCl_4$.

Similar treatment for $ClFe^{III}DBDPE$ requires an expression with $n = 3$ and yields $k_1 = 27 \pm 5$ $M^{-2}\ s^{-1}$ and $\kappa = 15 \pm 3$ M^2. The former also agrees with $k_1 = 27.3 \pm 1.5$ $M^{-1}\ s^{-1}$, from runs without added $HFeCl_4$.

Only a single determination with $ClFe^{III}TPP$ was carried out. It, too, showed an appreciable retardation by $HFeCl_4$, but a complete study was not attempted.

Competition Experiments for an Iron(II) Porphyrin Intermediate. The kinetic data suggest that the reaction may involve the intermediate $Fe^{II}P$. Since iron(II) porphyrins are capable of independent existence, experiments were carried with authentic samples of $Fe^{II}DPE$. We determined the relative amounts of H_4DPE^{2+} and $ClFe^{III}DPE$ produced upon addition of a sample of the iron(II) porphyrin to a solution containing both HCl and $HFeCl_4$ at known concentrations in large excess over the amount of the iron(II) porphyrin. The results of such a study are depicted in Figure 7. At the lowest [HCl] the spectrum corresponds primarily to that of $ClFe^{III}DPE$, and at the highest [HCl] nearly to the dication H_4DPE^{2+}, with smaller quantities of the iron(III) porphyrin. These data afford an independent estimate of κ of eq 6, 6 ± 2 M, compared to the kinetic value 3.7 ± 0.2 M. Considering the oxygen sensitivity of $Fe^{II}DPE$, and the slight solvent difference,[15] these results are in reasonable agreement. The larger value of κ found in the competition experiments corresponds to a higher yield of $ClFe^{III}DPE$ than expected, consistent with a small amount of air oxidation of $Fe^{II}DPE$ during handling or transfer.

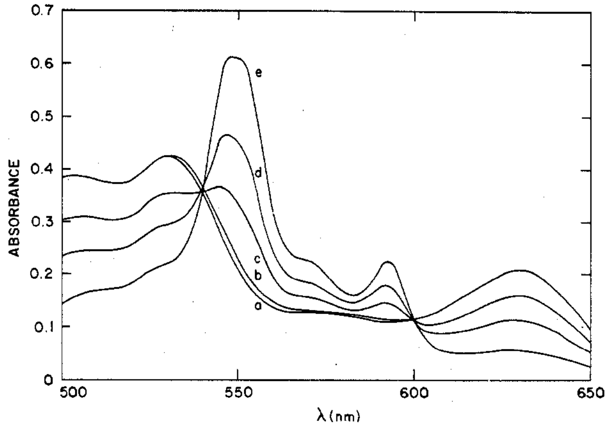


Figure 7. Product spectra of competition experiments for $Fe^{II}(DPE)$ between HCl and $HFeCl_4$. Each solution contains 4.75×10^{-3} M $HFeCl_4$. Curves b–e correspond to 0.014, 0.106, 0.270, and 0.936 M HCl. Curve a is the spectrum of pure $ClFe^{III}DPE$ with 0.014 M HCl.

Interpretation and Discussion

Rate Laws and Reaction Mechanism. It is convenient to discuss the kinetic results in terms of the mechanism in eq 8 and 9. Applying the steady-state approximation to the

$$ClFe^{III}P + Fe(II) + HCl \rightleftarrows HFeCl_4 + Fe^{II}P \quad (k_1, k_{-1}) \qquad (8)$$

$$Fe^{II}P \xrightarrow{nHCl} Fe(II) + H_4P^{2+} \quad (k_2) \qquad (9)$$

concentration of the iron(II) porphyrin, the rate law for this mechanism is given by eq 10, which agrees with the experimental expressions, eq 6, for $ClFe^{III}DPE$ ($n = 2$) and $ClFe^{III}DBDPE$ ($n = 3$). The parameter κ of eq 6 is seen to be k_{-1}/k_2.

$$\frac{-d[ClFe^{III}P]}{dt} = \frac{k_1[ClFe^{III}P][Fe(II)][HCl]}{1 + (k_{-1}/k_2)([HFeCl_4]/[HCl]^n)} \qquad (10)$$

The *n*th order HCl dependence for reaction 9 deserves comment. Demetalation reactions of divalent metalloporphyrins have been studied under a variety of conditions.[16] The commonly observed dependence upon acidity is a rate variation between second and fourth order in [HCl], often of a multiterm form. Thus the present second-order and third-order dependence for $Fe^{II}DPE$ and $Fe^{II}DBDPE$, respectively, are surprising neither in themselves nor in the change in apparent HCl dependence from one compound to the other.

The kinetic results obtained here substantiate the long-assumed mechanism; the kinetic evidence is supported by competition experiments for the intermediate role of the iron(II) porphyrin.

Experimental Section

Kinetic Measurements. Reaction rates were determined in strictly oxygen-free conditions, monitoring the absorbance at a fixed wavelength with time using a Cary Model 14 recording spectrophotometer. The wavelength used depended upon the concentration conditions, with several wavelengths and absorption bands being utilized.

After each run, the reaction solution was analyzed for chloride. The iron(II) solution was prepared independently for each run and analyzed at the start of the run. The kinetic data were treated according to standard methods for pseudo-first-order kinetics.

Competition Experiments. These measurements consisted of reducing the iron(III) porphyrin to the iron(II) species in an oxygen-free atmosphere, then transferring small portions to each of several solutions containing known quantities of HCl and $HFeCl_4$. The product is a mixture of the free porphyrin dication H_4P^{2+} and the iron(III) porphyrin,[17] whose relative concentrations could then be determined either from their known spectra or (better) by comparison with solutions from the same series of measurements at the extremes, i.e., with $[HFeCl_4]/[HCl] = 0$ and $\gg 1$. Absorbances were measured at the 550–555 nm maximum of the porphyrin dication. Several reducing agents were tried to prepare $Fe^{II}DPE$, namely, iron powder in 1:1 DMF–acetic acid, sodium dithionite in water–benzene, and Cr^{2+} in 1:1 benzene–acetic acid. Any of these iron(II) porphyrin solutions is extremely air sensitive, giving rise to one source of systematic error, namely, the formation of more $ClFe^{III}DPE$ than expected from the kinetic reactivity of $Fe^{II}P$ toward $HFeCl_4$ and HCl. Moreover, the necessity of preparing the $Fe^{II}P$ in a solvent other than the 95% HOAc–5% H_2O medium of the kinetic determinations means not only might $Fe^{II}P$ be introduced into the competition reaction possibly in a form containing different axial ligands but also that the final medium, and hence the quantitative comparison with the kinetic data, is slightly different in that small quantities of benzene were present.[15]

Materials. The iron porphyrins were prepared by standard methods. These preparations and the elemental analyses, melting points, and UV–visible spectra of the products are given in the supplementary materials.[12] Lithium chloride was recrystallized from acetic acid by the addition of benzene[9] and was dried under vacuum. Reagent grade *p*-toluene–sulfonic acid was twice recrystallized from acetic acid and dried at 50 °C. The acetic acid solvent was mostly the reagent grade material, but in some cases was refluxed with and distilled from chromium trioxide.[18] Water was triply distilled from alkaline permanganate in a tin-lined Barnstead sill. Chloroform was dried over calcium oxide for 24 h before use.[19] Benzene was washed with sulfuric acid and then with water and finally was distilled from calcium oxide.[20] Fisher A-540 and Alcoa F-20 activated alumina was used for chromatographic separations.

Solutions of Fe(III) were prepared by dissolving iron powder in glacial acetic acid containing HCl (0.1–1 M) with exposure to air. These solutions were used directly as a source of added $HFeCl_4$ or after addition of 5% H_2O were used to prepare the Fe(II) stock solutions for kinetic runs. The Fe(II) solutions were prepared only for immediate use by stirring with iron powder under an oxygen-free atmosphere of N_2 for about 1 hour; such solutions were shown to contain <1% Fe(III).

Solutions of HCl in acetic acid were obtained by bubbling the dry gas (either from a lecture bottle or generated by concentrated H_2SO_4 or concentrated HCl and solid sodium chloride), first through scrubbing towers (concentrated H_2SO_4 and glacial acetic acid) and then into the acetic acid solvent.

Analyses. The chloride content of stock solutions was determined by Volhard titration, after dilution with water to below 10% acetic acid by volume. The spent reaction solution from each kinetic run was analyzed for chloride.

Iron(III) solutions were analyzed spectrophotometrically after conversion to $Fe(phen)_3^{2+}$; this method agreed to within 1% of the total iron powder used. The iron(II) solutions were analyzed by cerium(IV) titration and/or by conversion to $Fe(phen)_3^{2+}$. The peak of $HFeCl_4$ at 361 nm (ϵ 7140 M^{-1} cm^{-1}) was used to establish that the Fe(II) stock solutions were essentially free of Fe(III).

The water content of glacial acetic acid was determined by the Karl Fischer method[21] and was <0.02 M H_2O. The water concentration in the kinetic runs was adjusted to 5.0% by volume, corresponding to 2.80 M H_2O.

The total iron content of iron porphyrins was analyzed spectrophotometrically as $Fe(phen)_3^{2+}$ after destructive oxidation of the evaporated residue with a mixture of concentrated nitric and sulfuric acids.[22]

Registry No. 1a, 19442-32-1; **1b**, 14688-94-9; **2**, 16456-81-8; $FeCl_2$, 7758-94-3; HCl, 7647-01-0; $HFeCl_4$, 16950-17-7; H_2DPE, 10589-94-3; H_2DBDPE, 14196-91-9.

Supplementary Material Available: Details of the preparation, analyses, and UV–visible spectra of $ClFe^{III}P$ samples, along with all the kinetic data (10 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Work performed for U.S. Energy Research and Development Administration under Contract No. W-7405-eng-82.

(2) (a) J. E. Falk, "Porphyrins and Metalloporphyrins", Elsevier, New York, N.Y., 1964, pp 129–135; (b) R. Hill, *Biochem. J.*, **19**, 345 (1925); (c) W. S. Caughey and A. H. Corwin, *J. Am. Chem. Soc.*, **77**, 1509 (1955).

(3) A. Hamsik, *Z. Physiol. Chem.*, **196**, 195 (1931).

(4) A. H. Corwin and R. Singh, *J. Org. Chem.*, **28**, 2476 (1963).

(5) P. S. Clezy and D. B. Morell, *Biochim. Biophys. Acta*, **71**, 150 (1963).

(6) H. Fischer, A. Treibs, and K. Zeile, *Z. Physiol. Chem.*, **195**, 1 (1931).

(7) D. B. Morell and M. Stewart, *Aust. J. Exp. Biol.*, **34**, 211 (1956).

(8) At the highest Fe(II) and HCl concentrations in the kinetic measurements of the dibromo derivative a slow secondary reaction leading to the destruction of $H_4(DBDPE)^{2+}$ was noted. The growth of a band at ca. 510 nm suggested [D. Mauzerall, *J. Am. Chem. Soc.*, **84**, 2347 (1962)] that the product of this slow reaction might be tetrahydroporphyrin resulting from a 4-equiv reduction of the dication. The reaction is so much slower than the main process (estimated half-time 3.8×10^3 s compared to 10.7 s for the first reaction) that the kinetic data for the main reaction were not affected although the spectrum of the product solution did drift with time.

(9) I. M. Kolthoff and S. Burckenstein, *J. Am. Chem. Soc.*, **78**, 1, 2974 (1956).

(10) (a) G. A. Gamlen and D. O. Jordan *J. Chem. Soc.*, 1435 (1953); (b) I. I. Antipova-Karataeva, Yu.A. Zolotuv, and I. V. Seryakova, *Zh. Neorg. Khim.*, **9**, 1712 (1968).

(11) (a) P. A. McCusker and S. M. S. Kennard, *J. Am. Chem. Soc.*, **81**, 2977 (1958); (b) C. Dragulescu and R. Pornsje, *Rev. Roum. Chim.*, **13**, 191 (1968); (c) R. J. Meyers, D. B. Metzler, and E. H. Swift, *J. Am. Chem. Soc.*, **72**, 3767 (1950).

(12) The individual kinetic runs, analyses, and spectra are reported as supplementary material.

(13) For the complex $ClFe^{III}DBDPE$, four additional runs lay outside the 0.1–0.7 M HCl range: one at 0.051 M, three with 0.78–1.01 M HCl. As seen in Figure 4 the data lie somewhat off the line described by the remaining points. The two-parameter expression, $k_{obsd} = A[Fe(II)] \cdot [HCl]^2/\{1 + B[HCl]^2\}$ accurately correlates all the data with $A = (1.93 \pm 0.17) \times 10^2\ M^{-3}\ s^{-1}$ and $B = 9.8 \pm 1.1\ M^{-2}$, but at the expense of an additional parameter. These changes might also be ascribed to changes in the chloride complexation of Fe(II) with [HCl], the extent of which is unknown in this medium.

(14) These runs encompassed a narrow range of [HCl] variation, 0.309–0.496 M, but [HCl] varied sufficiently to require correction to a "constant" value, 0.495 M. Values cited in the text are these corrected numbers, but uncorrected data are also available.[12]

(15) The solvent for the competition contained 0.37 M benzene, necessitated by the $Fe^{II}DPE$. A blank kinetic experiment gave k_1^{app} ca. 10% lower than otherwise expected.

(16) P. Hambright, *Coord. Chem. Rev.*, **6**, 247 (1971).

(17) The reaction also produces a small quantity of Fe(II) but at a level insufficient to catalyze further demetalation of $ClFe^{III}DPE$ in the time required for these determinations.

(18) W. C. Eichelberger and V. K. La Mer, *J. Am. Chem. Soc.*, **55**, 3633 (1933).

(19) W. S. Caughey, J. O. Alben, W. Y. Fujimoto, and J. L. York, *J. Org. Chem.*, **31**, 2631 (1966).

(20) I. A. Cohen and W. S. Caughey, *Biochemistry*, **7**, 636 (1968).

(21) J. Mitchell and D. M. Smith, "Aquametry", Interscience, New York, N.Y., 1948.

(22) E. B. Sandell, "Colorimetric Metal Analyses", 3rd ed, Interscience, New York, N.Y., 1959, p 552.